

PROCEEDINGS OF THE CHEMICAL SOCIETY

JUNE 1962

ONE HUNDRED AND TWENTY-FIRST ANNUAL GENERAL MEETING

THE One Hundred and Twenty-first Annual General Meeting was held in the Chemistry Department of the University of Sheffield on Wednesday, April 4th, 1962, at 9.15 a.m. The President, Lord Todd, was in the Chair.

After the notice convening the meeting had been read, Dr. J. Chatt, Honorary Secretary, presented the Report of Council. He stated that the number of Fellows had again increased, the growth during the year being higher than in any other year in the Society's history except 1960.

Referring to the *Journal*, he drew attention to the increase in the number of papers submitted and observed that the proportion of papers between the various branches of chemistry had generally been maintained. With regard to *Proceedings*, he said that, despite more stringent refereeing, the number of Communications had increased substantially and was giving rise to some concern.

Dealing with the other activities of the Society, Dr. Chatt referred to the symposia organised by the Society which had proved very popular; to the number of organisations which had joined as Library Subscribers increasing the membership of the Scheme by fifty per cent during the year; and to the interest in the Society's activities which had been aroused through the appointment of Liaison Officers. He remarked briefly on the Research Fund, pointing out that, despite the limited income, the Society was able to assist Fellows working at the smaller and less well-endowed establishments. He drew attention to arrangements made for Fellows to obtain *Index Chemicus* at a substantial discount.

Dr. Chatt then referred to the debt that the Society owed to those Fellows who gave freely of their services in arranging symposia, giving lectures, sitting on Committees, etc., and to whom, on behalf of the Council, he expressed his warmest thanks.

Ending on a personal note, Dr. Chatt referred to his six years of office and to the changes that had taken place during that time. He stated that the Honorary Secretaries' tasks were made much easier by the efficient work of the General Secretary and his office from which many innovations had originated. On the publications side, he paid tribute to the work of the Editors and their staff in dealing with the arrears of papers for publication which remained at the end of 1960 and which had now been published, and expressed his regret that their removal to yet another office was imminent.

The President then called upon Dr. J. W. Barrett, Honorary Treasurer, to present the accounts. Dr. Barrett reported that the General and Publications Fund Accounts were in sound condition and referred to the growth of Fellowship which had produced some £2000 more than the previous year. He pointed out that the Society had spent more money than in the previous year and that this was due to two main causes; the increased cost of producing a larger *Journal* and to the review of salaries of the permanent staff which resulted in increases of an exceptional nature. He added that the cost of capital improvements was lower than in the previous year and the work had now been finished in Burlington House. He stated that the Society had completed the year with a credit balance and, although he expected no

great changes in the coming months, he felt that costs must rise. However, the revenue from the sale of publications to non-Fellows was also increasing. Referring to the investments, he said that these were producing a larger income and that this was due to the wise policy of the Council when it decided some years ago to accept advice from the City. As a result, the Society had a sound portfolio and increased income.

Finally, Dr. Barrett reminded Fellows that this had been his first year as Honorary Treasurer and therefore he had perforce to be especially enquiring and curious of the management side of the Society. He had found a most satisfactory situation and paid special tribute to the help he had received from Mr. H. J. Morris who on retirement left behind a great record of service and younger staff well trained in the care of the Society's affairs.

Dr. F. A. Robinson referred to the marked increased cost of the *Journal* and asked the Honorary Treasurer if the Society could do anything about it during the present financial year. Dr. Barrett replied that an exceptional increase was not expected in the current year and, of the increased cost of some £22,000, about £16,000 included the cost of printing a very large number of pages of arrears of publication which had accumulated in the previous year. He added that, in any budget, anticipation of costs must depend on an accurate estimate of the number of pages to be printed, and if the estimate is correct the Publications Fund should be in balance at the end of the year.

The President remarked that the financial results gave the Society cause for congratulation. He also drew attention to two additional funds; the Ethel Behrens Fund, of the order of £2000, the income from which the Council had decided should be devoted to assisting undergraduate Fellows to attend the Anniversary Meetings of the Society; and the Robert Robinson Lectureship, of the order of £4000, the income from which would be used to endow a lectureship to be given in alternate years at the Anniversary Meetings in place of the Presidential Address which, in future, would be given only once during the Presidential term of office.

The President then moved the adoption of the Report and Accounts, Professor Sykes seconded the motion, and it was approved unanimously.

The President then announced the names of the following new members of Council elected to fill the vacancies caused by retirement:

President

Professor J. M. Robertson
Honorary Secretary
Dr. J. W. Linnett

Vice-Presidents who have not filled the office of President

Professor D. H. R. Barton
Dr. J. Chatt
Professor B. Lythgoe

*Elected Ordinary Members of Council
Constituency I (South-East England)*

Dr. G. W. A. Fowles
Dr. A. R. Katritzky
Dr. A. I. Vogel

Constituency II (Central and South-West England and South Wales)

Dr. W. J. Orville-Thomas

Constituency IV (North-East England)

Professor J. Baddiley
Professor F. S. Dainton
Dr. T. J. King

The President referred to Bye-Law 57 of the Society which stated that the Council shall hold at least eight ordinary meetings during the year and added that, although this number of meetings might be necessary in some years, the normal business of the Society could be conducted just as efficiently with fewer meetings and he thought it unnecessary to ask members of Council to travel long distances for a purely formal meeting. He called upon Dr. Barrett to propose the following motion:

"That the Bye-Laws of the Society be altered by deleting from Bye-Law 57 the word 'eight' and substituting therefor the word 'five'."

Dr. Chatt seconded the motion and it was carried unanimously.

On the motion of Dr. J. W. Barrett, seconded by Dr. J. Chatt, Messrs. W. B. Keen and Company, Finsbury Circus House, London, E.C.2, were appointed as auditors of the Society's Accounts for the year ended September 30th, 1962.

A vote of thanks to the President, Officers, Council, and Local Representatives for their services during the year was proposed by Professor G. Porter. He also congratulated the President on his elevation to a Life Peerage, particularly as it had happened during his term of office as President of the Society. The vote was carried with acclamation.

In reply, the President acknowledged the work of the Officers and Council and of the permanent officials of the Society. He added that the Society was in such good heart that he could hand over without any worry. He then declared the formal business of the Annual General Meeting terminated.

After an interval, the meeting was resumed at 10.15 a.m. in the Firth Hall. On behalf of the Society, the President made a Presentation of a Silver Salver and cheque to the retiring Finance Officer and re-

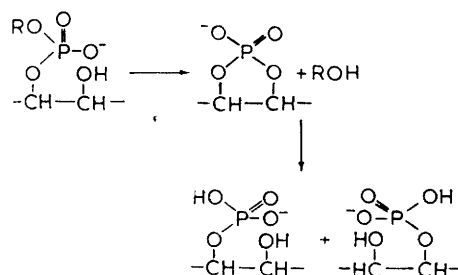
Professor J. M. Robertson, and asked him to take the Chair for the remainder of the meeting. Professor Robertson expressed his appreciation of the confidence shown in him by the Society and called upon Lord Todd to deliver his Presidential Address entitled "Some observations on Organic Phosphates."

The President next introduced the President-elect,

Some Observations on Organic Phosphates

In my Address to the Society a year ago¹ I discussed some of the problems then facing us in the field of polynucleotide synthesis—problems whose urgency has since been underlined by the striking developments in biological and biochemical studies on the rôle of nucleic acids in protein synthesis. In considering a topic for my Address on this occasion it seemed to me that it might be of some general interest if I dealt with a broader, but none the less related, topic by discussing some features of the chemistry of organic phosphates. The successful development of nucleotide chemistry has depended in large measure on the discovery of appropriate phosphorylation procedures and on studies of the chemical behaviour of esters of phosphoric and polyphosphoric acids. Phosphorylation studies, undertaken originally as part of nucleotide research, have yielded results of importance in other fields as well, by providing a rational explanation of certain biological processes, and by indicating possible lines of approach to the understanding of others. Before discussing some of the features of our current work, it may be useful as an illustration of the background to recall briefly a few of the important chemical developments in recent years where a knowledge of phosphate chemistry has proved highly relevant.

group. Such esters undergo hydrolysis with great ease to monoesters *via* a cyclic intermediate, the final product being usually a mixture of two isomeric monophosphate esters; the phosphate residue always remains attached to the glycol residue.



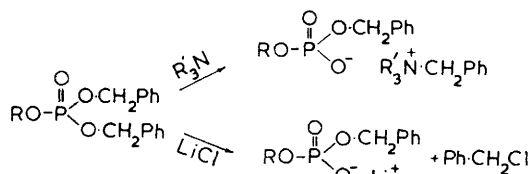
Again it may be recalled that in much of the work on nucleotide synthesis benzyl groups were commonly employed as protecting groups on phosphates, and it was necessary to develop methods whereby benzyl

* Delivered at the Anniversary Meeting of The Chemical Society at Sheffield on April 4th, 1962.

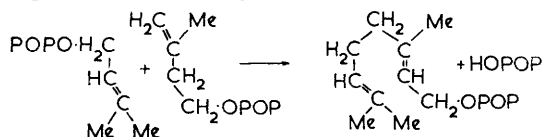
¹ *Proc. Chem. Soc.*, 1961, 187.

² Brown and Todd, *J.*, 1952, 52.

groups could be removed from an alkyl dibenzyl phosphate, either one at a time or together, under varying conditions. Notable among them were the methods of quaternisation³ and anionic fission⁴ by which one benzyl residue can be removed under mild conditions from a triester. The driving force in each of these methods is the strongly electrophilic character of the methylene group of the benzyl residue which is attacked, in the quaternisation method by a tertiary amine causing removal of the benzyl group by attachment to nitrogen in a quaternary ammonium cation, or by an anion such as Cl^- in anionic fission when benzyl chloride is produced. In reactions of this type the allyl group behaves in the same way as the benzyl.

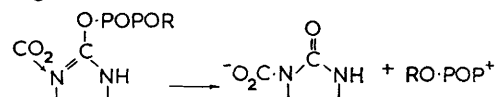


Although at the time these methods were discovered little thought was given to their possible extension to carbon-carbon bond formation by using a suitable olefin as nucleophile, it is clear that such an extension should be possible. And, indeed, the work of Bloch, Cornforth, and Lynen has shown that the biosynthesis of terpenoids and steroids rests on precisely such an extension.⁵ They have demonstrated that the "active isoprene" in biosynthesis is isopentenyl pyrophosphate. The mechanism of the process in which one molecule of isopentenyl pyrophosphate reacts with the isomeric 3,3-dimethylallyl pyrophosphate, yielding geranyl pyrophosphate with liberation of a molecule of pyrophosphate is strictly analogous to the laboratory processes of quaternisation and anionic fission. And, indeed, it can be demonstrated in the laboratory, since geranyl diphenyl phosphate passes with great ease into cyclic terpene with loss of diphenyl phosphate.



Finally mention may be made of the work of Lynen⁶ on the fixation of carbon dioxide by biotin to produce the so-called "active CO_2 " which is then available for a variety of biological reactions. He has shown that a phosphorus-containing intermediate is

formed from biotin—presumably the *O*-pyrophosphate or *O*-adenosyl pyrophosphate of the isourea form of biotin; attack by the positive carbon of the CO_2 molecule on the doubly bound nitrogen would clearly lead to its attachment, with simultaneous expulsion of the pyrophosphate group, yielding the biotin carbamic acid (as its anion) which is the "active CO_2 " of the biochemists. This mechanism for producing the carbamate could be predicted from the known behaviour of imidoil phosphates which act as phosphorylating agents when protonated on nitrogen.



These examples illustrate the way in which it is possible to reach a better understanding of many biological processes by studying relatively simple organic phosphates and polyphosphates, and in Cambridge my colleagues and I have been devoting a good deal of attention to this general approach. Some of our results and our reflections upon them may thus be of general interest.

At the risk of being repetitive I would once again draw attention to the fact that there are two distinct types of phosphorylation procedure in common use.^{1,7} The first type involves a second-order displacement mechanism and includes, in general, those methods based on reagents derived from phosphodiester (e.g., dibenzyl phosphorochloridate, tetraesters of pyrophosphoric acid) which yield as initial products phosphotriesters. Such methods are, of course, employed to prepare, not only simple phosphates, but also pyrophosphates and triphosphates. The second type employs monoesters of phosphoric acid which are "activated" by various means (e.g., reaction with arenesulphonyl halides, dicyclohexylcarbodi-imide, trichloroacetonitrile, diaryl or dialkyl phosphorochloridates) and yields phosphodiester; again methods of this type are applicable to pyrophosphate or triphosphate synthesis under appropriate conditions. All available evidence seems to support the view that methods of this second type proceed by production of a metaphosphate intermediate which, probably in the hypothetical monomeric form $(\text{RO} \cdot \text{PO}_2)$, is the true phosphorylating agent.

An instructive example of a metaphosphate-type method is found in oxidative phosphorylation in which quinol phosphates are used.⁸ Quinol phos-

³ Baddiley, Clark, Michalski, and Todd, *J.*, 1949, 815; Clark and Todd, *J.*, 1950, 2023.

⁴ Clark and Todd, *J.*, 1950, 2030.

⁵ For general review see Popjak and Cornforth, *Adv. Enzymol.*, 1960, 22, 281.

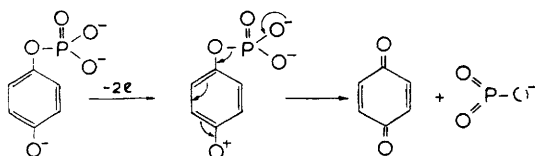
⁶ Cf., e.g., Symposium on Enzyme Reaction Mechanisms, *J. Cell. Comp. Physiol.*, 1959, 54, Suppl. 1, 45.

⁷ Todd, *Proc. Nat. Acad. Sci. U.S.A.*, 1959, 45, 1389.

⁸ Clark, Hutchinson, Kirby, and Todd, *J.*, 1961, 715.

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phates are very resistant to hydrolysis and do not readily break down in the absence of oxygen. But, in presence of oxidising agents (*e.g.*, bromine, ceric sulphate, quinones), they act as phosphorylating agents, yielding simultaneously the corresponding quinone. This reaction we formulate in the manner shown below, and the postulated production of monomeric metaphosphate is supported by a substantial body of evidence. Thus, if quinol phosphates are oxidised in aqueous phosphoric acid pyrophosphate is formed, while if they are oxidised in dimethylformamide the main product isolated is trimetaphosphate. Moreover, although both quinol phosphates and their monoesters undergo this reaction, quinol phosphate diesters (which cannot yield metaphosphate without hydrolysis) do not, even in the presence of reagents as powerful as ceric sulphate.

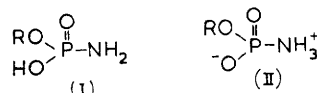


The behaviour of quinol phosphates on oxidation is of great interest in relation to the biological problem of oxidative phosphorylation, and it is difficult to believe that there is no connexion between these laboratory observations and the rôle of the ubiquinones and vitamins K in systems where oxidative phosphorylation occurs. As a laboratory demonstration of the possible rôle of such compounds, we have succeeded in synthesising adenosine-5' pyrophosphate (ADP) by oxidising a quinol phosphate in presence of muscle adenylic acid⁹ and adenosine-5' triphosphate (ATP) by oxidising *P*¹-2,3-dimethylnaphthoquinol *P*²-adenosine-5' pyrophosphate in presence of phosphate ion.¹⁰ The last-named example is of special interest since, formally, the reactive species produced in the oxidation is a mixed anhydride of metaphosphoric acid and muscle adenylic acid.

The production of metaphosphate as the reactive phosphorylating agent in the various methods of phosphorylation based on "activation" of a phosphomonoester is now fairly generally accepted and is supported, not only by the above observations on oxidative phosphorylation, but also by the ready

formation of trimetaphosphate from *P*¹*P*¹-diesters of pyrophosphoric acid.¹¹ Monomeric metaphosphates are, of course, unknown in the free state, but they seem more likely to be phosphorylating agents as such than in the trimeric form whose participation has recently been suggested¹² on somewhat insecure evidence in the case of carbodi-imide reactions.

It is interesting in connexion with the metaphosphate hypothesis to speculate on the way in which ATP (adenosine-5' triphosphate)—one of Nature's major phosphate transfer agents—may function. It is noteworthy that ATP functions by transferring either phosphate or nucleotide but rarely by transferring pyrophosphate, although if the transfer proceeded by a bimolecular displacement mechanism one would have thought that the central phosphorus atom would have been at least as readily attacked as either of the others. It seems possible that the central phosphate group acts as a kind of fulcrum, and that blockage of the acid functions on *P*¹ and *P*², either by metal-complex formation or by the protein component of an enzyme, leads to transfer of *P*³ as metaphosphate (*cf.* analogy with *P*¹*P*¹-diesters of pyrophosphoric acid). An analogous blocking of the groups on *P*² and *P*³ would lead to transfer of nucleotide as adenoside-5' metaphosphate, but on this type of mechanism transfer of pyrophosphate would not be expected. This is, of course, purely speculative, but it would certainly explain many of the experimental facts.



One important group of phosphorylating agents, the monoesters of phosphoramidic acid, presented an awkward problem in classification. Towards the end of last century Stokes¹³ reported that phosphoramidic acid gave, when heated, a polymeric material which has quite recently been identified as ammonium polymetaphosphate.¹⁴ Clark and Todd⁴ in 1950 prepared monobenzyl hydrogen phosphoramidate (I), showed that it lost ammonia when heated, and suggested that it could be regarded as a "base-metaphosphate complex" of the type described by Langheld.¹⁵ Later on, the use of monoesters of phosphoramidic acid as phosphorylating agents was described,^{16,17} and since then they have been widely used in pyro- and tri-phosphate synthesis. From

⁹ Clark, Hutchinson, and Todd, *J.*, 1961, 722.

¹⁰ D. W. Hutchinson, unpublished results.

¹¹ Brown and Hamer, *J.*, 1960, 1155.

¹² Weimann and Khorana, *Chem. Ind.*, 1962, 271.

¹³ Stokes, *Amer. Chem. J.*, 1893, **15**, 198.

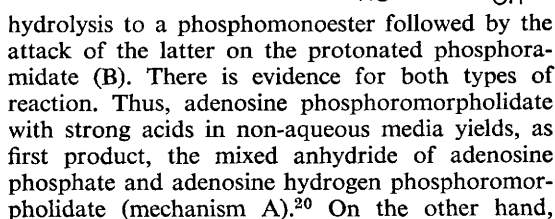
¹⁴ Becke-Goehring and Sambeth, *Chem. Ber.*, 1957, **90**, 2075.

¹⁵ Langheld, *Ber.*, 1910, **43**, 1857; 1911, **44**, 2076.

¹⁶ Chambers and Khorana, *Chem. Ind.*, 1956, 1022.

¹⁷ Clark, Kirby, and Todd, *J.*, 1957, 1497.

X-Ray crystallographic studies have shown that, in the solid state, the monoanion of phosphoramidic acid is zwitterionic.¹⁸ Studies in Cambridge, involving infrared spectroscopy,¹⁹ indicate that benzyl hydrogen phosphoramidate is zwitterionic in the crystalline state, but that when dissolved in dimethylformamide or dimethyl sulphoxide it exists as the neutral molecule. Benzyl hydrogen phosphoramidate crystallises as a hemihydrate and when kept at room temperature in the solid state it is slowly converted, after an initial lag period, into the diammonium salt of P^1P^2 -dibenzyl pyrophosphate;¹⁷ when carried out in dimethyl sulphoxide the reaction is of the second order with respect to phosphoramidate and hence no metaphosphate intermediate is involved.¹⁹ It may be mentioned that adenosine phosphoromorpholidate is similarly converted, on being kept, into diadenosine pyrophosphate.²⁰ The detailed mechanism of these reactions is unknown but a reasonable postulate would be attack on a protonated molecule of phosphoramidate by an anion leading to expulsion of 1 mol. of base and production of the pyrophosphate linkage. The attacking anion might be that of the phosphoramidate itself (A) or there might be initial


$$(B) \left\{ \begin{array}{l} \text{HO}^- + \text{RO}-\text{P}(=\text{O})(\text{OH})-\text{NH}_3^+ \longrightarrow \text{RO}-\text{P}(=\text{O})(\text{OH})_2 + \text{NH}_3 \\ \text{RO}-\text{P}(=\text{O})(\text{OH})-\text{O}^- + \text{RO}-\text{P}(=\text{O})(\text{OH})-\text{NH}_3^+ \longrightarrow \text{RO}-\text{P}(=\text{O})(\text{OH})-\text{O}-\text{P}(=\text{O})(\text{OH})\text{OR} + \text{NH}_3 \end{array} \right.$$

¹⁸ Hobbs, Corbridge, and Raistrick, *Acta Cryst.*, 1953, **6**, 621.

¹⁹ S. G. Warren, unpublished results.

²⁰ Moffatt and Khorana, *J. Amer. Chem. Soc.*, 1961, **83**, 649.

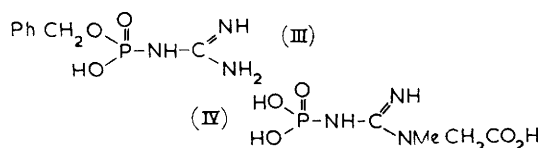
²¹ Moffatt and Khorana, *J. Amer. Chem. Soc.*, 1961, **83**, 663.

²² Rathler and Rosenberg, *Arch. Biochem.*, 1956, **65**, 319.

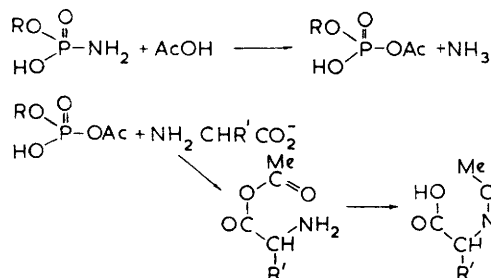
²³ Baddiley, Buchanan, and Letters, *J.*, 1956, 2812.

²⁴ G. W. Kirby and S. G. Warren, unpublished results.

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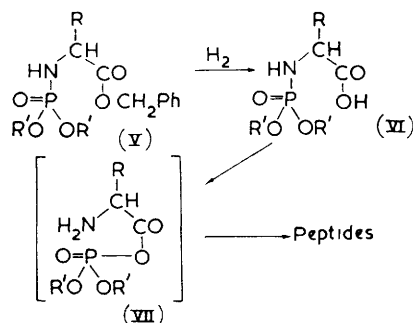


Monoesters of phosphoramidic acids react not only with phosphoric acid derivatives to yield pyrophosphates, but also with carboxylic acids to give mixed anhydrides. Thus, benzyl hydrogen phosphoramidate, when dissolved in glacial acetic acid, yields acetyl benzyl hydrogen phosphate, as shown by the fact that when the resulting solution is added to aqueous alkaline hydroxylamine acethydroxamic acid is formed. For this reason, mixtures of benzyl hydrogen phosphoramidate with carboxylic acids can be used as acylating reagents. The behaviour of such mixtures with amino-acids is of some interest.²⁵ A solution of benzyl hydrogen phosphoramidate in glacial acetic acid reacts at room temperature with the amino-acids glycine, leucine, alanine, and phenylalanine to give the corresponding acetamido-acids; in the absence of the phosphoramidate acylation is negligible. This reaction we interpret as probably proceeding by attack of the carboxylic group on the carbonyl group of the acetyl benzyl hydrogen phosphate followed by a rearrangement to the acetamido-acid by intramolecular acylation. The general scheme of reaction is set out in the annexed scheme.



If external carboxylate anions can bring about displacement reactions with phosphoramidates leading to mixed anhydrides it should be possible to bring about the same reactions intramolecularly. In particular, it should be possible to develop a method of polypeptide synthesis based on this idea. In order to test this hypothesis *N*-(diphenyl phosphoryl)glycine benzyl ester (V; R = H, R' = Ph) was prepared, and from it, by catalytic hydrogenation, the crystalline *N*-(diphenyl phosphoryl)glycine (VI; R = H, R' = Ph). In accordance with our expectation, the latter compound readily yielded polyglycine under acid conditions presumably by way of an intermediate (VII; R = H, R' = Ph). Similar oligo-

peptides have been obtained by using DL-phenylalanine, DL-leucine, and DL-valine.²⁶ As far as we are aware this is a new synthesis of polypeptides, but it is also of interest from another point of view. Could it be of significance in the biological synthesis of proteins?



Although considerable advances have recently been made in unravelling the complex course of protein biosynthesis and the part played in it by the nucleic acids, we do not yet know the mechanism by which polypeptide chains are formed in the ribosomes. We know that each amino-acid becomes attached ester-wise to the 2' or 3' position on the terminal nucleoside (adenosine) residue of its specific "soluble ribonucleic acid" (transfer RNA), the reagents bringing this about being apparently nucleotide-amino-acid anhydrides. In this form they are transferred to the ribosomes where they are arranged in specific order by a coding procedure involving the ribosomal ribonucleic acid, and then the polypeptide chain is formed. But the sequence of events in the ribosomes and the actual mechanism of polypeptide formation is still far from clear. It is possible that the transfer RNA attaches itself to the ribosomal RNA in such a way that the attached amino-acids are lined up so that direct polypeptide formation occurs. An alternative possibility, that the amino-acids might be first transferred to the internucleotidic phosphate groups on ribosomal RNA has in the past been difficult to accept, since the attachment of an amino-acid to a phosphodiester in the form of a mixed anhydride gives compounds so reactive that they would not be expected to have more than a transient existence. But the observed stability of *N*-(diphenyl phosphoryl)glycine, which can be handled and indeed crystallised, suggests that by attachment to an internucleotidic linkage through nitrogen amino-acids might be "stored" in relatively unreactive form until the appropriate sequence was built up. By acid-catalysis rearrangement to the anhydride form with immediate conversion into polypeptide could then

²⁵ J. F. P. Richter and M. Michalska, unpublished results.

²⁶ J. F. P. Richter and A. R. Macrae, unpublished results.

occur without damage to the polynucleotide chain. It is not suggested that this is indeed what happens; but, if it were found to fit the biological facts, then it could be accepted as being at any rate chemically reasonable.

It would be possible to discuss a number of other features of phosphate chemistry which may be sig-

nificant in biosynthetic processes and which may provide an approach to various aspects of enzyme action, but what I have discussed will, I hope, suffice to indicate to you some aspects of a broad and, I believe, important area of research where progress demands the joint efforts of organic chemists, biochemists, and biologists.

CHEMICAL SOCIETY ANNIVERSARY MEETING 1962 SYMPOSIA

Held at Sheffield on April 3rd–5th

Structure and Reactivity in Inorganic Chemistry

THIS symposium was held in two sessions, on April 4th and 5th. The size of the audiences was convincing, if rather uncomfortable, proof of keen interest in the speakers and their topics.

Dr. W. C. E. Higginson took the chair for the first session and introduced Dr. J. Lewis (University College, London), who gave a lecture on "Magnetism and the Structure of Inorganic Complexes." This was an excellent review of the magnetochemistry of transition elements and showed how the classical approach, in which the energy levels were assumed to be those of the free ion, and orbital contributions to the magnetic moments ignored, failed to account fully for the moments of many metal complexes. Dr. Lewis had found that many octahedral complexes for which a crystal-field treatment predicted no spin-orbit coupling had magnetic moments that were independent of temperature and equal to the classical spin-only value. For some tetrahedral nickel complexes in which orbital contributions were expected there was poor agreement between the experimental and the calculated variation of μ with temperature. Dr. Lewis competently explained how this could readily be accounted for by distortion of the ligand field around the central ion.

In the next lecture, "The Atomic and Electronic Structures of Nickel(II) Complexes," Professor F. A. Cotton (M.I.T.) opened by stating emphatically that it was now possible, by application of ligand-field theory to complexes of nickel(II), to distinguish octahedral from tetrahedral stereochemical configurations. The first criteria were magnetic, as previously discussed. The second were spectroscopic and were based on correlation of band positions with energy-level diagrams and on the band intensities. For square-planar compounds the position seemed less clear, but Professor Cotton showed how their "anomalously" solvent- and temperature-dependent electronic structures are explained by three main mechanisms: the co-ordination of solvent molecules, the Boltzmann distribution of close-lying singlet and triplet states, and, lastly, molecular association. The

last point was well illustrated when Professor Cotton considered the nickel(II)- β -diketone complexes. In these cases apparently the degree of molecular association can change from zero when *t*-butyl groups are the substituents of the diketone to essentially complete trimerisation when methyl groups are used.

The second session was opened by Professor A. W. Adamson, who presented Professor Fred Basolo of Northwestern University. Professor Adamson also remarked, in his humorous manner, that all statements were liable to be controversial. Under the title "Kinetics and Mechanisms of some Octahedral Metal Complexes," Professor Basolo divided the lecture into three interrelated parts. Studies on certain ammine-carboxylate complexes of cobalt(III), rhodium(III), and iridium(III) showed that in all cases the rates of acid hydrolysis were similar, thus suggesting that cleavage of the acyl-oxygen as against metal-oxygen bond took place.

The first syntheses and kinetics of the compounds, *cis*- and *trans*-[Rh(AA)₂Cl₂]⁺ where AA represents ethylenediamine or a substituted ethylenediamine were reported. A most surprising feature was that *trans*-[Rh(en)₂Cl₂]⁺ was hydrolysed at the same rate at either pH 1.0 or pH 13.0, in marked contrast to the corresponding cobalt(III) compound. New evidence was cited to support the theory that base hydrolysis in cobalt(III)-ammine complexes proceeds by an *S_N1cb* mechanism and not by simple *S_N2* displacements. The conclusion was that the hydroxyl ion is an ineffective nucleophile for metal complexes containing non-bonding *d*-electrons. In support, Professor Basolo quoted the *d*⁰-system [Si(acetylacetonate)₃]⁺ in which hydroxyl ion proved an effective reagent.

The last lecture, by Dr. R. G. Wilkins (Sheffield University), was entitled "The Fast Reactions of Metal Complexes." Dr. Wilkins first surveyed the exciting techniques being used in complex-ion kinetics, which enable rates of reactions to be measured which are complete in fractions of a

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second. This work was undertaken to illustrate the effects of ligand structure on the rates of formation and substitution of nickel(II) complexes and was concerned particularly with nickel-amine complexes. Dr. Wilkins presented a mass of detailed kinetic data on a variety of ligands containing from 1 to 6 nitrogen donor atoms. He considered it significant that the formation rates of complexes of nickel(II) with unidentate ligands are approximately equal to the water exchange rate and so indicates strongly that an S_N1 process more nearly describes the formation,

and that direct ligand entry is relatively unimportant. The most impressive part of the work was the resolution of the stepwise cleavage of Ni-N bonds during the acid dissociation of multidentate complexes, the nitrogen atoms being protonated as they were released.

After a short discussion Professor Adamson called on Dr. J. Chatt (I.C.I.) to propose a vote of thanks, after which the meeting closed. The symposium made it quite clear that to-day the chemistry of complexes is an intriguing and fast-moving subject.

P. G. PERKINS.

The Transition State*

A SYMPOSIUM on this topic was held during the Anniversary Meetings in Sheffield on April 3rd to 5th. In his address of welcome, Professor G. Porter remarked that although the transition-state theory had not entirely fulfilled its early promise, it was nevertheless the best and most widely used theory of reaction rates which we possessed.

Appropriately, the first contribution was from Professor H. Eyring, in which he discussed corrections to the idealised theory arising from departures from equilibrium kinetics. Since many activation processes in thermal reactions occur in stages, the reactants will pass over a number of potential barriers before reaction occurs. This was shown to lead to a transmission coefficient appreciably less than unity if the free-energy difference between successive intermediate states is small compared with RT cal./mole; but, as the free-energy difference increases, the transmission coefficient approaches unity. In association and adsorption in which energy must be dissipated in order to stabilise the products, it is the least energetic rather than the most energetic molecules which react.

The first session was concluded by a discussion of two papers on unimolecular decompositions in the gaseous phase. Professor N. B. Slater suggested that Kassel's model should be discarded as unrealistic; in his own theory, it is assumed that the energy is distributed between the normal vibrations of the molecule, and that dissociation can occur only when a critical co-ordinate exceeds a certain value. No energy exchange between truly harmonic vibrations can occur between collisions, a restriction which leads to calculated rate constants which are often smaller than experimental values. In practice, a limited flow of energy will occur because of the anharmonicity of the molecular vibrations, and Professor K. J. Laidler suggested that energy could flow only between those vibrations of the same symmetry as the reaction co-ordinate. A tentative configuration of the transition state can usually be deduced if a

reaction co-ordinate can be chosen which will give agreement with experiment. In discussion, however, several speakers stressed the importance of anharmonic coupling between vibrations of different symmetry in distorted molecules and questioned the validity of arguments based upon the symmetries of the reacting molecule and the activated complex.

With Professor E. A. Guggenheim in the chair, Professor K. S. Pitzer opened the second session with a paper on the calculation of transmission coefficients for reactions of the type $H + H_2 \rightarrow H_2 + H$. A semi-empirical equation due to Sato was used to describe the potential energy surface. Transmission coefficients were calculated for several different total energies, a linear collision being assumed. At low total energies, allowance for the bending of the activated complex appreciably reduces the transmission coefficient, and a correction for this is essential.

The remaining papers were concerned with reactions in solution and, in the first of these, Professor L. Melander discussed the transition state in electrophilic aromatic hydrogen exchange. The ratio of the rate constants for the electrophilic exchange of tritium and deuterium falls with increasing reactivity of the aromatic position. A transition state which includes both hydrogen atoms and takes their bending motion into account was shown to be qualitatively consistent with this observation.

The final paper of the session was read by Professor M. Szwarc and dealt with the transition state in electrophilic radical reactions. He showed that the ratio of the rate constants of addition of CF_3 radicals to an olefin and abstraction by CF_3 radicals from isobutane was much greater than the corresponding ratio for reactions of CH_3 radicals. This was interpreted in terms of polar transition states, the effect of the polarity being greater for addition than for abstraction, since the polarisability of a π -bond is greater than that of a σ -bond. Professor Szwarc considered that the transition state probably resembles

* A full report of the lectures and discussions at this symposium (but not at the other two) will be issued as Chemical Society Special Publication No. 16. This is expected to be available in October–November, 1962.

a σ -complex rather than a π -complex, since it appears to involve a particular carbon atom.

Since Mr. R. P. Bell was unfortunately unable to be present, Dr. J. W. Linnett took the chair for the final session. Sir Christopher Ingold began by pointing out that, whereas the idea of a transition state was extremely useful in reactions such as diene addition, there are many reactions in which it is ill-defined, and, in the benzidine rearrangement, its structure "must be like nothing else in this world." Despite much experimental work, "a cloud hangs over the high central region of the mechanistic route, wherein lies the transition state."

Professor H. C. Brown's paper, which may be destined to reach a wider public than most, as a result of the recent burglary of the Society's premises, was concerned with strained transition states. After assuring his audience that he was not one to shirk a controversy, Professor Brown discussed non-classical carbonium ions. Some of the structures suggested in the literature were likened to some of the more extreme forms of modern painting, and Professor Brown concluded by stressing the need for a sound

experimental basis for explanations in terms of non-classical structures.

Several sources of evidence for non-classical carbonium ions were discussed by Dr. A. Maccoll. Both isobutane and neopentane give the $C_2H_5^+$ ion in the mass spectrometer, possibly *via* a non-classical intermediate. It was shown that heterolytic dissociation energies derived from radical ionisation potentials could be correlated with the rate of heterolysis in polar solvents and of gas-phase elimination of alkyl halides, suggesting a transition state of the type (R^+X^-) .

The final paper was presented by Dr. G. Kohnstam and dealt with the interpretation of entropies and heat capacities of activation in solvolytic reactions. If one assumes that the transition state is highly polar, the values can be interpreted in terms of increased solvation. The interpretation of results obtained in largely aqueous solvents is highly controversial, as ensuing discussion showed.

The meeting was formally concluded by Professor K. W. Sykes, who thanked the contributors and organisers of the meeting.

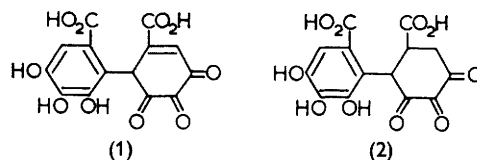
K. R. JENNINGS.

The Structure, Oxidation, and Biosynthesis of Naturally Occurring Phenols

THE 1962 Anniversary Meetings of the Chemical Society in Sheffield included a symposium on the above topic, divided into three sessions held on April, 3rd, 4th, and 5th, which were concerned respectively with the structure, the oxidation, and the biosynthesis of phenols. The chairmen for the three sessions were Sir Alexander Todd, Professor R. D. Haworth, and Professor E. R. H. Jones, respectively.

The first session opened with a paper by Professor K. Freudenberg who gave a masterly exposition of the biosynthetic approach to elucidation of the structure of lignin. He reviewed the degradative and synthetic evidence which suggested that lignin is biosynthesised from phenols of C_6-C_3 type by initial enzymic dehydrogenation to give phenoxy-radicals, the mesomeric forms of which react to form a variety of oligomers. The further combination of these oligomers either by radical coupling and substitution or by addition reactions of quinone methines possibly proceeds by non-enzymic means since the lignin produced is optically inactive. He believed that lignin has an ordered structure, although it was not possible to draw a final conclusion from the evidence now available. A discussion ensued among Sir Alexander Todd, Professor D. H. R. Barton, Professor K. Freudenberg, and Professor C. H. Hassall on whether dienone-phenol rearrangements of *in vivo* intermediates of lignin formation were induced enzymically, photochemically, or by acid-catalysis.

The second paper, given by Professor Otto Th. Schmidt was concerned with recent work on the ellagitannins, the biosynthetic scheme for which was



strengthened by the recent isolation of brevilagin I and II, which contain the dehydrohexahydroxydiphenic acid residue (1) and terchebin, which contains the isohexahydroxydiphenic acid residue (2). After describing the degradation of these ellagitannins he showed how reactions of compound (2) *in vitro* further confirmed the biosynthetic scheme.

Professor R. D. Haworth next described the application of methylation and methanolysis (degradation by transesterification with sodium methoxide) to the gallotannins. These showed that Chinese and Turkish gallotannin have structures based on penta-*O*-galloylglucose and a mixture of tetra-*O*-galloylglucoses, respectively, whilst tara tannin has a 3,4,5-tri-*O*-galloylquinic acid core.

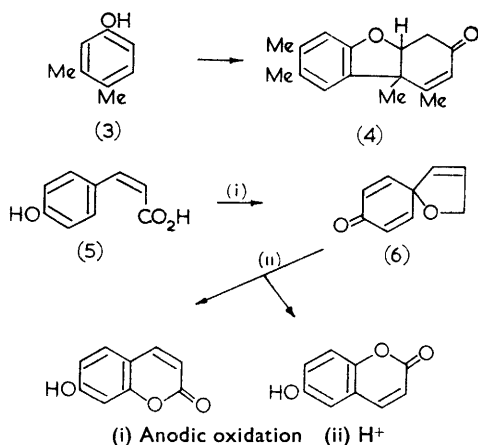
Professor D. H. R. Barton opened the second session with a lucid account of the mechanism and biogenetic role of oxidative phenolic coupling. The biosynthetic scheme for galanthamine was substantiated by the recent isolation of two postulated

intermediates, by a biosynthetically modelled laboratory synthesis of (–)-galanthamine, and by tracer experiments *in vivo* with postulated precursors. An unusual resolution of narwedine, the precursor of galanthamine produced either optical isomer in yields greater than 50%.

Further verification of the biosynthetic role of oxidative phenolic coupling was provided by Dr. A. R. Battersby by reference to tracer experiments with opium and Amaryllidaceae alkaloids *in vivo*. Specifically labelled tyrosine and norlaudanoline were incorporated into morphine in the predicted manner. Both (+)- and (–)-tetrahydropapaverine were incorporated into morphine, but to different extents, indicating enzymic control, whilst other tracer experiments substantiated the postulated biosynthetic order, thebaine → codeine → morphine.

Dr. S. Dagley was concerned with a different aspect of phenol oxidation, that of microbial degradation by hydroxylation and oxidative fission. After a summary of existing degradation pathways, new pathways motivated by recently discovered enzymes were described.

Returning to oxidative coupling of phenols Dr. A. I. Scott provided *in vitro* analogies of suspected *in vivo* oxidations: for example, the formation of griseofulvin and the depsidones pichrolichenic acid and diploicin by oxidation of phenolic precursors



with inorganic reagents. Enzymic oxidation of 3,4-xylenol (3) gave an optically inactive ketone (4), and griseofulvin produced enzymically *in vitro* was also racemic. He then suggested that coumarin biosynthesis might find analogy in the acid-catalysed rearrangements of the spirodienones (6) produced by

anodic oxidation of *cis*-4-hydroxycinnamic acid (5).

Starting the final session Professor A. J. Birch reviewed biosyntheses of aromatic compounds, especially those not based on shikimic acid. Among examples discussed was the biosynthesis of mycophenolic acid which incorporated mevalonate, acetate, and methionine. Since orsellinic acid was a precursor, nuclear methylation and substitution of the side chain (which was a geranyl remnant obtained from two molecules of mevalonate) occurred after aromatisation. He also discussed the biosynthesis of novobiocin and speculated on the origin of C₆–C₃ compounds of the eugenol type.

Dr. H. Grisebach showed that tracer experiments provided convincing evidence that flavanoids were biosynthetically derived from C₆–C₃ and acetate units by a scheme involving chalcone intermediates. The biosynthetic pathways to flavone and anthocyanin probably branched before the final oxidation state of the heterocyclic ring was established, and aryl (not aroyl) migration occurred in flavone biosynthesis. Dr. Grisebach then speculated upon the intermediate in which this migration occurred.

Professor C. H. Hassall gave an interesting demonstration of the application of the techniques of chemical genetics to the elucidation of biosynthetic problems inaccessible by the use of tracers and consideration of structural relationships. These methods revealed a common metabolic sequence for sulochrin, geodin, asteric acid, and geodoxin, which was verified by the reactions of their dechloro-analogues *in vitro*. A combination of these techniques with tracer methods revealed orcinol to be a precursor.

The final paper, given by Dr. J. D. Bu'Lock was concerned with a re-examination of the basic assumptions underlying isotope-incorporation studies with mould metabolites. This critical re-assessment was most appropriate at a time when these techniques are becoming more widely used.

Much of the material presented by six of the contributors was published recently in a collected form ("Recent Developments in the Chemistry of Natural Phenolic Compounds," Pergamon Press, London, 1961), but since each contributor disclosed new work this prior publication served to enhance rather than diminish the success of the symposium. The details of Professor Barton's galanthamine synthesis (*J.*, 1962, 806) appeared a few days after the symposium finished.

D. N. JONES.

THE ANNIVERSARY MEETING AT SHEFFIELD APRIL 2ND—5TH

EARLY April would not be the time recommended by Travel Agencies for a visit to the Peak District, and the Fates are in no wit kinder to Fellows of the Chemical Society than they had been to the residents during the devastating previous months. Indeed, it was not until the morning following the Meeting that Nature condescended to suggest that Winter might at last be satisfied; a mid-afternoon trip over Snake Pass on the previous day produced all the hazards of any mid-winter continental car-rally. Yet such was the enjoyment experienced at the Anniversary Meetings that these unpleasanties were not noticed.

Attendance at the Meeting was one of the biggest in the Society's history; such that the large lecture theatres were always crowded and, sometimes, inadequate to the extent that other accommodation had to be sought.

The Society's Annual General Meeting enabled the Honorary Officers to report on the continued success of the Stewardships of their Offices, and the paucity of questions from the floor indicated clearly the satisfaction of the Fellowship with the conduct of the Society's affairs. The Presidential address (see p. 199), which followed, must have satisfied all. Although appearing to deal with a narrow, specialised topic of organic chemistry, it nevertheless spanned a wide range of interests, drew attention to many queries in the natural and biological sciences, and must have suggested several lines of thought and study to listeners. Incidentally, it will probably make Chemical Society history in being the last occasion on which a President has been called on to deliver two Presidential addresses during his term of office. This easing of the Presidential burden has been made possible by the endowment of the "Robert Robinson Lectureship" (see *Proceedings*, 1962, 108).

The three symposia are fully reported elsewhere in this issue and one, on "The Transition State," is to form No. 16 in the Society's "Special Publication" series. Many of the papers read were stimulating and indeed challenging, and discussion of them often continued long after the scheduled closing of the session. All who contributed and joined in public discussions deserve our thanks and congratulations.

The programme of hospitality was much appreciated, not least by the ladies, who found much to

interest them. The works visits were a balanced mixture of chemical and local-industry interests and the latter particularly enabled the ladies to look into the background of much that they treasure in their own homes and to enable them to appreciate that the methods of skilled craftsmen have not been entirely swept away by the need for mass-production. The display of silverware at the Ladies' Reception given by the Mistress Cutler was spoken of most appreciatively. Fellows and visitors are indebted to these organisations and to others who gave hospitality, sometimes associated with works visits: United Coke and Chemicals Company Limited, The Shell Chemical Company, the Alkali Division, the Pharmaceuticals Division, and the Dyestuffs Division of Imperial Chemical Industries Limited, Batchelor's Foods Limited, Newton Chambers and Company Limited, and Samuel Fox and Company Limited.

Situated on the fringe of some of the loveliest country in England, Sheffield offers, to an extent that can be rivalled by few University Cities, trips to great, historic houses. Three were visited—Haddon Hall, Hardwick Hall, and Chatsworth House—and were a source of much pleasure; some stalwart Fellows, to allay the effects of generous luncheon hospitality, took the unusual exercise of walking the great gardens of one of these Houses to see the axemen tidying up the ravages of the winter's great gale.

Each day's work was rewarded by an evening's enjoyable relaxation—a Reception, Buffet, and Dance by invitation of the University, the well-attended Anniversary Dinner held in the University Gymnasium, and a Civic Reception in the Town Hall. Lord Hailsham, as principal speaker at the Dinner, told of his opinion that all science should be cultivated for the part it plays in promoting a higher level of culture in society at large and his belief that the corpus of human knowledge was essentially one and not two cultures—the arts and the sciences.

The 1962 Anniversary Meeting had all the markings of a well-conceived, properly organised, and efficiently run affair and all those who contributed officially (and unofficially) to making it the success it proved to be must receive our gratitude.

CORDAY-MORGAN MEDAL AND PRIZE

THE scheme for the administration of this Award (*Proceedings*, 1962, 135) has now been established by the Charity Commissioners and it will, in future, be subject to the revised rules approved by Council and given below (see also p. 236).

The Award, consisting of a Silver Medal and a monetary Prize which, for the year 1961, will amount to 400 guineas, is made annually to the chemist of either sex and of British Nationality who, in the judgement of the Council of the Chemical Society,

JUNE 1962

has published during the year in question, and in the immediately preceding five years, the most meritorious contribution to experimental chemistry, and who has not, at the date of publication, attained the age of thirty-six years.

Applications or recommendations in respect of the Award for the year 1961 must be received not later than December 31st, 1962, and applications for the Award for 1962 are due before the end of 1963.

Rules

1. The Award shall be known as the Corday-Morgan Medal and Prize.

2. The Award shall be made annually to the chemist of either sex and of British nationality who, in the judgement of the Council of the Chemical Society, shall have published during the year in question, and in the immediately preceding five years, the most meritorious contribution to experimental Chemistry, and who, at the date of publication, shall not have attained the age of thirty-six years. The date of publication of any journal shall be deemed to be the date at which the journal was first available to the public.

3. The Award shall not be made more than once to the same candidate. If in any one year two or more candidates are, in the opinion of the Council, of equal merit the Council may award a medal to each such candidate and divide the monetary prize equally between them.

4. The Council may at its discretion suspend the Award in any year in which no suitable candidate presents himself or is brought to the notice of the Council. In the event of such suspension a sum equal to the income otherwise available for the Award in that year shall be invested and added to the capital of the Trust Fund.

5. The Award shall consist of a silver Medal and a monetary Prize of an amount to be determined by Council having regard to the balance of the income of the Trust Fund for the year, after payment of the expenses incidental to the Award.

6. No restrictions shall be placed upon the branch of Chemistry for which the Award is granted, or upon the place in which the work is conducted.

7. The merits of the work of any candidate for the Award may be brought to the notice of the Council either by persons who desire to recommend the candidate or by the candidate himself.

8. Details of the Award shall be published annually in the *Proceedings of the Chemical Society* and elsewhere.

9. Applications, or recommendations for the Award shall be forwarded so that they shall reach the Society not later than the Thirty-first day of December in the year following that for which the Award is to be made. Applications, or recommendations, should be accompanied by the birth certificate of the candidate and a list of papers published by the candidate during the years in question (see Rule 2) and nine reprints (which will be returned) of each paper, or copies of any published work, on which the grant of the Award is to be judged.

The candidate may, if he wishes, submit with his application a statement on the background and main purpose of the research papers on which his application is to be judged, and may refer in such a statement to his previously published work.

10. Each candidate shall give the names of two persons with a knowledge of his work, to whom reference can be made by the Society.

11. The Award shall be presented at a meeting of the Society.

12. If any doubt shall arise as to the correct interpretation of these Rules, the matter shall be decided by the Council of the Society.

13. The Council may from time to time alter or add to the regulations for the administration of the Award, provided that no regulation shall be approved that is contrary to the terms of the Bequest as expressed in the Will of the late Sir Gilbert T. Morgan or to the conditions expressed by the Charity Commissioners for England and Wales.

XIXth INTERNATIONAL CONGRESS OF PURE AND APPLIED CHEMISTRY

LONDON, JULY 10th—17th, 1963

COPIES of the first circular are now available from The Honorary Secretary, XIXth International Congress of Pure and Applied Chemistry, 14 Belgrave Square, London, S.W.1.

The scientific programme of the Congress will consist of some 20 invited congress lectures in addition to a wide range of contributed papers. The papers presented in the division of Organic Chemistry will form the main theme; but certain aspects

of Inorganic Chemistry, Analytical Chemistry, and Applied Chemistry will also be discussed.

Each division of the Congress will comprise a number of sections and a proportion of these will meet concurrently during the period of the meeting. The specific topics to be discussed are outlined below.

Details regarding the submission of papers for the Congress will appear in the second circular to be issued in October, 1962.

Scope of Congress

A. Organic Chemistry

1. Reaction Mechanisms.
2. Physical Methods: to emphasise fundamental developments in techniques and substantial applications to structural problems.
3. Stereochemistry and Conformational Analysis.
4. Modern Aspects of Organometallic and Related Compounds.
5. Developments in Organic Synthesis.
6. Biogenesis.
7. Biologically Important Polymers.
8. Microbiological Products and Antibiotics.
9. Steroids and Terpenoids.

B. Inorganic Chemistry

1. Applications of the Newer Physical Methods (other than *X*-Ray Crystallography) to Structural Inorganic Chemistry: to include electron-spin

resonance, nuclear magnetic resonance, other forms of microwave spectroscopy, and polarography.

2. Inorganic chemistry of the Solid State.
3. Inorganic Chemistry of the Molten State.

C. Analytical Chemistry

1. Trace Analysis.
2. Separation Methods.
3. Electroanalysis.
4. Teaching of Analytical Chemistry.

D. Applied Chemistry

1. Adhesion of Surface Coatings.
2. Applied Chemistry of the Solid State.
3. Food Packaging Materials; Toxicological and Analytical Problems.
4. Industrial Carbon and Graphite.
5. Utilisation and Treatment of Wastes by Biological Methods.

A SYMPOSIUM ON NITROGEN HETEROCYCLIC CHEMISTRY

THIS meeting, arranged by the Hatfield College of Technology, with the support of the Chemical Society, attracted almost two hundred chemists to the College. In two days, May 10th and 11th, this "capacity crowd," as it would have been called in journalistic circles, listened to nine papers. That number in two days is certainly not a record, but is enough of a test of stamina to prove that at least two hundred people in the country take a fairly serious interest in nitrogen-heterocyclic chemistry.

The smooth way in which the conference proceeded demonstrated the excellence of the arrangements made by Dr. R. F. Robbins, Head of the Science Department at Hatfield. To him, and to Mr. E. Roberts, Registrar of the College, all who attended must be grateful. Our gratitude is also due to Dr. W. A. J. Chapman, Principal of the College, for sanctioning the use of the College's premises for the purpose of this meeting.

Heterocyclic chemistry, even when limited to the case of nitrogen compounds, is a subject of endless variety, and the topics discussed illustrated almost the whole range of the organic chemists' preoccupations; from the classical theme of the influence of substituents upon the behaviour of aromatic compounds, through the stereochemical problems of saturated systems, to the study of mechanism and the interpretation of physical properties.

The first session, under the Chairmanship of Professor W. Baker, saw the Symposium off to a brilliant start, with an account from Dr. J. W. Cornforth of his experiments towards a synthesis of vitamin B₁₂. An imaginary hydrolysis of the mole-

cule to give a complex keto-amine led him to consider isoxazoles as intermediates capable of providing such a keto-amine by characteristic reductive fission. The imaginary hydrolysis led on to deeply imaginative, sterically controlled syntheses of the fragments constituting the corners of the vitamin's molecule. At one stage Dr. Cornforth's scheme requires the stitching together of suitable fragments through 1,3-diketone structures, and an interesting side-product of these studies is a 1,3-diketone synthesis through the acylation of a methylene group activated by adjacent carbonyl and pyridinium groups.

Professor P. B. D. de la Mare followed Dr. Cornforth, with a discussion of electrophilic substitution in *N*-heterocycles. The fundamental requirement for progress here is a body of data permitting the quantitative comparison of the reactivities of fully identified substrates with the reactivity of benzene. Electrophilic attack on, say, quinoline, almost certainly occurs at nitrogen in the first instance. However, every electrophile is accompanied by a nucleophile, and in some reactions the isolated product arises from a complex sequence of electrophilic attack, nucleophilic addition, further attack, and elimination. It will clearly be some time before experiment indicates which of the several available theoretical treatments is relevant in the elementary sense of referring to processes which actually occur.

The second session of the meeting, under the Chairmanship of Professor de la Mare, heard Professor W. Baker on Meso-ionic compounds, Dr. J. D. Loudon on the synthesis of heterocyclic compounds by sulphur extrusion, and Dr. A. R. Katritzky on *N*-oxides.

The meso-ionic compounds contain six π -electrons associated with a five-membered ring. It is interesting to reflect, amidst all the current interest in non-benzenoid aromatics, that the sydnones, which fall within the definition of meso-ionic, are probably the only non-benzenoid compounds besides the tropolones, ferrocenes, and azulenes for which aromatic character has been claimed and in which the common electrophilic substitution at carbon have been observed.

Sulphur is a surprising element at any time, but never more so than in the extrusion reactions described by Dr. Loudon. Such extrusions have been observed in passage from 7- to 6-, 6- to 5-, and 5- to 4-membered rings. Dr. Loudon's studies were concerned originally with contraction of 7-membered thiepins, thiazepines, and thiadiazepines to 6-membered rings lacking sulphur. They provided an extraordinary wealth of synthetic materials, and an opportunity for a classical exercise in the study of substituent influences.

The recognition by Ochiai and den Hertog of the potentialities of pyridine 1-oxides was one of the most important developments in heterocyclic chemistry in recent years. Dr. Katritzky brought out the practical importance and theoretical interest of these compounds, showing how these features depend on the unusual ability of the *N*-oxide group both to accept and to donate electrons. The whole battery of physical methods was engaged in putting the comparison of pyridine 1-oxides with pyridine and benzene on a quantitative basis.

After the labours of the first day, the members of the conference were happy to retire to the laboratories of Messrs. Smith, Kline, and French Ltd. at Welwyn Garden City. There, after touring the splendidly equipped laboratories, they enjoyed the most profuse hospitality. The evening was enjoyable and valuable not only because we were able to enjoy the excellent food and splendid wines so generously provided by our hosts, but also because of the opportunity it provided for the renewal of old acquaintances and the beginning of new ones.

Whether or not such an evening helps to prepare for the next day's work is arguable, but there were no mass absences when on the following morning Professor A. Albert introduced the lecturers for the conference's third session; Professor D. H. Hey on new cyclisation reactions, and Dr. A. H. Jackson on porphyrin proton magnetic resonance spectra.

Professor Hey and his colleagues had begun with the aim of extending the Pschorr phenanthrene synthesis to the preparation of phenanthridone. The quite inexhaustible abilities of decomposing diazonium cations for displaying unexpected modes of reaction soon put to an end such limited ambitions. The formation of a spiro-dienone from diazotised

2-amino-*N*-ethyl-4'-methoxybenzanilide was only the first fruit of a rich harvest reaped from the virtuosity of these compounds.

With its large aromatic ring current, the porphin nucleus is a particularly interesting source of proton magnetic resonance spectra. Dr. Jackson showed how the main features of the spectra were related to the nature of the ring substitution. It is clear that proton magnetic resonance spectra will prove invaluable in structural studies in this field, as Dr. Jackson showed in the particular instance of the coproporphyrins. In addition they provide the theoretician with data of great interest.

The last session, under Professor Hey, heard papers from the present writer on quinolizidine stereochemistry, and from Dr. S. F. Mason on the electronic spectra of *N*-heterocycles.

The bicyclic quinolizidines make interesting subjects for the application of conformational arguments, both as regards the equilibria arising in them because of the stereochemical instability of tervalent nitrogen, and because of the influence of steric factors on the kinetic process of quaternary salt formation from these bases. Nuclear magnetic resonance spectra in particular promise to make a unique contribution towards the solution of these stereochemical problems.

Dr. Mason showed how the three types of electronic absorption spectra of interest in the *N*-heteroaromatic series, due to charge transfer, $n \rightarrow \pi^*$, and $\pi \rightarrow \pi^*$ excitation could be discussed in terms of a common model based on benzene orbitals. The correlations made over a large sequence of *N*-heteroaromatic nuclei were of appealing elegance. The introduction of strongly conjugating substituents required the use of the benzyl anion model, but again the unification achieved by surprisingly simple means must appeal strongly to organic chemists.

This Symposium is the third on heterocyclic chemistry to be held in recent years, following meetings at Exeter and in Canberra. In common with other branches of organic chemistry, heterocyclic chemistry grows at an ever increasing rate, and there can be no doubt that other meetings devoted to it will follow frequently in the coming years. It seems doubtful if any of these can be more enjoyable than this recent meeting at Hatfield. Hatfield College of Technology is indeed a particularly pleasant place for a function of this kind; its new and attractive buildings are adorned with numerous works of art, including examples by Barbara Hepworth and Ben Nicholson, which make it clear that the Two-Culture nonsense carries no weight here: it conveys that stimulating impression of active growth, and its staff is skilled in making visitors feel welcome. This was a memorable occasion.

K. SCHOFIELD.

THE BELGIAN CHEMICAL SOCIETY

1887—1962

At the initiative of a group of chemists in the sugar industry there was founded, on April 14th, 1887, the Belgian Association of Chemists which, since January 30th, 1904, has borne the name of Société chimique de Belgique.

Formed originally with the limited aim of solving problems in chemical analysis of sweets, foodstuffs, etc., this organisation has gradually enlarged its horizons and is today devoted to promoting the development of the chemical sciences.

From its inception, the Belgian Chemical Society has been the meeting-place of chemists who have chosen an industrial career and those who, in various capacities, are connected with the University. This peculiar feature is displayed in the fact that the Presidency of the Society is entrusted to a person of note, alternately from the academic and the industrial world.

In order to contribute to the dissemination of the work of its members, the Society publishes a scientific *Bulletin*, the pages of which are open for the results of original research. The subsidies granted for a number of years by the Ministry of National Education and by the Fondation Universitaire testify to the value of this periodical. Published under the title of *Bulletin des Sociétés chimiques belges*, it is edited in collaboration with the Flemish Union of Chemists.

The Society also collaborates in the production of the scientific news reports of the *Industrie Chimique Belge—Belgische Chemische Industrie*, a review published by the Federation of the Belgian Chemical Industries.

The Chemical Society encourages scientific research, not only by facilitating the dissemination of research work, but also by the annual grant of several awards. The latter are given in recognition of the best work by our young chemists in the light of their total research carried out during a period of ten years.

Further, the Central Committee of the Belgian Chemical Society, in collaboration with the Committees of the seven local branches (Brussels, Antwerp, Ghent, Liège, Mons, Charleroi, and Louvain), organise annually some fifty lectures covering the most varied aspects of chemistry.

These lectures are given in turn by Belgian and foreign scientists.

Finally, in common with the Flemish Union of Chemists, The Belgian Chemical Society organises a "Journée des Jeunes" twice a year, at which newly graduated licentiates and doctoral students report the results of their first labours and discuss them in an atmosphere of healthy rivalry.

The Belgian Chemical Society has taken part in a movement, developed at the initiative of the National Commission of Science, presided over by H.M. Leopold III, in favour of more effective support of scientific research by public authorities and of improvement in the contacts between University and Industry.

With this aim, an important meeting was organised by the Society in March, 1958, at which several speakers stressed the urgent need to promote the teaching of science at the secondary and higher levels, to assign larger budgets to university research laboratories, and to develop and stabilise the role of research in industry. A memorandum summarising the conclusions of an extensive enquiry addressed to industrial management and university teaching bodies was published in 1959 and forwarded to the National Commission of Science. The Chemical Society recorded with satisfaction that numerous recommendations drafted in this memorandum have been embodied in the final report of the Commission.

From June 12th to 15th, 1962, on the occasion of the seventy-fifth anniversary of the Belgian Chemical Society, a Symposium devoted to the organic chemistry of natural products will be held under the auspices of the International Union of Pure and Applied Chemistry. To date, we are able to give notice of the presentation of some 150 original communications by chemists of thirty-one nationalities and of seven plenary lectures by eminent scientists, including Lord Todd, Nobel Prize Winner. An academic session and various ceremonies will complete this international gathering, to which H.M. the King of Belgium has granted his distinguished patronage.

A. BRUYLANTS.

COMMUNICATIONS

Signs of Nuclear Resonance Coupling Constants in Saturated Aliphatic Systems

By H. FINEGOLD

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EARLIER studies of the significance of tenuous anomalies in the high-resolution nuclear resonance spectra of diethyl methylphosphonothionate¹ and diethyl sulphite² have evoked much interest,^{3,4} and recently Kaplan and Roberts⁵ have successfully applied an iterative computer programme to the complete analysis of the spectrum of diethyl sulphite, incorporating opposite signs for the vicinal and geminal coupling constants in the input data. This has suggested to us that the important general question of relative signs of coupling constants in saturated aliphatic systems requires complete re-

ship to be established uniquely. Calculations were finally checked against experimental measurements at 5704 gauss.

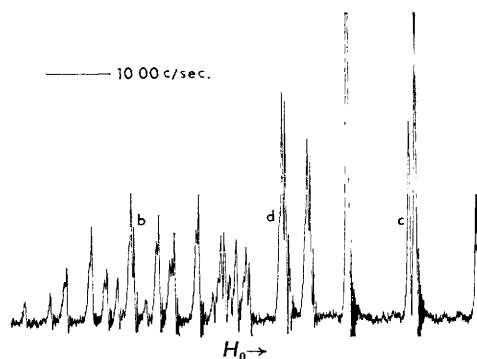
The results of the calculations are in the annexed Table (in c./sec.). The particular features to be noted in the above results are: (1) all three vicinal couplings must be of the same sign, and the signs of the vicinal and geminal couplings must be opposite; (2) there are two long-range couplings, opposite in sign to each other and having a unique relative sign relationship to all other coupling constants in the molecule; and (3) solvent effects are notable, not only in the

Compound	J_{ab}	J_{ac}	J_{ad}	J_{bc}	J_{bd}	J_{cd}	$(\gamma H_0) \cdot (1-\sigma_{ab})$	$(\gamma H_0) \cdot (1-\sigma_{bc})$	$(\gamma H_0) \cdot (1-\sigma_{cd})$
$\text{CH}_3^a\text{-CH}^b\text{Cl-CH}^c\text{H}^d\text{Cl}$ (20% in CCl_4)	∓ 6.56	± 0.10	∓ 0.29	∓ 9.05	∓ 4.65	± 11.10	147.02	34.10	14.48
$\text{CH}_3^a\text{-CH}^b\text{Br-CH}^c\text{H}^d\text{Br}$ (20% in CCl_4)	∓ 6.49	± 0.14	∓ 0.41	∓ 10.82	∓ 4.01	± 9.79	140.85	41.10	20.32
$\text{CH}_3\text{-CHBr-CH}_2\text{Br}$ (neat)	∓ 6.52	± 0.15	∓ 0.31	∓ 9.76	∓ 4.20	± 10.04	141.40	41.25	17.49
$\text{CH}_3\text{-CHBr-CH}_2\text{Br}$ (20% in C_6H_6)	∓ 6.55	± 0.15	∓ 0.30	∓ 10.00	∓ 4.20	± 9.86	137.76	40.46	17.65

examination. We here report on a study of asymmetric propane derivatives, including detailed results for 1,2-dichloropropane and 1,2-dibromopropane and indicative results for several 1,1-disubstituted propanes.

The 60 mc./sec. room temperature spectra of the dibromo- (see Figure) and dichloro-propane are relatively complex. This is attributable to the centre of asymmetry in the molecule, which is necessarily attended by three distinctively valued potential-energy minima in a 360° rotation about the $\text{C}_1\text{-C}_2$ bond. The unequal shielding values of the methylene protons give rise to an A_3BCD type spin system. In order to analyse this six-spin system, a small number of trial Hamiltonians were constructed, with approximations based on low degrees of mixing. Corrections terms were then introduced to achieve precise convergence between computed⁶ and experimental intensities and frequencies. The sensitivity of certain of the calculated intensities and frequencies to signs of the coupling constants permitted the sign relation-

shielding parameters,^{1,2} but also in the coupling constants.⁷ The geminal coupling, which would be expected to show no solvent effects if its magnitude



Nuclear magnetic resonance spectrum (60 mc./sec.) of 1,2-dibromopropane taken in 20% (v/v) CCl_4 solution (high-field band deleted). Indicated band origins correlate with labelled protons.

¹ Finegold, *J. Amer. Chem. Soc.*, 1960, **82**, 2641.

² Finegold, *Proc. Chem. Soc.*, 1960, 283.

³ Shafer, Davis, Vogel, Nagarajan, and Roberts, *Proc. Nat. Acad. Sci. U.S.A.*, 1961, **47**, 49.

⁴ Waugh and Cotton, *J. Phys. Chem.*, 1961, **65**, 562.

⁵ Kaplan and Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 4666.

⁶ Computations made with IBM 7090; programme written chiefly by A. A. Bothner-By, C. Naar-Colin, and their associates.

⁷ Freeman and Pachler, *Mol. Phys.*, 1962, **5**, 85.

depended principally on the methylenic HCH angle (whose value can be assumed constant throughout widely varying rotamer populations), shows substantial variation.

Three 1,1-disubstituted propanes of low symmetry—chloronitropropane, phenylpropanol, and ethylpropanol (pentan-3-ol)—were studied. Results of calculations on the experimental spectra indicated that the average magnitude of the vicinal coupling constants associated with the methyl group and geminal coupling constants was 7.1 and 10.6 c./sec., respectively, and that the relative signs of the vicinal

and geminal couplings were opposite in every case.

It appears that the consistent relative sign relationship in all of the above systems may be safely generalised, and opposite relative signs of the vicinal and the geminal coupling constants may be regarded as entirely typical of saturated aliphatic systems. If the valence-bond theory of coupling mechanism,⁸ which predicts like signs for geminal and vicinal couplings, is to be retained in its essential features, a greater contribution of polarisation factors to the sigma network associated with the coupling may perhaps have to be postulated.

(Received, April 16th, 1962.)

⁸ Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

The Unique Carbohydrate Portion of the Cardiac Glycoside, Gomphoside

By R. G. COOMBE and T. R. WATSON

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THE cardiac glycoside, gomphoside,¹ obtained from *Asclepias fruticosa*, is similar to several other glycosides, e.g., *Calotropis* glycosides obtained from the Asclepiadaceae,² in that it cannot be hydrolysed by any of the usual methods without decomposition of both the carbohydrate and the aglycone.

Evidence has been obtained which indicates that the carbohydrate of gomphoside has the unique structure shown in (I), i.e., is derived from a 4,6-di-deoxyhexosone. Gomphoside forms a diacetate and requires 1 mol. of periodate to produce compound (II), which forms a mono-2,4-dinitrophenylhydrazone. Acid hydrolysis of this compound (II) and

lysis of compound (II) in 2N-hydrochloric acid saturated with 2,4-dinitrophenylhydrazine gave a mixture of hydrazones which were identified as the derivatives of crotonaldehyde and glyoxylic acid.

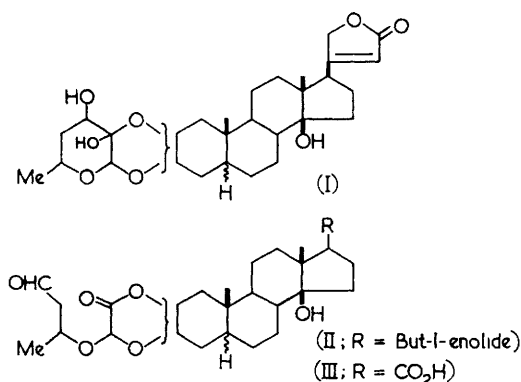
Compound (II) was not saponified by potassium hydrogen carbonate. Reduction with sodium borohydride and subsequent hydrolysis gave (–)-butane-1,3-diol, which was characterised as such and as the diphenylurethane. The presence of a $\text{CH}_3\text{CH}\cdot\text{O}$ group is confirmed by a doublet in the nuclear magnetic resonance spectrum of the glycoside having $\tau = 8.61$ and $J = 7$ c.p.s.

The ætanic acid (III) obtained by the degradation of the butenolide ring by Hunger and Reichstein's method³ shows infrared carbonyl at 1740, 1725, and 1715 cm^{-1} (in CHCl_3) which correspond to the δ -lactone, aldehyde, and carboxylic acid group, respectively. In addition, compound (II) could not be methylated with diazomethane.

The aglycone which is produced on hydrolysis of compound (II) contains a vicinal glycol system, as shown by periodate oxidation and is postulated as the $2\alpha,3\beta$ dihydroxy-5 ξ -carda-14,20(22)-dienolide.

We are indebted to Dr. J. N. Shoolery for running the nuclear magnetic resonance spectrum on a Varian Associates A60 instrument with deuteriochloroform as solvent and tetramethylsilane as internal reference.

(Received, April 16th, 1962.)



steam-distillation of the products into 2,4-dinitrophenylhydrazine reagent gave a quantitative yield of crotonaldehyde 2,4-dinitrophenylhydrazone. Hydro-

¹ Watson and Wright, *Austral. J. Chem.*, 1957, **10**, 79.

² Hesse and Reicheneder, *Annalen*, 1936, **526**, 252; cf. Hassall and Reyle, *J.*, 1959, 85.

³ Hunger and Reichstein, *Helv. Chim. Acta*, 1952, **35**, 1073.

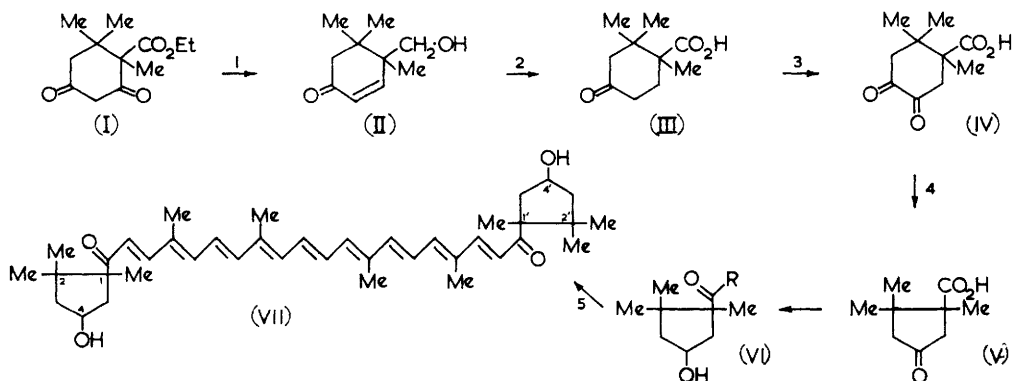
Stereochemistry of Capsorubin and Synthesis of its Optically Inactive Epimers

By R. D. G. COOPER, L. M. JACKMAN, and B. C. L. WEEDON

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CAPSORUBIN and capsanthin, which are believed to be derived from zeaxanthin, have characteristic end-groups that have been allocated a cyclopentane structure (cf. VII).¹⁻⁵ Whereas we favoured a *trans*-configuration for the two oxygen substituents on the five-membered ring from infrared light absorption¹ and nuclear magnetic resonance considerations,⁶ Karrer *et al.*³ claim to have proved a *cis*-relationship. We have now confirmed the novel ring structures, and established the *trans*-configuration of the oxygen substituents, by synthesis of optically inactive forms

R = Me). These condensed with crocetindial⁸ to give the "all-*trans*"-carotenoids (VII), presumably as mixtures of diastereoisomers of the DL- and *meso*-type. That from the *cis*-alcohol (VI; R = OH) had m.p. 203°, λ_{\max} . (in C₆H₆) 522, 488, and 457 (inflection) m μ , ν_{\max} . (in CHCl₃) 1650, 1582, 1541, 1006, 980, and 970 cm.⁻¹, τ (in CDCl₃) 9.03, 8.85, and 8.00 (relative intensities 2:1:2). That from the *trans*-alcohol (VI; R = OH) had m.p. 144–146°, λ_{\max} . (in C₆H₆) 519, 486 (ϵ 120,000), and 455 (inflection) m μ , ν_{\max} . (in CHCl₃) 3623, 1664, 1582,



Reagents: 1, (i) EtOH-*p*-Me-C₆H₄-SO₃H; (ii) LiAlH₄, (iii) H⁺. 2, (i) H₂-Pd-C, (ii) CrO₃. 3, O₂-KOBu^t. 4, (i) 5% KOH, (ii) H₃PO₄-NaBiO₃. 5, Crocetindial-5% KOH-EtOH.

of capsorubin and epicapsorubin.* The full stereochemistry of natural capsorubin is thus defined, since the absolute configuration at C-1 and C-1' is known,⁴ and those of the six-membered rings in capsanthin and zeaxanthin may now be provisionally assigned on reasonable biogenetic grounds.

Autoxidation of the keto-acid (III), m.p. 188°, obtained from the diketone-ester⁷ (I) via the keto-alcohol (II), m.p. 151°, gave the diosphenol (IV), m.p. 137°, which was converted into the keto-acid (V), m.p. 224°. Borohydride reduction yielded the *cis*- (isolated *via* the lactone, m.p. 181°) and the *trans*-hydroxy-acid (VI; R = OH), m.p. *ca.* 160° (decomp.) and 222°, respectively, which on treatment with methyl-lithium gave the hydroxy-ketones (VI;

1546, 1006, 980, and 970 cm.⁻¹, τ (in CDCl₃) 9.15, 8.80, 8.62, and 8.02 (relative intensities 1:1:1:2); unlike the above epimer, the latter did not separate on thin-layer chromatography from natural capsorubin, m.p. 201°, λ_{\max} . (in C₆H₆)⁹ 520, 486, and 455 m μ , ν_{\max} . (in CHCl₃)¹⁰ 3616, 1664, 1582, 1542, 1007, 980, and 970, τ (in CDCl₃)¹ 9.16, 8.80, 8.63, and 8.03 (relative intensities 1:1:1:2).

The authors thank Roche Products Limited and Hoffmann-La Roche Limited for chemicals and financial support (to R.D.G.C.). They are indebted to Varian Associates for the nuclear magnetic resonance spectra (methyl bands only are quoted).

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* The isomer differing from capsorubin in the configuration at both C-4 and C-4' is termed "epicapsorubin."

¹ Barber, Jackman, Warren, and Weedon, *Proc. Chem. Soc.*, 1960, 19; *J.*, 1961, 4019.

² Entschel and Karrer, *Helv. Chim. Acta*, 1960, **43**, 89.

³ Faigle and Karrer, *Helv. Chim. Acta*, 1961, **44**, 1257.

⁴ Faigle and Karrer, *Helv. Chim. Acta*, 1961, **44**, 1904.

⁵ Cholnoky and Szabolcs, *Experientia*, 1960, **43**, 483.

⁶ Unpublished work.

⁷ Crossley, *J.*, 1901, 138.

⁸ Isler, Gutmann, Lindlar, Montavon, Rüegg, Ryser, and Zeller, *Helv. Chim. Acta*, 1956, **39**, 463.

⁹ Karrer and Jucker, "Carotinoide," Birkhäuser, Basle, 1948.

¹⁰ Warren and Weedon, *J.*, 1958, 3972.

Pyrazolines from Tetracyanoethylene

By JUAN BASTÚS and JOSÉ CASTELLS

(DEPARTAMENTO DE QUÍMICA ORGÁNICA DE BARCELONA, PATRONATO "JUAN DE LA CIERVA"
DE INVESTIGACIÓN TÉCNICA (C.S.I.C.), UNIVERSIDAD DE BARCELONA, SPAIN)

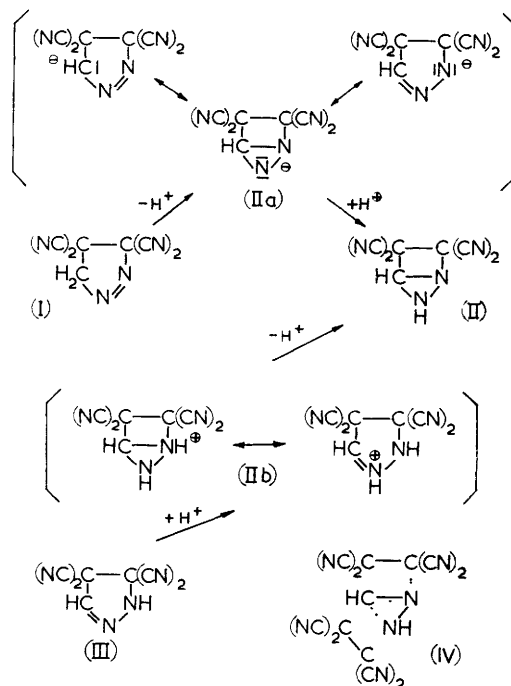
WHEN tetracyanoethylene in dry ether* suspension¹ is treated with one mol. of diazomethane in KOH-dried ether under nitrogen, 3,3,4,4-tetracyano-1-pyrazoline (I) (termed pyrazoline-I), m.p. 133° (decomp.), is obtained in 72% yield, the analytical sample being prepared by washing with benzene; this product has an infrared K=N stretching band at 1595 cm.⁻¹ (ref. 2a) but no N-H stretching band. Pyrazoline-I evolves nitrogen even at room temperature† and after 16 days is completely transformed into 1,1,2,2-tetracyanocyclopropane¹ (infrared spectral evidence). This extreme ease of "pyrolysis" must be related to the presence of the four strong electron-attracting cyano-substituents and to the presence of "preformed" N₂ in a 1-pyrazoline (contrast the stability of isomeric pyrazolines reported below).

Pyrazoline-I, (very carefully washed in the dark with dry benzene to remove all traces of tetracyanoethylene), slowly dissolves when treated with dry ether. After 15 minutes, filtration and evaporation afford an isomer, "pyrazoline"-II, m.p. 120° (decomp.), which infrared spectrum includes an N-H band at 3295 cm.⁻¹. "Pyrazoline"-II, when treated for about 90 minutes with a 5% solution of tetracyanoethylene in dry ether, yields, after removal of the solvent, a third isomer, pyrazoline-III, m.p. 126° (decomp.); the analytical sample was prepared by washing with benzene; its infrared spectrum also includes an N-H band (at 3333 cm.⁻¹).‡ Wet ether or dry ether containing a trace of hydrogen chloride isomerises pyrazoline-III back to "pyrazoline"-II. Both substances can be kept for several weeks with no apparent alteration.

Structures (II) and (III), respectively, seem to us the best choice for the two isomeric pyrazolines with an N-H bond. We assign the conventional structure of 4,4,5,5-tetracyano-2-pyrazoline (III) to pyrazoline-III because in the 1700–1500 cm.⁻¹ region of its spectrum there is a medium band at 1618 cm.⁻¹ which can be due to C=N st. and a weak one at 1595 cm.⁻¹ assignable to N-H b.;^{2b} "pyrazoline"-II, which shows a weak band at 1592 cm.⁻¹ (N-H b.), is consequently given the structure 2,2,3,3-tetracyano-1,5-diazabicyclo[2,1,0]pentane (II). To our knowledge, the diazabicyclopentane structure has not previously

been considered as a possible alternative for N-H pyrazolines, but there seems to be no theoretical objection to it; the recent preparation of one of the two possible isomers of cyclodiazomethane³ (diazirine) has bearing on this point.

The Chart summarises our views on the mechanisms of the reported isomerisations: an important analogy for the hybrid-ion formulations of anion (IIa) and cation (IIb) [and their subsequent evolution to structure (II) instead of (III)] is to be found



in the work of Silversmith and Roberts.⁴ The presence of four cyano-groups explains the ease of isomerisation of pyrazoline-I by such a weak basic agent as ether. The catalytic action of tetracyanoethylene in the conversion of "pyrazoline"-II into pyrazoline-III should be probably traced to its strong π -acid character,⁵ which could justify the formation of an intermediate such as (IV).

* Throughout, by dry ether is meant freshly distilled sodium-dried ether.

† Scratching of the substance may induce an explosive decomposition.

‡ The combined isomerisations explain why ether treatment of pyrazoline-I, which has not been carefully washed, leads directly to pyrazoline-III.

¹ Cf. Scribner, Sausen, and Prichard, *J. Org. Chem.*, 1960, **25**, 1440.

² Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 2nd edn., 1958, (a) p. 271, (b) p. 256.

³ Schmitz and Ohme, *Chem. Ber.*, 1962, **95**, 795.

⁴ Silversmith and Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 4083.

⁵ Merrifield and Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

During our work it was also realised that "pyrazoline"-II in dry benzene solution and under normal working conditions was completely isomerised to pyrazoline-III, but that the former could be recovered unaltered if a benzene solution was kept (60 min.) in the dark. This result can be explained if it is assumed that, for a benzene solution, light induces an incipient fragmentation of "pyrazoline"-II with formation of tetracyanoethylene;⁶ it is tempting to

accept that the π -basic properties of benzene play a role in facilitating this fragmentation ("pyrazoline"-II is stable in ether).

Infrared spectra were recorded as KBr pellets. We thank Professor J. Pascual for suggesting this work and for his interest and advice, Dr. F. Serratos for helpful comments, and Messrs. DuPont de Nemours and Co. for a gift of tetracyanoethylene. (Received, March 12th, 1962.)

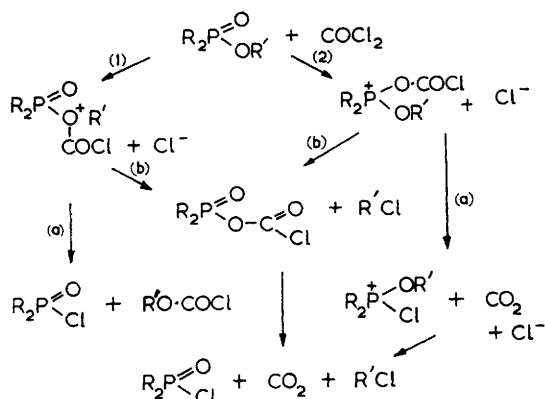
⁶ Cf. Rinehart and Van Auken, *J. Amer. Chem. Soc.*, 1960, **82**, 5251.

The Mechanism of Reaction of Carbonyl Chloride with Alkyl Phosphinates

By M. GREEN and R. F. HUDSON

(CYANAMID EUROPEAN RESEARCH INSTITUTE, GENEVA)

In order to obtain direct information on the relative nucleophilic reactivity of the two kinds of oxygen atoms in esters of quinquivalent phosphorus, the reaction between carbonyl chloride and a phosphinate ester with one of the oxygen atoms labelled with ¹⁸O has been investigated. In general, the annexed mechanisms are possible.



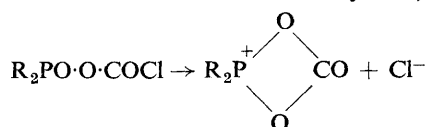
Mechanism 1(a) can be neglected since the corresponding chloroformate, which is stable under the reaction conditions, is not formed.

In order to differentiate between the other possibilities, benzyl [¹⁸O]alcohol was prepared¹ and converted into the ester by reaction with methylphenylphosphinyl chloride.

After reaction with a saturated solution of carbonyl chloride in carbon tetrachloride, the phosphinyl chloride was isolated and converted into the corresponding phosphinic acid. The lack of ¹⁸O exchange in this kind of reaction is now well established,² and is further substantiated by the present results. Treat-

ment with di-*p*-tolylcarbodi-imide gave the corresponding urea, which, on pyrolysis at 350° in the presence of activated bronze powder,³ gave a quantitative yield of carbon dioxide.

From water containing 1.70 atom % of ¹⁸O, carbon dioxide containing 0.833 (± 0.02) atom % was obtained. In view of the fact that half of the ¹⁸O is lost in the reaction of the phosphinic acid with the carbodi-imide, it follows that the phosphinyl chloride is produced with no change in isotope content (within the experimental error). The reaction therefore proceeds by mechanism (2) with the phosphoryl-oxygen atom as the nucleophilic centre, as suggested by Cadogan.³ The results also discount the possibility of the formation of a cyclic intermediate⁴ which could be formed from the mixed anhydride, viz.:



The reaction of carbonyl chloride with (+)-1-methylheptyl methylphenylphosphinate ($\alpha_D^{22} + 4.46^\circ$, homogeneous) prepared from (–)-1-methylheptyl alcohol ($\alpha_D^{22} - 7.6^\circ$, homogeneous) gave (+)-1-methylheptyl chloride, b.p. 55–56°/10 mm., $\alpha_D^{22} + 29.3^\circ$, homogeneous (yield, 90%) (Found: Cl 23.5. Calc. for C₈H₁₇Cl: Cl, 23.8%), and methylphenylphosphinyl chloride. This observation shows that the alkyl chloride is produced by an S_N2 displacement on a quasiphosphonium intermediate by chloride ions as shown in the above scheme.

We thank Dr. E. R. S. Winter of John & E. Sturge Ltd., Birmingham, for carrying out the ¹⁸O analyses. (Received, April 19th, 1962.)

¹ Von Doering and Dorfman, *J. Amer. Chem. Soc.*, 1953, **75**, 5595.

² Halmann, *J.*, 1959, 305.

³ Cadogan, *J.*, 1961, 3067.

⁴ Aaron, Uyeda, Frack, and Miller, *J. Amer. Chem. Soc.*, 1962, **84**, 617.

Tris(tri-*p*-fluorophenylphosphine)platinum(0)

By A. D. ALLEN and C. D. COOK

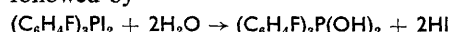
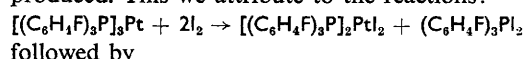
(DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO, TORONTO, CANADA)

It has recently been reported¹ that the triphenylphosphine complexes of platinum(0) described by Malatesta and Cariello² contain hydrogen and should be regarded as hydrides of bivalent platinum. During an investigation into platinum complexes containing substituted triarylphosphines, we have prepared an unusually stable compound of this type which appears to be tris(tri-*p*-fluorophenylphosphine)platinum(0).

Treatment of an ethanolic suspension of *cis*-dichlorobis(tri-*p*-fluorophenylphosphine)platinum(II) with hydrazine hydrate produces a golden-yellow precipitate, m.p. 136–139° (decomp.) (Found: C, 56.2; H, 3.2. C₅₄H₃₆F₉P₃Pt requires C, 56.7; H, 3.2%). This compound is stable in air and can be heated to 65° under a vacuum for several hours without detectable decomposition. In a 2% solution in benzene the molecular weight is 680, unchanged between 5 minutes and 5 hours. Nuclear magnetic resonance and infrared spectra show no sign of hydrogen bound to platinum.

Treatment with iodine in benzene followed by extraction with water and titration with alkali showed

that approximately two equivalents of acid had been produced. This we attribute to the reactions:



since similar treatment of the free phosphine also produces two equivalents of acid.

In carbon tetrachloride the compound decomposes without producing the chloroform expected from the reaction of a hydride complex.

No tetrakis-derivatives of platinum with tri-*p*-fluorophenylphosphine or tri-*p*-chlorophenylphosphine² have been isolated. The tendency of these substituted phosphines to accept *d*-electrons from the metal will be greater than that of triphenylphosphine. It appears that this stabilises the tri-coordinated compound and also discourages addition of a fourth phosphine.

We thank Dr. S. S. Danyluk for examination of the nuclear magnetic resonance spectrum.

(Received, April 4th, 1962.)

¹ Chopoorian, Lewis, and Nyholm, *Nature*, 1961, **190**, 528.

² Malatesta and Cariello, *J.*, 1958, 2323.

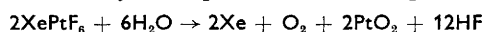
Xenon Hexafluoroplatinate(V) Xe⁺[PtF₆]⁻

By NEIL BARTLETT

(DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, B.C., CANADA)

A RECENT Communication¹ described the compound dioxygenyl hexafluoroplatinate(V), O₂⁺PtF₆⁻, which is formed when molecular oxygen is oxidised by platinum hexafluoride vapour. Since the first ionisation potential of molecular oxygen,² 12.2 eV, is comparable with that of xenon,² 12.13 eV, it appeared that xenon might also be oxidised by the hexafluoride.

Tensimetric titration of xenon (AIRCO "Reagent Grade") with platinum hexafluoride has proved the existence of a 1:1 compound, XePtF₆. This is an orange-yellow solid, which is insoluble in carbon tetrachloride, and has a negligible vapour pressure at room temperature. It sublimes in a vacuum when heated and the sublimate, when treated with water vapour, rapidly hydrolyses, xenon and oxygen being evolved and hydrated platinum dioxide deposited:



The composition of the evolved gas was established by mass-spectrometric analysis.

Although inert-gas clathrates have been described, this compound is believed to be the first xenon charge-transfer compound which is stable at room temperatures. Lattice-energy calculations for the xenon compound, by means of Kapustinskii's equation,³ give a value ~ 110 kcal. mole⁻¹, which is only 10 kcal. mole⁻¹ smaller than that calculated for the dioxygenyl compound. These values indicate that if the compounds are ionic the electron affinity of the platinum hexafluoride must have a minimum value of 170 kcal. mole⁻¹.

The author thanks Dr. David Frost for mass spectrometric analyses and the National Research Council, Ottawa, and the Research Corporation for financial support

(Received, May, 4th 1962.)

¹ Bartlett and Lohmann, *Proc. Chem. Soc.*, 1962, 115.

² Field and Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, 1957, pp. 114–116.

³ Kapustinskii, *Quart. Rev.*, 1956, **10**, 284.

Fourteen-membered Hydrogen-bonded Dimers of Some *meta*-Substituted Phenols

By F. A. L. ANET and J. M. MUCHOWSKI

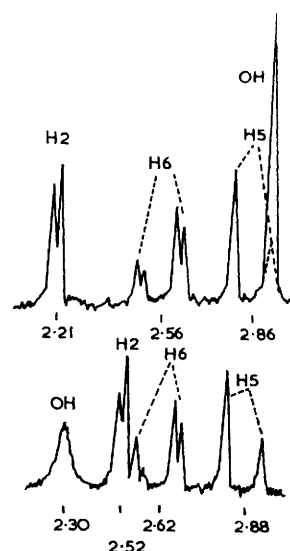
(DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OTTAWA, OTTAWA 2, CANADA)

ALTHOUGH phenols are known to associate in non-polar media by hydrogen-bonding, the aggregates so formed have no great stability.¹ We have now found that phenols with *meta*-substituents such as methoxycarbonyl or nitro-groups form unexpectedly stable dimers in non-polar solvents. Infrared and nuclear magnetic resonance studies indicate that the dimers contain two hydrogen bonds in a geometrically favourable fourteen-membered ring (e.g., I).

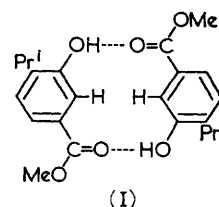
The effect was discovered during analysis of the nuclear magnetic resonance spectrum (60 Mc./sec.) of methyl 3-hydroxy-4-isopropylbenzoate (II) in carbon tetrachloride solution (0.27M). The bands of the aromatic protons were assigned (see Figure) on the basis of the expected coupling constants ($J_o = 6-8$, $J_m = 1.5-2$, $J_p < 1$ c./sec.), and analysis of the spectrum as an ABX system. However, the relative chemical shifts thus found for the aromatic protons were unexpected. From the effects of substituents,² it was expected that H-2 and H-6 would have very similar chemical shifts, with H-2 at perhaps very slightly higher field than H-6, whereas the assignments made on the basis of coupling constants placed H-2 at much lower field than H-6.

This anomaly was resolved when it was found that the chemical shift of H-2 was concentration-dependent, although only at such extremely low concentrations that the limit of the dilution shift could not be observed. A more satisfactory way of breaking the self-association was by addition of acetone or methanol. The addition of about one molar proportion of methanol (concn. ca. 1% v/v) resulted (see Figure) in a large upfield shift in the position of H-2, with little shift in H-6 and practically no shift in H-5. The phenolic hydroxyl proton became broad because of exchange with the methanol-hydroxyl proton and was shifted to low field because of the basicity of methanol. With the addition of a little more methanol, H-2 became practically coincident with H-6.

These effects are most simply explained if two molecules of the monomer are involved in a hydrogen-bonded dimer of structure (I). In this, each H-2 experiences the ring-current³ effect of two benzene rings, whereas in the monomer (or approximately so in a non-cyclic dimer) H-2 is affected by only one benzene ring. Whether structure (I) is



Nuclear magnetic resonance spectra of methyl 3-hydroxy-4-isopropylbenzoate. Top, in carbon tetrachloride. Bottom, in carbon tetrachloride containing 1% by volume of methanol. The chemical shifts in both cases are in p.p.m. with internal tetramethylsilane at 10.00. The OH bands were located by O-deuteration. The high-field regions of the spectra are not shown.



planar or not, the ring-current effect is of the required magnitude and direction.

The infrared spectrum of the ester was studied in carefully dried carbon tetrachloride solution at a path length of 5 cm. Except at concentrations below 10^{-4} M, two bands (3455 and 3613 cm^{-1}) were observed. By application of the treatment⁴ of Liddel and Becker, the equilibrium constant ($K = [\text{dimer}]/$

¹ Pimentel and McClellan, "The Hydrogen Bond," Freeman and Co., London, 1960, p. 377.

² Garnett, Henderson, Sollich, and Tiers, *Tetrahedron Letters*, 1961, 516.

³ Pople, Schneider, and Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 180.

⁴ Liddel and Becker, *Spectrochim. Acta*, 1958, 10, 70.

[monomer]²) was calculated to be 463 ± 10 mole/l. and was constant over a ten-fold concentration range. By comparison,¹ K for phenol in carbon tetrachloride has the value of about 1 mole/l.

For methyl *m*-hydroxybenzoate, K was equal to 544 ± 10 mole/l. In the case of *m*-nitrophenol, hydrogen bonding also persisted to low concentrations but K was not calculated. The nuclear mag-

netic resonance spectra of these compounds were too complicated for simple analysis, although marked changes were observed on addition of small amounts of methanol.

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Ion-pair Formation in Aqueous Solutions of Organic Electrolytes

By A. PACKTER and M. DONBROW

(SCHOOL OF PHARMACY, CHELSEA COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON)

SEVERAL workers¹ have reported marked interaction between long-chain aliphatic ammonium cations and arenesulphonate anions but the phenomenon has not been systematically studied.

The alkyltrimethylammonium salts of some simple arenesulphonic acids were prepared in aqueous solution by neutralisation of the acid by the appropriate base and the conductivities were measured by the usual techniques over the concentration range 10^{-4} N up to the solubility limit at 25° (10 – 200×10^{-4} N). The results are presented in the Figures. In the benzenesulphonic acid series, only the decyltrimethylammonium salt gave a Λ - c plot which deviated from the theoretical Onsager-Falkenhagen

equation.² However, the Λ - c plots for the salts of naphthalene-1-, anthraquinone-1-, and azobenzene-4-sulphonic acid deviated significantly from the theoretical curves. (The salts of anthracene-1-sulphonic acid did not give a suitable range of concentrations.) Pronounced ion-pair formation was indicated.

The degree of dissociation (α) at various salt concentrations was obtained from the Onsager-Falkenhagen equation:³

$$\Lambda = \Lambda_{\infty} - (B_2 + B_1\Lambda_{\infty})(\alpha c)^{0.5}/(1 + \kappa a)$$

(In these preliminary calculations, dimerisation effects have been neglected.)

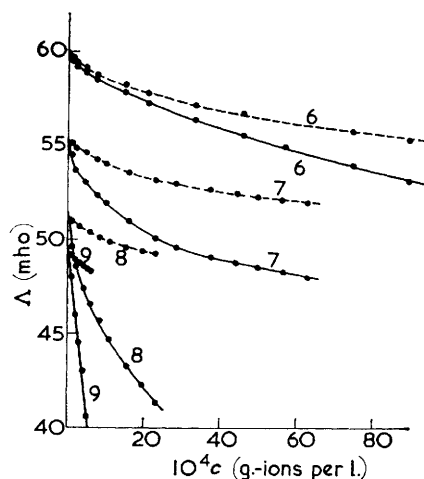
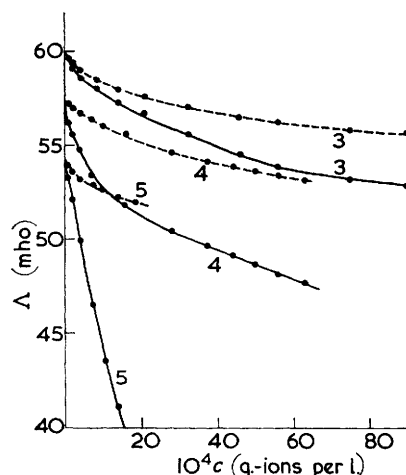
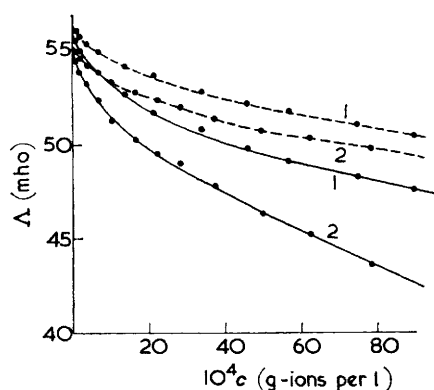
Curves no.	Ar·SO ₃ ·NMe ₃ R Ar	R	<i>I</i> (Å)	<i>K</i> (g.-ions per l.)	−Δ <i>G</i> ° <i>R</i> / <i>T</i> (kcal. per g. ion.)
—	Ph	Bu ⁿ	4.2	>0.3	<1
—	„	C ₆ H ₁₃	4.2	>0.3	<1
—	„	C ₈ H ₁₇	4.2	>0.3	<1
—	„	C ₁₀ H ₂₁	4.2	0.140	1.8
—	1-C ₁₀ H ₇	Bu ⁿ	5.2	>0.3	<1
—	„	C ₆ H ₁₃	6.6	>0.3	<1
1	„	C ₈ H ₁₇	7.2	0.140	1.8
2	„	C ₁₀ H ₂₁	7.2	0.049	2.7
—	C ₁₀ H ₇ O ₂ *	Bu ⁿ	5.2	>0.3	<1
3	„	C ₆ H ₁₃	6.6	0.103	2.3
4	„	C ₈ H ₁₇	8.0	0.040	3.2
5	„	C ₁₀ H ₂₁	9.4	0.0038	5.7
6	C ₁₂ H ₉ N ₂ †	Bu ⁿ	5.2	0.182	1.7
7	„	C ₆ H ₁₃	6.6	0.051	2.9
8	„	C ₈ H ₁₇	8.0	0.0098	4.6
9	„	C ₁₀ H ₂₁	9.4	0.00024	8.4

* Anthraquinone-1-sulphonate.

† Azobenzene-4-sulphonate.

¹ Colichman, *J. Amer. Chem. Soc.*, 1950, **72**, 1834; Mukherjee and Mysels, *ibid.*, 1955, **77**, 2937.

JUNE 1962



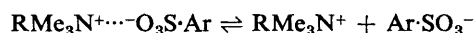
Plots of conductivity against concentration. Full lines are experimental, broken lines are calculated. Numerals key the substances listed in the Table.

² Robinson and Stokes, "Electrolyte Solutions," Butterworths, 1959, Chapter 7, p. 144.

³ Coates and Rigg, *Trans. Faraday Soc.*, 1961, **57**, 1637.

⁴ Higuchi, *J. Amer. Pharm. Assoc.*, 1957, **46**, 21.

Dissociation constants (K) for the equilibria



were then calculated.

Average K and $-\Delta G^\circ$ values are summarised in the Table, together with values of l , the length of "overlapping" organic sections³ common to the two ions of each salt (as measured from Courtauld models). Generally, l is determined by the long axis of the organic section of the smaller ion.

The $-\Delta G^\circ$ values increase with the length of "overlapping" organic portions common to the cation and anion of the salt and with the degree of "coacervation"⁴ of the whole salt from the aqueous phase.

The association is evidently caused predominately by interaction between the organic portions of the ions.

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Intermolecular Charge-transfer Bonds in *m*-Bromonitrobenzene

By T. L. CHARLTON and J. TROTTER

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MUCH attention has been devoted to complexes between halogen molecules, with a halogen atom acting as an electron acceptor, and donor molecules possessing lone pairs or π -electrons; in these there are short intermolecular distances indicative of charge-transfer bonds.¹ We have now found a

similar close approach in an aromatic halogen derivative, *m*-bromonitrobenzene.

Crystals of *m*-bromonitrobenzene are orthorhombic with four molecules in a unit cell of dimensions $a = 5.92$, $b = 21.52$, $c = 5.34$ Å, space group $Pbn2_1$; the structure has been determined by two-

¹ Hassel and Rømming, *Quart. Rev.*, 1962, **16**, 1.

dimensional *X*-ray methods. The molecule is planar within the limits of experimental error. There is an unusually short intermolecular contact involving a bromine atom and an aromatic ring; the bromine atom of each molecule is situated exactly above the midpoint of, and at a distance of 3.30 Å from, the C₁-C₆ bond of a molecule related to the first by the

glide plane operation *n*, the C-Br...C angle being 169°. The Br-C₁ and Br-C₆ contacts are 3.38 Å, in comparison with a van der Waals separation of 3.65 Å, and are thus indicative of charge-transfer bonds, which join the molecules together in chains along [101]. All the other intermolecular contacts are equal to, or greater than, the normal van der Waals

separations; the perpendicular distance between the planes of molecules related by translation *c* is 3.40 Å, close to the spacing in graphite.

The bromine-ring separation is very similar to the distance in the Br₂-benzene complex (3.36 Å), but in the latter each bromine atom is symmetrically situated with respect to all the C-C bonds of a particular aromatic ring.¹ The situation in *m*-bromonitrobenzene is quite different, and more closely related to that in the benzene-AgClO₄ complex, where there is interaction between silver ions and particular C-C bonds.²

The authors thank the National Research Council of Canada and the President's Research Fund, University of British Columbia, for financial support.

(Received, April 24th, 1962.)

² Smith and Rundle, *J. Amer. Chem. Soc.*, 1958, **80**, 5075.

The Structure of Gedunin

By Miss S. A. SUTHERLAND, G. A. SIM, and J. MONTEATH ROBERTSON

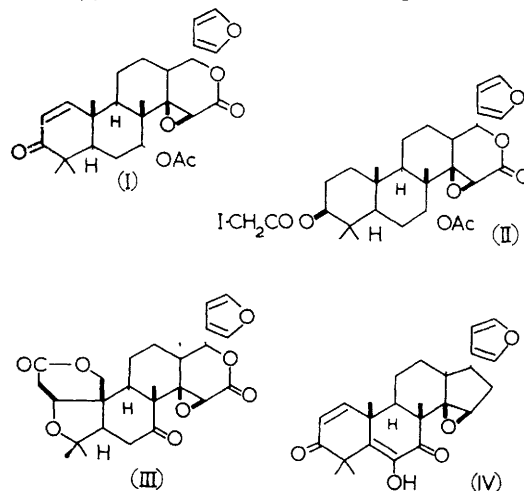
(CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW, W.2)

HALSALL and his co-workers¹ isolated from the heartwood of the West African timber *Entandrophragma angolense* a crystalline lactone, C₂₈H₃₄O₇, which they named gedunin; analogies with the chemistry of limonin² led them to propose³ (I) as the likely structure.

We have carried out an *X*-ray analysis of dihydrogedun-3β-yl iodoacetate, kindly supplied by Drs. T. J. King and F. E. King, who isolated dihydrogedunin from the heartwood of *Guarea thompsonii* and our *X*-ray results establish conclusively the constitution and relative stereochemistry shown in (II). Since gedunin is an αβ-unsaturated ketone³ our results also establish that gedunin is correctly formulated as (I). Gedunin is clearly a triterpenoid of the euphol⁴ type, intermediate in oxidation pattern between limonin^{2,5} (III) and cedrelone⁶ (IV).

Dihydrogedun-3β-yl iodoacetate crystallises in the orthorhombic system, space group *P*₂₁₂₁₂₁, with four molecules of C₃₀H₃₉IO₈ in a unit cell of dimensions *a* = 21.52, *b* = 10.57, *c* = 12.96 ± Å. In all 1201 independent structure amplitudes were measured. The crystal, and hence molecular, structure was

elucidated by Fourier methods. The value of *R* is now 22% and refinement is continuing.



We are indebted to Miss J. A. Spittal for assistance in the early stages of the analysis.

(Received, April 11th, 1962.)

¹ Akisanya, Bevan, Hirst, Halsall, and Taylor, *J.*, 1960, 3827.

² Barton, Pradhan, Sternhell, and Templeton, *J.*, 1961, 255; Arigoni, Barton, Corey, and Jeger, in collaboration with Cagliotti, Dev, Ferini, Glazier, Melera, Pradhan, Schaffner, Sternhell, Templeton, and Tobinaga, *Experientia*, 1960, **16**, 41.

³ Akisanya, Bevan, Halsall, Powell, and Taylor, *J.*, 1961, 3705.

⁴ Barton, McGhie, Pradhan, and Knight, *Chem. and Ind.*, 1954, 1325; *J.*, 1955, 876.

⁵ Arnott, Davie, Robertson, Sim, and Watson, *Experientia*, 1960, **16**, 49; *J.*, 1961, 4183.

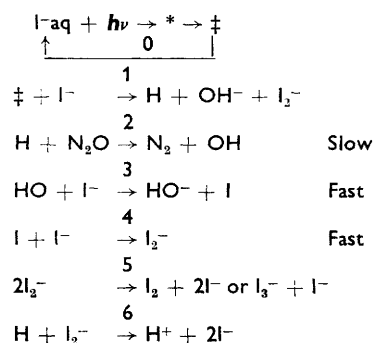
⁶ Grant, Hamilton, Hamor, Hodges, McGeachin, Raphael, Robertson, and Sim, *Proc. Chem. Soc.*, 1961, 444.

The Rates of Some Reactions of Hydrogen Atoms in Water at 25°C

By F. S. DANTON and S. A. SILLS

(DEPARTMENT OF PHYSICAL CHEMISTRY, THE UNIVERSITY, LEEDS 2)

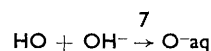
WHEN an aqueous solution of potassium iodide for which $3.5 < \text{pH} < 11$ and containing nitrous oxide is irradiated by light of wavelength 2537 Å the following reactions occur (* and ‡ denote photo-excited ions):



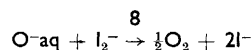
Consequently $\phi(\text{N}_2) = \phi(\text{I}_2)$ increases with concentration of nitrous oxide and potassium iodide to a limiting value of 0.165, which is the maximum attainable yield of hydrogen atoms as a result of the first two processes, and k_1/k_0 can be evaluated from the experimental results. At low $[\text{N}_2\text{O}]$ the rate of re-

action tends to become proportional to $(I_a[\text{N}_2\text{O}])^{2/3}$, and the rotating-sector technique can be used to obtain the values of k_2 , k_3 , and k_4 shown in the Table.

Change of pH below 3.5 and above 11 has the dramatic effects shown in the Figure. The sharp decline in $\phi(\text{I}_2)$, the constancy of $\phi(\text{N}_2)$, and the appearance of oxygen in yields such that $\phi(\text{N}_2) = \phi(\text{I}_2) + 2\phi(\text{O}_2) = 0.16$ when the pH is increased above pH 11 are caused by a simple competition between reaction 3 and reaction 7, the O^{-} emerging from the latter reaction destroying the intermediate



I_2^{-} in a reaction the stoichiometry of which is given by expression 8. The dependence of $\phi(\text{I}_2)$, and $\phi(\text{O}_2)$

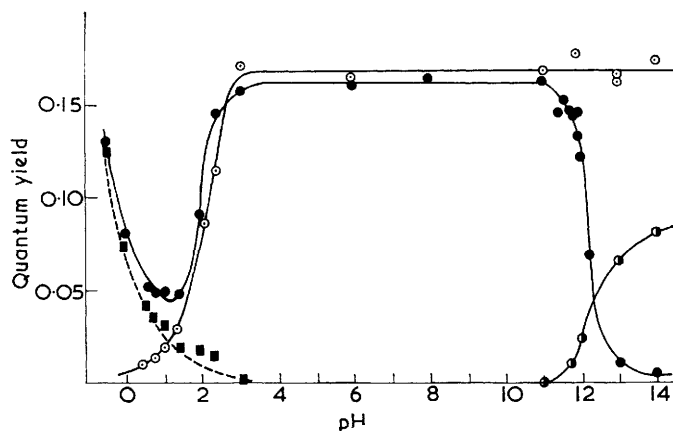


on pH leads to the value of k_3/k_7 shown in the Table.

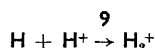
The striking decrease of $\phi(\text{N}_2)$, the increase of $\phi(\text{H}_2)$ from zero, and the minimum in $\phi(\text{I}_2)$ which occur when the pH is decreased below 3.5 are due to two causes. First, H^+ competes with N_2O for H , forming H_2^+ in reaction 9, which always oxidises

Data concerning rate processes in the photolysis of KI solutions

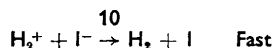
Limiting ϕ_{H} at high $[\text{KI}]$	0.16
$k_2(\text{H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH})$	$(1.25 \pm 0.5) \times 10^4 \text{ l. mole}^{-1} \text{ sec}^{-1}$
$k_9(\text{H} + \text{H}^+ \rightarrow \text{H}_2^+)$	$(2.6 \pm 1.1) \times 10^3 \text{ l. mole}^{-1} \text{ sec}^{-1}$
$k_6(\text{H} + \text{I}_2^{-} \rightarrow \text{H}^+ + 2\text{I}^{-})$	$(1.8 \pm 0.8) \times 10^7 \text{ l. mole}^{-1} \text{ sec}^{-1}$
$k_5(2\text{I}_2^{-} \rightarrow \text{I}_2 + 2\text{I}^{-} \text{ or } \text{I}_3^{-} + \text{I}^{-})$	$(2.2 \pm 0.8) \times 10^6 \text{ l. mole}^{-1} \text{ sec}^{-1}$
$k_3(\text{OH} + \text{I}^{-} \rightarrow \text{OH}^{-} + \text{I})/k_7(\text{OH} + \text{OH}^{-} \rightarrow \text{O}^{-\text{aq}})$	(4.5 ± 0.3)



The variation of $\phi(\text{N}_2) = 0$; $\phi(\text{I}_2) = \bullet$, $\phi(\text{H}_2) = \blacksquare$ and $\phi(\text{O}_2) = \circ$ with pH at 25°C. $\text{KI} = 0.276\text{M}$; $P_{\text{N}_2\text{O}} = 310 \text{ mm. Hg}$.

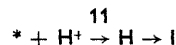


iodide according to expression 10. Consequently,



over this pH range, $\phi(\text{I}_2) = \phi(\text{H}_2) + \phi(\text{N}_2)$ and $\phi(\text{H}_2)/\phi(\text{N}_2) = k_9[\text{H}^+]/k_{10}[\text{N}_2\text{O}]$. Secondly, small concentrations of H^+ interfere with reaction (1), so that ϕ_{H} decreases as the pH changes from 3.0 to 1.2 but larger concentrations of H^+ facilitate the formation of H , presumably involving a reaction which

may be written according to equation 11, so that ϕ_{H} increases as the pH is further reduced.



The numerical values given in the Table permit prediction of values of $\phi(\text{I}_2)$ for certain deaerated, N_2O -free solutions which are in agreement with values which we have measured.

We are greatly indebted to the Distillers Company, Ltd., for generous financial help in this work.

(Received, March 8th, 1962.)

Perfluoroalkyl-bismuth and -thallium Compounds

By T. N. BELL, B. J. PULLMAN, and B. O. WEST

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REACTION of trifluoroiodomethane with alkyl derivatives of phosphorus,¹ arsenic,¹ antimony,¹ tin,^{2,3} and lead³ at moderate temperatures yields mixed alkyl-perfluoroalkyl compounds of these elements. In the reactions with trialkyl-phosphorus, -arsenic, and -antimony the appropriate tetra-alkyl-'onium iodide is also formed. It has now been found that trimethyl-bismuth reacts completely in the presence of an excess of trifluoroiodomethane at 100° to give dimethyl-trifluoromethylbismuth (82% conversion), methyl-bistrifluoromethylbismuth (18% conversion), and methyl iodide. The products were separated by vapour-phase chromatography (di-isodecyl phthalate as column packing; and nitrogen as carrier gas at 70°). No evidence for the production of tris-trifluoromethylbismuth was obtained. Methylbistrifluoromethylbismuth is formed readily when dimethyl-trifluoromethylbismuth is heated with an excess of trifluoroiodomethane at 100° but does not react with further trifluoroiodomethane in a further 48 hours at this temperature. The two alkylperfluoroalkylbismuth compounds are oxidised readily on exposure to air and ignite spontaneously under certain conditions. Their vapours are lachrymatory. Both compounds are rapidly hydrolysed by 5N-sodium hydroxide at room temperature, fluoroform being produced quantitatively. Dilute acid also hydrolyses the compounds, but slowly, liberating fluoroform. The boiling points are: BiMe_2CF_3 121°/760 mm.; $\text{BiMe}(\text{CF}_3)_2$ 132°/760 mm. (determined by the isoteniscope method). There is thus a rise in boiling point accompanying substitution of CF_3 for CH_3 in

BiMe_3 (b.p. 110°/760 mm.), which is contrary to the cases of the corresponding phosphorus, arsenic, and antimony compounds⁴ where the boiling points rise with the replacement of one CH_3 group in $(\text{CH}_3)_3\text{M}$ and then fall through $\text{CH}_3(\text{CF}_3)_2\text{M}$ to $(\text{CF}_3)_3\text{M}$. The observed decrease in decomposition temperature of $(\text{CF}_3)_3\text{M}$ compounds from phosphorus to antimony^{5,6} may suggest a high degree of thermal instability for tris-trifluoromethylbismuth.

Iodine reacts violently with each of the perfluoroalkylbismuth compounds at room temperature, but smoothly at -26°. Methyl iodide and trifluoroiodomethane are liberated and a mixture of methyl-trifluoromethylbismuth iodides remains. This observation is to be compared with that reported by earlier workers^{2,3} who find that alkyl groups are split preferentially from the alkylperfluoroalkyl-tin and -lead compounds by halogens.

Attempts to prepare thallium derivatives by the reaction of trimethylthallium and trifluoroiodomethane or heptafluoroiodopropane, or by the reaction of methyl-lithium with thallos iodide in the presence of heptafluoroiodopropane (cf. Gilman⁷) failed. In the former case dimethylthallium fluoride is produced even at -78°; in the latter, apart from a 10% conversion of thallos iodide into trimethylthallium, the reactants can be recovered unchanged.

We are grateful to the C.S.I.R.O. for a Post-Graduate Studentship to B.J.P.

(Received, April 2nd, 1962.)

¹ Haszeldine and West, *J.*, 1956, 3631.

² Clark and Willis, *J. Amer. Chem. Soc.*, 1960, **82**, 1888.

³ Kaesz, Phillips, and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6228.

⁴ Haszeldine and West, *J.*, 1956, 3880.

⁵ Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.

⁶ Dale, Emeléus, Haszeldine, and Moss, *J.*, 1957, 3708.

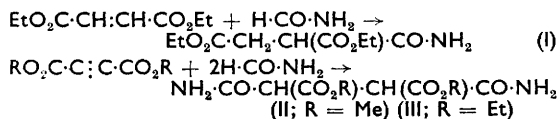
⁷ Gilman and Jones, *J. Amer. Chem. Soc.*, 1946, **68**, 517.

The Light-induced Addition of Formamide to Esters of Maleic, Fumaric, and Acetylenedicarboxylic Acid

By D. ELAD

(DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL)

THE light-induced addition of formamides to terminal olefins has been reported by us.¹ We have now found a similar addition to $\alpha\beta$ -conjugated ethylenic and acetylenic bonds. Two mol. of formamide add to the acetylenic bond.²



Irradiation³ of a solution of diethyl maleate or fumarate (8.5 g.) in formamide (135 g.), with the exclusion of oxygen, at room temperature gave the

ester (I) (25%), which on alkaline hydrolysis yielded the known tricarboxylic acid.

Similarly, irradiation of a solution of dimethyl acetylenedicarboxylate (5.5 g.) in formamide (135 g.) gave the diamide (II) (25%); use of diethyl acetylenedicarboxylate gave the analogue (III) (30%). Both products, on hydrolysis yielded ethane-1,1,2,2-tetracarboxylic acid.

We are indebted to Professor F. Sondheimer for his interest and to Dr. S. Pinchas for the infrared spectral measurements.

(Received, May 1st, 1962.)

¹ Elad, *Chem. and Ind.*, 1962, 362.

² Cf. Schlubach, Franzen, and Dahl, *Annalen*, 1954, 587, 124; Wiley and Harrell, *J. Org. Chem.*, 1960, 25, 903.

³ Hanau immersion quartz lamps Q 81.

Photochemistry of Hecogenin Derivatives: A Novel Cyclisation Reaction of C-Seco-steroids

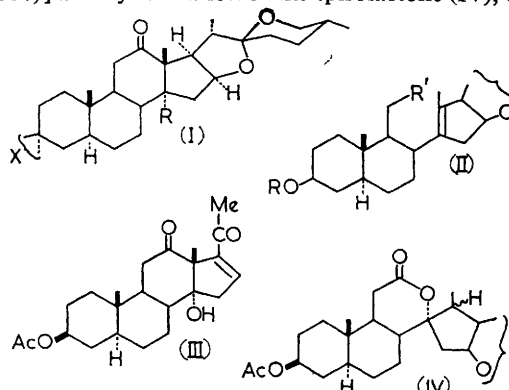
By PETER BLADON, W. McMEEKIN, and IVOR A. WILLIAMS

(CHEMISTRY DEPARTMENT, ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY, GLASGOW, C.1)

THE initial product of ultraviolet irradiation of hecogenin acetate (I; X = β -OAc, α -H, R = H) in dioxan solution was 3 β -acetoxy-12-oxo-12,13-seco-5 α ,25D-spirost-13-ene (lumihecogenin acetate) (II; R = Ac, R' = CHO), λ_{max} . 204 m μ (ϵ 4800), ν_{max} . (in KCl) 2740 (CHO), 1739 (OAc), 1709 (CHO), 1240 cm.⁻¹ (OAc). The presence of the aldehyde group was confirmed by the barely resolved triplet in the nuclear magnetic resonance spectrum at τ 0.85. By reduction with lithium aluminium hydride, lumihecogenin acetate was converted into the known^{1,2} anhydrohecolyl alcohol (II; R = H, R' = CH₂OH).

Oxidation of lumihecogenin acetate with chromium trioxide in aqueous sulphuric acid acetone³ gave 14 α -hydroxyhecogenin acetate (I; X = β -OAc, α -H, R = OH), ν_{max} . (in CCl₄) 3550 (OH), 1739 (OAc), 1706 (12-C=O), 1250 cm.⁻¹ (OAc). This is a general reaction, oxidation of anhydrohecolyl alcohol giving the corresponding 14 α -hydroxyhecogenone (I; X = O, R = OH). In these compounds the hydroxyl groups cannot be acetylated and are therefore tertiary. The presence of a hydroxyl group at position 14 (and not 17) was indicated by the conversion of 14 α -hydroxy-

hecogenin acetate by standard methods⁴ into 3 β -acetoxy-14 α -hydroxy-5 α -pregn-16-ene-12,20-dione (III), λ_{max} . 228.5 m μ (ϵ 7320) [cf. 3 β -acetoxy-5 α -pregn-16-ene-12,20-dione,⁵ λ_{max} . 227–230 m μ (ϵ 8510)] and by formation of the spiro lactone (IV), on



ultraviolet irradiation. The spiran (IV) had no ultraviolet absorption in the 205 m μ region and no hydroxyl absorption in the infrared spectrum. On

¹ Rothman, Wall, and Eddy, *J. Amer. Chem. Soc.*, 1954, 76, 527.

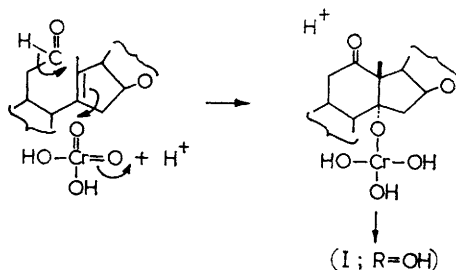
² Bladon and McMeekin, *J.*, 1961, 3504.

³ Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 2402.

⁴ Cameron, Evans, Hamlet, Hunt, Jones, and Long, *J.*, 1955, 2807.

⁵ Wagner, Moore, and Forker, *J. Amer. Chem. Soc.*, 1950, 72, 1856.

reduction with lithium aluminium hydride and treatment of the product with perchloric acid in methanol, it yielded anhydrohecolyl alcohol (II; $R = H$, $R' = CH_2OH$).



⁶ Waters, *Quart. Rev.*, 1958, **12**, 277.

⁷ Mayo, "Advances in Organic Chemistry," Interscience Publ. Inc., New York, 1960, Vol. II, p. 367; Mayo and Reid, *Quart. Rev.*, 1961, **15**, 393.

* In our earlier paper (ref. 2) we anticipated the presently disclosed findings on the position of the double bond.

These reactions show that in anhydrohecolyl alcohol and related compounds,¹ the double bond, the position of which has hitherto been uncertain,* is in the 13(14)- and not the 13(17)-position. The novel oxidation process is envisaged as proceeding by the mechanism shown (cf. Waters⁶). The photochemical transformations are in line with currently held theories (cf. Mayo⁷).

The authors thank Dr. A. Melera (Varian A.G., Zurich) for the nuclear magnetic resonance spectrum, and Dr. C. L. Hewett, Organon Laboratories Ltd., Newhouse, for a gift of a hecogenin acetate and loan of photochemical apparatus.

(Received, April 25th, 1962.)

The Catalytic Action of Anionic Catalysts

By ALWYN G. EVANS, J. C. EVANS, E. D. OWEN, and B. J. TABNER

(CHEMISTRY DEPARTMENT, UNIVERSITY COLLEGE, CARDIFF)

and J. E. BENNETT

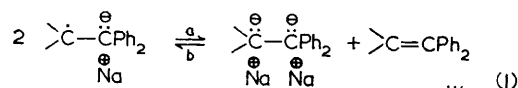
("SHELL" RESEARCH LTD., THORNTON RESEARCH CENTRE, CHESTER)

BUTYL-LITHIUM adds to 1,1-diphenylethylene, forming the ion pair $Bu\cdot CH_2\cdot CPh_2\cdot Li^+$ in benzene, but does not add to 1,1,3,3-tetraphenylbut-1-ene or tetraphenylethylene, owing, we believe, to the steric hindrance of the phenyl groups.¹ On mixing the tetraphenylbutene with sodium naphthalene in tetrahydrofuran, the green colour of the sodium naphthalene was immediately replaced by a red colour, showing that the electron had been transferred from the naphthalene to the olefin.² We now find the same behaviour for tetraphenylethylene. We have also brought tetrahydrofuran solutions of these two olefins into brief contact with a sodium film and then filtered the mixtures. Electron-spin resonance spectra (some of which are given in the Figure), and visible spectra of both types of solution have been measured.

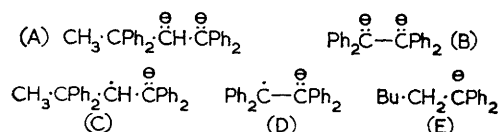
The electron-spin resonance spectra show that radicals are present in these solutions, and that their concentration increases with decrease in temperature. At room temperature the concentration of radicals is greater when tetraphenylethylene is used than when the tetraphenylbutene is used. The visible spectra at room temperature show a peak at 479 $m\mu$, and a shoulder at 432 $m\mu$ when the latter olefin is used, and a peak at 466 $m\mu$ and a shoulder at 700 $m\mu$ when the

former is used; with decrease in temperature, the heights of the peaks at 479 and 466 $m\mu$ decrease and the heights of the shoulders 432 and 700 $m\mu$ increase. [The spectrum of an unstable solution from the tetraphenylbutene (see ref. 2) has a peak at 432 and a shoulder at 479 $m\mu$.]

Thus, although the Bu^- ion cannot add to either of these olefins, an electron can. The radical ion formed by addition of an electron to the olefin, cannot dimerise because of steric hindrance (even a Bu^- ion cannot add on to these olefins) and to explain the change of radical concentration with temperature, we postulate the disproportionation reaction:



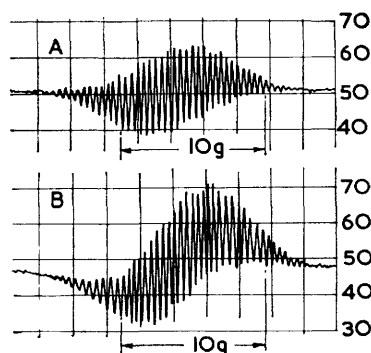
From our results we conclude that equilibrium (1) lies further to the right for the butene than for the



¹ Evans and George, *J.*, 1961, 4753.

² Evans, Evans, and Owen, *Proc. Chem. Soc.*, 1961, 339.

ethylene, and that reaction (1a) is endothermic. Since the absorptions at 479 and 466 $m\mu$ decrease with



(A) Electron-spin resonance spectrum of a solution, at room temperature, obtained by allowing 1.92 ml. of a tetrahydrofuran solution of $\text{Ph}_2\text{C}:\text{CPh}_2$ (2.05×10^{-2} mole l^{-1}) to come into brief contact with a sodium film, filtering, and then adding 5.92 ml. of a tetrahydrofuran solution of $\text{Ph}_2\text{C}:\text{CPh}_2$ (8.6×10^{-3} mole l^{-1}). (B) Same as A, at -100° .

decrease in temperature, and those at 432 and 700 $m\mu$ increase with decrease in temperature and with increase in radical concentration, we attribute these peaks to the species (A—D) as shown respectively. If, to obtain an estimate of the extinction coefficient, we assume that equilibrium (1) lies completely to the right, we obtain $\epsilon = 1.5 \times 10^4$ for (A) and 1.8×10^4 for (B) [compare $\epsilon = 1.6 \times 10^4$ for the monoion (E) absorption peak 428 $m\mu$].

When solutions formed by mixing sodium naphthalene with olefin in 1:1 molar ratio were treated with distilled water practically all the olefin was recovered unchanged. The predominant effect of the water is thus to remove the electron from the olefin. The probable reason for this is steric opposition to attachment of groups to these olefins, as shown by the inability of the Bu^- ion to add to either of them.

We thank D.S.I.R. for a Research Studentship (to J.C.E.), University of Wales for a Research Studentship (to B.J.T.), and "Shell" Research Ltd., for the use of the electron-spin resonance machine.

(Received, April 18th, 1962.)

The Dissociation Energy of the NH Radical

By M. A. A. CLYNE and B. A. THRUSH

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THERE appears to be very little direct thermochemical evidence on the dissociation energy of the NH radical and Gaydon's¹ recommended value of 85 ± 10 kcal./mole is based on a linear Birge-Sponer extrapolation of the ground state of NH to a limit at 92 kcal./mole.²

We have recently shown that the bond-dissociation energy of nitroxyl $D(\text{H}-\text{NO}) = 48.6$ kcal./mole,³ giving $\Delta H_f^\circ(\text{HNO})_g = 23.8$ kcal./mole at 298°K . HNO is isoelectronic with O_2 and with di-imide for which Foner and Hudson⁴ have determined $\Delta H_f^\circ(\text{N}_2\text{H}_2)_g = 48.7 \pm 5$ kcal./mole at 298°K . If, using Gaydon's value of $D(\text{N}-\text{H})$ as a reference point, we put $D(\text{N}-\text{H}) = (85 - x)$ kcal./mole we obtain $D(\text{HN}=\text{O}) = (114 + x)$ kcal./mole and $D(\text{HN}=\text{NH}) = (109 + 2x \pm 5)$ kcal./mole, which may be compared with $D(\text{O}=\text{O}) = 118$ kcal./mole. These bond energies should be fairly similar, since the species concerned are isoelectronic and all have

the same nuclear charge on each side of the bond concerned. For the related group of compounds with two fewer or with two more electrons one obtains:

$$\begin{aligned} D(\text{N}\equiv\text{N}) &= 225, & D(\text{H}_2\text{N}-\text{NH}_2) &= 60 \pm 3 \text{ kcal./mole} \\ D(\text{HC}\equiv\text{N}) &= 223.5, & D(\text{H}_2\text{N}-\text{OH}) &= 48 \pm 2 \text{ kcal./mole} \\ D(\text{HC}\equiv\text{CH}) &= 228, & D(\text{HO}-\text{OH}) &= 51 \text{ kcal./mole.} \end{aligned}$$

The experimental results for the heats of formation therefore support a value of $D(\text{N}-\text{H}) = 81 \pm 3$ kcal./mole, in excellent agreement with the value of 83 kcal./mole recently calculated by Companion and Ellison⁵ using a semi-empirical valence-bond treatment. Our value for $D(\text{N}-\text{H})$ together with $D(\text{NH}_2-\text{H}) = 104 \pm 2$ kcal./mole⁶ gives $D(\text{NH}-\text{H}) = 95 \pm 4$ kcal./mole.

(Received, May 3rd, 1962.)

¹ Gaydon, "Dissociation Energies," Chapman and Hall, London, 1953.

² Pannetier and Gaydon, *J. Chim. phys.*, 1951, **48**, 221.

³ Clyne and Thrush, *Trans. Faraday Soc.*, 1961, **57**, 1305. *Discuss. Faraday Soc.*, 1952, in the Press.

⁴ Foner and Hudson, *J. Chem. Phys.*, 1958, **28**, 719.

⁵ Companion and Ellison, *J. Chem. Phys.*, 1960, **32**, 1132.

⁶ Szwarc, *Proc. Roy. Soc.*, 1949, **A**, **198**, 267.

Substituent Effects of the $-\text{NH}_3^+$ and the $-\text{NMe}_3^+$ Group in Nitration

By MADELINE BRICKMAN, SHEENA JOHNSON, and J. H. RIDD

(WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1)

THE direct comparison of the substituent effects of the $-\text{NH}_3^+$ and the $-\text{NMe}_3^+$ group in nitration is complicated by preliminary proton loss from the $-\text{NH}_3^+$ group, leading to substitution in the neutral amino-compound. The contribution of this reaction path can be determined from a kinetic study of the nitration as a function of acidity. Such results for the nitration of aniline in concentrated sulphuric acid at 25° are tabulated below in terms of the stoicheio-

$\times 10^{13} \text{ mole}^{-1} \text{ sec}^{-1} \text{ l.}$) considerably exceeds that calculated from the encounter rate of the reactants ($\sim 10^9 \text{ mole}^{-1} \text{ sec}^{-1} \text{ l.}$). Thus, from the tabulated rate coefficients, the reactivity of the *para*-position in the anilinium ion appears to exceed slightly that of one of the *meta*-positions.

Nitration of the trimethylphenylammonium ion is usually considered to give only *meta*-substitution,² but from the infrared spectrum of the product, and

	Ph·NH ₃ ⁺				Ph·NMe ₃ ⁺	
H ₂ SO ₄ (%)	89.4	92.4	94.8	96.4	98.0	98.0
k_p (mole ⁻¹ sec. ⁻¹ l.)	1.36	0.945	0.590	0.454	0.259	0.0013
k_m (mole ⁻¹ sec. ⁻¹ l.)*	0.62	0.532	0.390	0.313	0.210	0.0055

* Calc. for a single *meta*-position.

metric second-order rate coefficients k_p and k_m for substitution at the *para*-position and at one of the *meta*-positions. In concentrations of sulphuric acid above 93%, the amount of *ortho*-substitution is very small (< 3%). *meta*-Substitution should be limited to reaction through the anilinium ion and, as might be expected, the decrease in its rate from 90% to 98% sulphuric acid is very similar to that reported¹ for the nitration of the trimethylphenylammonium ion and attributed to a medium effect. However, the rate profile for the *para*-substitution has a similar form; the ratio k_p/k_m changes by less than a factor of two over this range of acidity. Since the corresponding change in h_0 is by a factor of 14, it is improbable that reaction through the free amine contributes significantly to the nitration in 98% sulphuric acid. This conclusion is supported by the overall rate of *para*-substitution at this acidity; if a bimolecular rate coefficient is calculated by using the expected concentration of the free amine the value obtained (2.5

from the ultraviolet spectrum of the product after demethylation, we estimate that about 11% of *para*-substitution occurs. The rate coefficients tabulated for this substrate are calculated from this product analysis and from the kinetic study of Gillespie and Norton.¹ It appears that the replacement of the $-\text{NMe}_3^+$ group by the $-\text{NH}_3^+$ group increases the rate of *meta*-substitution by a factor of 38 and the rate of *para*-substitution by a factor of about 200.

The reason for this difference in the electron-donating effects of these groups is not yet clear. Possible interpretations include the effects of N-H hyperconjugation³ and of hydrogen bonding with the medium;⁴ it may also be useful to consider the mobility of the N-H protons in the transition state. We hope that a current study of related compounds and of medium effects will help to distinguish between these possibilities.

One of us (M.B.) thanks the D.S.I.R. for a maintenance award. (Received, May 1st, 1962.)

¹ Gillespie and Norton, *J.*, 1953, 971.

² Vorländer and Siebert, *Ber.*, 1919, 52, 294.

³ de la Mare, *Tetrahedron*, 1959, 5, 107.

⁴ Willi, *Z. phys. Chem. (Frankfurt)*, 1961, 27, 233.

Biosynthesis of Berberine

By IAN D. SPENSER and J. R. GEAR

(DEPARTMENT OF CHEMISTRY, MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA)

RECENTLY we reported the isolation of labelled hydrastine and berberine from plants of *Hydrastis canadensis* L. to which [¹⁴C]tyrosine^{1,2} and [¹⁴C]-

dopamine² had been administered. Stepwise degradation of the radio-hydrastine demonstrated that tyrosine^{1,2} and dopamine² both served as specific

¹ Gear and Spenser, *Nature*, 1961, 191, 1393.

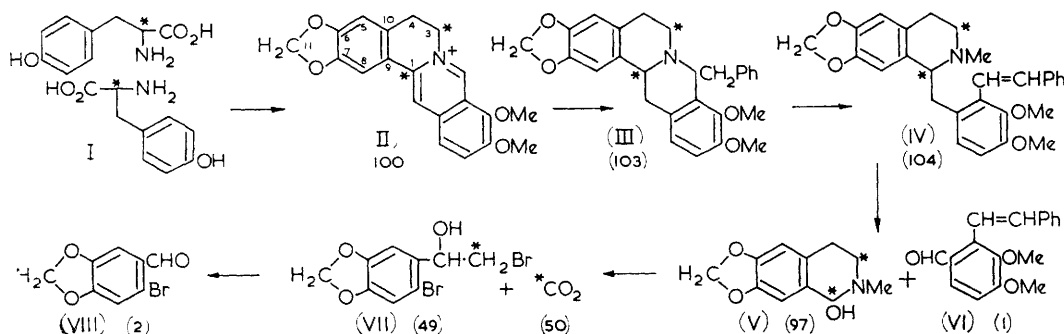
² Spenser and Gear, *J. Amer. Chem. Soc.*, 1962, 84, 1059.

JUNE 1962

precursors of this phthalide-isoquinoline alkaloid.

We have now completed the systematic degradation of radio-berberine (specific activity* 10.5×10^4 counts min.⁻¹ mmole⁻¹), obtained from plants which had grown for 17 days in the presence of DL-[2-¹⁴C]-tyrosine (I) (total activity 8.68×10^7 counts min.⁻¹, specific activity 5.15×10^8 counts min.⁻¹ mmole⁻¹). As predicted by biogenetic hypothesis,³ radioactivity was confined to carbon atoms 1 and 3 of the berberine nucleus.[†]

Berberine (II), isolated from the plants as the



* Denotes radiocarbon. Relative specific activities (berberine = 100) are given in parentheses.

hydrochloride, was converted into hydrastinine (V) by a modification of the method originated by Freund and Fleischer.⁵ A Grignard reaction with benzyl chloride gave benzylidihydroberberine which was reduced with sodium borohydride to benzyltetrahydroberberine (III). Conversion into the methiodide and Hofmann degradation gave de-N-methyltetrahydrostyrylberberine (IV). Oxidation of this led to inactive 3,4-dimethoxy-2-styrylbenzaldehyde (VIII).[‡]

* The specific activity of the sample, originally reported¹ as 12.4×10^4 counts min.⁻¹ mmole⁻¹, dropped to a constant value of 10.5×10^4 after further recrystallisation.

† It had been shown⁴ that in *Coptis japonica* Makino DL-[2-¹⁴C]tyrosine gave rise to berberine containing radioactivity of unknown distribution in the nucleus of the alkaloid.

³ Robinson, "The Structural Relations of Natural Products," Clarendon Press, Oxford, 1955.

⁴ Imaseki, Oneyama, and Tajima, *J. Pharm. Soc. Japan*, 1960, **80**, 1802.

⁵ Freund and Fleischer, *Annalen*, 1913, **397**, 30.

hyde (VI) and hydrastinine (V), which retained all the activity of the original berberine. Hydrastinine, degraded as previously described,¹ gave the bromide (VII) (carbon atoms 3—11 of berberine) and carbon dioxide (carbon atom 1), which was assayed after conversion into benzoic acid. Oxidation of the bromide (VII) gave 6-bromopiperonaldehyde (VIII) (carbon atoms 4—11), which was isolated as the acetone derivative.

The relative specific activities of berberine and its degradation products are summarised in the Chart.

The degradation sequence shows that tyrosine serves as a specific precursor of berberine and that two tyrosine units participate in the biosynthesis of the alkaloid.

Financial assistance by the National Research Council of Canada and by the Ontario Research Foundation is gratefully acknowledged.

(Received, April 6th, 1962.)

Electron-spin Resonance Spectra of Ketyls of Benzophenone

By P. B. AYSCOUGH and R. WILSON

(DEPARTMENT OF PHYSICAL CHEMISTRY, THE UNIVERSITY, LEEDS, 2)

AROMATIC ketyls, formed by the reaction of alkali metals with aromatic ketones, are believed to exist as contact ion-pairs in ethers. The valency-electron of the alkali metal is transferred to the lowest unoccupied $2p\pi$ -orbital of the ketone where it can interact with the nuclear spins of the ring protons to produce hyperfine structure in the electron-spin

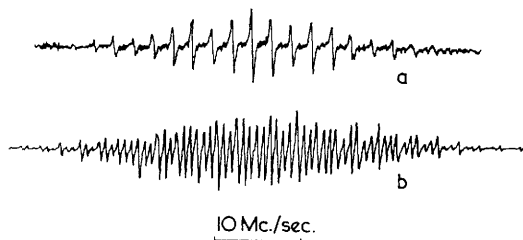
resonance spectra. In previous work, only the magnitude of the interaction with the sodium atom in the sodium ketyl has been established with any certainty because of the complexity of the spectra.¹ No interaction with potassium was observed in an examination of the potassium ketyl.²

The anion of benzophenone can be prepared by

¹ Adam and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 1518.

² Kojakova and Syrkin, *Doklady Akad. Nauk S.S.S.R.*, 1958, **131**, 346.

electrolytic reduction of the ketone.³ Using the technique described by Geske and Maki,⁴ we have observed the simple spectrum shown in Fig. a from a



Electron-spin resonance spectra of (a) the anion and (b) the sodium ketyl of benzophenone, at 25°.

$2 \times 10^{-3}M$ -solution of benzophenone in methyl cyanide containing 0.1M-tetraethylammonium perchlorate as electrolyte. At least twenty-three equally spaced lines, each about 0.04 Mc./sec. wide, may be seen under high power. Such a small number of narrow lines can be observed only if the hyperfine splitting constants of the four *ortho*-, four *meta*-, and two *para*-protons are in a simple integral ratio. This has been shown to be 3:1:4, from which twenty-five lines are predicted, with relative intensities 1:4:6:8:19:32:34:44:71:80:72:88:106:88:72:80:71:44:34:32:19:8:6:4:1. The outermost lines are not seen but the remainder have the correct relative intensities. Absolute values of the hyperfine interaction constants ($\pm 2\%$), measured by comparison with the standard spectrum of triphenylmethyl,⁵ are given in the Table, together with those obtained for the sodium and potassium ketyls.

Spectra were also observed from solutions ($\sim 5 \times 10^{-4}M$) containing the sodium and potassium ketyls of benzophenone in 1,2-dimethoxyethane (Fig. b).

³ Austen, Given, Ingram, and Peover, *Nature*, 1958, **182**, 1784.

⁴ Geske and Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671.

⁵ Ayscough, McCann, and Wilson, *Proc. Chem. Soc.*, 1961, 16.

⁶ Atherton and Weissman, *J. Amer. Chem. Soc.*, 1961, **83**, 1330.

Hyperfine splitting constants (Mc./sec.) for the ortho-, meta-, and para-protons and the cation in benzophenone ketyls.

	a_o	a_m	a_p	a_M
Ph_2CO^-	6.96	2.32	9.28	—
$\text{Ph}_2\text{CO}^-\text{Na}^+$	7.23	2.41	9.63	3.15
$\text{Ph}_2\text{CO}^-\text{K}^+$	7.08	2.35	9.66	0.64

These much more complex spectra are derived from the basic pattern observed in the anion with an additional splitting caused by interaction with the sodium or potassium nucleus ($I = 3/2$). These interactions are approximately four-thirds and one-third, respectively, of that of the *meta*-protons, so that the total number of observable lines is considerably reduced by superposition. Exact values were obtained by computing theoretical spectra as described earlier.⁵ If the species observed during electrolysis is the free anion, it appears that the cation has a negligible effect on the distribution of the unpaired electron in the aromatic system. This is not surprising since the hyperfine interactions with the alkali metal corresponds to an unpaired spin density on the metal of $< 1\%$, as in the case of the sodium naphthalenide ion-pair.⁶ The sodium and potassium hyperfine splittings also vary in a manner similar to that observed for the sodium naphthalenide ion-pair in various solvents. However, in contrast to these systems, variation of the concentration of the sodium ketyl from about $10^{-4}M$ to $10^{-2}M$ affects only the line width, from which it is concluded that under our experimental conditions dissociation of the ion-pair is negligible.

We are indebted to D.S.I.R. for purchasing the spectrometer and providing a research grant (for R.W.).

(Received, April 9th, 1962.)

Total Synthesis of (\pm)-Gibberic Acid

By H. J. E. LOEWENTHAL

(CHEMISTRY DEPARTMENT, MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASS., U.S.A.)

and S. K. MALHOTRA

(CHANDLER LABORATORIES, COLUMBIA UNIVERSITY, NEW YORK, U.S.A.)

THE novel type of ring closure to the bicyclo[3,2,1]-octane system previously utilised in a synthesis of (\pm)-gibberone¹ has now been successfully applied to

a stereospecific synthesis of (\pm)-gibberic acid (I), the racemate of a key intermediate^{2,3} in the degradation of gibberellic acid.

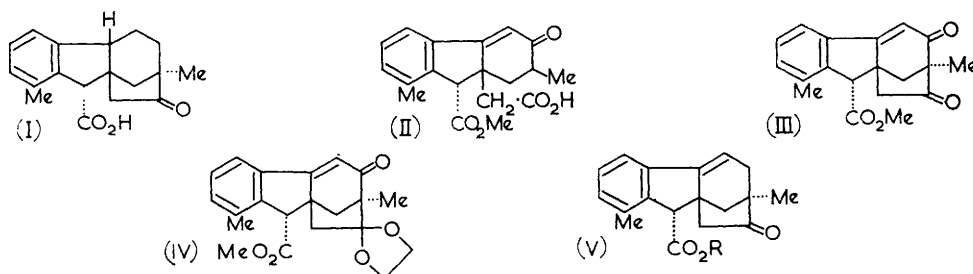
¹ Loewenthal, *Proc. Chem. Soc.*, 1960, 355.

² Cross, *J.*, 1954, 4670.

³ Stork and Newman, *J. Amer. Chem. Soc.*, 1959, **81**, 3168.

Dimethyl (2-methoxycarbonyl-6-methylphenyl)-succinate,⁴ on cyclisation with sodium hydride in benzene–dimethylformamide, gave dimethyl 7-methyl-3-oxoindane-1,2-dicarboxylate, whose alkylation with ethyl bromoacetate and sodium hydride in benzene–dimethylformamide, followed by acid hydrolysis, led to 3-carboxy-4-methyl-1-oxoindan-2-ylacetic acid. The dimethyl ester of this product, on reaction with isopropenyl methyl ketone in methanolic sodium methoxide, afforded in 80% yield the

hydrolysed with alkali, and the resulting mixture of acids was separated by chromatography of their methyl esters, giving as chief product the monoketal-ester (IV). Wolff–Kischner reduction of this, followed by ketal cleavage and esterification, gave methyl (\pm)-dehydrogibberate (V; R = Me). The derived acid (V; R = H), m.p. 220–222° (decomp.), λ_{\max} . 259 (ϵ 15,500), 269 (ϵ 13,500), 288 (ϵ 3400), and 299 $m\mu$ (ϵ 3000) (in MeOH), on catalytic hydrogenation gave (\pm)-gibberic acid (I), m.p. 175–177°. The



expected¹ half-ester (II), m.p. 200–201° (decomp.), λ_{\max} . 231 (ϵ 9100), 235 (ϵ 9100), and 296 $m\mu$ (ϵ 31,400) (in MeOH). Cyclisation of this with the boron trifluoride–ether complex in acetic acid–acetic anhydride gave in nearly 80% yield the diketo-ester (III), m.p. 148.5–149°, λ_{\max} . 236.5 (ϵ 8400), 298 (ϵ 20,600), and 324 $m\mu$ (ϵ 14,100) (in MeOH). This was converted into the ketal with ethylene glycol and toluene-*p*-sulphonic acid in benzene, the product was

infrared spectrum of the latter, in CHCl_3 solution was identical with that of (+)-gibberic acid, m.p. 155–155.5°, obtained by degradation of gibberellic acid.²

We are greatly indebted to Professor G. Stork (Columbia University) for valuable assistance, and to Professor G. Büchi (M.I.T.) for the hospitality of his laboratory. (Received, March 23rd, 1962.)

⁴ Malhotra, Ph.D. Thesis, Columbia University, 1961.

NEWS AND ANNOUNCEMENTS

Programme of Meetings, 1962–63.—The Council has agreed that, as an experiment, scientific meetings held during the first part of the session 1962–63 should start at 6 p.m. instead of at 7.30 p.m. This decision is subject to review in the late autumn of 1962.

The Harrison Memorial Prize.—The Selection Committee, consisting of the Presidents of The Chemical Society, The Royal Institute of Chemistry, The Society of Chemical Industry, and The Pharmaceutical Society, will, in 1963, consider making an award of the Harrison Memorial Prize.

The Prize, which consists of a bronze plaque and a monetary payment of 100 guineas, will be awarded to the chemist of either sex who, being a natural-born British subject and not at the time over thirty years of age, shall, in the opinion of the Selection Committee, during the five years ending December 1st,

1962, have conducted the most meritorious and promising original investigations in Chemistry and published the results of those investigations in a scientific periodical or periodicals.

Applications, five copies of which must be submitted, should include the full names of the applicant; age (birth certificate to be enclosed); degrees (with name of University); any other qualifications and experience; titles, and reprints if available, of published papers (with co-authors' names); where research was carried out; testimonials and references, and any other relevant particulars.

The Selection Committee is prepared to consider applications, nominations, or information as to candidates who have not attained the age of thirty years at December 1st, 1962, and are otherwise eligible for the Prize.

Any such communications must be received by the

President of the Chemical Society, Burlington House, London, W.1, not later than December 31st, 1962.

Ethel Behrens Fund.—This is a new fund, the purpose of which is to provide grants towards the travelling expenses, including maintenance, of Fellows of the Society studying at a University or Technical College in the British Isles for the first University degree, or other equivalent qualification, to enable them to attend the Anniversary Meetings of the Society and any Scientific Symposia or Discussions in conjunction therewith. The first awards are to be made in connection with the Anniversary Meetings to be held in Cardiff in March, 1963.

Forms of application, together with regulations governing the award of travel grants, may be obtained from the General Secretary and must be returned by February 15th, 1963.

Research Fund.—The Research Fund of the Chemical Society provides grants for the assistance of research in all branches of Chemistry. Applications for grants will be considered in December, 1962, and should be submitted on the appropriate form not later than November 15th, 1962. The total amount available for distribution is approximately £1,000, and applications from Fellows will receive prior consideration.

Forms of application, together with the regulations governing the award of grants, may be obtained from the General Secretary.

Local Representatives.—*Dr. C. C. Barker* has been appointed as the Local Representative for Hull in succession to *Dr. G. C. Bond*, who has resigned.

Liaison Officers.—The following Fellows have agreed to act as Chemical Society Liaison Officers:
Brighton Technical College . . Mr. J. D. Donald
Royal Naval College, Greenwich Dr. J. H. Pryor
University of Glasgow . . Dr. S. J. Thomson
Organon Laboratories Ltd.,
Newhouse-by-Motherwell . . Dr. C. L. Hewett

Election of New Fellows.—258 Candidates, whose names were published in *Proceedings* for April, have been elected to the Fellowship.

Deaths.—We regret to announce the deaths of the following: *Dr. A. G. Foster* (25.5.62), of Royal Holloway College; *Mr. V. C. Hewlett* (12.4.62), formerly Chairman, C. J. Hewlett and Sons, Ltd.; *Mr. S. J. Pentecost* (3.5.62), Director, Hicking Pentecost and Co. Ltd., and a Fellow for over 75 years; *Dr. E. A. H. Roberts* (13.3.62), Research Manager, Indian Tea Association (London); and *Dr. S. Smith* (23.5.62), formerly Director, Wellcome Chemical Research Laboratories.

Royal Society Visiting Professorship.—The Council of the Royal Society has appointed *Professor M. Szwarc*, Research Professor at the State University

College of Forestry at Syracuse University, New York, U.S.A., to be the Royal Society Visiting Professor for the academic year 1962—63. He is expected to take appointment on August 1st, 1963, and to work at the University of Liverpool on ionic and anionic and stereospecific polymerisation.

The Bragg Lectures.—At intervals of three years or so, a lecture will be given to commemorate the work of Sir William Bragg and his son, Sir Lawrence Bragg. It will be given in one or other of the centres in which the Braggs' work has been done—Cambridge, Leeds, London, and Manchester—and if possible, repeated in more than one of them.

The first Bragg lecture will be given in June, 1962, the centenary of W. H. Bragg's birth, by Professor P. P. Ewald, F.R.S, Emeritus Professor of Physics at the Polytechnic Institute of Brooklyn, U.S.A., on "William Henry Bragg and the New Crystallography." It will be given twice, in Leeds on Thursday, June 7th, at 5.15 p.m. in the Arts Lecture Theatre of the University (admission free, no tickets), and in London on Wednesday, June 13th, at 5.15 p.m. in the Royal Institution, 21 Albemarle Street, London, W.1 (admission free, by ticket obtainable from the Secretary of the Royal Institution).

Symposia, etc.—The 2nd International Symposium on Passivity, sponsored jointly by the Electrochemical Society, the German Bunsen Society for Physical Chemistry and the Faraday Society, will be held in Toronto, Canada, on September 3rd—7th, 1962. Further enquiries should be addressed to Mr. Cohen, National Research Council of Canada, Ottawa, Ontario, Canada.

An International Metal Congress will be held in Vienna on September 23rd—27th, 1962. Further enquiries should be addressed to Metall-u. Farben A.G., Kärntnerstrasse 7, Vienna I, Austria.

The 14th International Plastics Congress will be held in Turin on October 1st—3rd, 1962, in connection with the 12th International Technical Exhibition. Further enquiries should be addressed to Segretaria, Congresso Internazionale delle Materie Plastiche, Corso Galileo Ferraris, 60, Turin, Italy.

The First Australian Conference on Electrochemistry, under the joint sponsorship of the Royal Australian Chemical Institute, the University of Tasmania, and the University of New South Wales, will be held in Sydney on February 13—15th, and in Hobart on February 18—20th, 1963. Further enquiries should be addressed to the Honorary Secretary, Sydney Committee, Dr. F. Gutmann, Department of Physical Chemistry, University of New South Wales, P.O. Box 1, Kensington, New South Wales.

The 2nd International Congress on Metallic Corrosion will be held in New York on March 11—15th, 1963. Further enquiries should be addressed to the

National Association of Corrosion Engineers, 1061 M & M Building, Houston 2, Texas, U.S.A.

Personal.—Honorary Membership of the City and Guilds of London Institute has been conferred upon *Mr. A. Baker* in recognition of distinguished services to that Institute.

Professor D. H. R. Barton is to give the Minnesota Mining and Manufacturing Company (Canada) Special Lecture Series in Chemistry at the University of Western Ontario, in July, 1962.

Mr. R. P. Bell has been elected a Foreign Member of the Royal Danish Academy of Science and Letters.

Professor Endre Berner has retired from the Chair of Chemistry at the University of Oslo.

Dr. J. Biggs, Assistant Lecturer in Chemistry at Hull University, has been appointed Lecturer with effect from October 1st, 1962.

Mr. B. K. Blenkinship has resigned from the position of Chief Chemist of the South African Breweries Ltd., to take up a new appointment as Assistant to the General Manager (Production) of Dominion Breweries Ltd., Auckland, C.I., New Zealand.

Miss Gaynor Corfield, of the Chemistry Department of the University College of Wales, Aberystwyth, has been elected to the Gritton Postgraduate Research Award at Sydney University, New South Wales, where she will pursue further research studies under the direction of Professor R. J. W. Le Fèvre.

Dr. J. S. G. Cox has been appointed Development Director of Genatosan Ltd.

Dr. D. W. Davies, Research Fellow, University of Keele, has been appointed Lecturer in Theoretical Chemistry at the University of Groningen from June 1st, 1962.

Dr. B. K. Davison has joined the International Nickel Company (Mond) Limited as a Development Chemist.

Dr. H. C. Dunn, U.K.A.E.A., Risley, has now returned from Japan.

Mr. C. Fox, formerly Lecturer in Chemistry, Rotherham College of Technology, has taken up an appointment as a Technical Officer, Research Department, Imperial Chemical Industries Limited, Heavy Organic Chemicals Division, Billingham.

Dr. T. R. Griffiths, of the North-East Essex Technical College and School of Art, has been granted one year's leave of absence and will take up an appointment in August as Visiting Scientist at Oak Ridge National Laboratories, Oak Ridge, Tennessee, U.S.A.

Dr. R. D. Guthrie and *Dr. S. Trippett* have been appointed to Senior Lectureships at the University of Leicester from October next.

Professor S. H. Harper, Department of Chemistry, University College of Rhodesia and Nyasaland, is visiting England until the beginning of August.

Professor T. P. Hilditch, of Liverpool, has been awarded the Lampitt Medal by the Council of the Society of Chemical Industry.

Sir Christopher Ingold, Emeritus Professor of Chemistry in the University of London, is spending some weeks in Ireland as Visiting Professor of Chemistry in University College, Dublin.

Mr. G. C. Israel has resigned his position as Professor of Chemistry at the University of Ghana and has taken up an appointment as Principal Lecturer in Chemistry at the Welsh College of Advanced Technology, Cardiff.

Dr. A. R. Katritzky of Cambridge University has been appointed Professor of Chemistry at the University of East Anglia. He is at present lecturing in Poland by invitation of the Polish Academy of Sciences.

Dr. D. F. C. Morris has been appointed Reader in the Department of Chemistry, Brunel College, London.

Dr. J. A. K. Quartey, Lecturer in Chemistry at the University of Ghana, has been elected to a Fellowship for 1962—5 at Churchill College, Cambridge.

Dr. R. J. W. Reynolds has been appointed to the staff of the new Imperial Chemical Industries Petrochemicals and Polymers Laboratory to assist the Head of the Laboratory, Dr. D. S. Davies, in drawing up the preliminary programme and to manage a part of the research team when it is set up later in the year.

Professor J. B. Speakman, Professor of Textile Industries, University of Leeds, has been elected President of the Textile Institute.

Dr. F. S. Spring, Research Director of Laporte Industries Ltd., has been appointed Chairman of Howards & Sons Ltd.

Professor Börje Steenberg, of the Royal Institute of Technology, Sweden, was presented with the "Stora Ekmansmedaljen" award at the annual meeting of the Swedish Association of Pulp and Paper Engineers.

Dr. D. E. Wheeler, Managing Director of The Wellcome Foundation Ltd., has been appointed President of the Association of the British Pharmaceutical Industry.

APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objections to the election of these candidates should communicate with the Honorary Secretaries within ten days of the publication of this issue of *Proceedings*. Such objections will be treated as confidential. The forms of application are available in the Rooms of the Society for inspection by Fellows.)

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ADDITIONS TO THE LIBRARY

The chemical industry in Europe: a study prepared by the Chemical Products Committee. 1960—1961. Pp. 178. Organisation for Economic Co-operation and Development. Paris. 1962. (Presented by the publisher.)

Bibliography of publications dealing with the polarographic method in 1960. J. Reyrovsky. Pp. 101. Československé Akademie VED. 1962. (Presented by the publisher.)

Radiation chemistry of polymeric systems. A. Chapiro. (High Polymers, vol. 15.) Pp. 712. Interscience. New York. 1962.

Absorption spectra and chemical bonding in complexes. C. K. Jørgensen. Pp. 352. Pergamon Press. Oxford. 1962.

Recent advances in processing cereals: papers read at a symposium organised by the Food Group, held at the Royal Society of Medicine, London, 1961. (S.C.I. Monograph No. 16). Pp. 199. Society of Chemical Industry. London. 1962. (Presented by the publisher.)

New approaches to the study of catalysis. P. H. Emmett. (36th Annuals Priestley Lecture.) Pp. 157. Pennsylvania State University. Pennsylvania. 1962. (Presented by the publisher.)

Organic chemistry of bivalent sulfur. E. E. Reid. Vol. 4. Pp. 437. Chemical Publishing Co. New York. 1962.

Methods in carbohydrate chemistry. Edited by R. L. Whistler and M. L. Wolfrom. Vol. 1. Pp. 589. Academic Press. New York. 1962.

The chemistry of flavonoid compounds. Edited by T. A. Geissman. Pp. 666. Pergamon Press. Oxford. 1962. (Presented by the publisher.)

Natural organic macromolecules. B. Jørgensen. Pp. 464. Pergamon Press. Oxford. 1962. (Presented by the publisher.)

Comparative biochemistry: a comprehensive treatise. Edited by M. Florkin and H. S. Mason. Vol. 3. Pp. 959. Academic Press. New York. 1962.

Les méthodes de la chimie analytique: analyse quantitative minérale. G. Charlot. 4th edn. Pp. 1024. Masson. Paris. 1961.

Toxicity of arsenic compounds. W. D. Buchanan. Pp. 151. Elsevier. Amsterdam. 1962.

The production of chemicals from reactors. Part 6. Anhydrous hydrazine from the pile and fission fragment irradiation of liquid ammonia. D. A. Landsman and C. M. Noble. Pp. 18. A.E.R.E. Harwell, Berks. 1961.

Eighth symposium (International) on Combustion, held at the California Institute of Technology, Pasadena, California, 1960, and published for the Combustion Institute. Pp. 1164. Williams and Wilkins Co. Baltimore. 1962.

NEW JOURNALS

Journal of Catalysis, from 1962, **1**.

Photochemistry and Photobiology, from 1962, **1**.

CORDAY-MORGAN MEDAL AND PRIZE

ADDENDUM

The scheme for the administration of this Award (*Proceedings*, 1962, 135,208) has now been established by the Charity Commissioners who have requested that the following be published:

CHARITY COMMISSION

The Corday-Morgan Medal and Prize Fund administered by the Chemical Society.

Scheme for the amendment of the terms of the Will.

The Charity Commissioners have made an order establishing a scheme for this and other purposes. Copies can be obtained by written request to the Charity Commission, 14 Ryder Street, London, S.W.1 (quoting ref. No. JEH-129779-A), and may also be seen at that address.

It will, in future, be subject to the revised rules approved by Council and given on pp. 208—209.