PROCEEDINGS
OF THE
CHEMICAL SOCIETY

JUNE 1963

ONE HUNDRED AND TWENTY-SECOND ANNUAL GENERAL MEETING

THE One Hundred and Twenty-second Annual General Meeting was held in the Reardon Smith Lecture Theatre of the National Museum of Wales, Park Place, Cardiff, on Thursday, March 28th, 1963, at 9.30 a.m. The President, Professor J. M. Robertson, was in the Chair.

The President referred with deep regret to the death on the previous Tuesday of Dr. A. D. Mitchell, who had retired as Assistant Editor at the end of 1962 after 36 years' service to the publications of the Society, and to whom it had been intended to make a presentation that morning.

The notice convening the meeting having been read, Professor A. W. Johnson, Honorary Secretary, presented the Report of Council. Referring to the continued rise in Fellowship, he pointed out that the net growth of 11·9% during the year was the largest for many years.

Dealing with publications, he referred to the large increase in the number of papers submitted for publication in the *Journal* which was unlikely to abate, and stated that the Editorial staff had been increased to deal with the extra volume of work. He also referred to Dr. Cahn's appointment as Director of Publications Research to investigate the future trends in the method of presentation of papers. Professor Johnson said that greater stringency had been exercised in the selection of Communications for *Proceedings* which had resulted in fewer being published than in the previous year. He added that details of the Society's other publications in the Report of Council illustrated the great activity in all fields of publication.

In his comments on the other activities of the Society, Professor Johnson referred to the much greater use of the photocopying service and the increased number of books borrowed during the year, reflecting the successful administration of the Library. He remarked briefly on the Research Fund, stating that, as usual, more requests had been received than could be met from the income of the Fund. He recalled that the Robert Robinson Lectureship has been founded during the year and the first lecture would be given in Birmingham in 1964; that grants had already been made under the Ethel Behrens Fund. He spoke of the debt the Society owed to the Local Representatives and Liaison Officers whose services were gratefully acknowledged.

The President called upon the Honorary Treasurer, Dr. J. W. Barrett, to present the Financial Report and Accounts. Dealing with the General Purposes Account, Dr. Barrett said that the growth in Fellowship had produced a larger income but, unfortunately, expenditure was also increasing. Administration costs were rising slowly but the cost per Fellow appeared to be contained.

Referring to the Publications Fund, Dr. Barrett stated that although the income had risen, costs were increasing faster, but because the 1961—62 *Journal* was abnormally large, the rise was not apparent from the account. Taken over the last two years, expenditure on the *Journal* and *Proceedings* had risen from £68,000 to £88,000 so that the trend was upward and would continue so. He anticipated a greater number of printed pages during the current year at a greater cost per page. He added that steps must be taken to maintain the Society's finances and to find a solution to the problems of publication of original research.

With regard to the Library Account, Dr. Barrett stated that the income was derived from transfers from the General Purposes Account and contributions from the Chemical Council and contributing Societies. He added that capital and maintenance expenditure had climbed over the last five years at almost a 10% compound rate of interest. He considered that the present division of expenditure on the Library could not be allowed to continue as the Society carried a far greater burden than the contributing Societies.

The Treasurer described the balance sheet as strong and healthy, and considered that the Society was in a strong position to meet commitments. There was, therefore, no need for alarm but the Society must be conscious of the need to look closely at the future. Dealing with the Investments, he stated that the Society had received excellent service from J. Henry Shroder Wagg & Co. Limited, and that both the General Purposes and the Trust Funds had increased in value and had produced more income during the year.

Finally, referring briefly with the day-to-day administration of the Society, he stated that internal Staff changes brought about during the year had proved successful and to the advantage of the Fellowship.

The President spoke of the expansion of the Fellowship and expressed his appreciation of the work of Local Representatives and Liaison Officers. He added that the Society's main duty was as a publishing body and the Council was taking very active measures to investigate and deal with the problems of publication looming ahead. He added that he was hopeful that the Society's accommodation needs would be met, some progress having been made during the years, and he viewed the future with confidence. He concluded by expressing his personal thanks and those of the Officers to the General Secretary and his staff for their work on the Society's behalf during the past year.

The President then moved the adoption of the Report and Accounts. Professor K. W. 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 vacancies caused by retirement:

Vice-Presidents who have not filled the Office of President

(Appointments made by the Council)
Sir Harry Melville
Mr. M. W. Perrin

Elected Ordinary Members of Council

Constituency I

Dr. L. Crombie
Professor B. C. L. Weedon

Constituency II

Dr. A. B. Foster

Constituency III

Professor J. Lewis

Constituency V

Professor P. L. Pauson

On the motion of Dr. J. W. Barrett, seconded by Dr. J. W. Linnett, Messrs. W. B. Keen and Co., Finsbury Circus House, London, E.C.2, were appointed as auditors of the Society's Accounts for the year ended September 30th, 1963.

A vote of thanks to the President, Officers, Council, Committees, and Local Representatives for their services during the year was proposed by Mr. E. A. Cooke and carried with acclamation. The President thanked Mr. Cooke for his remarks and declared the formal business of the Annual General Meeting terminated.

After an interval, the meeting was resumed at 10.30 a.m. when the President presented the Harrison Memorial Prize for 1962 to Dr. A. Carrington in consideration of his contributions to the study of theoretical chemistry, especially by virtue of his work on electron-spin resonance.

The President then gave his Presidential Address entitled "Contributions of *X*-Ray Analysis to Natural Product Chemistry." At the conclusion of the Address, a vote of thanks to the President, proposed by Professor A. W. Johnson, was carried with acclamation.

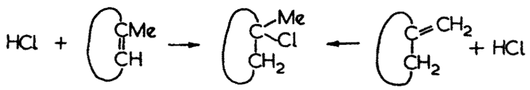
TILDEN LECTURE*

Stereoselectivity in the Reactions of Cyclic Compounds

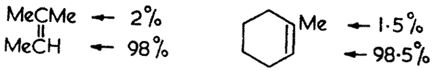
By H. B. HENBEST
(QUEEN'S UNIVERSITY, BELFAST, N. IRELAND)

THIS lecture will be chiefly concerned with one aspect of the topic covered by the general title: directive effects in additions to substituted cyclic compounds. These properties of cyclic compounds have been studied only recently, although directive effects in the addition reactions of some substituted acyclic olefins gave rise to one of the earliest generalisations in organic chemistry (Markovnikov rule, 1870). Additions to cycloalkenes in which a substituent group is in a position remote from the double bond will form the main part of this Lecture. Finally, some reactions of similarly substituted saturated and unsaturated cyclic ketones will be discussed.

When the addition reactions of substituted and unsubstituted cycloalkenes in general are considered, we see that the factors governing the production of structural isomers and stereoisomers can be divided into two classes: those that are special to ring systems and those that are also apparent in the reactions of acyclic olefins. Reactions covered by the Markovnikov rule come, for example, into the second group. Thus tertiary chlorides are formed by the addition of hydrogen chloride to both cyclic and acyclic trialkylated olefins. In cyclic systems addition of hydrogen chloride can give the same product starting from an endo- or an exo-cyclic olefin; the direction of addition is also independent of ring size.

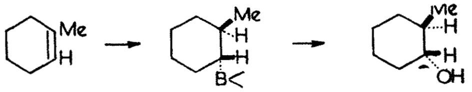


In the hydroboration of acyclic and cyclic trisubstituted olefins the isomers formed predominantly are those in which the boron group is attached to the secondary carbon:

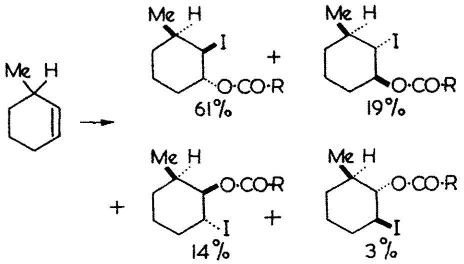


By contrast, one or two methyl groups at the allylic position in cyclohexene have virtually no effect on the direction of hydroboration, for example, equal amounts of 2,2-dimethyl- and 3,3-dimethyl-cyclohexanol are obtained starting from 3,3-dimethyl-cyclohexene.[1]

The formation of geometrical isomers in additions to cycloalkenes poses two questions: (*a*) is there *cis* or *trans* addition of the reagent to the double bond, and (*b*) is this affected by a substituent on the ring? Many stereoselective reactions of olefins (cyclic and acyclic) come under (*a*), for example, *cis*-hydroxylation *via* the addition of osmium tetroxide, and the *cis*-addition of boron hydride that occurs in hydroboronation:

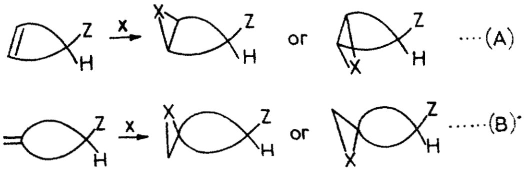


Specific *trans*-addition is well illustrated by the formation of diaxial compounds from suitable cyclohexenes and halogens. The illustrated reaction of 3-methylcyclohexene with iodine 3,5-dinitrobenzoate provides a more complex example of *trans*-addition: all four geometrical isomers are produced but in unequal proportions.[2]



(R =3,5-Dinitrophenyl)

Question (*b*) above may be symbolised as in schemes (A) and (B). If the substituent Z is without



influence upon the reaction, a 50:50 mixture of *cis*- and *trans*-product will be obtained. A difference from this ratio is a measure of the directive effect of Z.[3]

The most readily available substituted cycloalkenes

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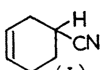
* Delivered before The Society at the University, Oxford, on February 12th, 1962; at the University, Bristol, on February 13th; at Imperial College, London, on May 10th; and at the University, Southampton, on May 11th, 1962.

[1] Brown, "Hydroboration," Benjamin, Inc., New York, 1962.

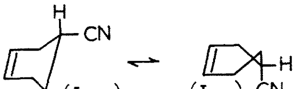
[2] Lemieux and Kavadias, unpublished work. We thank Professor R. U. Lemieux for this example.

[3] Cf. Henbest, Nicholls, Jackson, Wilson, Crossley, Meyers, and McElhinney, *Bull. Soc. chim. France*, 1960, 1365.

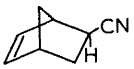
for the study of such directive effects are 4-substituted cyclohexenes (*e.g.*, I) and α- and β-substituted bicyclo[2,2,1]heptenes (*e.g.*, II; *exo* and *endo*). Although some reactions of these compounds have been investigated, the structures of the molecules are not suitable for definitive work on the directive effect of a substituent upon addition reactions.



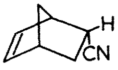
(I)



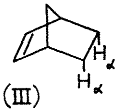
(I, *eq*) (I, *ax*)



(II, *exo*)



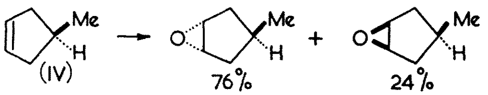
(II, *endo*)



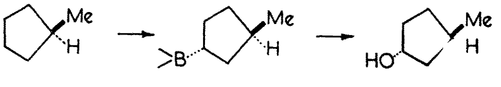
(III)

Results from 4-cyanocyclohexene are bedevilled by the fact that this molecule is flexible; the nitrile group can be in an equatorial or an axial conformation during a reaction (cf. I, *eq*, and I, *ax*). The bicycloheptenes (II; *exo* and *endo*) have a different disadvantage. In the parent hydrocarbon (III), reagents are known[4] to have a strong preference for approach to the β-face, presumably because of the hindrance towards α-face attack imposed by the hydrogens marked H_α in (III). An α-directive effect due to the nitrile group in the reactions of the substituted compounds (II; *exo* and *endo*) would need to be very strong in order to overcome the normal preference for the formation of β-orientated products.

4-Substituted cyclopentenes (*e.g.*, IV) are much more suitable compounds; in each there is a plane of symmetry through the substituent and the centre of the double bond, and there can be no directive effect other than that caused by the substituent. 4-Methylcyclopentene (IV) was synthesised[5] in order to find out if a methyl group at a homoallylic position would afford a directive effect (probably steric). Its reaction with peroxylauric acid gave more *trans*- than *cis*-epoxy-compound. Change of solvent (from cyclopentane to acetonitrile) did not change the *cis*:*trans* product ratio, suggesting that the alkyl group was exerting a steric and not a polar effect (see below). 4-Methylcyclopentene is a simple counterpart of steroidal olefins where axial β-methyl groups in angular positions cause reagents to react at the α-face of the molecule; for example, cholest-2-ene in reaction with a peroxy-acid gives at least 85% of the 2α,3α-epoxide.



A steric directive effect is also presumably involved in the reaction of 4-methylcyclopentene with diborane, from which a 75% yield of *trans*-3-methylcyclopentanol is obtained after oxidation of the intermediate organoborane:



Similarly, hydroboronation of cholest-2-ene affords a preponderance of α-alcohols (cholestan-3α-ol, 45%; cholestan-2α-ol, 23%), although cholestan-3β-ol (20%) is also produced.[6] Initial carbon-to-boron bond formation at a point farthest from the 10β-methyl group is involved in the production of the 3α-alcohol.

Addition of acetyl hypobromite to 4-methylcyclopentene is also stereoselective. Treatment of the total product with alkali gave the *cis*-methyl epoxide (VI) in good yield, showing that the bromoacetate (V) had been formed in the initial step. The direction of addition in this case may be caused by steric repulsion between the methyl group and the bromine atom, the latter being effectively larger than acetoxyl.

Earlier experiments (with steroids, see below) had shown that a remote polar substituent could influence the stereochemistry of epoxide formation from $\alpha\beta$-unsaturated ketones and alkaline hydrogen peroxide.

These observations raised the general question: do polar substituents show directive effects across two or more saturated rings in other (perhaps simpler one-step) additions? In order to obtain an unequivocal answer for reactions at an isolated double bond, the unsaturated nitriles (VII, VIII, and IX) were synthesised.[7] Compounds (VIII) and (IX) have fairly rigid structures owing to the *trans*-junctions; the distance between the olefinic bond and the polar group in each molecule can be calculated fairly accurately. As with (VII), differences from a 50:50 product ratio in the reactions of (VIII) and (IX) are a measure of the effect of the remote substituent.

The formation of epoxides from these unsaturated nitriles was investigated because the geometrical con-

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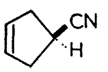
[4] Walborsky and Loncrini, *J. Amer. Chem. Soc.*, 1954, **76**, 5396; Kwart and Vosburgh, *ibid.*, p. 5400; Wiberg and Saegebarth, *ibid.*, 1957, **79**, 2822; Henbest and Nicholls, *J.*, 1959, 221.

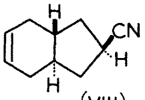
[5] Henbest and McCullough, *Proc. Chem. Soc.*, 1962, 74, and unpublished work.

[6] Hassner and Pillar, *J. Org. Chem.*, 1962, **27**, 2914.

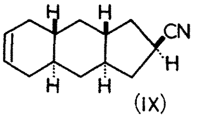
[7] Crossley, Darby, Henbest, McCullough, Nicholls, and Stewart, *Tetrahedron Letters*, 1961, 398.



(VII)



(VIII)

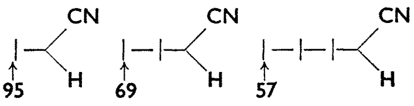


(IX)

figuration of the epoxy-nitriles could be determined with certainty by dipole-moment measurements, and because the direct reaction with a peroxy-acid proceeds in high yield (> 90%), obeys a second-order kinetic law accurately, is stereospecific and nonreversible, and can be carried out in a variety of organic solvents.

Addition of oxygen on the side of the molecule *trans* to the substituent is predominant in the reactions of the three unsaturated nitriles with peroxylauric acid in a hydrocarbon, *e.g.*, cyclopentane. The percentage *trans*-attack is given on the following diagrams, which are simplified side elevations of the molecules (VII), (VIII), and (IX):

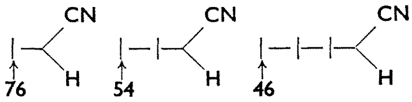
Peroxylauric acid in cyclopentane



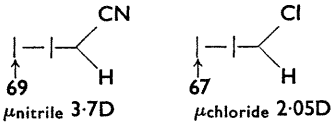
The *cis*:*trans* product ratios in the mono- and bicyclic series were determined by gas–liquid chromatography and are accurate to *ca.* 1%. The isomeric products from the tricyclic unsaturated nitrile were separated by adsorption chromatography and the ratio here is less accurate (*ca.* 3%); the *trans*-directive effect of the nitrile group is only just discernible across three rings.

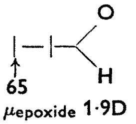
This *trans*-directive effect may be polar or steric in origin. The ratios are dependent on the polarity of the solvent, a strong indication that the directive effect is polar. (It will be recalled that the ratio of the *cis*- and *trans*-epoxy-compounds from 4-methylcyclopentene is independent of solvent.) In acetonitrile, almost random attack of peroxy-acid occurs with the bi- and tri-cyclic compounds, but the monocyclic 4-cyanocyclopentene, still gives more *trans*- (76%) than *cis*-compound:

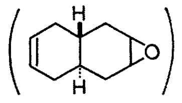
Peroxylauric acid in acetonitrile



The possibility that the directive effect of the nitrile substituent results from dipole–dipole interaction between it and the transition state of the olefin–peroxy-acid reaction receives support from the fact that the extent of *trans*-attack depends on the dipole moment of the remote group. The bicyclic cyanide and chloride, and the bicyclic epoxide (epoxy-*trans*-hexalin) are compared:

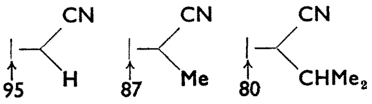




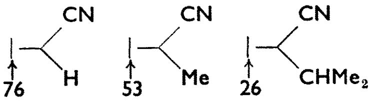


Methyl derivatives of the mono- and bi-cyclic nitriles (VII and VIII) were prepared in order to evaluate possible steric effects. As expected, in the monocyclic series, a methyl group decreased the amount of reaction *trans* to the nitrile group, and an isopropyl group had an even larger effect.

Peroxylauric acid in cyclopentane

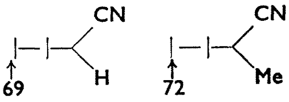


Peroxylauric acid in acetonitrile



Similar methylation of the bicyclic unsaturated nitrile, followed by reaction with the peroxy-acid, gave an *increased* proportion of *trans*-compound compared with the reaction of the unmethylated starting material. Thus, in contrast with the monocyclic series, there is more attack *cis* to the alkyl group in the bicyclic compound:

Peroxylauric acid in cyclopentane



This small but real effect of the methyl substituent may be due to one or both of two reasons: (*a*) the dipole moment of the remote group may be larger [adjacent alkylation increases the moment of a nitrile group: acetonitrile (3·48D, propionitrile (3·57D, isobutyronitrile (3·61D)]; (*b*) the larger methyl group will, for conformational reasons, increase the angle between the nitrile group and the general plane of the ring system. (Calculations confirm that the polar directive effect of the nitrile group will increase if it moves towards a more perpendicular position.) The dipole moments of the products are in line with both of these possibilities:[8]

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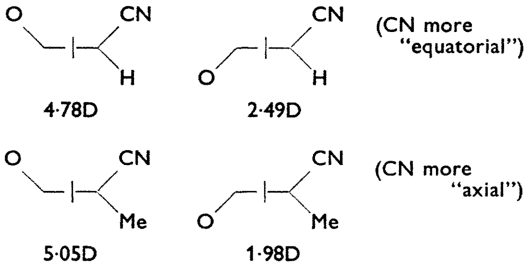
[8] We thank Mr. R. J. Bishop and Dr. L. E. Sutton (Oxford) for these values.



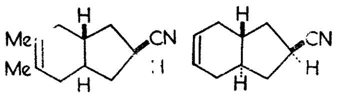
The magnitudes of the *cis* and *trans* dipole–dipole interactions in the reactions will depend on the moments of each polar substituent and transition state, the distances and angles between them, and the dielectric of the intervening medium. Some of these factors can be estimated more accurately than others. By making reasonable assumptions fairly good agreement between experimental and calculated values can be obtained. The following simplified expression can be used to examine the distance factor:

$$\Delta U_m \times r_m^3 = \Delta U_b \times r_b^3 = \Delta U_t \times r_t^3.$$

ΔU is the potential energy difference for *cis* and *trans* reaction for mono(m)-, bi(b)-, and tri(t)-cyclic compounds, and r is the distance between each pair of dipoles (average of *cis*- and *trans*-distances). The experimental ratio for the bicyclic nitrile (69:31 in cyclopentane) gives a ΔU_b value of 480 cal. mole^{-1}, which can be used to give calculated values of ΔU_m and ΔU_t:

	Calculated	Experimental
ΔU_m	2260	1750 (± 50)
ΔU_t	160	165 (± 75)

Dipole–dipole interactions should be increased by replacement of the two olefinic hydrogens by methyl groups as a larger positive charge may then be supported in the vicinity of the ring-carbon atoms; the dipole moment of the transition state should be increased and the *cis*:*trans* product ratio magnified. This effect was observed when cyclopentane (but not acetonitrile) was used as reaction solvent for the following bicyclic compounds:[9]



	trans-Reaction (%)	
Peroxylauric acid in cyclopentane	74	69
Peroxylauric acid in acetonitrile	54	54

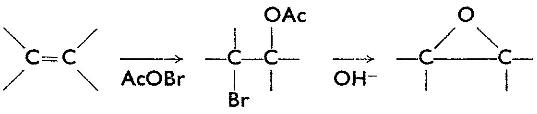
A more extensive survey (see Table) of solvent effects was made in the case of the reaction of 4-cyanocyclohexene (I) with peroxylauric acid.[9]

trans-*Epoxy-nitrile (%) from 4-cyanocyclohexene in the solvents named*

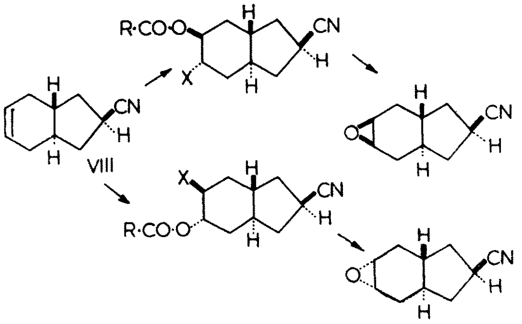
Hydrocarbons		*Halides*	
Cyclopentane	82	1-Chloropropane	80
Benzene	81	2-Chloropropane	79
Ethers		*Ketones*	
Isopropyl ether	82	Cyclohexanone	75
Diethyl ether	80	Butan-2-one	75
Tetrahydrofuran	79	Acetone	74
Alcohols		*Nitriles*	
t-Butanol	80	Isobutyronitrile	69
Butan-2-ol	80	Acetonitrile	68
Propan-2-ol	79·5		
Cyclohexanol	79	*Nitroalkane*	
Ethylene glycol	79	Nitromethane	69
Methanol	78		
Ethanol	78		
Butan-1-ol	78		

The amount of *trans*-product is greatest in the least polar solvents, but closer examination shows that the values do not depend only on the bulk dielectric constant of the solvent or on the dipole moments of individual solvent molecules (*e.g.*, reactions in cyclopentane and isopropyl ether afford the same ratio); specific solvation factors are undoubtedly also involved. The accessibility of a polar atom or group in the solvent molecules may be a factor of some importance (cf. the values obtained in the three ethers).

As noted already, epoxides can be prepared by reaction of an olefin with acetyl hypobromite followed by treatment of the bromoacetate with alkali:



In cyclic compounds the configuration of the epoxide is the same as that of the acetate group in its precursor. In order to find the effect of a remote polar substituent on the initial addition, the bicyclic nitrile (VIII) was treated with various acyl hypohalites



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[9] Henbest and Stewart, unpublished results.

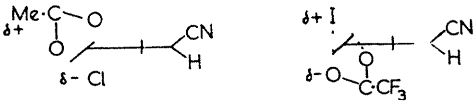
(generated from the appropriate silver salt and halogen in carbon tetrachloride). The total products were treated with alkali and analysed by gas chromatography.

	AcOCl	AcOBr	$F_3C·CO·OBr$	AcOI	$F_3C·CO·OI$
trans-Epoxide (%)	31	38*	45	47*	59

* See text.

Change of solvent from carbon tetrachloride to acetonitrile in the reactions marked with an asterisk changes the ratio to 50:50, indicating that a polar directive effect is also operative in these additions.[7]

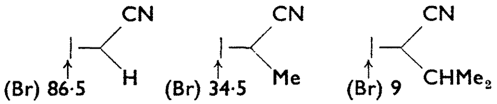
Although less is known about the mechanism of the olefin–acyl hypohalite reaction, the picture (C) of two of the transition states may be proposed. The reactions depicted are those in which the strongest directive effects were observed.



(C)

The + and − charges are placed on the transition-state side of each diagram so that dipole–dipole interactions with the nitrile group are most favourable. In the formation of these major products, acetoxyl and iodine assume positive charges whereas trifluoroacetoxyl and chlorine more readily assume negative charges. Precedents for such trends are available for more ionic forms of these atoms and groups.

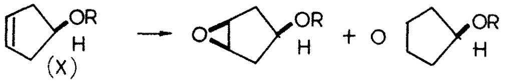
In the addition of acetyl hypobromite to monocyclic compounds, this polar directive effect is opposed by a steric effect; a methyl group, and to a greater extent, an isopropyl group, diminish the proportion of bromine attack on that side of the molecule.



Directive effects of another kind may be caused by association of the reagent with the substituent by some form of partial bonding. The reagent would then be held, albeit temporarily, on the same side of the ring as the substituent and the probability of *cis*-attack could be increased. Such an effect was first observed in the reactions of certain allylic cyclohex-2-enols with peroxy-acids in which *cis*-hydroxy-epoxides are formed; hydrogen bonding between the hydroxyl substituent and the reagent was postulated as occurring in these reactions.[10] *cis*-Attack of peroxyacid was also encountered with the allylic amide, 3-benzamidocyclohexene.[11] The predominant formation of *trans*-epoxy-compounds from allylic ethers and esters, and the large negative entropy of activation (see Table) in the cyclohex-2-enol–peroxybenzoic acid reaction,[12] are consistent with the chelative mechanism proposed for the latter.

Reactions of peroxybenzoic acid with:	$\Delta H\ddagger$ (kcal. mole^{-1})	$\Delta S\ddagger$ (cal. deg.$^{-1}$ mole^{-1})
cyclohexene	10·42	−32·9
3-hydroxycyclohexene	8·35	−41·0
3-methoxycyclohexene	12·36	−30·7

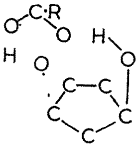
A *cis*-epoxy-alcohol can also be obtained in high yield (80—90%) from the reaction of a peroxy-acid with the homoallylic cyclopent-3-enol (X; R = H). The hydroxyl group in this compound is well placed to participate in the transition state of the *cis*-reaction (cf. XI).[13] The yield of *cis*-product (see Table) is good when cyclopentane or acetonitrile is used as reaction solvent, but in ether or propan-2-ol, a higher proportion of *trans*-epoxy-alcohol is produced, probably because the hydroxyl group of the unsaturated alcohol tends to be hydrogen bonded to the oxygenated solvent instead of to the peroxy-acid. The chelative mechanism cannot operate in the reaction of 4-methoxycyclopentene (X; R = Me) with peroxy-acid. In this case the general polar directive effect causes the *trans*-epoxy-compound to be formed predominantly, and the dependence of *cis*:*trans* ratio upon solvent is similar to that for 4-cyanocyclopentene.



(C)

trans-Epoxy-compound (%)

Solvent	R = H	R = Me
Cyclopentane	10	92
Acetonitrile	21	67
Diethyl ether	37	91
Methanol	57	57



(XI)

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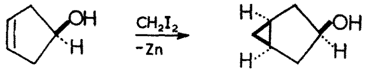
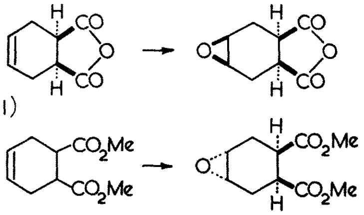
[10] Henbest and Wilson, *J.*, 1957, 1958.
[11] Goodman, Winstein, and Boschan, *J. Amer. Chem. Soc.*, 1958, **80**, 4312.
[12] Henbest and Nicholls, unpublished results.
[13] Darby, Henbest, and McClenaghan, *Chem. and Ind.*, 1962, 462.

Other *cis*-directive effects that depend upon special interactions between reagents and functional groups may be expected. The specific addition of a methylene unit *cis* to the hydroxyl group of 4-hydroxycyclopentene appears to be an example;[14] co-ordination of the hydroxyl group to an intermediate organometallic species is possible during the addition.



Another instance is the *cis*-attack of peroxy-acid on the anhydride[15] (XII). We have confirmed this

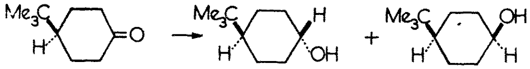


(XII)

(XIII)

result, and have shown that 90% or more of the *cis*-epoxide is formed in benzene, acetonitrile, or chloroform. In contrast, the related diester gives the *trans*-epoxide (XIII) as the main product (80% in cyclohexane and 73% in acetonitrile). Intermediate addition of the peroxy-acid to one of the carbonyl groups of the anhydride (XII) could be responsible for the observed *cis*-selectivity.

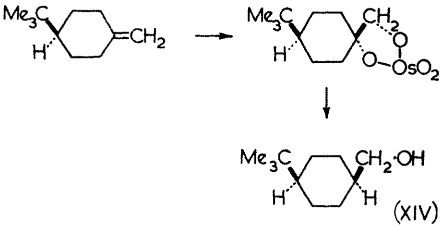
Remotely placed substituents can also influence the direction of addition of reagents to exocyclic double bonds, including that of a keto-group.[16] Most information is available in the cyclohexane series where the reactions of alkyl-substituted compounds should be first considered.[17] The major product from the reduction of alkylcyclohexanones by metal hydrides in solution is usually the more stable (equatorial) alcohol formed by addition of hydrogen from the axial direction.



	(Axial addition of hydrogen)	(Equatorial addition of hydrogen)
$LiAlH_4$	92	8
$NaBH_4$	89	11
Equilibrium ratio	79	21

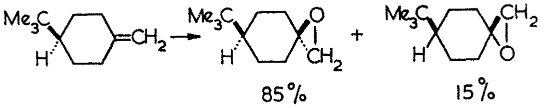
The results given above for the conformationally rigid 4-t-butylcyclohexanone show that the yield of equatorial alcohol can be higher than that present in the equilibrium mixture of alcohols. Thermodynamic control by the *O*-aluminium or *O*-boron complex formed in the reaction accounts for this difference; indeed, when a mixture of lithium aluminium hydride and aluminium chloride is used for reduction the final yield of equatorial alcohol can be virtually quantitative owing to the exceptionally bulky $-OAlCl_2$ intermediate.[18]

Another factor that may help to decide the direction of addition to an exocyclic bond of a cyclohexane derivative in its chair conformation is that the two sides of the ring are topologically different and can therefore present different degrees of steric hindrance to an approaching reagent. For this reason a large reagent would be more likely to add from an equatorial than an axial direction. The addition of osmium tetroxide to 4-t-butylmethylenecyclohexane is a good example: the diol (XIV) is formed in 90% yield (after hydrolysis of the intermediate adduct).[19] Hydrogenation catalysts are also bulky and a preference for equatorial approach is often observed, although the ratios obtained can be dependent on other factors, *e.g.*, the pressure of hydrogen.[20,21] In cases of 4-t-butylcyclohexanone and 4-t-butylmethylenecyclohexane the products obtained by addition of hydrogen from an equatorial direction are known to be the less stable isomers.



(XIV)

On the other hand, a peroxy-acid is relatively small and the reaction of peroxylauric acid with 4-t-butylmethylenecyclohexane gives mainly the product of axial attack.[22] This reaction may be controlled by steric or thermodynamic factors (or both). With regard to the latter, the chief product would also be expected to be the more stable isomer. This



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[14] Winstein and Sonnenburg, *J. Amer. Chem. Soc.*, 1961, **83**, 3235.

[15] Gray, Heitmeier, and Kraus, *J. Amer. Chem. Soc.*, 1962, **84**, 89.

[16] Combe and Henbest, *Tetrahedron Letters*, 1961, 404.

[17] Dauben, Fonken, and Noyce, *J. Amer. Chem. Soc.*, 1956, **78**, 2579; Dauben and Bozak, *J. Org. Chem.*, 1959, **24**, 1596; Jones and Wise, *J. Amer. Chem. Soc.*, 1962, **84**, 997.

[18] Eliel and Rerick, *J. Amer. Chem. Soc.*, 1960, **82**, 1367.

[19] Cross and Whitham, unpublished results. We thank Dr. G. H. Whitham (Birmingham) for this information.

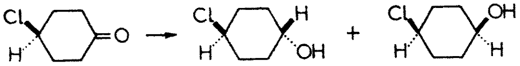
[20] Eliel and Ro, *J. Amer. Chem. Soc.*, 1957, **79**, 5997.

[21] Communication from S. Siegel, quoted by Sauvage, Baker, and Hussey, *J. Amer. Chem. Soc.*, 1960, **82**, 6090.

[22] Henbest and McKervey, unpublished results.

may be suggested from a knowledge of *A* values of groups (methyl 1·74; hydroxyl 0·78)[23] with structures similar to those of the methylene and epoxide functions.

Compared with the behaviour of a 4-alkylcyclohexanone, reduction of 4-chlorocyclohexanone with sodium borohydride yields a greater proportion of *cis*-compound:[16]

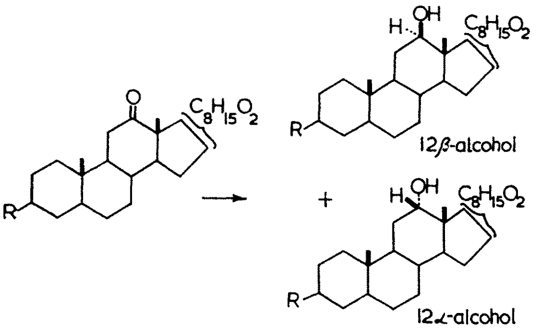


(XV) (XVI)

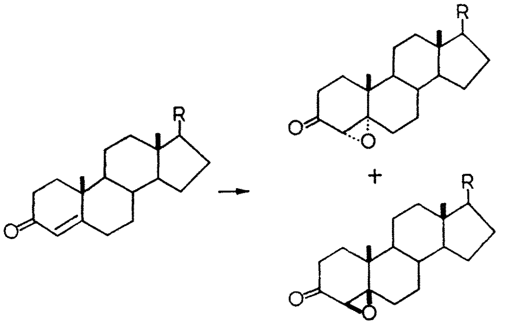
	(XV)	(XVI)
$NaBH_4$ in methanol	41	59
$NaBH_4$ in propan-2-ol	37	63
Equilibrium ratio	55	45

The formation of more axial alcohol from the chloroketone can be explained by dipole–dipole interactions between the C–Cl group and the transition state for hydride addition.[16] [The unusually high proportion (45%) of *cis*-isomer in the equilibrium mixture of the chloro-alcohols shows that dipole–dipole interactions are also present in the ground states of these molecules.] This conclusion is supported by study of the kinetics of the reduction of various 4-substituted cyclohexanones because a linear free-energy relation is found when log (reaction rate) is plotted against the σ_I value of the 4-substituent. The increased preference for the formation of *cis*-product when an electron-attracting substituent is present is reflected in the ρ_{cis} and ρ_{trans} values (3·78 and 1·96, respectively).[24]

This effect of chlorine upon the borohydride reduction of a ketone can be transmitted across three saturated rings; the proportion of 12α(axial)-alcohol from a 12-oxotigogenin is increased when a halogen atom is present at position 3 (see Table). From the quantitative point of view even stronger long-range directive effects are observed in the reactions of 17-substituted 3-oxo-Δ^4-steroids with alkaline hydrogen peroxide.[25] The β-epoxide is the normal product, but up to 30% of the α-epoxide is formed when an electron-attracting substituent is present at position 17. A significant result is that the ratio α:β-epoxide is changed only slightly when the configuration of the 17-substituent is reversed (it may be noted that 3α- and 3β-chlorine both have the effect of increasing the proportion of 12α-alcohol obtained in the reduction of 12-oxotigogenins). These results suggest that the positive end of the dipole (δ+ at C-17) is responsible for the directive effect, the substituent (the negative end of the dipole) being embedded in the polar solvent and therefore relatively ineffective. The directive effect then depends upon the relative sizes of the electrostatic interactions between the partial positive charge at C-17 and the two anionic reaction intermediates formed by initial α- or β-addition of hydroperoxide anion at position 5. As the charges in each pair are unlike, favourable interactions may develop in both cases, but in the intermediate from β-addition of hydroperoxide ion the steroid molecule is bent, which allows polar solvent molecules to interpose themselves partially between the line of charges; this does not occur with the more planar intermediate from α-addition of hydroperoxide ion.



	R = H	R = α-Cl	R = β-Cl
	% 12α-Alcohol (± 3%)		
$NaBH_4$ in tetrahydrofuran	22	33	29
$NaBH_4$ in acetonitrile	9	12	17



R	α-Epoxide (%)	β-Epoxide (%)
H or alkyl	0	100
β-Ac	26	74
α-OH	27	73
β-OH	30	70

Numerous possibilities remain for the further investigation of the influence of near and remote groups upon the reactions of alicyclic molecules. A greater variety of directive effects may be found in the reactions of these molecules than in the substitution of aromatic compounds. Already we see that steric factors in addition can be studied with the aid of 4-methylcyclopentene, and that the reactions of rigid bicyclic molecules such as (VIII) provide insight into the polarity of certain transition states.

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[23] Lewin and Winstein, *J. Amer. Chem. Soc.*, 1962, **84**, 2464.

[24] Kwart and Takeshita, *J. Amer. Chem. Soc.*, 1962, **84**, 2833.

[25] Henbest and Jackson, unpublished results.

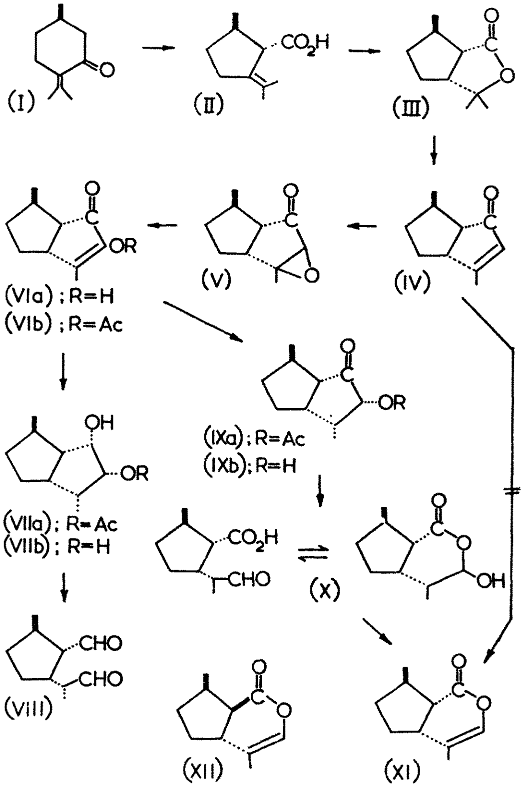
COMMUNICATIONS

A Stereospecific Synthesis of the Enantiomer of Natural Iridodial, and of Natural Nepetalactone

By S. A. ACHMAD and G. W. K. CAVILL

(SCHOOL OF CHEMISTRY, THE UNIVERSITY OF NEW SOUTH WALES, AUSTRALIA)

trans-PULEGENIC ACID (II), the starting material for these syntheses, results from the action of sodium methoxide in methanol,[1] or in dimethoxyethane,[2]* on pulegone dibromide which, in turn, is formed from (+)-pulegone (I).[3,4]† Treatment of the *trans*-acid (II) with 10N-hydrochloric acid in methanol gives the γ-lactone (III; 90%) which is then transformed into the bicyclo-octenone (IV; 28%) by the action of phosphorus pentoxide in phosphoric acid. Use of the bicyclo-octenone (IV) as an intermediate in the synthesis of two cyclopentanoid monoterpenes[5] is now described.



Epoxidation of (IV) with alkaline hydrogen peroxide solution gives the oxo-epoxide (V; 52%) which is converted into the hydroxybicyclo-octenone (VIa; 80%) by sulphuric acid in acetic acid. Complete hydrogenation (Adams catalyst) of its acetate (VIb; 89%) yields the diol monoacetate (98%), which is assigned structure (VIIa). Hydrolysis of (VIIa) gives the crystalline diol (VIIb; 89%). Finally, fission of this diol with sodium periodate in aqueous ethanol yields (VIII), the enantiomer of one of the forms of natural iridodial.[6] Gas chromatography of (VIII) gives one peak, whereas natural iridodial shows two peaks. Synthetic iridodial (VIII), after treatment with aqueous acetic acid, gives a product whose gas-chromatographic retention times and infrared spectrum are in agreement with those of the natural product.

Peracid oxidation of the bicyclo-octenone (IV) should give the nepetalactone (XI) but this direct transformation has not yet been achieved. Alternatively, partial hydrogenation (Adams catalyst) of (VIb) gives the saturated acetoxy-ketone (IXa; 85%), whence alkaline hydrolysis yields the parent ketol (IXb; 73%). Oxidation of this ketol with lead tetra-acetate in acetic acid, gives the nepetalic acids (as X) which, on pyrolysis, are converted into the enantiomer of natural nepetalactone (XI; 63%). Gas chromatography shows one peak identical in retention time with that of the natural product. The infrared spectrum of (XI) corresponds closely to that of natural nepetalactone, which contains E XI and a proportion of E XII.[7] Conversion of synthetic nepetalactone (XI) into the nepetalinic acids, of known configuration, is in progress.

The authors acknowledge the award of a Colombo Plan Scholarship (to S.A.A.), and thank Dr. E. J. Eisenbraun for a specimen of natural nepetalactone.

(*Received, April 1st*, 1963.)

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* We agree with Wolinsky, Wolf, and Gibson[1] on the stereochemistry of the pulegenic acids, but disagree with their interpretation of the Favorskii transformations[2] which are involved.

† (+)-Pulegone, as supplied by Keith Harris and Co. Ltd., Sydney, has $[\alpha]^{25}_{D}$ + 24·1°.

[1] Wolinsky, Wolf, and Gibson, *J. Org. Chem.*, 1963, **28**, 274.

[2] Achmad and Cavill, unpublished work.

[3] Wallach, *Annalen*, 1917, **414**, 233, and earlier papers.

[4] von Rupe and Schafer, *Helv. Chim. Acta*, 1928, **11**, 466.

[5] For a review, see Cavill, *Rev. Pure and Appl. Chem.*, 1960, **10**, 169.

[6] Cavill and Ford, *Austral. J. Chem.*, 1960, **13**, 296.

[7] Bates, Eisenbraun, and McElvain, *J. Amer. Chem. Soc.*, 1958, **80**, 3420, and earlier papers.

Study of Organic Molecular Complexes by Polarography

By M. E. PEOVER

(NATIONAL CHEMICAL LABORATORY, TEDDINGTON, MIDDLESEX)

SOME of the first determinations of the stabilities of organic complexes were made in the course of aqueous potentiometric titrations of redox systems in which dimers are formed between the reduced and the oxidised species.[1] However, such systems constitute special examples of a much wider group of donor–acceptor interactions, "charge-transfer" interations.[2]

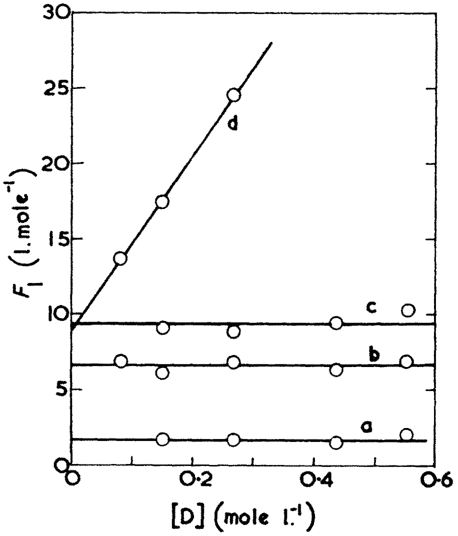
Under polarographic conditions in aprotic solvents of moderate dielectric constant, most aromatic acceptor molecules have been found to exhibit reversible oxidation–reduction behaviour,[3] $A + e \rightleftharpoons A^-$. We find this is also true in some solvents of low dielectric constant (chloroform, methylene chloride, benzotrifluoride, tetrahydrofuran) in which donor–acceptor interactions tend to be strongest. In the presence of a compound forming a complex with A but not with A^-, the polarography of the $A \rightleftharpoons A^-$ system should be altered in a manner which depends on the free-energy of formation of the donor–acceptor complex. We find that organic donor–acceptor interactions are readily studied in this way.

Special problems of technique encountered are: a high concentration of supporting electrolyte is required to eliminate migration currents (0·5M-NBu_4ClO_4 is satisfactory); a high cell resistance, which was overcome by using a controlled-potential device;[4] a suitable reference electrode, for which the half-cell Ag|AgI, AgI(sat.), 0·05M-NBu_4I, 0·5M-NBu_4ClO_4 in the chosen solvent was found satisfactory; and occasional adsorption phenomena, usually eliminated by a trace of a polymer.

Adding hexamethylbenzene to a chloroform solution of, say, tetracyanoethylene shifts the first wave in the polarogram of the latter to more negative potentials (*e.g.*, a shift of 50 mv is obtained with 0·55M-hexamethylbenzene); the polarogram remains reversible, indicating rapid dissociation of the complex, that is confirmed by a.c. polarograms. The shifts in half-wave potential, Δ, from the value in the absence of added hexamethylbenzene, can be analysed by conventional metal-ion ligand theory:[5]

$$F_0 = \frac{I_S}{I_C}\,\text{antilog}_{10}\,\frac{F\Delta}{2{\cdot}303\boldsymbol{R}T} = 1 + K_1[D] + K_2[D]^2 + \ldots K_n[D]^n$$

in which K_1, K_2... are successive formation constants, and I_S/I_C is the ratio of the diffusion current of simple and complex species at the donor concentration [D], ([D] $\gg$ [A]). Plots of $F_1 = (F_0 - 1)/[D]$ against [D] are shown for a number of acceptor molecules. The plots giving lines parallel to the *x*-axis indicate 1:1 association with *y*-intercepts of K_1. The dichlorodicyanoquinone plot shows that association with two hexamethylbenzene molecules occurs; the intercept gives K_1, the slope K_2. The K_1 values are lower than are obtained from observations on the charge-transfer bands in pure chloroform. Probably the supporting electrolyte ion-pairs have the same effect as adding a small quantity of polar solvent. The polarographic method assumes that the donor concentration at the surface of the electrode is the same as in the bulk of the solution and that there is no influence from the electric field in the vicinity of the electrode.



Complex formation, as a function of hexamethylbenzene concentration, with (a) *tetracyanoquinodimethane,* (b) *chloranil,* (c) *tetracyanoethylene,* (d) 2,3-*dichloro*-5,6-*dicyanoquinone, in* $CHCl_3$–0·5N-NBu_4ClO_4, *at* 25°. Acceptor concn. 5 — 8 × 10^{-4}M.

Studies in chloroform solution are limited to the stronger acceptor molecules because of reduction of

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[1] Michaelis and Fletcher, *J. Amer. Chem. Soc.*, 1937, **59**, 2460; Michaelis and Schubert, *Chem. Rev.*, 1938, **22**, 437.
[2] Mulliken, *J. Chem. Phys.*, 1951, **19**, 514.
[3] Peover, *Nature*, 1961, **191**, 702; *Trans. Faraday Soc.*, 1962, **58**, 1656, 2370.
[4] Arthur and Vanderkam, *Analyt. Chem.*, 1961, **33**, 765.
[5] See Irving, *Adv. Polarography*, 1960, 42.

the solvent at negative potentials; most acceptors can be studied in methylene chloride. If the acceptor does not give a reversible reduction wave the donor component may undergo reversible oxidation (*e.g.*, tetramethyl-*p*-phenylenediamine). When the half-wave potentials of donor and acceptor are similar, a redox process giving free-radical ion formation occurs[6] as well as complex formation. The polarographic method allows a precise study of the energetics of these various processes. Other advantages are (i) the method is independent of the assumptions of the spectroscopic method, (ii) it is applicable where charge-transfer absorptions are concealed or ambiguous, and (iii) interaction with transient species capable of electrochemical generation can be studied.

(*Received, April 6th,* 1963.)

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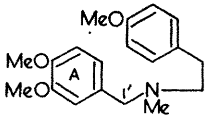
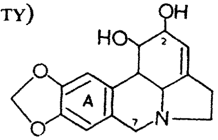
[6] Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1962, p. 186; Allison, Peover, and Gough, *Nature*, 1963, **197**, 764.

Biosynthesis in the Amaryllidaceae: Further Evidence on the C_6–C_1 Unit and the Methylenedioxy-group

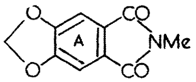
By D. A. ARCHER, S. W. BREUER, R. BINKS, A. R. BATTERSBY, and W. C. WILDMAN
(THE ROBERT ROBINSON LABORATORIES, UNIVERSITY OF LIVERPOOL, AND THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF BRISTOL AND IOWA STATE UNIVERSITY)



(I)



(II)



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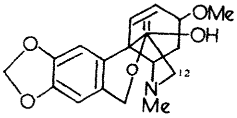
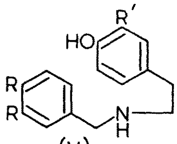
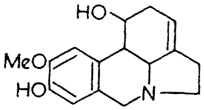


(IV)



(V)



(VI)

THE conversion of phenylalanine into the C_6–C_1 unit which is built into belladine[1] (I) and lycorine[1,2] (II) may occur (*a*) *via* phenylserine and then fission[2] or (*b*) by way of cinnamic acid[1] as for the phenolic cinnamic acids.[3] The tracer evidence below supports the latter pathway.

Sodium *trans*-[3-^{14}C]cinnamate fed to *Nerine bowdenii* plants yielded radioactive alkaloids. The lycorine (II; 1·00 C*, incorporation 0·02%), was oxidised and the product isolated as *N*-methylhydrastimide[4] (III; 0·97 C*). Degradation of the belladine (I; 1·00 C*), as earlier,[1] proved that ring A and atom $C_{1'}$, together carry almost all (0·94 C*) of the total activity of the molecule.

Sprekelia formosissima plants were fed with [7-^{14}C]benzaldehyde; the isolated tazettine (IV) was weakly radioactive (0·005% incorporation). Degradation[5] to *NN*-dimethylglycine showed 5% of the total activity in this unit. This result and the poor incorporation compared with other precursors[5] suggest that benzaldehyde is not on the biosynthetic pathway. Also [1'-^{14}C]bisdeoxynorbelladine (V; R = R' = H) fed to the same species led to tazettine (IV) and haemanthamine of negligible activity.

The stage at which introduction of the hydroxyl group at position-2 of lycorine occurs has been studied by feeding [1'-^{14}C]hydroxynorbelladine (V; R = R' = OH) to "Twink" double *Narcissus* plants. The incorporations into lycorine (II) and norpluviine (VI) were $6{\cdot}8 \times 10^{-4}$% and $1{\cdot}7 \times 10^{-3}$%, respectively; the incorporations[6] from norbelladine (V; R = OH, R' = H) into these alkaloids were 0·24% and 0·74%, respectively. This suggests that hydroxylation occurs at a later stage in the biosynthesis and experiments to test this are in hand.

The methylene group of the methylenedioxy-system of haemanthamine has been proved[7] to originate from an *O*-methyl group. Support for this origin in the case of lycorine has been obtained by feeding L-[*methyl*-^{14}C]methionine[8] to "Twink" daffodils. The isolated lycorine (II) and norpluviine (VI) were labelled almost exclusively at the methylene group (0·95 C*) and at the *O*-methyl group (1·01 C*), respectively.

This investigation was supported in part by a Public Health Service Research Grant to Iowa State University of Science and Technology, from the National Heart Institute.

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[1] Wildman, Battersby, and Breuer, *J. Amer. Chem. Soc.*, 1962, **84**, 4599.
[2] Suhadolnik, Fischer, and Zulalian, *J. Amer. Chem. Soc.*, 1962, **84**, 4348.
[3] McCalla and Neish, *Canad. J. Biochem. and Physiol.*, 1959, **37**, 537; Neish, *Phytochem.*, 1961, **1**, 1.
[4] Warnhoff and Wildman, *J. Amer. Chem. Soc.*, 1957, **79**, 2192.
[5] Wildman, Fales, and Battersby, *J. Amer. Chem. Soc.*, 1962, **84**, 681.
[6] Battersby, Binks, Breuer, Fales, and Wildman, *Proc. Chem. Soc.*, 1961, 243.
[7] Barton, Kirby, and Taylor, *Proc. Chem. Soc.*, 1962, 340.
[8] Cf. Sribney and Kirkwood, *Nature*, 1953, **171**, 931.

The Kinetics of the Dissociation of Weak Acids measured by a Rotating Platinum Disc Electrode

By W. J. ALBERY and R. P. BELL
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THE kinetics of the fast forward and backward reactions of an equilibrium between reducible and irreducible species in solution have been widely studied by polarography. It has been known for some time that similar studies could be carried out with a rotating platinum disc electrode, and in fact Vielstich and Jahn[1] have investigated the dissociation rates of a number of weak acids.

The rotating disc electrode has advantages over the mercury drop in that the speed of rotation can be easily varied and accurately measured; the corresponding quantity in polarography, the drop time, is not such a convenient experimental variable. Furthermore, platinum has a much lower overvoltage for the discharge of hydrogen than mercury and so reactions involving protons can be studied directly and no depolariser is needed. But unfortunately, when the potential of the rotating electrode is made large enough to make the electrode reaction very much faster than the diffusion of protons to the disc, so that the limiting diffusion current can be measured, water itself begins to be decomposed on the electrode. This means that one observes only a point of inflexion in the current–voltage curve, rather than a substantial plateau. Calculations of rate constants based on such points of inflexion are likely to have a large error.

We have developed a modification of the method, which allows the current due to the decomposition of water to be balanced and hence the true limiting current to be measured. Two cells, each with a rotating electrode, are used. One is filled with a standard hydrochloric acid solution, the other with the weak acid buffer to be studied. They are made part of a Wheatstone bridge circuit. The ratio of the values of the two resistances in the other arms of the circuit is the same as the areas of the two discs. This ensures that when the bridge is balanced, not only is there the same potential difference at both electrodes, but also the same current density. Under these conditions the decomposition of water per unit area should be identical on each disc, and hence the current due to the electrode reaction

$$H^+ + e \rightarrow \tfrac{1}{2}H_2$$

should also be equal. At the potentials used the "water current" is still considerably smaller than the "H$^+$ current" and so the above assumptions need only be a first-order approximation.

To find the balancing conditions, the "weak-acid electrode" is rotated at a known speed. A series of voltages are applied across the Wheatstone bridge. At each voltage the speed of the "strong-acid electrode" is adjusted until the bridge is balanced. A range of about 0·15 v is found over which this speed alters by less than 2%. This corresponds to the plateau in the normal current–voltage diagram.

At this point, from previous work[2,3,4] we find that

$$\text{Flux} = \frac{C_{H^+}}{\dfrac{\mu_{H^+}}{\sqrt{\omega_{H^+}}}} = \frac{C_{HA}}{\dfrac{\mu_{HA}}{\sqrt{\omega_{HA}}} + \sqrt{\dfrac{[A^-]}{D_{H^+}k_d K}}},$$

where subscript H$^+$ refers to the strong acid and subscript HA to the weak acid.

$$\text{Also, } \mu = 1{\cdot}8\,\nu^{-\frac{1}{6}}\,D^{-\frac{2}{3}}\left\{0{\cdot}8934 + 0{\cdot}316\left(\frac{D}{\nu}\right)^{0\cdot36}\right\},$$

where D is the diffusion coefficient in cm.^{2} sec.$^{-1}$, ν the kinematic viscosity in cm.^{2} sec.$^{-1}$, C the concentration, ω the velocity of rotation in radians sec.$^{-1}$, k_d the first-order rate constant for the dissociation $HA \rightarrow H^+ + A^-$ in sec.$^{-1}$, K the dissociation constant for the weak acid in moles l.$^{-1}$, and [A$^-$] the calculated concentration of weak acid anion at the electrode. Rearranging one gets:

$$\sqrt{\frac{\omega_{HA}}{\omega_{H^+}}} = \frac{C_{H^+}}{C_{HA}}\cdot\frac{\mu_{HA}}{\mu_{H^+}} + \frac{C_{H^+}\sqrt{\omega_{HA}}}{C_{HA}\mu_{H^+}}\sqrt{\frac{[A^-]}{D_{H^+}k_d K}}\,.$$

Since μ varies as $D^{-\frac{2}{3}}$ and since $D_{H^+} \sim 8 \times D_{HA}$, C_{HA} is made about 4 × C_{H^+} so that $\omega_{H^+} \sim \omega_{HA}$.

To prevent migration of reactants due to the electric field it is usual to use an excess of an inert salt in the cell. But, since the larger the concentration of A$^-$ the larger will be the kinetic terms, we have used KA only. The excess of salt both carries the current and acts as the buffer.

Measurements have been made on solutions containing: 2 × 10^{-2}M-acetic acid in 0·1M- and in 0·3M-potassium acetate, and on 3 × 10^{-2}M-trimethylacetic acid in 0·1M- and in 0·3M-potassium trimethylacetate. The strong-acid solution used throughout was 5 × 10^{-3}M-hydrochloric in 0·1M-potassium chloride.

The limiting current of the strong-acid solution by itself agreed with the theoretically calculated current to about 1%. For acetic acid the intercept term $(C_{H^+}\mu_{HA}/C_{HA}\mu_{H^+})$ for the plot of $\sqrt{(\omega_{HA}/\omega_{H^+})}$ against $\sqrt{\omega_{HA}}$ agreed with theory to within the

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[1] Vielstich and Jahn, *Z. Elektrochem.*, 1960, **64**, 43.
[2] Koutecky and Levich, *Zhur. fiz. Khim.*, 1958, **32**, 1565.
[3] Dogonadse, *Zhur. fiz. Khim.*, 1958, **32**, 2437.
[4] Gregory and Riddiford, *J. Chem. Soc.*, 1956, 3756.

experimental error of 3%. The diffusion coefficient of trimethylacetic acid has not yet been measured. An estimate for the intercept based on the relative mobilities of AcO^- and $Me_3C{\cdot}CO_2^-$ was within 4% of the experimental value for 0·1M-potassium trimethylacetate. There was a much larger discrepancy for a 0·3M-solution, but in this case the viscosity of the solution is 1·15 times that of pure water and so it is likely that the estimated value is in error.

The results obtained for k_d at 25°C in sec.$^{-1}$ were:

0·1M-KOAc	$9{\cdot}7 \times 10^5$	0·1M-$KO_2C{\cdot}CMe_3$	$1{\cdot}26 \times 10^5$
0·3M-KOAc	$7{\cdot}6 \times 10^5$	0·3M-$KO_2C{\cdot}CMe_3$	$1{\cdot}31 \times 10^5$

On correcting for the drop in $D_+ + D_-$ caused by the salt solutions and on averaging, one gets the following values at infinite dilution:

	k_d (sec.$^{-1}$)	k_r (mole^{-1} l. sec.$^{-1}$)
Acetic acid	$9{\cdot}1 \times 10^5$	$5{\cdot}2 \times 10^{10}$
Trimethylacetic acid	$1{\cdot}42 \times 10^5$	$1{\cdot}53 \times 10^{10}$

The experimental error is estimated at ± 10%. The average value for acetic acid agrees well with that of Eigen and Eyring, which was obtained by a relaxation technique, the dispersion of an electric field being measured.[5] The low value for the recombination reaction between H^+ and $Me_3C{\cdot}CO_2^-$ must be due to the large steric blocking effect of the t-butyl group.

One of us (W.J.A.) thanks the Gas Council for a research scholarship.

(*Received, April 5th,* 1963.)

[5] Eigen and Eyring, *J. Amer. Chem. Soc.*, 1962, **84**, 3254.

The Synthesis of Cycloartane

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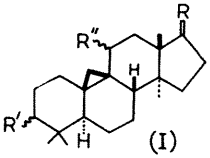
WE wish to report the synthesis of cycloartane[1] (I; $R = C_8H_{17}$, $R' = R'' = H$), the parent hydrocarbon of an expanding group[2] of pentacyclic triterpenoids.

Photolysis[3] of the nitrite (II; $R = C_8H_{17}$, $R' = NO$, $R'' = Me$), m.p. 124—127°, $[\alpha]_D + 95°$, of 3β-acetoxylanostan-11β-ol gave the 19-oximino-derivative (II; $R = C_8H_{17}$, $R' = H$, $R'' = CH{=}N{\cdot}OH$), m.p. 199—203°, $[\alpha]_D + 84°$, together with 3β-acetoxylanostan-11β-ol and some 3β-acetoxylanostan-11-one. There was little, if any, attack upon C-18. Reduction of the oxime with lithium aluminium hydride gave 19-aminolanostan-3β,11β-diol, m.p. 219—222°, $[\alpha]_D + 46°$. Dehydration of the oxime with sodium acetate–acetic anhydride on the steam-bath gave the acetoxy-nitrile (II; $R = C_8H_{17}$, $R' = H$, $R'' = CN$), m.p. 259—260°, $[\alpha]_D + 69°$, which with phosphorus oxychloride and pyridine afforded the olefin (III; $R = C_8H_{17}$, $R' = Ac$, $R'' = CN$), m.p. 151—153°, $[\alpha]_D + 51°$. Reduction of the latter with lithium aluminium hydride furnished the amine (III; $R = C_8H_{17}$, $R' = H$, $R'' = CH_2{\cdot}NH_2$), m.p. 243—244°, $[\alpha]_D + 75°$. Deamination with sodium nitrite in dioxan-acetic acid–water gave the diol (I; $R = C_8H_{17}$, $R' = \beta$-OH, $R'' = \alpha$OH), m.p. 171—174°, $[\alpha]_D + 34°$, which, on chromic acid oxidation, afforded the dione (I; $R = C_8H_{17}$, $R' = (:O)$), m.p. 168—171°, $[\alpha]_D + 74°$. Wolf-Kishner reduction of the latter under forcing conditions[4] gave cycloartane (m.p., mixed m.p., $[\alpha]_D$, and analysis).



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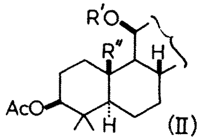

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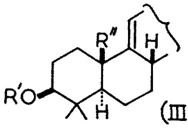

(III)

Since lanosterol, from which the 3β-acetoxylanostan-11β-ol was prepared, has been synthesised from cholesterol[5] the present work constitutes a (formal) total synthesis of cycloartane.

Satisfactory spectral and analytical data have been obtained for all new compounds. $[\alpha]_D$ are in chloroform (approx. 1%).

(*Received, April 1st,* 1963.)

[1] Barton, *J.*, 1951, 1444.
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[3] Barton, Beaton, Geller, and Pechet, *J. Amer. Chem. Soc.*, 1960, **82**, 2640; 1961, **83**, 4076.
[4] Barton, Ives, and Thomas, *J.*, 1955, 2056.
[5] Woodward, Patchett, Barton, Ives, and Kelly, *J.*, 1957, 1131.

Perloline

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R. E. CORBETT, THE LATE J. MURRAY, and B. J. SWEETMAN
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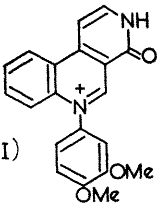
PERLOLINE,[1] the main alkaloid of perennial rye-grass (*Lolium perenne* L.), and its salts are of the form $C_{20}H_{17}N_2O_3,X,yH_2O$; in the free base, perloline, that crystallises from ethyl cellosolve–water (1:1), $X = OH$, $y = O$; in the perchlorate, m.p. 280° (decomp.), $\nu_{max.}$ ($C = N^+$) 1695 $cm.^{-1}$, $X = ClO_4$, $y = 1$ or 0; in the nitrate, m.p. 185—190° (decomp.), $X = NO_3$, $y = 1$ or 0; in the mercurichloride (red form), m.p. *ca.* 210° (effervescence), $X = \frac{1}{2}(HgCl_4)$, $y = 1$.

Hydrogenation in acetic acid or reduction by lithium aluminium hydride in tetrahydrofuran of perloline gave a product, $C_{20}H_{18}N_2O_3$, m.p. 220° (decomp.) (with an ultraviolet absorption spectrum similar to that of dimethylaniline), which was readily reoxidised to perloline. Acetylation of perloline gave an *N*-acetyl derivative (formed by acetic anhydride in pyridine), m.p. 232° (decomp.), $\nu_{max.}$ ($C = O$) 1650 $cm.^{-1}$ (broad), or an *O*-acetate (formed in refluxing acetic anhydride), m.p. 296° (decomp.), $\nu_{max.}$ ($C = O$) 1766 and 1650 $cm.^{-1}$.

The degradation of perloline and its derivatives in various ways to perlolidine, $C_{12}H_8N_2O$ (formula defined by nuclear magnetic resonance and mass spectroscopy), is interpreted as removal of a dimethoxyphenyl residue attached to nitrogen, since pyrocatechol was obtained on selenium dehydrogenation, and pyrocatechol, guaiacol, and veratrole are obtained on pyrolysis of perloline, but oxidation did not yield veratric acid. A by-product in the oxidation of perloline with potassium ferricyanide was a substance $C_{20}H_{16}N_2O_4,2H_2O$, m.p. 288° (decomp.), regarded as the lactam which would result from oxidation of a carbinolamine function. With nitric acid, both perloline and perlolidine gave picric acid, diagnostic of a benzene residue.

A crystal-structure analysis of the red form of perloline mercurichloride has been carried out at Glasgow. The crystals are orthorhombic, space group *Pnna*, with eight sets of $C_{20}H_{17}N_2O_3,\frac{1}{2}(HgCl_4),H_2O$ in the unit cell of sides $a = 12{\cdot}83$, $b = 16{\cdot}63$, $c = 18{\cdot}85$ Å. The mercury atoms were located from Patterson sections and the lighter atoms (other than hydrogen) by three-dimensional Fourier methods, from 2077 independent structure-amplitudes. The value of R is now 13·9%.

The $HgCl_4^{2-}$ anion is tetrahedral, with an average Hg–Cl of distance 2·50 Å. The water molecule is independent of the alkaloid cation which is therefore the protonated form of anhydroperloline and has structure (I). Perloline then has structure (II), and as removal of the dimethoxyphenyl group gives perlolidine, $\nu_{max.}$ (N–H) 3148, ($C = O$) 1665 $cm.^{-1}$, which also occurs in perennial rye-grass, the structure of this alkaloid is defined as (III). In agreement with the result of the *X*-ray analysis, the nuclear magnetic resonance spectrum of anhydroperloline shows the presence of 16 protons, 6 of which are in the methoxyl region, and the remainder aromatic.



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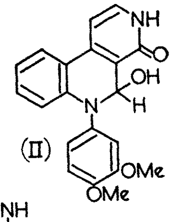

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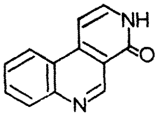

(III)

This diazaphenanthrene ring system has not previously been reported in a natural product. The positions of the nitrogen atoms suggest that a tryptamine precursor may be involved in the biogenesis.

The extensive calculations were carried out on the Glasgow University DEUCE computor with programmes devised by Drs. J. S. Rollett[2] and J. G. Sime[3]. We are grateful to Professor J. M. Robertson, C.B.E., F.R.S., for his interest, to Dr. K. Biemann

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[1] For a summary of the previously published chemistry see T. A. Henry, "The Plant Alkaloids," J. and A. Churchill Ltd., London, 1949, p. 749.

[2] Rollett, in "Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961, p. 87.

[3] Sime, ref. 2, p. 301.

(M.I.T.) for mass spectroscopy, and to Dr. A. Melera (Varian A.G., Zurich) for n. m. r. spectroscopy. Part of this work was commenced during the tenure of an I.C.I. Fellowship, Cambridge, 1951—52 (W.I.T.) and continued under a Lord Beaverbrook graduate scholarship, University of New Brunswick, 1952—53 (R.H.B.).

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Exchange Processes in the Reaction of Boron Trichloride with Triethylamine–Boron Trifluoride

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ALTHOUGH reactions in which one tervalent boron compound in a Lewis base complex is replaced by a second are well known, little information is available on their mechanisms. In the reaction of boron trifluoride with the trimethylamine complexes of organoboron dichlorides to give organoboron difluorides,[1] boron–nitrogen bond cleavage occurs, accompanied by halogen transfer. Replacement of boron trifluoride from its trimethylamine complex by boron trichloride is almost quantitative at 205°. At this temperature, the reaction may involve partial dissociation of the complex followed by rapid interaction of free trimethylamine with boron trichloride, although a bimolecular displacement of boron trifluoride by the trichloride at lower temperatures was suggested.[2] The reaction[3] of amine–boranes with a deficiency of boron trichloride or tribromide to give compounds of the type $R^1R^2R^3N,BH_yHal_{3-y}$ led, however, to suggestions that this reaction proceeds *via* hydrogen–halogen exchange, without the breaking of boron–nitrogen bonds.

The heterogeneous reaction of boron trichloride with triethylamine–boron trifluoride has now been investigated:

$$Et_3N,BF_3 + BCl_3 \rightleftharpoons Et_3N,BCl_3 + BF_3.$$

Isotopic dilution techniques established that the observed replacement involves two distinct pathways. Under sufficiently mild conditions, boron trifluoride is formed rapidly without significant B–N bond cleavage, while under more vigorous conditions, processes involving exchange of boron atoms bonded to the donor atom become important.

Triethylamine–boron trifluoride was treated with a slight deficiency of boron trichloride at temperatures between −80° and 60° The change of pressure over the mixture of complex and boron halide and the infrared spectrum of the volatile components showed that free boron trifluoride appears in a few minutes even at −80°.

In dilution experiments, isotopically normal boron trichloride (boron content taken as 20·0% of ^{10}B) was added to ^{10}B-enriched triethylamine–boron trifluoride (boron content 91·2% of ^{10}B). At the end of the reaction time, material volatile at 0° was removed (quantitative recovery, based on boron trichloride taken). This mixture of halides was kept at room temperature for 1 hr. The trifluoride was separated from the trichloride by repeated vacuum-line fractionation and analysed mass spectrometrically. Results of two typical experiments are summarised in the Table.

Temp.	Time (hr.)	$(C_2H_5)_3N,BF_3$ (mmole)	BCl_3 (mmole)	BF_3(%) in products	^{10}B Content (%)
0°	4	4.68	4.50	64.8	24.0
60°	16	5.14	4.99	70.3	57.2

At 0°, although 65% "replacement" of boron trifluoride was observed, the isotopic composition of the trichloride–trifluoride mixture corresponds to exchange with added trichloride of only about 5% of the boron originally in the complex. Formation of boron trifluoride at 0° thus occurs principally without cleavage of boron–nitrogen bonds, most probably by halogen exchange between ter- and quadrivalent boron. Less exact isotope ratios from the infrared spectrum of the halide mixture obtained by treating isotopically normal triethylamine–boron trichloride with ^{10}B-enriched boron trifluoride at 0° indicate that halogen exchange is the principal process by which boron trichloride is formed in the reverse reaction. At 60°, however, boron–nitrogen bonds are broken and re-formed, and the isotopic composition of the halide mixture obtained is close to that expected (56·0% of ^{10}B) for complete isotopic equilibration of the boron in the sample. This could occur either through partial dissociation of the various complexes present and competitive re-association of the components, or by a true displacement reaction.

The author thanks Mr. E. E. Hughes for the mass spectrometric analyses.

(*Received, April 10th*, 1963.)

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[1] Brinckman and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6235; Brinckman, Ph.D. Thesis, Harvard University, 1960.

[2] Dutton, Paterson, and Onyszchuk, *Proc. Chem. Soc.*, 1960, 149.

[3] Ratajczak, *Bull. Soc. chim. France*, 1960, 487; Nöth and Beyer, *Chem. Ber.*, 1960, **93**, 2251.

Six-co-ordinate Complexes of Bivalent Platinum and Nickel

By N. C. Stephenson and G. A. Jeffrey
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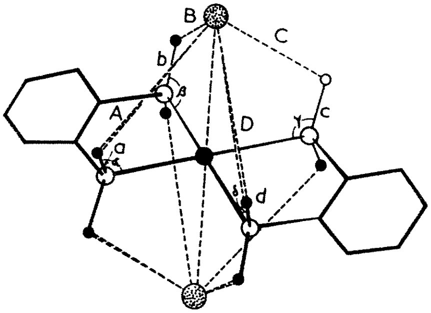
Pittsburgh 13, Pa., U.S.A.)

The study of diamagnetic d^8-complexes was, until recently, concerned with the investigation of their square-planar four-fold co-ordination. *o*-Phenylenebisdimethylarsine (diarsine) forms complexes of bivalent platinum, palladium, and nickel which have been shown to exist as five-co-ordinate cations $[M^{II}(diarsine)_2Halogen]^+$ in solution[1] and six-co-ordinate molecules $[M^{II}(diarsine)_2I_2]$ in the solid state.[2] We have elucidated the complete crystal structures of the complexes (i) $Pt(diarsine)_2Cl_2$ and (ii) $Ni(diarsine)_2I_2$. The crystal data are: (i) $a = 9{\cdot}66$, $b = 16{\cdot}60$, $c = 18{\cdot}02$ Å, Z = 4, space group *Pcan*; (ii) $a = 9{\cdot}49$, $b = 9{\cdot}25$, $c = 16{\cdot}94$ Å, $\beta = 114{\cdot}0°$, Z = 2, space group $P2_1/c$. The cell dimensions were obtained from zero-layer precession and Weissenberg photographs and are accurate to about 0·5%. Three-dimensional data for each compound were recorded on multifilm Weissenberg photographs and were estimated visually; respectively, 1649 and 1688 independent structure amplitudes were determined for the two compounds.

The position of the heavy atoms were obtained from two-dimensional Patterson and Fourier syntheses. The heavy atoms determined the majority of the structure phases, and the carbon atoms were located from three-dimensional difference Fourier syntheses. The refinement of positional and anisotropic thermal parameters for all atoms was carried out by means of successive differential syntheses with Shiono's IBM 7070 programmes.[3] The final *R* values are 12% and 11% for the platinum and the nickel compound, respectively.

The arrangement of the halogen ions and diarsine chelates around the transition metals is shown in the Figure. In both cases the central atom is surrounded by four arsenic atoms in a square plane, and two halogens complete the structure which, in total, is distorted-octahedral. The bond lengths and angles are given in the Table.



Hatched circles = Halogen. Open circles = arsenic. Large filled circles = metal. Small filled circles = methyl.

Bond distances (Å) *and angles.*

									Mean e.s.d.
Ni–As		2·28		2·30		2·28		2·30	0·002
$As–CH_3$	a	1·92	b	1·87	c	2·01	d	1·93	0·03
$I \cdots CH_3$	A	3·78	B	3·84	C	3·87	D	3·74	0·03
$Ni–As–CH_3$	α	117·3°	β	120·1°	γ	121·4°	δ	118·9°	0·90
Pt–As		2·38		2·37		2·38		2·37	0·004
$As–CH_3$	a	2·05	b	2·04	c	1·91	d	1·87	0·04
$Cl \cdot\cdot CH_3$	A	4·42	B	4·16	C	4·22	D	4·48	0·04
$Pt–As–CH_3$	α	114·1°	β	109·5°	γ	119·1°	δ	119·3°	1·20

The Ni–As bond distances are significantly shorter than the normal covalent sum (2·57 Å) for the two elements ($\Delta/\sigma > 30$). The Pt–As bond distances are also appreciably shorter than the sum of the square covalent radius for platinum(II) and the tetrahedral covalent radius for arsenic (1·31 + 1·18 = 2·49 Å). This bond distance is the same as that found[2] for the Pt–As bond in the compound $Pt(diarsine)_2I_2$. The shortening is probably due to interaction between the less stable and unfilled ligand *d* orbitals and the filled metal *d* orbitals. In this case the metal *d* orbitals are stabilised by the interaction and the separation Δ between t_{2g} and e_g orbitals is thus increased.

The Pt–Cl bond is considered to be ionic. This bond distance (4·16 Å) exceeds the sum of the ionic radius of chlorine and the van der Waals radius of bivalent platinum (1·81 + 2·07 = 3·88 Å). The chloride ion is cushioned on four methyl groups and the approach distances do not indicate a strong inter-

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[1] Harris, Nyholm, and Phillips, *J.*, 1960, 4379.
[2] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.
[3] Programmes no. 330 and 376, World List of Crystallographic Computer programmes, 1961, I.U.Cr.

action with the square-planar cations. The estimated standard deviation in the Pt–As–CH_3 angle is 1·2°, so that the distortions from the normal tetrahedral angle are significant.

The short Ni–I bond distances of 3·21 Å and the close approach of each iodide ion to the four *cis*-oriented methyl groups suggest a strong interaction between nickel and the two iodide ions. There is a significant distortion of the Ni–As–CH_3 angles (σ = 0·74°) from the tetrahedral value.

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Isomerisation of Toluenesulphonic Acids in Aqueous Sulphuric Acid

By A. C. M. WANDERS and H. CERFONTAIN

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RECENT publications by Spryskov[1] on the sulphonation of toluene in concentrated aqueous sulphuric acid at elevated temperatures and prolonged reaction time prompt us to report a kinetic study of the isomerisation of the toluenesulphonic acids in aqueous sulphuric acid.

The isomerisations were studied in 74·0 ± 0·3 wt.-% aqueous sulphuric acid at 140·8° ± 0·5° under homogeneous conditions. The method of analysis was similar to that described previously.[2] Material balances were better than 90%. Toluene-*p*- and -*m*-sulphonic acid both isomerise to yield a mixture of mostly toluene-*m*- and -*p*-sulphonic acid with only a small amount of *ortho*-isomer. On isomerisation of the *ortho*-isomer rapid formation of the *para*-isomer is observed, although eventually a similar equilibrium mixture is obtained as in the former cases. A complicating factor in the isomerisation is the formation of toluene-2,4-disulphonic acid from toluene-*p*- and -*o*-sulphonic acid. However, its rate of formation is slow compared with the rates of isomerisation under study. Sulphonation of toluene-*m*-sulphonic acid does not take place. From the limiting values of [*meta*]/[*para*] and [*ortho*]/[*para*] at high reaction time (1·60 ± 0·15 and 0·085 ± 0·015, respectively) the equilibrium composition was calculated as *para* 37·2 ± 2·2%, *meta* 59·6 ± 2·5%, and *ortho* 3·2 ± 0·6%. Toluene-*m*-sulphonic acid is apparently thermodynamically the most and toluene-*o*-sulphonic acid the least stable isomer. Our results conflict with previous observations[3] stating that toluene-*p*- and -*o*-sulphonic acid, on isomerisation, do not yield any -*m*-sulphonic acid.

The apparent rate constants for isomerisation, determined graphically from initial rate of disappearance of the parent isomer and from the initial rates of formation of the other isomers, listed in the Table, illustrate once more the relative instability of the *ortho*-isomer under the reaction conditions used. The values of k_{pm}/k_{mp} and k_{po}/k_{op} calculated from the initial rates agree within the limits of experimental error with those obtained from the equilibrium composition.

Apparent isomerisation rate constants (*all* × 10^6, *sec.*$^{-1}$)*

	k_{pm}	k_{po}	k_{mp}	k_{mo}	k_{op}	k_{om}
†	13 ± 2	16 ± 5	6·7 ± 0·5	0·2 ± 0·1	320 ± 20	40 ± 20
‡		26 ± 5	7·1 ± 0·8			90 ± 40

*k_{pm} denotes the apparent rate constant *para* → *meta*, etc.

† Determined from initial rate of formation of the new isomer.

‡ Determined as the difference between the rate constant of disappearance of the parent compound and that of formation of the other isomer.

The apparent rate constants of isomerisation can be correlated satisfactorily with desulphonation rate constants and sulphonation isomer-distribution.[4] This allows description of the isomerisation as an intermolecular process, *viz.*, desulphonation followed by rapid sulphonation[5] and does not need π-complex mechanisms proposed previously.[6]

(*Received, March 27th*, 1963.)

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[1] Spryskov, *Isvest. V.U.Z., M.V.O., S.S.S.R., Khim. i Khim. Tekhnol.*, 1961, **4**, 981; *Chem. Abs.*, 1962, **57**, 16,464c; *J. Gen. Chem.* (*U.S.S.R.*), 1960, **30**, 2433.

[2] Cerfontain, Duin, and Vollbracht, *Analyt. Chem.*, in the press.

[3] Holleman and Caland, *Ber.*, 1911, **44**, 2504; Muramoto, *Kagaku to Kogyo* (*Osaka*), 1959, **33**, 259; *Chem. Abs.*, 1960, **54**, 12,041b.

[4] Cerfontain, Kort, Sixma, and Wanders, unpublished work.

[5] Shilov and Vainshtain, *Ukrain. khim. Zhur.*, 1955, **21**, 58; *Chem. Abs.*, 1955, **49**, 8845b.

[6] Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949, p. 230; Syrkin, Yakerson, and Shnol, *J. Gen. Chem.* (*U.S.S.R.*), 1959, **29**, 189.

The Effect of Solvent Changes on the Stabilities of Initial and Transition States in Solvolysis by S_N Mechanisms

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FOR the solvolysis of an organic halide, the first-order rate coefficient (k_1) is related to its value in some reference solvent (k_1^0) by

$$k_1/k_1^0 = \gamma/\gamma\ddagger, \quad . \quad . \quad . \quad (1)$$

where the relative activity coefficients, γ and $\gamma\ddagger$, reflect the effect of solvent changes on the stabilities of the initial and transition states, respectively. Previous determinations of γ and $\gamma\ddagger$ are confined to a few volatile halides, mainly t-butyl chloride,[1] and may not always be very accurate.[2] We now report these parameters for the reaction of sparingly soluble chlorides with aqueous acetone.

Relative rates and activity coefficients for solvolysis in aqueous acetone.

[Activity coefficients from k_1 *via* eqn. (1) and either solubilities (which yield γ), or zeroth-order rates for hydrolysis in permanently saturated solutions (which yield $\gamma\ddagger$).]

	Mechanism S_N2			Mechanism S_N1					
	$4\text{-}NO_2\cdot C_6H_4\cdot CH_2Cl$*			$4\text{-}NO_2\cdot C_6H_4\cdot CHPhCl$*			$4\text{-}NO_2\cdot C_6H_4\cdot CHCl\cdot C_6H_4\cdot Ph\text{-}4$†		
% Acetone	$-\log k_1/k_1^\circ$	$-\log\gamma$	$-\log\gamma\ddagger$	$-\log k_1/k_1^\circ$	$-\log\gamma$	$-\log\gamma\ddagger$	$-\log k_1/k_1^\circ$	$-\log\gamma$	$-\log\gamma\ddagger$
45	0·161	0·258	0·096	0·343	0·351	0·008	—	—	—
50	0·314	0·556	0·242	0·789	0·788	−0·001	—	—	—
55	0·436	0·744	0·317	1·149	1·078	−0·071	—	—	—
60	0·555	0·916	0·376	—	—	—	—	—	—
70	—	—	—	—	—	—	1·319	1·427	0·108
85	—	—	—	—	—	—	2·582	2·375	−0·207

* At 0° or 1·62°; reference solvent 40% acetone. † At 20·18°; reference solvent 50% acetone.

The results in the Table show that the reduction in rate caused by decreasing the water content arises from an increase in the stability of the initial state; transition-state effects make only a small contribution to k_1/k_1^0 in S_N1 solvolysis ($\log k_1/k_1^0 \sim \log\gamma$) and actually oppose the observed change in rate in the S_N2 reaction ($\log k_1/k_1^0$ and $\log\gamma\ddagger$ have the same sign). The previous work yields initial-state contributions to k_1/k_1^0 which are considerably smaller in aqueous alcohols[1a,3] than those now observed, and almost negligible for changes from water to deuterium oxide.[1b,4]

The present variations of $\log\gamma$ and $\log\gamma\ddagger$ with solvent composition (see Table) are qualitatively consistent with the assumption that the initial state is associated with, say, n_a molecules of acetone, and the transition state with n_a molecules of acetone and n_W molecules of water. The small effect of solvent changes on the stability of the transition state for S_N1 hydrolysis probably arises from opposing changes of roughly equal magnitude in the facilities for solvation by acetone and by water. The decrease of $\log\gamma\ddagger$ in S_N2 hydrolysis as the solvent is made less aqueous then suggests that the transition state now requires proportionally less participation by water (*i.e.*, a smaller value of n_W/n_a) than for mechanism S_N1, in agreement with conclusions based on the heat capacities of activation[5] and with earlier views.[6]

In the present systems, the rate of S_N2 hydrolysis is considerably less sensitive to solvent changes than when mechanism S_N1 is operating, as generally observed.[6] It can be seen that this arises, at least partly, from the greater stabilisation (or smaller destabilisation) of the transition state in S_N1 hydrolysis as the ionising power of the solvent is increased. Our results do not, therefore, invalidate earlier interpretations[6] of the different effects of solvent changes on the rates of S_N1 and S_N2 solvolysis. They do, however, show that initial-state effects can be extremely important in determining the magnitude of k_1/k_1^0, irrespective of the mechanism which is operating.

(*Received, April 26th*, 1963.)

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[1] (*a*) Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 5937; (*b*) Clarke, Taft, and Williams, *ibid.*, 1962, **84**, 2292; Clarke and Taft, *ibid.*, p. 2295.

[2] Olson, Ruebsamen, and Clifford, *J. Amer. Chem. Soc.*, 1954, **76**, 5255.

[3] Bird, Hughes, and Ingold, *J. Chem. Soc.*, 1943, 255.

[4] Swain and Thornton, *J. Amer. Chem. Soc.*, 1962, **84**, 822.

[5] Kohnstam, "The Transition State," *Chem. Soc. Special Publ.* 1962, No. 16, p. 179.

[6] Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.

Long-range Thallium–Proton Spin–Spin Coupling Constants

By J. P. MAHER and D. F. EVANS
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PREVIOUSLY[1] it was shown that in the diethylthallium cation the ^{205}Tl–H(CH_3) coupling constant is larger than that for ^{205}Tl–H(CH_2) and of opposite sign. This behaviour is typical of ethyl groups bonded to elements in Periods II—VI, with a nuclear spin of $\frac{1}{2}$.[2,3] To account for these anomalous constants it has been suggested that other mechanisms beside Fermi contact are important,[2] or that *d*-electron hybridisation is involved.[3] However, it has recently been shown that in saturated organic compounds the geminal and vicinal H–H coupling constants are also of opposite sign. Our present results for the ^{205}Tl–H coupling constants suggest that they may involve essentially the same mechanism as the H–H coupling constants, namely *via* Fermi contact involving the 6*s* orbital of the thallium atom.

The results obtained for phenylthallium compounds are given in the Table. The uniform increase in these coupling constants from triphenylthallium to the monophenylthallium cation is a general feature for organothallium compounds, regardless of the group attached to the thallium. The ratios for the ^{205}Tl–H coupling constants in R_3Tl, R_2Tl^+, and RTl^{2+} are approximately 1:1·7:4·0.[4] If the ^{205}Tl–H coupling constants in the monophenylthallium cation are divided by about 130, the values obtained are similar, in both magnitude and relative sign, to the corresponding H–H coupling constants in aromatic compounds, namely $J_{H\text{-}H\,(ortho)}$ ± 6—9; $J_{H\text{-}H\,(meta)}$ ± 1—3; $J_{H\text{-}H\,(para)}$ ± 0—1 c./sec.[5] The ^{205}Tl–H(CH_3) coupling constants in the monotolyl cations are respectively 104·2, 50·1, and 61·0 ± 0·5 c./sec. for the *ortho*-, *meta*-, and *para*-methyl groups. In mesitylene the *ortho* and *para* H–H(CH_3) coupling constants are, respectively, 0·89 and 0·45 c./sec.,[6] and the ^{205}Tl–H coupling constants are again about 130 times greater than the H–H coupling constants. That the ^{205}Tl–H(*para*-CH_3) coupling constant is larger than the corresponding *meta* coupling constant is consistent with results of calculations of the π-contribution to H–H coupling constants in aromatic systems by Acrivos[6] and by McConnell.[7] These results suggest that, as for the corresponding H–H coupling constants, the thallium coupling to the *ortho* and *meta* ring protons is transmitted mainly *via* the σ-electrons of the benzene ring. In contrast, for the *para* coupling, transmission *via* the π-electrons is important.[7] The ^{205}Tl–H(*meta*) coupling constant, like the H–H(*meta*) coupling constant, is anomalously large in comparison, for in the di-n-propylthallium cation the coupling constants are *J* for ^{205}Tl–H(αCH_2) $= \pm$ 341; *J* for ^{205}Tl–H(βCH_2) $= \mp$ 469; *J* for ^{205}Tl–H(γCH_3) $= \mp 20{\cdot}5 \pm 0{\cdot}5$ c./sec.

TABLE. *Coupling constants*, J, *in* c./sec.

	^{205}Tl–H(*ortho*)	^{205}Tl–H(*meta*)	^{205}Tl–H(*para*)
*$PhTl^{2+}$	±948	±365	±123
*Ph_2Tl^+	451	139	$51{\cdot}_7$
Ph_3Tl†	±259	±80 ± 5	±35 ± 5

	^{205}Tl–H(*trans*)	^{205}Tl–H(*cis*)	^{205}Tl–H(*gem*)
*$(CH_2{=}CH)Tl^{2+}$	3750	1806	2004
*$(CH_2{=}CH)_2Tl^+$	1618	805	842

* As the perchlorate in D_2O. † In trimethylamine.

In the divinylthallium and vinylthallium cations the *cis* and *trans* coupling constants have roughly the expected relative magnitudes (see Table) compared with the usual H–H coupling constants in vinyl derivatives.[8] The geminal coupling constant, however, is anomalously large. It is noted that the *trans* ^{205}Tl–H coupling constant in the $(CH_2 = CH)Tl^{2+}$ cation is the largest proton coupling constant yet reported.

The very large magnitudes of these ^{205}Tl–H coupling constants can be qualitatively understood

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[1] Maher and Evans, *Proc. Chem. Soc.*, 1961, 208.
[2] Narasimhan and Rogers, *J. Chem. Phys.*, 1961, **34**, 1049.
[3] Stafford and Baldeschwieler, *J. Amer. Chem. Soc.*, 1961, **83**, 4473.
[4] Authors' unpublished data.
[5] Banwell and Sheppard, *Discuss. Faraday Soc.*, in the press.
[6] Acrivos, *Mol. Phys.*, 1962, **5**, 1.
[7] McConnell, *J. Chem. Phys.*, 1959, **30**, 126.
[8] Schaeffer, *Canad. J. Chem.*, 1962, **40**, 1.

on the basis of the Fermi contact interaction, as arising from the large effective nuclear charge of the thallium atom.[9] Also, Klose[10] has made valence-bond calculations, based on Karplus's method,[11] of coupling constants in ethyl groups bonded to heavy atoms and has obtained results of the right order of magnitude. The increase of the coupling constants in the series R_3Tl, R_2Tl^+, and RTl^{2+} may be partly due to the increase in the *s*-character of the thallium–carbon bond (cf. Holmes and Kivelson[12]) and partly to the increased effective nuclear charge of the thallium. It seems likely that a similar interpretation is applicable to other proton coupling constants involving heavy elements of Groups II—IV, such as mercury and lead.

Proton resonance spectra were measured on a Varian V4311 spectrometer at 56·45 Mc./sec., and the relative signs of the coupling constants were determined by using double irradiation.[1] We thank the Department of Scientific and Industrial Research for financial support (to J.P.M.).

(*Received, April 26th*, 1963.)

[9] Schneider and Buckingham, *Discuss. Faraday Soc.*, in the press.
[10] Klose, *Ann. Physik*, 1962, **9**, 262.
[11] Karplus, *J. Chem. Phys.*, 1959, **30**, 11.
[12] Holmes and Kivelson, *J. Amer. Chem. Soc.*, 1961, **83**, 3903.

The Reaction of Bicyclo[2,2,1]heptadiene with Methylphosphonous Dichloride

By M. GREEN

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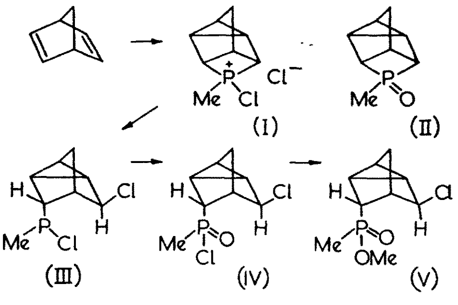
RECENTLY, bicyclo[2,2,1]heptadiene has been reported to react with boron trichloride,[1] phenylboron dichloride,[1] stannic chloride,[2] phenyltin trichloride,[2] and germanium tetrabromide,[2] to give substituted nortricyclenes. It has now been found that methylphosphonous dichloride reacts with bicyclo[2,2,1]heptadiene in the absence of light and oxygen to give a crystalline 1:1 adduct (I).

This adduct with sulphur dioxide or aqueous sodium hydrogen carbonate gave a neutral phosphine oxide (II), m.p. 157°, $\nu_{\text{max.}}$ 3·25, 8·40, 12·55 μ, that resisted hydrogenation. The proton magnetic resonance spectrum of this oxide, measured in benzene, had peaks at (τ 8·07, 8·13) complex, τ 8·43 complex, (τ 8·66, 8·85) doublet, (τ 8·89, 8·91, 8·93) complex with area ratios 1·95, 2·8, 3·4, 3, respectively. The doublet at (τ 8·66, 8·85) collapsed into a singlet (τ 8·76) and a simplification of the complex (τ 8·07, 8·13) occurred on application of the spin-decoupling technique to the ^{31}P atom. This doublet can therefore be assigned to the group ($P–CH_3$).

Pyrolysis of the adduct (I) at 180°/0·1 mm. gave a liquid phosphonous chloride (III), $\nu_{\text{max.}}$ 3·25, 12·55 μ, whose proton magnetic resonance spectrum in benzene* had peaks at τ 5·66 singlet, (τ 7·79, 7·97) complex, τ 8·31 singlet, τ 8·76 complex, τ 8·90 complex, τ 9·04 complex, with area ratios 0·85, 1·26, 1·0, 2·93, 3·94, 0·96, respectively. The peak at τ 5·66 can be assigned to the group CHCl. This singlet could not be split under conditions of high resolution.

Reaction of this chloride (III) with chlorine and then sulphur dioxide gave a liquid phosphonyl chloride (IV), $\nu_{\text{max.}}$ 3·25, 8·1, 12·55 μ, demonstrating that the former is a tervalent-phosphorus chloride. A liquid phosphinate ester (V), $\nu_{\text{max.}}$ 3·25, 8·25, 12·55 μ, was formed when the product (IV) reacted with an excess of methanol, suggesting that one of the chlorine atoms in (IV) is attached to a carbon atom.

The presence of peaks at 3·25 and 12·55 μ and the absence of absorption between 5·0 and 6·9 μ in the infrared spectra of (II—V) suggest[3] that these compounds are substituted nortricyclenes. The overlap of peaks prevents a detailed analysis of the proton magnetic resonance spectra; however, the spectra are compatible with substituted nortricyclene structures. It is suggested that these compounds have the structures formulated. The presence of the group



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* The nuclear magnetic resonance spectra of compounds (II) and (III) were also measured in CCl_4; no peaks corresponding to olefinic or aromatic protons were then observed.

[1] Joy and Lappert, *Proc. Chem. Soc.*, 1960, 353.
[2] Rabel and West, *J. Amer. Chem. Soc.*, 1962, **84**, 4169.
[3] Pollard, *Spectrochim. Acta*, 1962, **18**, 837.

CHCl as a singlet in the proton magnetic resonance spectrum of (III) and the known[4] dependence of the coupling constant between vicinal hydrogen atoms on the dihedral angle suggests a structure (III) in which the chlorine atom of the CHCl group occupies an *exo*-position.

The ready reaction of methylphosphonous dichloride with bicyclo[2,2,1]heptadiene is probably due to the importance of a homoconjugative effect.[5] A detailed mechanism of this reaction cannot be suggested on the basis of the evidence described; however, it is of significance that no unsaturated isomer of compound (II) or (III) was detected.

(*Received, April 5th,* 1963.)

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[4] Karplus, *J. Chem. Phys.*, 1959, **30**, 11; Anet, *Canad. J. Chem.*, 1961, **39**, 789.

[5] Winstein and Shatavsky, *Chem. and Ind.*, 1956, 59.

The Mechanism of Pyrophosphate Formation from Phosphoramidates

By V. M. CLARK and S. G. WARREN
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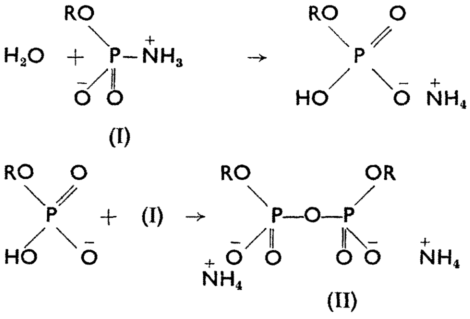
SINCE the initial reports[1,2] of the use of phosphoramidates in the synthesis of pyrophosphates, further development has led to a highly flexible method by which a wide variety of unsymmetrical pyrophosphates, including ATP [1] and coenzyme A [3] has been synthesised. The mechanism of formation of the pyrophosphate link in these reactions has, however, awaited elucidation.

We report a kinetic investigation of the formation of the diammonium salt of P^1,P^2-dibenzyl pyrophosphate (II) by thermal treatment of benzyl hydrogen phosphoramidate (I).[1] A pathway involving a metaphosphate intermediate[4] would presumably be of first order with respect to phosphoramidate since the intermediate would be highly reactive, and its formation therefore rate-determining. On the other hand, for a pathway involving external nucleophilic attack on the phosphorus atom second-order kinetics would be observed.[5]

In dry dioxan at 70°, benzyl hydrogen phosphoramidate (I) has a half-life of 3 hr. Analysis of the infrared absorption bands corresponding to phosphoryl (P=O) stretching (1200 cm.$^{-1}$ in the pyrophosphate and 1270 cm.$^{-1}$ in the phosphoramidate) showed that the reaction followed a second-order rate law with respect to (I). An induction period (prior to pyrophosphate formation) of approximately 1 hr. was observed, but this disappeared on addition of two molar equivalents of water at the outset of the reaction. It therefore seemed likely that hydrolysis of the substrate occurred before phosphorylation. This was confirmed by chromatographic and spectrophotometric identification of the benzyl hydrogen phosphate anion in the reaction mixture.

These observations lead us to suggest the sequence:



(R = $C_6H_5 \cdot CH_2$)

A bimolecular mechanism appears to be common to all displacements of phosphoramidates. Thus, (I) has been used to extend the phosphate chains of both AMP and ADP,[1] without protection of the hydroxyl groups of the 2′ and 3′ positions of the ribose moiety (a highly reactive intermediary metaphosphate would not show such selectivity). Furthermore, diethyl phosphoramidate undergoes cleavage of the P–N link when treated with gaseous hydrogen chloride to give diethyl phosphorochloridate,[6] and with phenyl dihydrogen phosphate in benzene, a pyrophosphate triester is obtained which reacts further with the monophenyl phosphate to yield, ultimately, *sym*-diphenyl dihydrogen pyrophosphate.[7] Since the initial material in the last two examples is a diester of phosphoramidic acid it is clear that no metaphosphate can arise in this reaction.

The results here reported differentiate the reactions of phosphoramidates from those involving carbo-

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[1] Clark, Kirby, and Todd, *J.*, 1957, 1497.

[2] Chambers and Khorana, *J. Amer. Chem. Soc.*, 1958, **80**, 3749, 3756.

[3] Moffatt and Khorana, *J. Amer. Chem. Soc.*, 1961, **83**, 663.

[4] Todd, *Proc. Nat. Acad. Sci. U.S.A.*, 1959, **45**, 1389; Butcher and Westheimer, *J. Amer. Chem. Soc.*, 1957, **77**, 2420; Kumamoto and Westheimer, *ibid.*, p. 2515.

[5] Dostrovsky and Halmann, *J.*, 1953, 503; Hudson and Keay, *J.*, 1956, 2463, 1960, 1859.

[6] Skrowaczewska and Mastalerz, *Roczniki Chem.*, 1955, **29**, 415.

[7] Richter, Ph.D. Thesis, Cambridge, 1961.

di-imides[8] and the oxidation of quinol phosphates[9] since acceptable evidence for the formation of metaphosphate intermediates has been presented in these cases.

We gratefully acknowledge the award of a Senior Scholarship by Trinity College and of a D.S.I.R. maintenance allowance (to S.G.W.).

(*Received, April 22nd,* 1963.)

[8] Weimann and Khorana, *J. Amer. Chem. Soc.*, 1962, **84**, 4329.
[9] Clark, Hutchinson, Kirby, and Todd, *J.*, 1961, 715.

The Constitution of Munetone

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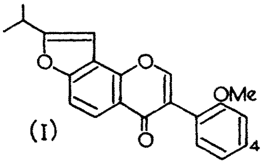
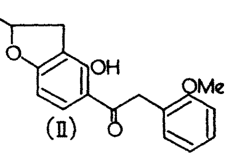
and M. F. SAINSBURY
(BRISTOL TECHNICAL COLLEGE)

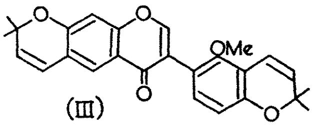
THE isoflavone munetone was originally given the constitution (I),[1] which was unusual in two respects. Like tlatlancuayin,[2] munetone was described as lacking an oxygen-containing substituent in the 4′-position, yet this is frequently present in natural isoflavones;[3] and the structure (I) contained an isoprenoid C_5 residue unique in structural type among natural phenolic compounds.[4] Synthetical studies have now shown that this structure for munetone requires considerable revision.



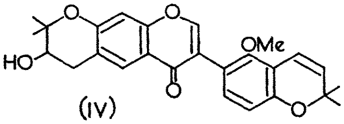
(I)



(II)



(III)



(IV)

The Hoesch reaction[5] of dihydrotubanol[6] with 2-methoxybenzyl cyanide gave the deoxybenzoin (II) which, by reaction with ethyl orthoformate[3,7] followed by dehydrogenation,[8] gave a product of expected structure (I). This material was different from natural munetone, but the nuclear magnetic resonance spectrum of the synthetic isoflavone corresponding to the deoxybenzoin (II) fully supported its structure. The nuclear magnetic resonance spectrum of natural munetone, kindly supplied by Dr. N. L. Dutta, was incompatible with the structure (I) and showed that the formula of munetone should be changed from $C_{21}H_{18}O_4$ to $C_{25}H_{24}O_5$. The 24 protons could then be assigned to two 2,2-dimethylchromen residues,[9] a methoxyl group, an isoflavonoid proton in the 2-position, and two pairs of aromatic protons. One pair of aromatic protons formed an AB system (J 8·5 c./sec.) and the other pair was associated with two singlets slightly broadened by weak coupling (J 0·6 c./sec.). These characteristics and the chemical shifts[10] uniquely define the structure of munetone as (III).

This revised structure (III) for munetone is established by its partial synthesis from mundulone (IV).[11] Mundulone methanesulphonate and ethanolic sodium hydroxide gave a deoxybenzoin identical with munetol,[1] which by reaction with ethyl orthoformate[3,7] gave munetone (III).

(*Received, April 8th,* 1963.)

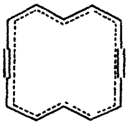
[1] Dutta, *J. Indian Chem. Soc.*, 1956, **33**, 716; 1959, **36**, 165; 1962, **39**, 475.
[2] Crabbé. Leeming, and Djerassi, *J. Amer. Chem. Soc.*, 1958, **80**, 5258.
[3] Venkataraman, "Fortschritte der Chemie Organischer Naturstoffe," ed. L. Zechmeister, Springer-Verlag, 1959, Vol. XVII, p. 1; Ollis, "The Chemistry of Flavonoid Compounds," ed. T. A. Geissman, Pergamon, Oxford, 1961, p. 353.
[4] Ollis and Sutherland, "Recent Developments in the Chemistry of Natural Phenolic Compounds," ed. W. D. Ollis, Pergamon, Oxford, 1961, p. 74.
[5] Spoerri and Du Bois, *Org. Reactions*, 1949, **5**, 387.
[6] Miyano and Matsui, *Chem. Ber.*, 1959, **92**, 2491.
[7] Sathe and Venkataraman, *Current Sci. (India)*, 1949, **18**, 373.
[8] Sarin, Sehgal, and Seshadri, *J. Sci. Ind. Res. (India)*, 1957, **16**, *B*, 61.
[9] Burrows, Ollis, and Jackman, *Proc. Chem. Soc.*, 1960, 177.
[10] Dyke, Ollis, and Sainsbury, unpublished work.
[11] Burrows, Finch, Ollis, and Sutherland, *Proc. Chem. Soc.*, 1959, 150.

The Electron Distribution in 1,8-Bisdehydro[14]annulene

By N. A. BAILEY and R. MASON

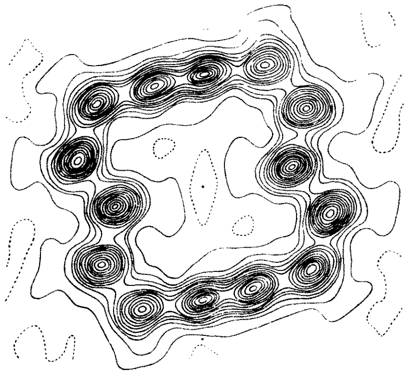
(CRYSTALLOGRAPHY LABORATORY, DEPARTMENT OF CHEMISTRY,
IMPERIAL COLLEGE, LONDON, S.W.7)

THE identification of an unusual hydrocarbon, 1,8-bisdehydro[14]annulene, $C_{14}H_{10}$ (I), has recently been reported.[1] Its aromaticity, which is consistent with Hückel's rules, is established by the chemical shifts of the inner and the outer protons in the nuclear magnetic resonance spectrum and by the preliminary *X*-ray results. The molecule is particularly interesting in so far as it is not possible to represent the bonding in the molecule, which is required to be strictly centrosymmetric,[1] by the usual Kekulé formulations.

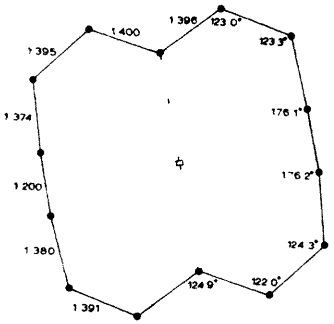


(I)

A complete least-squares analysis of the room-temperature three-dimensional *X*-ray data has now been completed ($R = 0{\cdot}078$); the Figures show both the electron distribution in the molecular plane and the carbon–carbon bond lengths (Å) and bond angles which have average standard deviations of 0·008 Å and 0·4°, respectively.



The molecule is planar (r.m.s. deviation 0·004 Å) and has essentially *mmm* (D_{2h}) symmetry. Apart from the triple bond, the carbon–carbon bond lengths correspond to a π-bond order identical with that of benzene. The shortening of the bonds adjacent to the triple bond arises from the change of atomic radius of carbon on rehybridisation from an sp^2 to an sp valency state[2,3] rather than from increased π-bonding. π-Electron delocalisation in the molecule is complete and the present geometry is being used as the basis of self-consistent-field molecular-orbital calculations.



All the hydrogen atoms have been located by difference Fourier analysis, the average carbon–hydrogen bond length being 1·08 ± 0·05 Å. The separation of the inner hydrogen atoms, which are essentially coplanar with the carbon framework, is only 1·85 Å; this value suggests a van der Waals radius for hydrogen of approximately 0·95 Å rather than the usually accepted 1·25 Å.[4] Relief of some of the repulsion between these non-bonded hydrogen atoms is reflected in the increase of the external bond angle at the carbon atoms to which they are bonded. The remaining angular deviations from strict trigonal and digonal symmetry may also be explained in terms of intramolecular electron correlation effects.

The complete difference density shows features similar to those that have been reported earlier[5] and, together with other details of the analysis, will be discussed elsewhere.

We are grateful to Professor F. Sondheimer and Dr. Y. Gaoni for providing us with a sample of the compound, and to Mrs. J. Dollimore, Mr. O. S. Mills, and Drs. J. S. Rollett and R. Sparks for copies of their Mercury computer programmes. One of us (N.A.B.) acknowledges the receipt of a Morganite Research Studentship.

(*Received, April 19th*, 1963.)

[1] Sondheimer, Gaoni, Jackman, Bailey, and Mason, *J. Amer. Chem. Soc.*, 1962, **84**, 4595.

[2] Coulson, Victor Henri Memorial Volume, Liège, Desoer, 1948, p. 15.

[3] Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 105.

[4] Pauling, "The Nature of the Chemical Bond," 3rd edn., Oxford University Press, 1960, p. 260.

[5] Mason, *Proc. Roy. Soc.*, 1960, *A*, **258**, 302.

The Phosphorescence and Delayed Fluorescence Lifetimes of Pyrene in Liquid Paraffin

B. STEVENS and M. S. WALKER
(DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, SHEFFIELD 10)

PARKER and HATCHARD[1] have convincingly demonstrated that the delayed component of fluorescence emitted by dissolved aromatic hydrocarbons originates in the interaction of two triplet-state molecules. If any further confirmation is required it is that the rate constants k_D and k_T for the respective decay of delayed-fluorescence intensity and of triplet-state concentration be reliably measured for the same outgassed solution under the same conditions; such measurements should establish the relationship

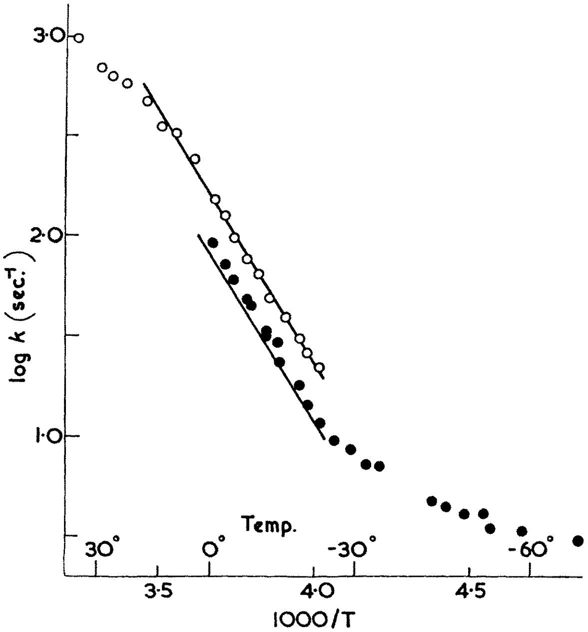
$$k_D/k_T = 2 \quad , \qquad . \;.\; . \quad (1)$$

which this mechanism requires.

A 0·01M-solution of pyrene in outgassed liquid paraffin emits both delayed fluorescence and phosphorescence over the temperature range from 0° to −30°. We have measured the decay constants k_D and k_T for each emission component (isolated by appropriate optical filters), using an apparatus previously constructed[2] for recording luminescence decay curves with decay constants in the region of 1—10^4 sec.$^{-1}$. In all cases the decay was exponential over the region of observation and standard errors in the measured decay constants, obtained from least squares plots of log intensity against time, amounted to less than 5%; control experiments established that the temperature of the solution was within 0·5° of the measured temperature of the refrigerant over the temperature range covered.

Values of log k are plotted against reciprocal temperature in the Figure. The upper line drawn through the log k_D points is a least-squares plot for the data between 0° and −30°; the lower line, drawn with the same slope but displaced vertically by −log 2 [in accordance with equation (1)], is in good agreement with the experimentally observed variation of log k_T with $T°K^{-1}$ over the same temperature range. A statistical treatment of the log k values in this range leads to the relationship $k_D/k_T = 1·7 \pm 0·3$, in support of Parker and Hatchard's mechanism for delayed fluorescence.

At lower temperatures k_T approaches the value $k_T° = 3·0$ sec.$^{-1}$ recorded for the frozen solution at −196°; the corresponding lifetime of 0·33 sec. can be compared with the value of ~ 0·2 sec. in EPA previously observed.[3] A similar variation in k_T with temperature has been reported for 9,10-dibromoanthracene by Porter and Stief,[4] the data in our Figure corresponding to the high and intermediate viscosity regions (2) and (3) recognised by these authors. However, a plot of log $(k_T - k_T°)$ against reciprocal temperature, supplemented by log $(k_D/2 - k_T°)$ in the higher temperature region, is quite linear over the range from 20° to −60°, which indicates that one first-order triplet-quenching process is dominant in this region. Moreover the correspondence between the observed activation energy of 11 ± 2 kcal./mole and that of ~ 12 kcal./mole for viscous flow of this solvent[5] signifies that this quenching process is viscosity-dependent.[4]



Plot of log k_D *(open circles) and log* k_T *(solid circles) against reciprocal of absolute temperature for* 0·01M*-solution of pyrene in liquid paraffin.*

This research has been made possible through the support of the U.S. Department of Army through its European Research Office.

(*Received, April* 17*th*, 1963.)

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[1] Parker and Hatchard, *Proc. Chem. Soc.*, 1962, 147, 386; *Proc. Roy. Soc.*, 1962, *A*, **269**, 574; *Trans. Faraday Soc.*, 1963, **59**, 284.

[2] Stevens and Hutton, *Proc. Phys. Soc.*, 1963, **81**, 566.

[3] McClure, *J. Chem. Phys.*, 1949, **17**, 905.

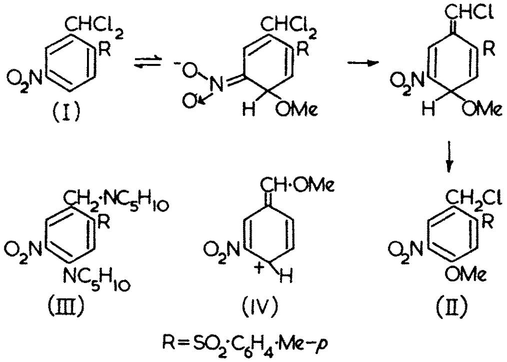
[4] Porter and Stief, *Nature*, 1962, **195**, 991.

[5] Stief, private communication.

Abnormal Nucleophilic Substitution of 3-Nitrobenzylidene Chlorides

By J. D. LOUDON and D. M. SMITH
(CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW)

A NOVEL and interesting variant of nucleophilic substitution at an aromatic centre is provided by the action of sodium methoxide on the benzylidene chloride (I). Entry of methoxide ion into the aromatic nucleus, with expulsion of a chloride ion from the side-chain, leads to the methoxybenzyl chloride (II), of which the structure has been proved by independent synthesis. Similar attack by ethoxide ion yields the corresponding ethoxybenzyl chloride in 70% yield. On the other hand, by the action of piperidine on the compound (I), both chlorine atoms are replaced and the normal benzylidenedipiperidine (I; NC_5H_{10} for each Cl) is formed together with the abnormal product (III).



These reactions extend and elucidate some observations by Kliegl and Hölle,[1] which have been overlooked in current surveys. Kliegl and Hölle found that 3-nitrobenzylidene chloride in reactions with sodium methoxide, ethoxide, and n-propoxide gave small, but in that order increasing, proportions of 2,5- and 4,3-alkoxynitrobenzyl alkyl ethers at the expense of the normal acetals. The toluene-*p*-sulphonyl group in compound (I) may be expected to assist the abnormal reaction (*a*) by contributing to electrophilicity in the nucleus and (*b*) by hindering the approach of an external reagent to the chlorine-bearing carbon atom. The practical result, by defining the initial stage as in (I) → (II), disposes of the possibility that the abnormal reaction proceeds through an acetal-type of intermediate and a derived entity such as (IV).

(*Received, April 5th*, 1963).

[1] Kliegl and Hölle, *Ber.*, 1926, **59**, 901.

Naturally Occurring Aliphatic Nitro-compounds; The Endecaphyllins

By R. A. FINNEGAN, W. H. MUELLER, and M. P. MORRIS*
(DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO, U.S.A.)

ALTHOUGH the toxicity of *Indigofera endecaphylla* Jacq. has been recognised for several years,[1] chemical examination[2-4] has led to the isolation of but a single pure substance, β-nitropropionic acid,[2] previously obtained by hydrolysis of hiptagin[5] and karakin.[6,7] These, along with 1-nitro-2-phenylethane,[8] appear to be the only previously reported naturally occurring aliphatic nitro-compounds.[9]

Our work with an acetone extract of the leaves and stems of *I. endecaphylla* was prompted by observations that the toxic properties of β-nitropropionic acid[2,3,10] apparently do not correspond to those of the whole plant.[4] Silica-gel chromatography has now provided, in addition to this acid, a number of crystalline compounds, including six aliphatic nitro-compounds. These compounds, called endecaphyllin A—E, are listed in the Table, along with a seventh nitro-compound (X) which was isolated directly from the crude extract.

The presence of $CH_2{\cdot}NO_2$ groups in these substances was indicated by infrared bands near 1550 cm.$^{-1}$, by ultraviolet maxima near 270 mμ, and by chemical tests.[11] The sizes of the extinction coefficients for the ultraviolet bands support the

* Food and Drug Administration, Washington, D.C.

[1] Warmke, Freyre, and Morris, *Agron. J.*, 1952, **44**, 517; Nordfeldt, Henke, Morita, Matsumoto, Takahashi, Younge, Willers, and Cross, Univ. Hawaii, Agric. Exp. Station, Tech. Bull. No. 15, July, 1952; Emmel and Ritchey, *J. Amer. Soc. Agron.*, 1941, **33**, 675.

[2] Morris, Pagan, and Warmke, *Science*, 1954, **119**, 322.

[3] Cooke, *Arch. Biochem. Biophys.*, 1955, **55**, 114.

[4] Hutton, Windrum, and Kratzing, *J. Nutrit.*, 1958, **64**, 321; 1958, **65**, 429; Coleman, Windrum, and Hutton, *ibid.* 1960, **70**, 267.

[5] Gorter, *Bull. Jard. Bot. Buitenzorg.*, 1920, **2**, 187.

[6] Carter and McChesney, *Nature*, 1949, **164**, 575; Carrie, *J. Soc. Chem. Ind.*, 1934, **53**, 288T; Carter, *ibid.*, 1943. **62**, 238T.

[7] Carter, *J. Sci. Food Agric.*, 1951, **2**, 54.

[8] Gottlieb and Magalhaes, *J. Org. Chem.*, 1959, **24**, 2070.

[9] Cf. Pailer, "Fortschritte der Chemie organischer Naturstoffe," 1960, Vol. XVIII, p. 55.

[10] Rosenberg and Zoebisch, *Agron. J.*, 1952, **44**, 315.

Endecaphyllin	M.p.	Formula
A	120—122°	$C_{15}H_{21}N_3O_{15}$
B	125—126·5	$C_{15}H_{21}N_3O_{15}$
B_1	129—130	$C_{16}H_{23}N_3O_{15}$
C	150—152·5	$C_{15}H_{21}N_3O_{15}$
D	145—146	$C_{12}H_{18}N_2O_{12}$
E	132—134	$C_{12}H_{18}N_2O_{12}$
X	104—105·5	$C_{18}H_{24}N_4O_{18}$

conclusion that all the nitrogen atoms are present in nitro-groups. The materials are non-basic, and amide absorption bands are absent from the infrared spectra which show, in addition to the nitro-bands, hydroxyl and saturated-ester absorption. Further, hydrogenation results accorded with those expected for complete reduction of all nitro- to amino-groups.

Paper chromatography of endecaphyllin hydrolysates resulted in the detection of β-D-glucose and β-nitropropionic acid along with several unidentified compounds which probably result from partial hydrolysis.

The combined analytical, spectral, and chemical properties allow the formulation of endecaphyllin A, B, and C as isomeric tri-*O*-(β-nitropropionyl)-D-glucopyranose derivatives (I; n = 3), D and C as analogous diesters (I; n = 2), and X as a tetraester (I; *n* = 4). Compound B_1 is probably a triester of methyl β-D-glucopyranoside (this glycoside also occurs free in the plant).

(I) $C_6H_{12-n}O_6(CO{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2)_n$

The melting point and rotation of endecaphyllin A are nearly identical with those reported for karakin,[7] 1,4,6-tri-*O*-(β-nitropropionyl)-D-glucopyranoside, and it is possible that the two substances are identical. However, conditions reported[7] to provide karakin diacetate (m.p. 103°) afforded only a monoacetate of endecaphyllin A (m.p. 125·5—126·5°). The detailed structures of the endecaphyllins are expected to result from degradative and synthetic work now in progress.

This investigation was supported by The Division of General Medical Sciences, U.S. Public Health Service.

(*Received, March 8th*, 1963.)

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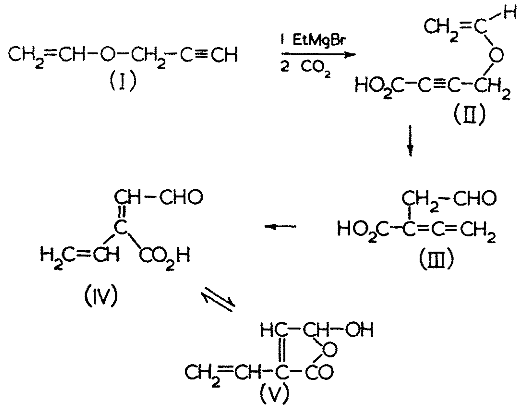
[11] Noller, "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, Pa., 1951, p. 255; Dannley and Kitko, *Analyt. Chem.*, 1960, **32**, 1682; Meyer and Locher, *Ber.*, 1874, **7**, 1510.

The Synthesis of the Antibiotic P.A. 147 [5-Hydroxy-3-vinylfuran-2(5*H*)-one]

By D. K. BLACK and S. R. LANDOR
(WOOLWICH POLYTECHNIC, LONDON, S.E.18)

THE powerful antibiotic P.A. 147 previously isolated from a *Streptomyces* strain[1,2] and identified as 5-hydroxy-3-vinylfuran-2(5*H*)-one[1,2] (V) has been synthesised through an allenic intermediate. The Grignard reagent from propargyl vinyl ether* (I) and ethylmagnesium bromide gave the acid (II) on treatment with carbon dioxide. This acid was passed in a stream of nitrogen† through an electrically heated tube containing glass wool, and the products were condensed in a cooled trap and chromatographed on deactivated alumina. This led to the lactol (V), a yellow oil, $\nu_{max.}$ 3400, 1780, 1750, 1640, $\lambda_{max.}$ 245 mμ (ε 8800). After titration with 0·1N-sodium hydroxide it had $\lambda_{max.}$ 273 mμ (ε 19,320), which is typical for the conjugated dienal system present in the anion of the open-chain acid (IV). Hydrogenation (two equivalents of hydrogen absorbed) gave the saturated lactol, whose semicarbazone, m.p. 158° (lit,[1] 158—159°) had the correct analysis.



It is suggested that a Claisen-Cope type rearrangement of the acid (II) gives the unisolated allenic aldehyde (III) which rapidly changes prototropically to the 2,4-dienal and the lactol (V) with which it is in equilibrium.

We thank the D.S.I.R. for a maintenance grant to D.K.B.

(*Received, May 3rd*, 1963.)

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[1] Els, Sobin, and Celmer, *J. Amer. Chem. Soc.*, 1958, **80**, 878.

[2] Akita, Okami, Suzuki, Maeda, Takeuchi, and Umezawa, *J. Antibiotics*, *A*, 1962, 130.

* Prepared by interaction of dipropargyl acetal and boron trichloride, followed by treatment with trimethylamine and pyrolysis of the complex; this unpublished general method for the preparation of allyl and propargyl vinyl ethers was developed in our laboratory.

† We had previously shown (Black, Landor, and, in part, Demetriou, unpublished work) that propargyl vinyl ethers could be converted into allenic aldehydes; cf. parallel work on propargyl acetals by Jones, Loder, and Whiting (*Proc. Chem. Soc.*, 1960, 180).

NEWS AND ANNOUNCEMENTS

Library.—On Thursday, July 4th the Library will close at 5 p.m. It will also close at 6 p.m. on Friday, August 2nd, and will re-open at 9.30 a.m. on Wednesday, August 7th, 1963.

The Corday-Morgan Medal and Prize.—This Award, consisting of a Silver Medal and a monetary Prize of 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, 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. If, in the opinion of the Council, two or more candidates are of equal merit, a medal may be awarded to each and the prize divided equally among them. Copies of the rules governing the Award may be obtained from the General Secretary of the Society. Applications or recommendations in respect of the Award for the year 1962 must be received not later than December 31st, 1963, and applications for the Award for 1963 are due before the end of 1964.

Election of New Fellows.—69 Candidates were elected to the Fellowship in May, 1963.

Deaths.—We regret to announce the deaths of the following: *Mr. G. Adams* (30.3.63), Stourbridge, a Fellow since 1914; *Dr. R. F. Hunter* (2.5.63), Research Co-ordinator at Bakelite Limited, Birmingham; *Dr. D. C. Quin* (21.4.63), Research Chemist at the Distillers Company Limited, Epsom; and *Lt.-Col. F. M. Potter* (3.5.63), Director, Scottish Tar Distillers, Falkirk.

Medway College of Technology.—A two-day Symposium on "Recent Work in Biosynthesis," will be held, with the support of the Society, at the Medway College of Technology, on September 19—20th, 1963. Speakers will include Professor D. H. R. Barton, Professor A. R. Battersby, and Dr. J. W. Cornforth, and further details and application forms may be obtained from the Organisers, Department of Science, Medway College of Technology, Horsted, Maidstone Road, Chatham, Kent.

Visit to University College of Rhodesia and Nyasaland.—*Professor F. Sebba*, Professor of Physical Chemistry at the University of the Witwatersrand, recently visited the Department of Chemistry under the auspices of the Chemical Society. He gave three lectures to mixed audiences of students, staff and local scientists, entitled "Physical Chemistry of Mineral Flotation," "Ion Flotation," and "Recent Advances in Catalysis." He also visited the Government Metallurgical Laboratory and the Mazoe Consolidated Gold Mine.

Imperial College of Science and Technology.—Courtaulds Limited have agreed to provide the sum of £20,000 to help *Professor A. R. Ubbelohde*, Head of the Department of Chemical Engineering and Chemical Technology, with the many needs in connection with a major new extension for the Department which is being erected as part of the College's Jubilee Expansion Scheme.

Van't Hoff Fund.—The Committee of the Van't Hoff Fund for the endowment of investigations in the field of pure and applied chemistry invites applications for grants from the fund.

The amount available for next year is about 2,000 Dutch guilders. Applications should be sent by registered post to Het Bestuur der Koninklijke Nederlandse Akademie van Wetenschappen, bestemd voor de Commissie van het "Van't Hoff Fonds," Trippenhuis, Kloveniersburgwal 29, Amsterdam, before December 1st, 1963. The purpose for which the grant is required, the reasons for the application, and the amount desired must be stated.

Grants from the Fund for 1963 were awarded to *Dr. G. Billek* (Vienna), *Dr. J. Schell* (Ghent), and *Dr. S. G. Tandon* (Jabalpur, India).

R.I.C. Film Index.—The third edition of the "Index of Chemistry Films" is now available. It contains up-to-date details of about 1,200 films and 300 filmstrips on chemistry and related topics, classified by subject, followed by the addresses of the distributors and an alphabetical list of titles. The date of production of each film is also given. Copies may be obtained from the Royal Institute of Chemistry, 30 Russell Square, London, W.C.1, price 7/6.

International Symposia, etc.—The Sixth International Congress of Nutrition, under the auspices of the International Union of Nutritional Sciences, will be held in Edinburgh on August 9—15th, 1963. Further enquiries should be addressed to Miss A. D. Watson, Honorary Organising Secretary, Clinical Chemistry Department, Royal Infirmary, Edinburgh 3.

The Fifth International Symposium on Gas Chromatography organised by the Institute of Petroleum Gas Chromatography Discussion Group will be held at Brighton on September 8—10th, 1964. Intending delegates, or those wishing to submit papers, should write to the Organising Office, Fifth International Symposium on Gas Chromatography, 61 New Cavendish Street, London, W.1.

Personal.—*The Hon. R. J. Asheton* has been appointed to the board of Borax (Holdings) Ltd.

Dr. R. W. Bailey has been elected Chairman of the Manawatu Branch of the New Zealand Institute of Chemistry.

Dr. V. C. Barry has been elected Treasurer of the Royal Irish Academy.

Mr. S. G. Brooker has been elected Vice-President of the New Zealand Institute of Chemistry.

Dr. E. Bullock, formerly of Nottingham University, has been appointed Head of the Department of Chemistry, of the Memorial University of Newfoundland, Canada.

Dr. J. I. G. Cadogan has been appointed to the Purdie Chair of Chemistry in St. Salvator's College, St. Andrews, from October 1st, 1963.

Mr. W. E. Cash has been appointed Technical Adviser to the Chairman of the Chemical and Plastics Group, Distillers Company Limited.

Mr. H. A. Collinson has been re-elected Vice-Chairman of the British Plastics Federation.

Mr. P. Day has been elected to a Junior Research Fellowship in Chemistry at St. John's College, Oxford, as from October 1st, 1963.

Mr. J. A. Dean has been appointed Manager of the Research and Development Department of A. Boake, Roberts & Company Limited.

Dr. A. J. Downs has been promoted from Senior Demonstrator to Lecturer in Inorganic Chemistry at King's College, Newcastle-upon-Tyne.

Dr. A. Fischer, of the University of Canterbury, N.Z., has been promoted to a Senior Lectureship.

The Honorary Degree of D.Sc. has been conferred on *Sir Howard W. Florey*, Honorary Fellow, by the University of Hull.

The University of Sussex have announced that the following have been appointed Lecturers in Chemistry: *Dr. M. H. Ford-Smith*, *Dr. R. D. Guthrie*, *Dr. J. G. Stamper*.

Dr. W. P. Grove, Director, Radiochemical Centre, Amersham, was present as observer at the National Conference on Atomic Energy, Isotopes and Radiation, Pretoria, in April, and afterwards lectured at the University of Natal, Pietermaritzburg.

Mr. P. D. Gujral is now Assistant Editor in the Publications and Information Directorate, C.S.I.R., New Delhi, working for the Indian Journal of Chemistry and the Journal of Scientific and Industrial Research.

Dr. D. Hall, who has returned to the University of Auckland, N.Z., after a study period at the University of Pittsburgh, has been promoted to Associate Professor.

The title of Professor of Nuclear Technology has been conferred on *Mr. G. R. Hall* in respect of his post at the Imperial College of Science and Technology, London.

Mr. K. H. Handy, Works Manager of Monsanto Chemicals Limited, Ruabon, is to become General Manager of Production at the London Headquarters.

Professor S. H. Harper, after having served for seven years as Dean of the Faculty of Science of University College of Rhodesia and Nyasaland, has been appointed Vice-Principal whilst retaining the Headship of the Department of Chemistry. Recent Staff appointments include *Dr. J. G. Sheppard* as Lecturer in Physical Chemistry and *Mr. R. M. Letcher* as Assistant Lecturer in Organic Chemistry.

The Royal Society and the Leverhulme Trust announce that *Professor R. D. Haworth*, who retires this year as Firth Professor of Chemistry and Head of the Chemistry Department, University of Sheffield, will visit Madras University as Visiting Professor in the field of Organic Chemistry.

Mr. D. Layton has been appointed Deputy Head of the Department of Education at Leeds University from July 1st, 1963.

Dr. R. Lessing and *Mr. R. C. Odams* have been elected to the Council of the British Chemical Plant Manufacturers, with Mr. Odams as Vice-Chairman.

Professor D. R. Llewellyn has been appointed Assistant Vice-Chancellor of the University of Auckland, N.Z., with special responsibility for buildings.

Mr. W. R. Longworth has been appointed Planning Controller at Fisons Fertilizers Limited.

Dr. A. Maccoll, Reader in Chemistry at University College, has been appointed to a Chair of Chemistry tenable at that College.

Mr. P. J. March has been appointed General Manager of the Plastics and Rubbers Division of Shell Chemical Company Limited.

Professor C. A. McDowell, of The University of British Columbia will be spending the 1963—64 academic year in the Department of Theoretical Chemistry, University of Cambridge.

Mr. W. D. Morton has become General Manager of G.E.C. Witton Engineering Works.

Dr. L. N. Mulay, formerly of the University of Cincinnati, has been appointed an Associate Professor at the Pennsylvania State University, University Park, Pennsylvania.

Dr. K. R. Payne has been appointed General Manager of L. Light and Company Limited in succession to *Mr. G. R. Jones*.

Professor G. Porter, at present Professor of Physical Chemistry, is to be the Firth Professor of Chemistry and Head of the Department of Chemistry of Sheffield University as from October 1st, 1963. He has also been elected Professor of Chemistry at the Royal Institution, an honorary appointment which is a revival of a Professorship which has not been occupied since 1868.

Mr. P. Powell has been elected to a Junior Research Fellowship at Merton College, Oxford.

Dr. R. E. Richards, Fellow of Lincoln College, Oxford, Reader in Physical Chemistry, has been appointed to Dr. Lee's Professorship in Chemistry, with effect from October 1st, 1964, in succession to *Sir Cyril Hinshelwood.*

Dr. P. S. Sarin, of Brandeis University, has been appointed a Research Fellow in Medicine at the Harvard Medical School.

Dr. J. Shorter has been appointed a Senior Lecturer in the University of Hull.

Dr. B. P. Straughan, a Fellow of King's College, Newcastle-upon-Tyne, has been appointed as Research Assistant in Inorganic Chemistry.

Dr. J. M. Tedder has been appointed Reader in Organic Chemistry at the University of Sheffield.

Honorary degrees of Doctor of Science were conferred on *Lord Todd*, *Sir Harry Melville*, and *Dr. V. Prelog* at Liverpool University on May 4th, 1963.

Mr. J. Vaughan, of the University of Canterbury, N.Z., has been appointed to the newly-created second Chair of Chemistry in that University.

Sir Owen Wansborough-Jones has retired as a member of the National Research Development Corporation on the expiry of his period of appointment.

Professor F. L. Warren, of the University of Natal, has been appointed a member of the Scientific Advisory Council recently created by the Government of South Africa.

Dr. R. G. Wilkins, of the University of Sheffield, has accepted a post at the State University of New York.

Mr. J. Wright has been promoted to a Lectureship at the University of Canterbury, N.Z.

OBITUARY NOTICE

WILLIAM CHARLTON

1902—1962

WILLIAM CHARLTON was born in December, 1902 in Newcastle-on-Tyne, and was educated there at Rutherford College Boys' School and Armstrong College of the University of Durham, where in 1925 he gained First Class Honours in the B.Sc. examination. At this time, his professor, W. N. (later Sir Norman) Haworth, moved to Birmingham and Charlton went with him as one of his first research students. There he played a small but useful part in the work of that now famous school in laying the foundations of our knowledge of sugar chemistry. He was a collaborator in the important paper (Charlton, Haworth, and Peat, *J.*, 1926, p. 89) in which conclusive evidence is adduced for the pyranose structure of glucose and related sugars. It was followed by papers on "The Constitution of the Disaccharide Melibiose and its relation to Raffinose" (Charlton, Haworth, and Hickinbottom, *J.*, 1927, 1527), "The Structure of 2,3,4-trimethylglucoside" (Charlton, Haworth, and Herbert, *J.*, 1931, 2855) and "The Constitution of α- and β-fructose diacetones" (Anderson, Charlton, Haworth, and Nicholson, *J.*, 1925, 1337).

He was awarded the degree of Ph.D. at Birmingham in 1928 as a result of this work and then joined Imperial Chemical Industries Ltd. For the first two years he was seconded to work with J. Kenner at Manchester. This was at a time when Imperial Chemical Industries Ltd. was laying the foundations of the close association with British Universities it has held since and that set the pattern which has since been copied by most of the major chemical firms in this country and the U.S.A. He worked with Kenner at the (then) Manchester College of Technology until the end of 1930 and published papers on nitration of oximes (Charlton, Earl, Kenner, and Luciano, *J.*, 1932, 30) and on the synthesis of polyhydric alcohols related to carbohydrates (Charlton and Kenner, *J.*, 1932, 750).

At the end of this period he was posted to the Research Department of the then Imperial Chemical Industries Ltd. Dyestuffs Group at Blackley and worked there for the rest of his life. His early researches were on dyestuff intermediates and dyes of the thioindigoid class, the manufacture of which was, at that time, being developed at Blackley. In 1937 he was transferred to the Synthetic Resins Section of the department, the main interest of which, at that time, was in the so-called alkyd resins, the polycondensation products of glycerol and similar polyhydric alcohols with phthalic anhydride and the anhydrides of other polycarboxylic acids, which have become of great industrial importance as media for paints and in coating compositions generally. From this date on this was to prove his life's work. He rose in due course to become Head of his Section and the success of Imperial Chemical Industries Ltd. in this field of endeavour owes much to his leadership and his own personal work.

Charlton was a quiet, retiring, and reserved man. In his work he did not spare himself and he set himself the highest standards of achievement. He gave the most careful thought to any problem before making up his mind but when he had once reached a decision he adhered to it. Among the large technical staff at Blackley he had few intimates but he was always most friendly and helpful and was held in the highest esteem by all his colleagues. His outside interests matched his character and personality. He was a keen and very knowledgeable bibliophile with a particular interest in mediaeval French literature. At times he entertained his selected associates with free translations from this source. He was keenly interested in music and also in its electrical reproduction, and he played both the piano and the organ with skill and feeling.

His last years were clouded by ill-health. He had to spend periodical spells in hospital for physical examinations: unpleasant visits, to which he faced up with outstanding fortitude and good humour. In fact, only his closer associates knew of them. He was very upset by the death of his wife some two years ago and himself died of a heart attack in hospital last December. He leaves a son, Alan, a botanist, at present studying for a higher degree at Manchester University.

H. A. PIGGOTT.

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