NOTES

266. *The Polarography of Quinoline Derivatives. Part IX.*[1] *Amperometric Titrations with 8-Hydroxyquinaldinic Acid.*

By W. R. TURNER and JOHN T. STOCK.

QUINALDINIC ACID,[2] quinoline-8-carboxylic acid,[3] and quinolin-8-ol [4] have been used as amperometric titrants for approximately millimolar solutions of metal ions. The active groupings of quinaldinic acid and of quinolin-8-ol are both present in 8-hydroxyquinaldinic acid. This acid, which resembles the other three compounds in being polarographically reducible,[1] is a potential amperometric titrant for metal ions even when these are polarographically inactive. The titration with 8-hydroxyquinaldinic acid of thorium in the concentration range 0·5 to 3 mM is precise to within 3% and accurate to within 5%.

Experimental.—The apparatus and general techniques were as in Part VIII. The 0·100M titrant was prepared from the calculated weight of 8-hydroxyquinaldinic acid (HQA) [1] and its equivalent of sodium hydroxide. Stock solutions of lead nitrate, ferric chloride, and uranyl acetate were standardized by conventional methods.[5] Analytical grade thorium nitrate was used.

Unless otherwise indicated, 50-ml. portions of 0·5M-ammonium acetate (pH 7·0) that were 1mM in the desired metal were titrated after deoxygenation. The titrant was added in 0·1-ml. portions at intervals of 5 min. After each addition, the mixture was stirred magnetically for 30 sec., and the current was read just before the next portion of titrant was added. All potentials are with reference to the saturated calomel electrode.

Screening tests. The dropwise addition of 0·5 ml. of 0·01M-metal ion solution to 5-ml. portions of 2 mM-HQA in 0·5M-ammonium acetate (pH 7·0) gave precipitates in the following cases: Fe^{2+} (red-brown), Fe^{3+} (green-black), UO_2^{2+} (orange), Pb^{2+}, Th^{4+}, and ZrO^{2+} (all yellow). A yellow coloration was obtained with Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Al^{3+}. The coloration with Cu^{2+} was yellow-green. No reaction was observed with Mg^{2+} or Cr^{3+}. Repetition in 0·5M-ammonia–0·5M-ammonium chloride (pH 9·4) gave similar results; the only additional precipitate was with Al^{3+} (white). No precipitation was observed in 0·5M-acetic acid–0·5M-sodium acetate (pH 4·6). The deep green colour given by HQA and traces of ferric iron has been noted by Irving and Pinnington.[6]

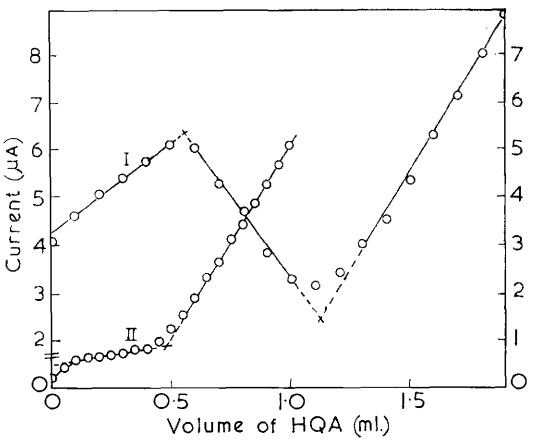
[1] Part VIII, W. R. Turner and J. T. Stock, preceding Paper.
[2] J. T. Stock, *J.*, 1949, 1793.
[3] J. T. Stock, *J.*, 1949, 2470.
[4] J. T. Stock, *Metallurgia*, 1949, **40**, 179, 229.
[5] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," Wiley, New York, 1953, 2nd edn., pp. 227, 392, and 471.
[6] H. Irving and A. R. Pinnington, *J.*, 1954, 3782.

No precipitation occurred at pH 4·6, 7·0, or 9·4 when this test was applied to 8-amino-, 8-chloro-, 8-methoxy-, 8-methyl-, or 8-nitro-quinaldine, or to 8-methyl- or 8-nitro-quinaldinic acid.[1] With 5mM-8-methoxyquinaldinic acid, only Fe^{2+} gave a precipitate (red) at pH 7·0 or a coloration (orange) at pH 4·6. The yellow colour of a pH 4·6 solution of 8-methoxyquinaldinic acid was discharged by the addition of Co^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+}. The precipitating properties of 8-hydroxyquinaldine [1] are well known.[7]

Amperometric titrations. (a) *Uranyl ion.* Titration at a potential of −0·8v gave an L-type curve,[8] with considerable scatter of the points that defined the excess-uranyl branch. The average titre (5 runs) was 8—9% above that required for an HQA-to-uranyl molar ratio of 2 to 1. Repetition at a potential of −1·4v did not give the expected V-type curve.[8] Instead the current rose initially as shown by curve I. Such effects are common when nonequilibrium conditions such as supersaturation exist. However, the reproducibility of the titration curve and the location of the peak midway between the start and the end point suggest that the first

Titration of 50-ml. portions of Th^{4+} at pH 7·0.

Concn. (mM)	Concn. found (mM)	Average devn. (%)	Average error (%)
0·500	0·468, 0·492, 0·480, 0·466, 0·488	2·0	−4·2
1·000	0·964, 0·970, 0·956, 0·936, 0·936	1·4	−4·8
2·000	1·98, 2·01, 1·97, 2·00, 2·08	1·5	+0·1
3·000	2·92, 3·10, 3·20, 3·08, 3·24	2·8	+3·7



Titration of 50 ml. of 1mM-metal ion with 0·1M-HQA at −1·4 v.

Curve I, left ordinate, uranyl; II, right ordinate, thorium.

stage of the titration involves the formation of an electroreducible 1-to-1 molar complex of HQA and uranyl ion. The average titre (5 runs) was 12% above the requirement for an HQA-to-uranyl molar ratio of 2 to 1.

(b) *Thorium.* Titration at a potential of −1·4v gave a curve of reversed-L type (curve II).[8] The end point occurred at a HQA-to-thorium molar ratio of 1 to 1. Typical results are given in the Table. The titre of 1mM-thorium was unaffected by the presence of fluoride ion up to a concentration of 0·2mM. Higher concentrations of fluoride increased the titre; the error in the presence of 1mM-fluoride was about 30%. Negative errors, expected to arise from the interaction of fluoride and thorium ions, were not observed.

(c) *Lead.* In the titration of a potential of −0·8v, the current *increased* from the start; no end point indication was obtained. The solution became intensely yellow, but precipitation did not occur. A mixture of uranyl and lead ions at respective concentrations of 1 and 0·4mM gave an L-type curve at this potential. The post end-point current was about one-third of the initial current, and the titre was about 25% in excess of that required for uranyl ion alone. Partial coprecipitation of lead appears to occur under these conditions.

(d) *Ferric iron.* A greenish-black coloration was obtained; otherwise, the behaviour of

[7] R. G. W. Hollingshead, " Oxine and its Derivatives," Butterworths, London, Vol. 3, Ch. XXXVIII.
[8] J. T. Stock, *Analyst*, 1947, **72**, 291.

ferric ion was similar to that of lead. Although an L-type curve was obtained when the titration was carried out in 0·5*M*-sodium citrate, the results were low and imprecise.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF CONNECTICUT,
STORRS, CONNECTICUT, U.S.A.

[Present address (W. R. T.): DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICHIGAN, U.S.A.] [*Received, August 10th*, 1964.]

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267. *Structure of the Fulminate Ion.*

By KARTAR SINGH and N. N. BANERJI.

THE fulminate ion has a linear arrangement of atoms, and the end carbon atom has an unusual valency. A study of the force constants of this compound should be useful in elucidating the nature of the chemical bonds within the ion. In the present investigations, infrared spectra of ordinary and nitrogen-15 labelled mercury fulminate have been examined, and the force constants of the various bonds have been derived. These results provide interesting information about the nature of bonds within the ion.

Experimental.—Mercury fulminate was prepared by the action of alcohol on mercuric nitrate in nitric acid. A pure product was obtained by dissolving the crystals in 50% ammonium hydroxide, neutralizing the solution with acetic acid, and washing the product successively with water and alcohol.

An isotopically enriched sample was prepared by making use of [^{15}N]nitric acid (sp. gr. 1·32 with an enrichment of 78%), supplied by the Atomic Energy Commission, Bombay.

Infrared spectra were examined in Nujol, because fulminate may react with potassium bromide if pellets are prepared by pressing. A Perkin-Elmer 221 instrument was used.

Results.—Observed absorption peaks are given in Table 1. The frequencies ν_1, ν_2, and ν_3 are reproducible within an error of 0·60, 0·62, and 0·40%, respectively.

TABLE 1.

Absorption frequencies of mercury fulminate.

Frequency (cm.$^{-1}$)	$^{16}O^{14}N^{12}C$	$^{16}O^{15}N^{12}C$	Observed	Calc.
Symmetric	1220	1220	—	7
Antisymmetric	2202	2165	37	—
Bending	480	477	—	—

On enrichment of the sample with nitrogen-15, an additional sharp peak appears at 2165 cm.$^{-1}$. This is shown in the Figure. This peak is $\Delta\nu_3$ 37 cm.$^{-1}$ from the antisymmetric peak in ordinary fulminate. The symmetric peak (ν_1) is broad. The Redlich–Teller product rule, though strictly applicable to frequencies with no undertones, has been used to find the shift, which may occur as a result of enrichment of the sample, in the symmetric frequency ν_1. The calculated shift is $\Delta\nu_1$ 7 cm.$^{-1}$. It has been difficult to observe a shift of this magnitude as the ν_1 peak is broad.

DISCUSSION

On the basis of simplified valence force field the potential energy is given by the expression

$$2V = f_1(\Delta r_1)^2 + f_2(\Delta r_2)^2 + 2f_{12}(\Delta r_1)(\Delta r_2) + f_\alpha r_1 r_2 (\Delta\alpha)^2 \quad (1)$$

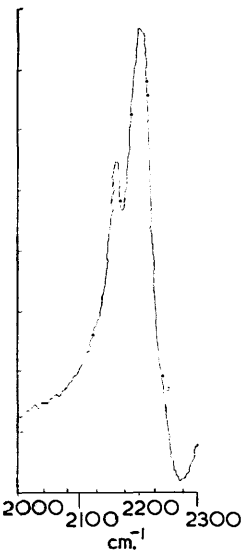
where f_1 and f_2 are force constants of the bands between oxygen and nitrogen and nitrogen

and carbon, f_α is the bending force constant. The solution of secular equation gives the following relationships

$$\lambda_1 + \lambda_3 = \left(\frac{1}{m_O} + \frac{1}{m_N}\right) f_1 + \left(\frac{1}{m_N} + \frac{1}{m_C}\right) f_2 - \frac{2}{m_N} f_{12} \quad (2)$$

$$\lambda_1 \lambda_3 = \left(\frac{m_O + m_N + m_C}{m_O m_N m_C}\right)(f_1 f_2 - f_{12}^2) \quad (3)$$

where m_O, m_N, and m_C are masses of the oxygen, nitrogen, and carbon atoms, $\lambda = 4\pi^2\nu^2$,



Absorption in the region of the antisymmetric vibration of labelled mercury fulminate.

and f_{12} is the interaction constant. The bending force constant can be obtained from the expression

$$4\pi^2\nu_2^2 = \frac{f_\delta}{r_1^2 r_2^2}\left(\frac{r_1^2}{m_C} + \frac{r_2^2}{m_O} + \frac{(r_1 + r_2)^2}{m_N}\right) \quad (4)$$

where r_1 and r_2 are the lengths of the ON and NC bonds. These equations have been used in calculating the force constants. The observed frequencies of normal fulminate and isotopically enriched fulminate have been employed in these calculations. The values of f_1 and f_2 have been obtained by solving equations (2) and (3) for various values of f_{12}.

It has been observed that, with $f_{12} = 1{\cdot}25 \times 10^5$ dynes/cm., the two sets of frequencies for ordinary and enriched mercury fulminate give the same values of f_1 and f_2. By assigning this value to f_{12}, a set of values of f_1, f_2, f_{12}, and f_δ for the fulminate ion have been obtained. These values are given in Table 2 together with the corresponding values of force constants for N_2O,[1] HCN,[2] NO_2 (nitrite),[3] and $^+NO_2$ (nitronium ion).[3,4]

The dispersions in values of f_1, f_2, and f_{12} are 0·19, 0·07, and 0·05. The stretching force constant for the N–C bond in fulminate is $17{\cdot}18 \times 10^5$ dynes/cm. The corresponding value for the CN bond in nitriles is $16{\cdot}7 \times 10^5$ dynes/cm. It is apparent that the N–C bond in the fulminate ion is approximately a triple bond. The force constant of the N–O bond in

[1] Richardson and Wilson, *J. Chem. Phys.*, 1950, **18**, 694.
[2] Wilson, Decius, and Cross, " Molecular Vibrations," McGraw-Hill Co., 1955, p. 178.
[3] Jonathan, *J. Mol. Spectroscopy*, 1960, **4**, 75.
[4] Smith and Linnett, *Trans. Faraday Soc.*, 1956, **52**, 891.

TABLE 2.

Values for force constants (dynes/cm.) and interaction constants for normal and isotopically enriched fulminate and other groups.

	f_1	f_2	f_{12}	f_δ/r_1r_2
ONC	$9{\cdot}56 \times 10^5$	$17{\cdot}18 \times 10^5$	$1{\cdot}25 \times 10^5$	$0{\cdot}31 \times 10^5$
NNO	$11{\cdot}50 \times 10^5$	$18{\cdot}98 \times 10^5$	$1{\cdot}43 \times 10^5$	$0{\cdot}49 \times 10^5$
HCN	$5{\cdot}7 \times 10^5$	$18{\cdot}6 \times 10^5$	$-0{\cdot}22 \times 10^5$	$0{\cdot}20 \times 10^5$
ONO	$7{\cdot}7 \times 10^5$	—	$2{\cdot}0 \pm 0{\cdot}5 \times 10^5$	$1{\cdot}2 \pm 0{\cdot}1 \times 10^5$
$^+NO_2$	$17{\cdot}3 \times 10^5$	—	—	—

fulminate is $9{\cdot}56 \times 10^5$ dynes/cm.; the force constant for the N–O bonds in the nitrite and the nitronium ion $\overset{+}{N}O_2$ are $7{\cdot}6 \times 10^5$ dynes/cm. and $17{\cdot}0 \times 10^5$ dynes/cm., respectively. These results show that both the O–N and N–C bonds are stronger than the single O–N bond and the triple N≡C bond; this is because of the presence of formal charges. The structure of the fulminate ion is that of a resonance hybrid of the canonical structures

(I) $\bar{O}-\overset{+}{N}\equiv C$ and $\bar{O}=\overset{+}{N}=C$ (II)

These results support the view that structure (I) makes a major contribution to the resonance hybrid.

MINISTRY OF DEFENCE, NEW DELHI, INDIA. [*Received, October 25th*, 1963.]

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268. *The Isolation of a Hitherto Undescribed Sulphate of Cytosine and an Improved Preparation of the Intermediate* 1-*Cyano*-2,2-*Diethoxyethane.*

By J. A. HILL and W. J. LE QUESNE.

THIS Note records a synthesis of cytosine as the hemisulphate, $C_4H_5N_3O,\frac{1}{2}H_2SO_4$, in 22% overall yield from commercially available materials and of the corresponding sulphate of [2-^{14}C]cytosine in 34·5% yield from [^{14}C]urea.

The synthetic route was a modification of the method of Bendich, Getler, and Brown,[1] which involved condensation of triethyl orthoformate with ethyl bromoacetate to give ethyl 3,3-diethoxypropionate,[2] followed by conversion [3] of this ester into 1-cyano-2,2-diethoxyethane via ββ-diethoxypropionamide, and condensation of the nitrile with urea to give cytosine in 11% overall yield. Although ethyl ββ-diethoxypropionate is now prepared from triethyl orthoformate and keten in an improved yield,[4] the three-stage preparation of the nitrile was found to be tedious, and as 1-bromo-2,2-diethoxyethane was commercially available, use was made of the recently developed method [5] for the conversion of halides into cyanides in high yield under mild conditions. Previous attempts to convert the bromoacetal into the cyanoacetal had been made,[3,6,7] but the highest yield recorded was 14%.

Reaction of a mixture of 1-bromo-2,2-diethoxyethane, sodium cyanide, and dimethyl sulphoxide gave an oil which was fractionated slowly under reduced pressure to give a 38%

[1] Bendich, Getler, and Brown, *J. Biol. Chem.*, 1949, **177**, 565.
[2] Tschitschibabin, *J. prakt. Chem.*, 1906, **73**, 326.
[3] McElvain and Clarke, *J. Amer. Chem. Soc.*, 1947, **69**, 2657.
[4] Crosby and Berthold, *J. Org. Chem.*, 1962, **27**, 3083.
[5] Friedman and Shechter, *J. Org. Chem.*, 1960, **25**, 877.
[6] Hartung and Adkins, *J. Amer. Chem. Soc.*, 1927, **49**, 2517; 1947, **69**, 1535.
[7] Uhle and Jacobs, *J. Org. Chem.*, 1945, **10**, 81.

recovery of starting material and 43% of 1-cyano-2,2-diethoxyethane. The yield of nitrile allowing for starting material recovered was 69%. Only one experiment was performed at this stage and these yields may thus be capable of improvement.

1-Cyano-2,2-diethoxyethane was condensed with urea by a modification of the method of Bendich *et al.*[1] Bendich *et al.*[1] precipitated cytosine by addition of acetic acid to an alkaline solution of the product until the pH was 7·0—7·5. We found that precipitation of the product at pH 6—7 consistently gave a crystalline cytosine sulphate of composition $C_4H_5N_3O,\frac{1}{2}H_2SO_4$. A barium chloride–hydrochloric acid test confirmed the presence of sulphate ions, and the ultraviolet spectrum indicated a molecular weight in agreement with the above formulation. The yield of $C_4H_5N_3O,\frac{1}{2}H_2SO_4$ from urea was 34·5%, and from 1-cyano-2,2-diethoxyethane 32%, thus giving an overall yield of 22% from 1-bromo-2,2-diethoxyethane.

Since this sulphate, containing one half of a molecule of sulphuric acid per molecule of cytosine, can also be obtained by addition of ethanol to a solution of one mole of cytosine hydrate in approximately one mole of 2N-sulphuric acid, it obviously crystallises from solutions over quite a wide range of pH. A 0·04M-aqueous solution of the sulphate has a pH of 3·2.

When optimum conditions had been established, [^{14}C]urea was treated with 1-cyano-2,2-diethoxyethane to give [2-^{14}C]cytosine sulphate with a specific activity of 21·5 mc/mmole. The latter was identical in all respects with the samples of inactive material.

It is pertinent to note that cytidine sulphate obtained from synthetic cytidine in a similar manner has the composition $C_9H_{13}N_3O_5,\frac{1}{2}H_2SO_4$.[8]

Experimental.—Infrared spectra (i.r.) were determined in carbon disulphide solution on a Grubb–Parsons G.S.3 Grating Spectrometer by Mr. B. H. Baxter. Ultraviolet spectra were determined on a Unicam S.P. 500 spectrometer.

1-*Cyano*-2,2-*diethoxyethane*. 1-Bromo-2,2-diethoxyethane (36·1 g., 0·183 mole) was added during 30 min. to a warm (60°) stirred mixture of sodium cyanide (78%; 12·9 g., 0·205 mole) in dimethyl sulphoxide (75 ml.). The stirred mixture was then heated at 70° for 4 hr. Isolation of the product in the usual manner gave a yellow oil which was carefully fractionated under reduced pressure through a 20-cm. lagged Dufton column during 4 hr. Three fractions were obtained as follows: (i) 13·5 g. (38% recovery) of 1-bromo-2,2-diethoxyethane, b. p. 60—82°/12 mm., (lit.,[9] b. p. 62—63°/15 mm.), $\nu_{max.}$ includes 684 cm.$^{-1}$ (CBr stretching), 2254 cm.$^{-1}$ absent; (ii) 1·7 g. (6%) of an intermediate fraction, b. p. 82—90°/12 mm., consisting of approx. 80% cyanide and 20% bromide (calculated from the i.r. spectrum); (iii) 11·3 g. (43%) of 1-cyano-2,2-diethoxyethane, b. p. 90—91°/12 mm. (lit.,[7] b. p. 99°/14 mm.), $\nu_{max.}$ includes 2254 cm.$^{-1}$ (CN stretching), 684 cm.$^{-1}$ absent. The yield of nitrile allowing for starting material recovered was 69%.

[2-^{14}*C*]*Cytosine sulphate*. [^{14}C]Urea (100·5 mg.; 39·54 mc.) was dissolved in anhydrous butanol (1·1 ml.) under a stream of dry nitrogen in a flask immersed in an oil-bath at room temperature. Under carbon dioxide-free conditions sodium (507 mg.) was added to anhydrous butanol (16·5 ml.) under a stream of dry nitrogen, and the mixture was heated under reflux until complete solution had occurred (about 20 min.). Part of the above sodium butoxide solution (1·30 ml.) was then carefully added to the butanol solution of urea with rapid stirring under nitrogen, followed by 1-cyano-2,2-diethoxyethane (0·27 ml.; 260 mg.), and the mixture was heated under reflux with fast stirring for 2¼ hr. After cooling to room temperature overnight, the mixture was evaporated almost to dryness (rotary evaporator), and the yellow residue was dissolved in hot 2N-sulphuric acid (2·1 ml.). Ether (5 ml.) was added and pipetted off after shaking the mixture to remove residual butanol. The aqueous solution was heated for 5 min., and pipetted hot on to a charcoal column (12 mm. length × 4 mm. diameter). The column was kept warm in a stream of hot air, and the solution was forced through the column by compressed air into a filter beaker. The reaction flask was washed with more hot 2N-sulphuric acid (0·4, 0·2, and 0·4 ml.) and the washings were also passed through the column.

[8] Howard, Lythgoe, and Todd, *J.*, 1947, 1052.
[9] McElvain and Kundiger, *Org. Synth.*, 1943, **23**, 8.

The filter beaker was immersed in a bath at 70—80°, and after 10 min., the solution was brought to pH 9 with ammonia (*d* 0·88). Glacial acetic acid was then carefully added at *ca.* 80° until the pH was between 6 and 7, and the mixture was allowed to cool and kept at 0° overnight. The crystalline product was collected, recrystallised four times from water (including one further decolorisation with charcoal), and dried at 110°/10^{-6} mm. for 3 hr. The yield of [2-^{14}C]cytosine sulphate was 92·2 mg. (34·5% based on [^{14}C]urea; 32% based on 1-cyano-2,2-diethoxyethane), with a specific activity of 21·5 mc/mole. The product had $\lambda_{max.}$ 275 mμ (ε 11,010) in N-sulphuric acid, whilst cytosine hydrate had $\lambda_{max.}$ 275 mμ (ε 10,710) in N-sulphuric acid under the same conditions, thus indicating an apparent purity of 102%. Ratios of absorption were as follows: $\varepsilon_{250}/\varepsilon_{260}$ = 0·47 (lit.,[10] 0·48); $\varepsilon_{280}/\varepsilon_{260}$ = 1·50 (lit.,[10] 1·50); $\varepsilon_{290}/\varepsilon_{260}$ = 0·72 (lit.,[10] 0·77). Inverse dilution analysis (with cytosine, converted into sulphate after addition) gave the apparent radiochemical purity as 103%. Paper chromatography, descending on Whatman 3 MM paper, followed by autoradiography gave the following values: (i) in propan-2-ol : hydrochloric acid : water (65 : 17 : 18) the radiochemical purity was >99%, and the R_F value = 0·45; (ii) in ethanol : 0·2% hydrochloric acid (75 : 25) the radiochemical purity was >98%, and the R_F value 0·44; (iii) in propan-2-ol : water : trichloroacetic acid (70 ml. : 30ml. : 5 g.) the radiochemical purity was >98%, and the R_F value 0·58.

Cytosine sulphate from cytosine hydrate. Cytosine hydrate (1·0 g.; previously tested for degree of hydration) was dissolved in 2N-sulphuric acid (8·4 ml., 1·05 mol.) at 75° with stirring, and ethanol (15 ml.) was added quickly. The *sulphate* crystallised and after cooling, the crystals were collected, washed with ethanol, and dried at 110°/10^{-6} mm. for 3 hr. (Found: C, 30·0; H, 3·7; N, 26·0; S, 9·9. Calc. for $C_4H_5N_3O,\frac{1}{2}H_2SO_4$: C, 30·0; H, 3·8; N, 26·2; S, 10·0%); $\lambda_{max.}$ (in N-sulphuric acid) 275 mμ (ε 11,230, assuming *M*, 160·14). The pH of a 0·04M-aqueous solution of cytosine sulphate at 20° was 3·2 (cf. 7·4 for free cytosine under the same conditions).

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THE RADIOCHEMICAL CENTRE, AMERSHAM, BUCKS.

[Present address (J. A. H.): SOUTHERN DYESTUFF COMPANY, P.O. BOX 10098, CHARLOTTE 1, NORTH CAROLINA, U.S.A.] [*Received, March 18th*, 1964.]

[10] " Specifications and Criteria for Biochemical Compounds," NAS–NRC Publication 719, National Academy of Sciences, Washington, D.C., 1960, P-10.

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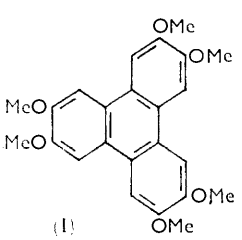
269. 2,3,6,7,10,11-*Hexamethoxytriphenylene.*

By FRITZ-HANS MARQUARDT.

IT is known that in the course of Friedel–Crafts reactions, by-products are formed in low yield by intermolecular dehydrogenating condensation of the aromatic component of the reaction mixture.[1] Experience has shown that with derivatives of benzene as the aromatic component, the products are diphenyls, *i.e.*, the condensation does not proceed further than the linking of two aryl residues. The purpose of this Note is to report the isolation and identification of a rather unusual product of such a reaction, 2,3,6,7,10,11-hexamethoxytriphenylene (I), which results from a dehydrogenating cyclotrimerization of veratrole.



(I)

The location of the methoxy groups was determined by means of the nuclear magnetic resonance spectrum, which consisted of only two bands: one at δ 4·14 p.p.m., for the eighteen protons of the methoxy-groups, and one at δ 7·79 p.p.m. for the six aromatic protons indicating that all the methoxy-groups were in equivalent positions.

[1] For a review see Olah, " Friedel–Crafts and related reactions," Interscience Publishers Inc., New York, 1963, Vol. I, part 2, p. 979.

Experimental.—Veratrole (1 mol.) was acetylated with acetyl chloride (1 mol.) in the presence of aluminium chloride (1 mol.) at −5° in toluene for 3 hr. The crude neutral product was distilled *in vacuo* at 129°/1 mm. to remove 3,4-dimethoxyacetophenone. Trituration of the residue with ethyl acetate afforded a solid 0·08%, which was purified by recrystallisation from chloroform; it had m. p. 314·5—316° (corrected) [Found: C, 70·6; H, 6·0; O, 23·2; OMe, 22·02%; *M* (mass spectrum), 408. $C_{24}H_{24}O_6$ requires C, 70·6; H, 5·9; O, 23·5; 6 OMe, 22·1%; *M* 408].

The nuclear magnetic resonance spectrum was determined at 60 Mc. with $CDCl_3$ as solvent and with tetramethylsilane as internal reference.

Thanks are offered to Dr. Padowetz for analytical data, to Dr. Zürcher for the nuclear magnetic resonance spectrum and to Dr. Hürzeler for the mass spectrum.

PHARMACEUTICAL DIVISION, CIBA LIMITED,
BASLE, SWITZERLAND.

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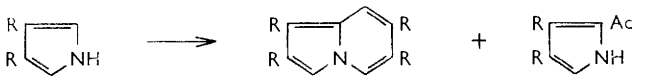
270. *The Self-condensation of 3,4-Dialkylpyrroles.*

By R. BONNETT, I. A. D. GALE, and G. F. STEPHENSON.

IN an extension of earlier observations [1] on the acid-catalysed self-condensation of pyrroles the behaviour of 3,4-dimethylpyrrole and 3,4-diethylpyrrole has been examined. Acid treatment of pyrroles of this substitution pattern might be expected to cause trimerisation.[2] However, in several experiments with 3,4-diethylpyrrole no trimer could be isolated, and under the specific conditions which cause the trimerisation of the parent compound [2] the diethylpyrrole was recovered.

An alternative mode of reaction leading to the indolizine system can be envisaged (cf. the reaction [3] with 2,4-dimethylpyrrole) and self-condensation in this manner has now been realised with both pyrroles. Thus, 3,4-diethylpyrrole, under forcing conditions in the presence of zinc acetate, gave an indolizine, formulated on the basis of the earlier example [3] as 1,2,6,7-tetraethylindolizine (I; R = Et) (24%), together with 2-acetyl-3,4-diethylpyrrole (10%). An analogous reaction occurred with 3,4-dimethylpyrrole. The condensation of acetonylacetone with 3,4-diethylpyrrole similarly gave 1,2-diethyl-5,8-dimethylindolizine: this reaction required a shorter time and proceeded in much better yield



(I)

than the self-condensations, and was not accompanied by the formation of isolable quantities of 2-acetyl-3,4-diethylpyrrole. In the self-condensation it was observed that the yield of indolizine was improved by the presence of water (~20%) in the reaction medium. The water probably inhibits the alternative reaction, the acetylation of the pyrrole; but it might take part in one or more possible hydrolytic steps involving, for example, the pyrrole itself or the pyrrolinylpyrrole presumed to be formed as an intermediate.[3]

The indolizines decomposed gradually when kept at room temperature, but could be kept for long periods with little decomposition at −20° under nitrogen in the dark.

[1] Bonnett and White, *J.*, 1963, 1648.
[2] Potts and Smith, *J.*, 1957, 4018.
[3] Saxton, *J.*, 1951, 3239; compare also the recently reported condensations involving 2,3,4-trialkylpyrroles; Atkinson, Grigg, and Johnson, *J.*, 1964, 893.

Ethanolic solutions fluoresced brilliantly in ultraviolet light and had characteristic ultraviolet spectra which showed the expected transformation to spectra of the vinylpyridine type [4] when the solutions were acidified.

Experimental.—Ultraviolet spectra were measured in 95% ethanol: wavelength values in parenthesis refer to inflections.

Self-condensation of 3,4-*Dimethylpyrrole.*—3,4-Dimethylpyrrole (3·45 g.), zinc acetate dihydrate (17 g.), and aqueous acetic acid (80% v/v, 100 ml.) were refluxed under nitrogen for 40 hr. The bulk of the solvent was distilled, the residue was basified (aqueous sodium hydroxide) and the mixture was steam-distilled: during the distillation some crude indolizine (0·57 g.; m. p. 106—108°) was deposited in the condenser. The distillate (~700 ml.) was acidified (acetic acid) and extracted with ether (3 × 170 ml.). The extract was dried ($MgSO_4$), evaporated, and the residue crystallised (charcoal) from light petroleum (b. p. 60—80°) to give 2-acetyl-3,4-dimethylpyrrole (0·03 g., 1·3%), m. p. 131—132·5°, identical with an authentic sample.

The steam-distillate was basified (aqueous sodium hydroxide) and extracted with ether (3 × 170 ml.). The extract was dried and evaporated to give crude 1,2,6,7-*tetramethylindolizine* (I; R = Me) (total 0·825 g., 26%). Crystallisation from ethanol gave needles, m. p. 109—109·5°, which turned green on storage (Found: C, 83·15; H, 8·6; N, 8·0. $C_{12}H_{15}N$ requires C, 83·2; H, 8·7; N, 8·1%); $\lambda_{max.}$ 248, (283), 294, 308, and 358 mμ (log ε 4·50, 3·28, 3·40, 3·32, and 3·16, respectively); on acidification (HCl) $\lambda_{max.}$ 225, 250, and 326 mμ (log ε 4·38, 3·96, and 3·79, respectively).

Self-condensation of 3,4-*Diethylpyrrole.*—3,4-Diethylpyrrole (1 g.), zinc acetate dihydrate (5 g.), and aqueous acetic acid (80% v/v, 50 ml.) were refluxed under nitrogen for 48 hr. The solution was steam-distilled, basified, and steam-distilled again. The combined distillates (~1 l.) were basified and extracted with ether. The extract was dried (Na_2SO_4), the ether was removed under nitrogen, and the residue was chromatographed on alumina (Spence " H " type). Elution with ether brought off the indolizine fraction, which was concentrated under nitrogen and distilled to give a low-boiling fraction (0·08 g., mainly unchanged diethylpyrrole) and at bath ~110°/0·15 mm., 1,2,6,7-*tetraethylindolizine* (I; R = Et) (0·22 g., 24%) (Found: C, 83·3; H, 10·2; N, 6·1. $C_{16}H_{23}N$ requires C, 83·8; H, 10·1; N, 6·1%); $\lambda_{max.}$ 248, 287, 297, 309, and 360 mμ (log ε 4·50, 3·34, 3·49, 3·48, and 3·30, respectively).

Elution with ethanol followed by concentration and sublimation of the residue gave 2-*acetyl*-3,4-*diethylpyrrole* (0·14 g., 10%), m. p. 86—89°, raised to 93—94° after crystallisation from petroleum (b. p. 60—80°) and sublimation (Found: C, 72·9; H, 9·15; N, 8·6. $C_{10}H_{15}NO$ requires C, 72·7; H, 9·15; N, 8·5%); $\nu_{max.}$ (Nujol) 3220 and 1627 $cm.^{-1}$; $\lambda_{max.}$ 299 mμ (log ε 4·21).

Condensation of 3,4-*Diethylpyrrole with Acetonylacetone.*—3,4-Diethylpyrrole (1 g.), acetonylacetone (1·5 g.), zinc acetate dihydrate (1·5 g.), and aqueous acetic acid (90% v/v, 50 ml.) were refluxed under nitrogen for 24 hr. The mixture was steam-distilled, basified, and steam-distilled again. The combined distillates (~500 ml.) were basified and extracted with ether. The extract was washed, dried, and concentrated to give an oil which was chromatographed on alumina (Spence " H " type), the indolizine being eluted with ether. Concentration of the ether and distillation gave 1,2-*diethyl*-5,8-*dimethylindolizine* as an oil (1·4 g., 79%), b. p. 117—121°/1·2 mm., which solidified on storage, m. p. 29—32° (Found: C, 83·3; H, 9·6; N, 7·1. $C_{14}H_{19}N$ requires C, 83·5; H, 9·5; N, 7·0%); $\lambda_{max.}$ 241, (281), 292, 305, and 341 mμ (log ε 4·56, 3·41, 3·62, 3·73, and 3·45, respectively).

2-*Acetyl*-3,4-*dimethylpyrrole.*—This was prepared in 36% yield by the action of acetyl chloride on the Grignard derivative of 3,4-dimethylpyrrole (cf. ref. 5). Recrystallisation (charcoal) from petroleum (b. p. 60—80°) gave crystals, m. p. 132·5—133·5° (Found: C, 69·9; H, 8·0; N, 10·3%. $C_8H_{11}NO$ requires C, 70·0; H, 8·1; N, 10·2%); $\nu_{max.}$ (Nujol) 3280 and 1625 $cm.^{-1}$, $\lambda_{max.}$ 296 mμ (log ε 4·29).

The awards of maintenance grants by the D.S.I.R. (to G. F. S.) and by the Petroleum Research Fund (to I. A. D. G.) are gratefully acknowledged.

CHEMISTRY DEPARTMENT, QUEEN MARY COLLEGE, LONDON E.1. [*Received, April 15th,* 1964.]

[4] Favini, *Gazzetta*, 1963, **93**, 635.
[5] Oddo, *Ber.*, 1910, **43**, 1012.

271. *Electron Impact Studies of Some Aromatic Fluorocarbons.*

By J. L. Cotter.

This Note reports some mass-spectral, ionization-potential, and appearance-potential measurements made on perfluorobiphenyl, perfluoro-*p*-terphenyl, and perfluoro-*p*-quaterphenyl.

The ionization potentials of these compounds, together with the appearance potentials of selected ions derived from perfluorobiphenyl and perfluoro-*p*-terphenyl are given in the Table.

Ionization and appearance potentials.

Molecule	Ion (singly charged positive ion)	Relative intensity (%)	I.P. or A.P. (ev)	No. of detmns.
C_6F_6	C_6F_6		10·1 ± 0·1	2
$C_{12}F_{10}$	$C_{12}F_{10}$	100·0	10·0 ± 0·1	5
$C_{12}F_{10}$	$C_{12}F_9$	10·0	16·7 ± 0·1	3
$C_{12}F_{10}$	$C_{12}F_8$	8·89	18·4 ± 0·3	2
$C_{12}F_{10}$	$C_{11}F_7$	27·8	17·2 ± 0·1	2
$C_{18}F_{14}$	$C_{18}F_{14}$	100·0	9·85 ± 0·3	5
$C_{18}F_{14}$	$C_{18}F_{13}$	4·38	17·5 ± 0·3	4
$C_{18}F_{14}$	$C_{18}F_{12}$	3·40	19·9	1
$C_{18}F_{14}$	$C_{17}F_{11}$	16·6	18·2 ± 0·1	2
$C_{24}F_{18}$	$C_{21}F_{18}$		9·9 ± 0·1	2

In the mass spectrum of perfluorobiphenyl, if all ions with $m/e = 167$ correspond to the doubly charged molecular ion, then the ratio of the intensities of doubly charged to singly charged ions of $(^{12}C)_{12}(^{19}F)_{10}$ should be the same as the ratio of doubly charged to singly charged ions of $(^{12}C)_{11}(^{13}C)_1(^{19}F)_{10}$. Experimentally, the ratio of the peak intensities at m/e 167 and m/e 334 (0·0955) was found to be identical, within the experimental error, with the ratio of the peak intensities at m/e 167·5 and m/e 335 (0·0960). The apparent absence of the pentafluorophenyl ion ($m/e = 167$) from the mass spectrum of perfluorobiphenyl, and the relatively low intensity of this ion in the mass spectrum of perfluoro-*p*-terphenyl, shows that disruptive processes leading to the formation of this ion, by cleavage of the interannular bonds, are not among the preferred fragmentation modes of these molecules. The behaviour of biphenyl on electron impact, parallels that of its perfluoro-analogue in that the phenyl ion is absent from the biphenyl mass spectrum.[1]

In the mass spectrum of perfluoro-*p*-terphenyl, the ratio of the peak intensities at m/e 241 and m/e 482 was found to be 0·154; while the ratio of the peak intensities at m/e 241·5 and m/e 483 was 0·116. It follows that about 75% of the peak intensity at m/e 241 was due to the doubly charged molecular ion $C_{18}F_{14}^{2+}$, and 25% to the fragment ion $C_9F_7^+$.

The appearance potential of the ion $C_{18}H_{13}^+$ from $C_{18}F_{14}$ is 0·8 ev greater than the appearance potential of the ion $C_{12}F_9^+$ from $C_{12}F_{10}$. If the assumptions are made that the carbon–fluorine bond dissociation energies in these molecules are not greatly different and that the difference in the ionization potentials of the radicals $C_{18}F_{13}$ and $C_{12}F_9$ is the same as the difference in the ionization potentials of the corresponding molecules, then the large difference in the appearance potentials of these two ions, would imply that a considerable amount of excess energy is involved in the dissociative process:

$$C_{18}F_{14} + e \longrightarrow C_{18}F_{13}^+ + F + 2e$$

Experimental.—Perfluorobenzene, b. p. 80°, and perfluorobiphenyl, m. p. 68—69°, were supplied by the Imperial Smelting Corporation Ltd., and used without further purification, Samples of perfluoro-*p*-terphenyl, m. p. 191·5—193·5°, and perfluoro-*p*-quaterphenyl, m. p. 234°. were kindly furnished by Mr. Thrower. No mass fragment heavier than those corresponding to the molecular ions was found in the mass spectra of these samples.

The mass spectra and ionization efficiency curves were obtained on an Associated Electrical Industries Ltd. mass spectrometer M.S.2-H. The mass spectra were obtained with 70v electrons. The temperature of the heated inlet system of the mass spectrometer was 270° for

[1] Hall and Elder, *J. Chem. Phys.*, 1959, **31**, 1420.

experiments with perfluorobiphenyl and perfluoro-*p*-terphenyl, and 365° for perfluoro-*p*-quaterphenyl.

Mainly as a result of the inhomogeneity in energy of the bombarding electrons, the correct determination of ionization and appearance potentials from experimentally determined ionization efficiency curves is not unequivocal. The procedure adopted in this research to obtain critical voltages is that due to Dibeler and Reese.[2] Either argon or krypton was used to calibrate the electron energy scale, the choice of gas being made so as to avoid interference with fragment ions of the same *m/e* ratio as the inert gas ion. As a check on the experimental technique the ionization potential of perfluorobenzene was redetermined and the value obtained 10·1 ev is in agreement with previously determined values, 9·9 ev [3] and 10·0 ev.[4]

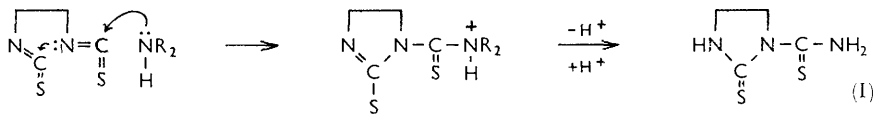
ROYAL AIRCRAFT ESTABLISHMENT, FARNBOROUGH, HANTS. [*Received, April 23rd,* 1964.]

[2] Dibeler and Reese, *J. Res. Nat. Bur. Stand.*, 1955, **54**, 127.
[3] Dibeler and Reese, *J. Chem. Phys.*, 1957, **26**, 304.
[4] Majer and Patrick, *Trans. Faraday Soc.*, 1962, **58**, 17.

272. 1-*Thiocarbamoylimidazolidine-2-thione.*

By M. MAMMI, F. D'ANGELI, and (the late) S. BEZZI.

ETHYLENE DI-ISOTHIOCYANATE, $(CH_2{\cdot}NCS)_2$, reacts with excess of concentrated aqueous ammonia, to yield, besides small amounts of the expected dithiourea, $(CH_2{\cdot}NH{\cdot}CS{\cdot}NH_2)_2$, a mono-adduct to which a triazepine structure had been assigned,[1] but which we have shown by *X*-ray structure analysis to be 1-thiocarbamoylimidazolidine-2-thione (I); crystallographic details will be reported elsewhere.[2]



(I)

Formation of (I) conceivably results from a reaction, competing with the one leading to the dithiourea, in which the carbon atom of an isothiocyanate group is not attacked by a molecule of ammonia but by the nitrogen atom of the functional group reacting with ammonia.

This type of cycloaddition also occurs with other nucleophiles such as primary and secondary amines and thiols. Imidazole structures similar to (I) have been shown to belong to several of these mono-adducts so formed, although an independent synthesis of (I) itself was not achieved.[3]

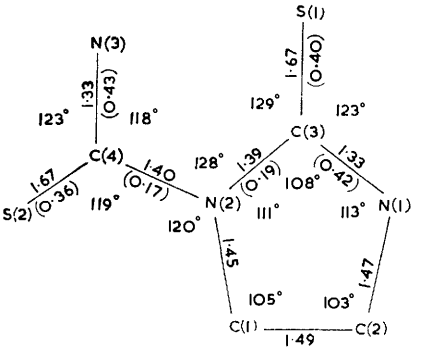
The structure analysis, carried out on the projections (100) and (010) ($R = 0{\cdot}065$ and 0·082, respectively) led to the values shown in the Figure; the values for double-bond character were calculated by the Pauling equation.[4]

In agreement with the fact that (I) is a 1,3-substituted dithiobiuret, its structure is quite similar to that in biuret hydrate [5] and in bis(biuret)cadmium chloride.[6] In (I), as well as in biuret, a *trans* configuration is present, and the distance N(3)–S(1) (2·971 Å) shows the existence of an internal hydrogen bond, as in biuret.[7,8] The structure for (I) in the Figure is also in agreement with data for ethylenethiourea (imidazolidine-2-thione).[9]

Within experimental error, the ring atoms lie on a plane with which C(3)–S(1) and

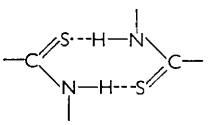
[1] G. D. Thorn and R. A. Ludwig, *Canad. J. Chem.*, 1954, **32**, 872.
[2] M. Mammi, G. Valle, G. Cojazzi, and V. Busetti, unpublished data. See also preliminary communication at the 6th International Congress of the Internat. Union of Crystallography, Rome, 1963.
[3] F. D'Angeli, A. Bandel, and V. Giormani, *J. Org. Chem.*, 1963, **28**, 1596; F. D'Angeli, C. Di Bello and V. Giormani, unpublished results.
[4] L. Pauling, " The Nature of the Chemical Bond," 2nd edn., Cornell U.P., Ithaca, New York, 1948.
[5] E. W. Hughes, H. L. Yakel, and H. C. Freeman, *Acta Cryst.*, 1961, **14**, 345.
[6] L. Cavalca, M. Nardelli, and G. Fava, *Acta Cryst.*, 1960, **13**, 594.
[7] I. C. Kogon, *J. Amer. Chem. Soc.*, 1957, **79**, 2253.
[8] W. D. Kumler and M. L. Calvin, *J. Amer. Chem. Soc.*, 1960, **82**, 6305.
[9] P. J. Wheatley, *Acta Cryst.*, 1953, **6**, 369.

N(2)–C(4) bonds form angles of 1·4 and 2·2°, respectively. Double-bond values indicate a formal negative charge of about 0·6 electron on each sulphur atom and a formal positive charge of about 0·4 on each nitrogen; these values fit with zero charges on atoms C(3) and C(4), whose total bond orders are very close to 4.



Bond lengths and angles in 1-thiocarbamoylimidazolidine-2-thione. Values for double-bond character are given in parentheses.

The results indicate a high contribution by polar structures compared with the uncharged structure (I). For each of the two groups of atoms, N(1)C(3)S(1)N(2) and N(3)C(4)S(2)N(2), three resonance formulæ can be written, namely, >N–C(:S)–N<, >N⁺=C(S⁻)–N<, and >N–C(S⁻)=N⁺<. Possible combinations give rise to nine formulæ, among which eight are allowed to contribute to the resonance hybrid; each of the four which bear a positive charge on N(2) conceivably contributes to the extent of 9%, and each of the others about 16%.



These results agree with the type of crystal packing, which shows that each sulphur atom is surrounded by nitrogen atoms and *vice versa*. Further, the molecules are linked, through centres of symmetry, by hydrogen bonds. Since two bridges occur in each molecule, with intermolecular distances of 3·40 and 3·45 Å, infinite chains result.

VIII Sezione del Centro Nazionale di Chimica delle Macromolecole,
Istituto di Chimica Organica dell'Università,
Padova, Italy.

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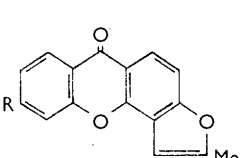
273. *Furano-compounds. Part III.*[1] *Synthesis of 5′-Methyl- and 5′,6-Dimethyl-furano(3′,2′:4,3)xanthones.*

By Gurubasav S. Puranik and S. Rajagopal.

Continuing our work[1,2] on synthesis and biogenetic significance of furanoxanthones, especially methyl-substituted one, we synthesised two new α-methylfuranoxanthones (I; R = H or Me). The substituents may affect the pharmacology of the furanoxanthones. By analogy with the oxidation pattern of karanjin,[3] 3-hydroxyxanthone was selected as the initial material on which to build the furan ring. Two methods for the furan ring closure of the 4-allyl-3-hydroxyxanthones were adopted. The first, based on Scheinmann and Suschitzky's work,[4] gives dihydrofurano-compounds, which were dehydrogenated by treatment with *N*-bromosuccinimide in presence of benzoyl peroxide followed by dehydrobromination by pyridine.[5] The second route is an adaptation of the method of Adams and Rindfusz[6] involving addition of bromine to 3-acetoxy-4-allyl-derivatives followed by cyclisation and dehydrobromination. Infrared data agree with earlier observations.[1]



(I)

[1] Part II, Puranik and Rajagopal, *J. Org. Chem.*, 1964, **29**, 1089.
[2] Puranik and Rajagopal, *Ber.*, 1963, **96**, 976.
[3] Beal and Katti, *J. Amer. Pharm. Assoc.*, 1926, **14**, 1086.
[4] Scheinmann and Suschitzky, *Tetrahedron*, 1959, **7**, 31.
[5] Geissman and Halsall, *J. Amer. Chem. Soc.*, 1951, **73**, 1280.
[6] Adams and Rindfusz, *J. Amer. Chem. Soc.*, 1919, **41**, 648.

Experimental.—3-*Allyloxyxanthone.* Reaction of 3-hydroxyxanthone (2·5 g.) with allyl bromide (2 g.) and calcined potassium carbonate (11 g.) in acetone (300 c.c.) gave the *allyl ether* (3 g.) as plates (from alcohol), m. p. 137° (Found: C, 76·3; H, 4·9. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%).

4-*Allyl*-3-*hydroxyxanthone.* 3-Allyloxyxanthone (2·7 g.) in dimethylaniline (21 c.c.) was refluxed for 3 hr. Acidification with hydrochloric acid gave 4-*allyl*-3-*hydroxyxanthone* (2·5 g.) as needles (from alcohol), m. p. 253° (Found: C, 76·1; H, 4·9. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%).

3-*Acetoxy*-4-*allylxanthone.* This, prepared by heating 4-allyl-3-hydroxyxanthone (1·2 g.) with acetic anhydride (10 c.c.) and a drop of syrupy phosphoric acid, was obtained as *needles* (from alcohol), m. p. 126°. It gave no colour with ethanolic ferric chloride (Found: C, 73·5; H, 5·0. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8%).

4′,5′-*Dihydro*-5′-*methylfurano*(3′,2′:4,3)*xanthone.* 3-Allyl-4-hydroxyxanthone (2·2 g.) in glacial acetic acid (250 c.c.) was saturated under nitrogen with hydrogen bromide gas in the presence of traces of diphenylamine. The mixture was set aside in the dark at room temperature for four days and then worked up. 4-β-*Bromopropyl*-3-*hydroxyxanthone* (1·3 g.) was obtained as needles (from alcohol), m. p. 213° (decomp.) (Found: C, 57·3; H, 4·5; Br, 23·6. $C_{16}H_{13}BrO_3$ requires C, 57·7; H, 4·0; Br, 24·0%).

This bromo-derivative (1 g.) suspended in acetone (200 c.c.) was treated with potassium carbonate (2 g.) and refluxed for 6 hr. The *dihydrofurano-compound* (0·55 g.) was obtained as pale yellow needles (from alcohol), m. p. 180° (Found: C, 76·3; H, 4·9. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%).

5′-*Methylfurano*(3′,2′:4,3)*xanthone.* A solution of 4′,5′-dihydro-5′-methylfurano(3′,2′:4,3)-xanthone (0·38 g.) in dry carbon tetrachloride (30 c.c.) containing a trace of benzoyl peroxide was treated with *N*-bromosuccinimide (0·25 g.) and the mixture refluxed on a steam-bath for 20 min. The succinimide that separated was filtered off and the filtrate on evaporation left a brownish solid (0·55 g.) which crystallised as shining needles (from alcohol), m. p. 142°.

Dehydrobromination. The above substance in pyridine (5 c.c.) was refluxed for 1 hr., cooled, and acidified with 2N-hydrochloric acid. The resulting precipitate was extracted with ethyl acetate to yield a yellow *substance* (0·12 g.) which crystallised as yellow rectangular rods (from alcohol), m. p. 170° (Found: C, 76·5; H, 4·3. $C_{16}H_{10}O_3$ requires C, 76·8; H, 4·0%); $\nu_{max.}$ 1630s, 1470m, 1060s, and 881w.

3-*Acetoxy*-4-(2′,3′-*dibromopropyl*)*xanthone.* A solution of bromine (0·8 g.) in glacial acetic acid (5 c.c.) was added dropwise to a well stirred solution of 3-acetoxy-4-allylxanthone (1 g.) in glacial acetic acid (10 c.c.), at room temperature. The reaction mixture was diluted with water (50 c.c.) and the *solid* which separated (2 g.) was obtained as small needles (from alcohol), m. p. 162° (Found: C, 45·3; H, 3·4; Br, 35·5. $C_{18}H_{14}Br_2O_4$ requires C, 45·4; H, 3·1; Br, 35·2%).

5′-*Methylfurano*(3′,2′:4,3)*xanthone.* A solution of 3-acetoxy-4-(2′,3′-dibromopropyl)xanthone (1·14 g.) and potassium hydroxide (3 g.) in ethanol (75 c.c.; 95%) refluxed for 2 hr. and worked up gave the furanoxanthone (0·3 g.), rectangular rods (from alcohol), m. p. 170°, undepressed by admixture with the sample obtained as above.

3-*Allyloxy*-6-*methylxanthone.* Allylation of 3-hydroxyxanthone (2 g.) in acetone (300 c.c.) with allyl bromide (1·6 g.) and calcined potassium carbonate (9 g.) yielded the 3-*allyl ether* (2·2 g.) as thin rectangular plates (from alcohol), m. p. 137° (Found: C, 76·5; H, 5·1. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%).

4-*Allyl*-3-*hydroxy*-6-*methylxanthone.* The above allyl ether (2 g.) when heated with dimethylaniline (18 c.c.) for 3 hr. gave 4-*allyl*-3-*hydroxy*-6-*methylxanthone* (2 g.) as long needles (from alcohol), m. p. 253° (Found: C, 76·8; H, 5·2. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%).

4-*Allyl*-3-*acetoxy*-6-*methylxanthone.* This, prepared by heating 4-allyl-3-hydroxy-6-methylxanthone (1·3 g.) with acetic anhydride (10 c.c.) and fused sodium acetate (2 g.), was obtained (1·4 g.) as colourless long *needles* (from alcohol), m. p. 178°. It gave no colour with ethanolic ferric chloride (Found: C, 74·3; H, 5·4. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%).

3-*Acetoxy*-4-(2′,3′-*dibromopropyl*)-6-*methylxanthone.* Treatment of 3-acetoxy-4-allyl-6-methylxanthone (0·6 g.) in chloroform (8 c.c.) at room temperature with bromine (0·4 g.) in chloroform (8 c.c.) gave the dibromo-compound (0·8 g.) as *needles* (from alcohol), m. p. 184° (Found: C, 48·5; H, 3·1; Br, 34·1. $C_{19}H_{16}Br_2O_4$ requires C, 48·7; H, 3·4; Br, 34·2%).

5′,6-*Dimethylfurano*(3′,2′:4,3)*xanthone.* The foregoing dibromo-compound (0·6 g.) when

heated with alcoholic potassium hydroxide (6 g. in 150 c.c.) for 2 hr. gave 5′,6-dimethylfurano-(3′,2′:4,3)xanthone (0·3 g.) as shining needles (from alcohol), m. p. 225° (Found: C, 77·5; H, 4·3. $C_{17}H_{12}O_3$ requires C, 77·3; H, 4·6%); $\nu_{max.}$ 1630w, 1478m, 1070s, and 889w.

We thank Professor S. Siddappa for his interest, and the Government of India, Ministry of Scientific Research and Cultural Affairs, for a Research Training Scholarship (to G. S. P.).

DEPARTMENT OF CHEMISTRY, KARNATAK UNIVERSITY,
DHARWAR-3, INDIA. [*Received, May 5th*, 1964.]

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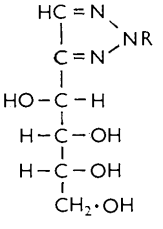
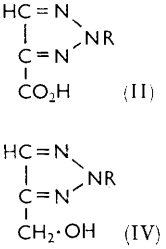
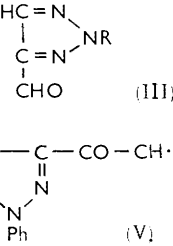
274. *The Scope and Mechanism of Carbohydrate Osotriazole Formation. Part XIV.* o-Halogenophenyl and Other Triazole Derivatives.*

By H. EL KHADEM, Z. M. EL-SHAFEI, and M. H. MESHREKI.

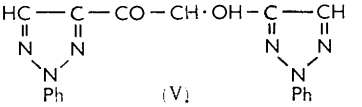
WHEN *o*-halogenophenylosazones are converted into osotriazoles with copper sulphate, a simultaneous dehydrogenation is caused by the reduced copper precipitated during the reaction;[1-4] therefore no *o*-halogenophenylosotriazole has been prepared. We have now converted D-*arabino*-hexose *o*-chlorophenylosazone into the 4-bromo-2-chlorophenylosotriazole (I; R = 4-bromo-2-chlorophenyl) by the action of bromine water. The latter converts[4,5] phenylosazones into osotriazoles and brominates them in the 4-position. The position of the bromine was established when the same compound was obtained from D-*arabino*-hexose 4-bromo-2-chlorophenylosazone by treatment with bromine water. Although this constitutes the first preparation of an *o*-halogenophenylosotriazole, it is by no means a satisfactory general reaction, since bromine water cannot be used for the preparation of monosubstituted derivatives which it brominates,[5] or of iodo-derivatives which undergo transhalogenation.[3] Attempts to carry out this reaction with other halogens proved unsuccessful; iodine in aqueous potassium iodide failed to react with *o*-chloro-, *o*-bromo-, or *o*-iodo-phenylosazones and bubbling chlorine gas into an aqueous suspension of these osazones only resulted in amorphous mixtures. We have oxidised a number of substituted phenylosotriazoles (I). Potassium permanganate gave the corresponding 2-aryl-4-carboxy-1,2,3-triazoles (II), while periodic acid gave the 4-formyl analogues (III). Reduction of the latter gave the corresponding 2-aryl-4-hydroxymethyl-1,2,3-triazoles (IV).


(I)


(II)


(III)

(IV)


(V)

The aromatic character of the triazole ring[2,6] gives the 4-formyl derivatives (III) the properties of aromatic aldehydes. Boiling with alkali converts (III) into a mixture of acid (II) and alcohol (IV) by a Cannizzaro-type reaction, while potassium cyanide gives the benzoin analogue (V).

Experimental.—D-arabino-*Hexose 4-bromo-2-chlorophenylosazone.* D-Glucose (10 g.) in water (200 ml.) was treated successively with 4-bromo-2-chlorophenylhydrazine hydrochloride (35 g.), sodium acetate (35 g.), and a few drops of acetic acid, and then heated on the water-bath

* Part XIII, El Khadem, and El-Shafei, *Tetrahedron Letters*, 1963, 1887; Part XII, El Khadem, Meshreki, and Labib, *J.*, 1964, 2306.

[1] El Khadem and El-Shafei, *J.*, 1959, 1655.
[2] El Khadem, El-Shafei, and Mohammed, *J.*, 1960, 3993.
[3] El Khadem, El-Shafei, and Meshreki, *J.*, 1961, 2957.
[4] El Khadem, *Adv. Carbohydrate Chem.*, 1963, **18**, 111.
[5] El Khadem and El-Shafei, *J.*, 1958, 3117.
[6] El Khadem, *J.*, 1961, 3146.

for 2 hr. The *osazone* which separated (12 g.) crystallised from ethanol–water in needles, m. p. 230° (decomp.), moderately soluble in boiling ethanol and methanol and insoluble in ether or water (Found: N, 9·6. $C_{18}H_{18}Br_2Cl_2N_4O_4$ requires N, 9·6%).

D-arabino-*Hexose* 4-*bromo*-2-*chlorophenylosotriazole*. (*a*) D-*arabino*-Hexose *o*-chlorophenylosazone (2 g.) in water (150 ml.), was treated in the cold with bromine (3 ml.) and kept overnight at room temperature with occasional shaking. The mass obtained was filtered off (1 g.), washed with water and ethanol, and crystallised from water–ethanol in *needles*, m. p. 173°, moderately soluble in hot ethanol and methanol and insoluble in water (Found: C, 37·9; H, 3·5; N, 11·0. $C_{12}H_{13}BrClN_3O_4$ requires C, 38·1; H, 3·4; N, 11·1%).

(*b*) D-*arabino*-Hexose 4-bromo-2-chlorophenylosazone (2 g.), similarly treated with bromine as in (*a*), gave the same product (1·2 g.), m. p. and mixed m. p. 173° (Found: C, 38·1; H, 3·6; N, 11·1%).

D-arabino-*Hexose* 4-*bromo*-2,5-*dimethylphenylosazone*. D-Glucose (10 g.) was heated with 4-bromo-2,5-dimethylphenylhydrazine hydrochloride (40 g.) and sodium acetate as above. The *osazone* (10 g.) crystallised from ethanol in needles, m. p. 215° (decomp.) (solubility as above) (Found: C, 45·8; H, 5·0; N, 9·5. $C_{22}H_{28}Br_2N_4O_4$ requires C, 46·2; H, 4·9; N, 9·8%).

D-arabino-*Hexose* 4-*bromo*-2,5-*dimethylphenylosotriazole*. D-*arabino*-Hexose 4-bromo-2,5-dimethylphenylosazone (2 g.) was suspended in water (100 ml.) and treated with bromine (3 ml.) as above. The *osotriazole* (1 g.) crystallised from ethanol in needles, m. p. 157° (solubility as above) (Found: C, 45·5; H, 4·8. $C_{14}H_{18}BrN_3O_4$ requires C, 45·2; H, 4·8%).

2-*Aryl*-1,2,3-*triazole*-4-*carboxylic acids* (II). A boiling suspension of the osotriazole (2 g.) in water (200 ml.) was treated with potassium permanganate (6 g.) until a pink colour persisted. The hot mixture was filtered, decolourised by sulphur dioxide and acidified. The *acid* which separated, recrystallised from water–ethanol; it was soluble in hot ethanol and methanol and insoluble in water (see Table).

2-*Aryl*-4-*formyl*-1,2,3-*triazoles* (III). D-*arabino*-Hexose arylosotriazole (1 mmole) was treated with periodic acid ($HIO_4,2H_2O$) (0·8 g., 3·5 mmoles) dissolved in water (10 ml.), and the mixture kept overnight at room temperature with occasional shaking. The crystalline *product* (see Table) was filtered off, washed with water and recrystallised from water–ethanol. It was soluble in ethanol and methanol, and insoluble in acetone or water.

Substituted 2-phenyl-1,2,3-triazole-4-carboxylic acids (II; R = substituted phenyl).

			Found (%)				Required (%)		
Subst. in Ph	M. p.	Yield (%)	C	H	N	Formula	C	H	N
2,4-Br_2	200°	32	30·3	1·9	11·3	$C_9H_5Br_2N_3O_2,H_2O$	29·6	1·9	11·5
4-Br-2-Cl	215	35	33·2	2·3	—	$C_9H_5BrClN_3O_2,H_2O$	33·7	2·2	—
3,4-$(CO_2H)_2$ [2*]	218	28	44·9	3·1	14·7	$C_{11}H_7N_3O_6,H_2O$	44·7	3·1	14·2

Substituted 4-formyl-2-phenyl-1,2,3-triazoles (III; R = substituted phenyl).

3,4-Cl_2 [3]	142°	52	45·1	2·7	17·9	$C_9H_5Cl_2N_3O$	44·6	2·1	17·4
2,5-Me_2 [7]	49—50	58	65·9	5·4	—	$C_{11}H_{11}N_3O$	65·7	5·5	—
3,4-O·CH_2·O [7]	137	62	55·8	3·5	19·2	$C_{10}H_7N_3O_3$	55·3	3·2	19·4

Substituted 4-hydroxymethyl-2-phenyl-1,2,3-triazoles (IV; R = substituted phenyl).

Unsubst.[9]	72°	80	61·8	5·0	23·8	$C_9H_9N_3O$	61·7	5·1	24·0
p-Cl [10]	97	82	—	—	20·0	$C_9H_8ClN_3O$	—	—	20·0
p-Br [10]	100	82	42·9	3·3	16·7	$C_9H_8BrN_3O$	42·5	3·2	16·5
m-Cl [10]	104	80	52·0	4·3	20·5	$C_9H_8ClN_3O$	51·6	3·8	20·0
p-CO_2H [7]	250	85	54·7	3·7	18·9	$C_{10}H_9N_3O_3$	54·8	4·1	19·2
p-NHAc [7]	174	85	—	—	24·0	$C_{11}H_{12}N_4O_2$	—	—	24·1
p-Me [7]	72	82	63·6	6·1	22·2	$C_{10}H_{11}N_3O$	63·5	5·8	22·2
4-Br-3-Me [10]	78	82	—	—	16·2	$C_{10}H_{10}BrN_3O$	—	—	15·7
4-Br-3-Cl [7]	98	80	37·3	2·4	14·6	$C_9H_7BrClN_3O$	37·4	2·4	14·6
m-Me [7]	58	80	63·8	5·8	22·0	$C_{10}H_{11}N_3O$	63·5	5·8	22·2

* Prepared from D-*arabino*-hexose 3,4-dimethylphenylosotriazole.

2-*Aryl*-4-*hydroxymethyl*-1,2,3-*triazoles* (IV). A solution of 2-aryl-4-formyl-1,2,3-triazole (0·5 g.) in dry isopropyl alcohol (150 ml.), was treated with aluminium isopropoxide [8] (2 g.), and

[7] Bishay, El Khadem, and El-Shafei, *J.*, 1963, 4980.

[8] Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., Ltd., London, 1959, p. 883.

[9] von Pechmann, *Ber.*, 1888, **21**, 2751; Hann and Hudson, *J. Amer. Chem. Soc.*, 1944, **66**, 735.

[10] El Khadem, Kolkaila, and Meshreki, *J.*, 1963, 3531.

heated on the water-bath for 3 hr., during which the alcohol distilled off. The residue obtained was treated with cold 50% hydrochloric acid, and the crystals filtered off, washed, and dried (see Table). The *product* crystallised from water–ethanol and was soluble in ethanol and methanol and insoluble in acetone or water.

Action of alkali on 4-formyl-2-phenyl-1,2,3-triazole. 4-Formyl-2-phenyl 1,2,3-triazole [9] (0·3 g.) was treated in the cold with a solution of potassium hydroxide (0·27 g.) in water (25 ml.) and the mixture kept overnight at room temperature with occasional shaking. Water (25 ml.) was added and the mixture extracted with ether and the ethereal solution washed with sodium hydrogen sulphite, sodium hydrogen carbonate, and water, and dried. *4-Hydroxymethyl-2-phenyl-1,2,3-triazole* (0·1 g.) left after evaporation of the ether crystallised from water–ethanol in needles, m. p. 72° (Found: C, 61·8; H, 5·0; N, 23·9. $C_9H_9N_3O$ requires C, 61·7; H, 5·1; N, 24·0%). The aqueous layer was treated with hydrochloric acid and the crystals filtered off, washed, and dried (0·13 g.). 2-Phenyl-1,2,3-triazole-4-carboxylic acid recrystallised from water–ethanol in needles, m. p. and mixed [11] m. p. 191° (Found: N, 22·0. Calc. for $C_9H_7N_3O_2$: N, 22·2%).

Action of alkali on 2-p-bromophenyl-4-formyl-1,2,3-triazole. 2-*p*-Bromophenyl-4-formyl-1,2,3-triazole [10] (0·3 g.) was similarly treated with potassium hydroxide solution yielding 2-p-*bromophenyl-4-hydroxymethyl-1,2,3-triazole*, m. p. and mixed m. p. 100° (Found: C, 42·5; H, 2·9; N, 16·5. $C_9H_8BrN_3O$ requires C, 42·5; H, 3·2; N, 16·5%), and 2-*p*-bromophenyl-1,2,3-triazole-4-carboxylic acid,[5] m. p. and mixed m. p. 236° (Found: N, 15·2. Calc. for $C_9H_6BrN_3O_2$: N, 15·7%).

Action of potassium cyanide on 4-formyl-2-phenyl-1,2,3-triazole. A solution of 4-formyl-2-phenyl-1,2,3-triazole [9] (0·5 g.) in ethanol (50 ml.) was treated with a solution of potassium cyanide (0·5 g.) in water (20 ml.) and refluxed for 30 min. On concentration, (±)-*2-oxo-1,2-bis(2-phenyl-1,2,3-triazol-4-yl)ethanol* (V) separated, was washed, and dried (0·2 g.). It crystallised from ethanol in needles, m. p. 280°, soluble in hot ethanol and methanol and insoluble in water (Found: C, 62·1; H, 3·7. $C_{18}H_{14}N_6O_2$ requires C, 62·4; H, 4·0%).

FACULTY OF SCIENCE, ALEXANDRIA UNIVERSITY,
ALEXANDRIA, U.A.R.

[*Received, May 11th,* 1964.]

[11] Hardegger and Schreier, *Helv. Chim. Acta*, 1952, **35**, 232.

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275. 8-*Nitro*-1-*naphthol.*

By D. C. MORRISON.

A previous report [1] showed that the product of decomposition of 8-nitronaphthalene-1-diazonium salts in aqueous acid medium, which had been regarded as 8-nitro-1-naphthol,[2] was a hydroxynaphthaquinone oxime. It was also indicated that the synthesis of 8-nitro-1-naphthol by Bell,[3] involving nitration of 1-naphthyl *m*-nitrobenzenesulphonate followed by hydrolysis, could not be repeated.

It has now been found that Bell's nitration can be repeated if slightly modified (final addition of 1—2 ml. of water, and ice-cooling for crystallization). The 8-nitro-1-naphthyl ester obtained was identical with that resulting from esterification of 8-nitro-1-naphthol with *m*-nitrobenzenesulphonyl chloride and pyridine. The main nitration product, however, was the 4-nitro-1-naphthyl ester, and in one run a trace of the 5-nitro-ester was found.

Of other methods investigated for the synthesis of 8-nitro-1-naphthol, the only successful one involved the removal of the diazo-group from 8-nitro-2-diazo-1-naphthol [4] by use of cuprous oxide and ethanol,[5] but the product was obtained in only 30—32% yield and was difficult to purify, yellow crystals being eventually produced having pK_a 9·2.

[1] D. C. Morrison and D. W. Heinritz, *J. Org. Chem.*, 1962, **27**, 2229.
[2] N. N. Vorozhtzov and V. V. Kozlov, *Ber.*, 1936, **69**, *B*, 416.
[3] F. Bell, *J.*, 1933, 286.
[4] F. Gaess and A. Ammelburg, *Ber.*, 1894, **27**, 2211.
[5] H. H. Hodgson and H. S. Turner, *J.*, 1943, 86; 1944, 8.

Hydrogenation of the nitro-naphthol in methanol containing a little hydrochloric acid gave the hydrochloride of 8-amino-1-naphthol. 8-Nitro-1-naphthol was further characterized as the methyl ether and the benzoate.

Experimental.—1,8-Dinitro-2-toluene-*p*-sulphonamidonaphthalene was hydrolysed in concentrated sulphuric acid, and the amine diazotized in the same medium by nitrosylsulphuric acid. The resulting solution was poured into a large excess of ice–water, left for several days at room temperature, and the diazo-naphthol filtered off.[4,6] The diazo-group was not removed either by refluxing with zinc and ethanol or by the hypophosphorous acid procedure.

8-*Nitro*-1-*naphthol.* A mixture of sulphuric acid (*d* 1·84) (60 ml.) and acetic acid (60 ml.) was cooled to 5—10° and treated with the diazo-naphthol (6 g., 0·028 mole). After stirring for ½ hr. or more to ensure solution, the liquid was added to a stirred suspension of yellow cuprous oxide (20 g.) in absolute ethanol (180 ml.) during 15—20 min. at 55—75°. The liquid was then kept at 75—80° for ¾ hr., some of the ethanol being boiled off. After cooling and filtration, most of the ethanol was removed under a vacuum, water was added, and the dark tar produced was repeatedly extracted with warm water and filtered. The crude brown nitro-naphthol, which was deposited from the combined extracts on standing overnight, was filtered off and the filtrates saturated with salt, and filtered, to obtain more product (total yield 1·59 g., 30%). The product was recrystallised from water containing a few drops of acetic acid, and from benzene–hexane. The tendency to form an oil renders purification difficult. The best product was yellow and had m. p. 130—133° (Found: C, 63·5; H, 4·0; N, 7·15. Calc. for $C_{10}H_7NO_3$: C, 63·5; H, 3·7; N, 7·4%). The nitro-naphthol is slowly volatile in steam, giving a yellow distillate. The solution in aqueous sodium hydroxide is red or red-brown, as is the 5-nitro-isomer (4-nitro-1-naphthol is orange in alkaline solution).

A solution of the compound in methanol, with palladium catalyst, absorbed 96·4% of the theoretical amount of hydrogen. The catalyst was filtered off, and hydrochloric acid was added to the solution which was evaporated to dryness under a vacuum. A grey powder was obtained, with the same infrared spectrum as 8-amino-1-naphthol hydrochloride obtained by alkali fusion [7] of 8-aminonaphthalene-1-sulphonic acid.

8-*Nitro*-1-*methoxynaphthalene.* A suspension of 8-nitro-1-naphthol (0·9 g., 4·76 mmoles) in water (10 ml.) was treated alternately at 40—60° with dimethyl sulphate and 40% aqueous sodium hydroxide until a total of 2 ml. of the former and 5 ml. of the latter had been added. The mixture was digested for 15 min. at 50° and cooled. After ensuring that the liquid was alkaline, the solid was filtered off, washed, and steam-distilled for several hours. The distillate was extracted with ether, which was removed to yield the methoxy-derivative (0·56 g., 58%). Recrystallization from aqueous methanol gave yellow-white crystals, m. p. 94—95·5° (Found: C, 64·85; H, 4·1; N, 6·75. Calc. for $C_{11}H_9NO_3$: C, 65·0; H, 4·4; N, 6·9%).

8-*Nitro*-1-*naphthyl benzoate.* The benzoate was obtained in the usual way by use of benzoyl chloride and an anhydrous pyridine solution. The mixture was set aside overnight, poured into water, and an excess of dilute hydrochloric acid added. After several hours the oil which was first precipitated turned into a *solid*, m. p. 125—126° (from aqueous methanol); a second form was sometimes found, when less water was present, m. p. 123—123·5° (Found: N, 4·85. $C_{17}H_{11}NO_4$ requires N, 4·8%).

HYMAN LABORATORIES INC., BERKELEY, CALIFORNIA.

[Present address: CHEMAGRO CORP., KANSAS CITY, MISSOURI, U.S.A.]

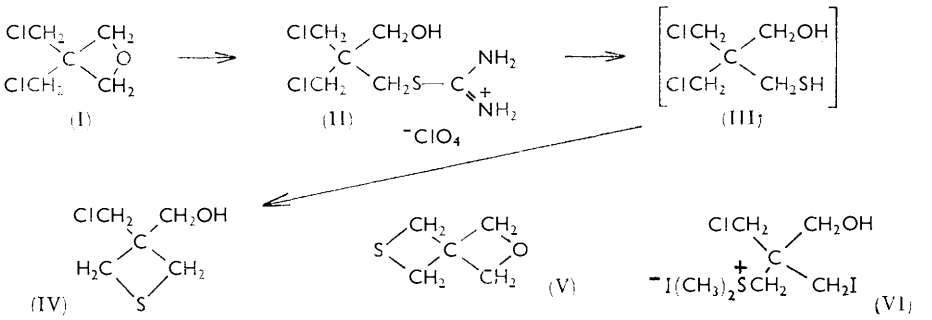
[*Received, May 15th*, 1964.]

[6] F. Bell, *J.*, 1929, 2784.
[7] L. C. Raiford and E. P. Clark, *J. Amer. Chem. Soc.*, 1926, **48**, 487.

276. 3-*Chloromethyl*-3-*hydroxymethylthiacyclobutane*.

By J. D. Downer and J. E. Colchester.

It has been reported [1] that 2,2-diethyl-3-mercaptopropanol is obtained by the reaction of 3,3-diethyloxacyclobutane with thiourea in the presence of perchloric acid and subsequent treatment of the intermediate thiouronium salt with alkali. When 3,3-bischloromethyloxacyclobutane [2] (I) reacted with thiourea under the same conditions we obtained the expected intermediate thiouronium perchlorate (II) but treatment of this salt with potassium hydroxide gave a colourless oil, C_5H_9ClOS, and not the expected 2,2-bischloromethyl-3-mercaptopropanol (III). The molecular weight, elemental analyses and



"hydroxyl" content of the product indicated that dehydrochlorination of the 2,2-bischloromethyl-3-mercaptopropanol had occurred. The infrared absorption spectrum of the product failed to reveal the presence of either SH or C–O–C groupings. Vigorous treatment of the product with potassium hydroxide removed a further molecule of hydrogen chloride giving the known 2-oxa-6-thiaspiro[3,3]heptane [2] (V) which was characterized as the sulphone. The product was therefore formulated as 3-chloromethyl-3-hydroxymethylthiacyclobutane (IV). Convincing proof of this structure was obtained when the thiacyclobutane (IV) was refluxed with methyl iodide. Fission of the ring occurred with the formation of the sulphonium iodide (VI). The thiacyclobutane (IV) was further characterized by formation of a crystalline carbonate, sulphite, and α-naphthylurethane.

Experimental.—3,3-Bischloromethyloxacyclobutane (310 g.), ethanol (500 ml.), and water (100 ml.) were mixed with thiourea (200 g.). Perchloric acid (306 g. of 70% aqueous solution) was added dropwise during 2·25 hr., the temperature of the reaction being maintained at 30°. After this period the temperature was raised to 50° for 2 hr. The solution was then left at room temperature overnight. The *perchlorate* of 2,2-bischloromethyl-3-thioureidopropanol (Found: N, 8·4; S, 10·1. $C_6H_{13}Cl_3N_2O_5S$ requires N, 8·5; S, 9·7%) was filtered off. This salt was refluxed for 40 min. with potassium hydroxide (112 g.) in water (200 ml.). A heavy oil separated which was extracted from the mixture with benzene. The benzene solution was dried ($MgSO_4$) and evaporated. Distillation of the residual oil gave 3-*chloromethyl*-3-*hydroxymethylthiacyclobutane* (150 g., 49%), b. p. 120°/8 mm., n_D^{20} 1·5497 [Found: C, 39·2; H, 6·3; S, 21·0; OH, 6·5 meq/g.; *M* (v.p. osmometry), 158. C_5H_9ClOS requires C, 39·3; H, 5·9; S, 21·0%; OH, 6·6 meq/g.; *M*, 153].

3-Chloromethyl-3-hydroxymethylthiacyclobutane (15·3 g.) was refluxed with potassium hydroxide (5·3 g.) in ethanol (100 ml.) for 16 hr. The potassium chloride which formed was filtered off, the ethanol evaporated, and the residue dissolved in ether. The ethereal solution was washed with water, dried ($MgSO_4$), and evaporated. Distillation of the residue gave 2-oxa-6-thiaspiro[3,3]heptane (10 g.), b. p. 78°/5 mm. (lit.,[2] 60°/3 mm.). This compound (7·5 g.) was caused to react with 30% hydrogen peroxide (12·5 g.) and glacial acetic acid (12 ml.) at 10°. Volatile material was evaporated from the reaction mixture; the residue solidified on cooling.

[1] C. S. Rondestvedt, *J. Org. Chem.*, 1961, **26**, 3024.
[2] T. W. Campbell, *J. Org. Chem.*, 1957, **22**, 1029.

Recrystallization from methanol gave the sulphone, 6-sulphonyl 2-oxaspiro[3,3]heptane, m. p. 162° (lit.,[2] 161—162°) (Found: S, 21·3. Calc. for $C_5H_8O_3S$: S, 21·6%).

α-Naphthyl isocyanate (8·5 g.) and 3-chloromethyl-3-hydroxymethylthiacyclobutane (7·2 g.) in carbon tetrachloride (50 ml.) were heated to 90° for 30 min. The solvent was removed; the mixture solidified on cooling. Recrystallization from methanol gave the *α-naphthylurethane*, m. p. 142—143° (Found: C, 59·8; H, 5·2; Cl, 10·7; N, 4·4; S, 10·0. $C_{16}H_{16}ClNO_2S$ requires C, 59·7; H, 5·0; Cl, 11·0; N, 4·4; S, 10·0%.

A cooled 10% solution of carbonyl chloride (5 g.) in toluene was added to a cooled solution of 3-chloromethyl-3-hydroxymethylthiacyclobutane (15·3 g.) and pyridine (15·8 g.) in chloroform (100 ml.) at such a rate that the temperature was maintained at 25° for 20 hr. The pyridine hydrochloride was filtered off, the toluene–chloroform solution evaporated to low bulk, and the residue dissolved in ether and washed with water. The ethereal solution was dried ($MgSO_4$) and evaporated; the residue solidified on cooling. Recrystallization first from light petroleum (b. p. 30—40°) and then from methanol yielded the *carbonate*, m. p. 82° (Found: Cl, 21·5; S, 19·7. $C_{11}H_{16}Cl_2O_3S_2$ requires Cl, 21·4; S, 19·4%).

Thionyl chloride (6 g.) was added to a cooled solution of 3-chloromethyl-3-hydroxymethylthiacyclobutane (15·3 g.) in toluene (150 ml.) and pyridine (15·8 g.). When the addition was complete, the toluene solution was washed with water, dried ($MgSO_4$) and the toluene evaporated. The residue crystallized on standing and was recrystallized from methanol to give the *sulphite*, m. p. 65—66° (Found: S, 27·3. $C_{10}H_{16}Cl_2O_3S_3$ requires S, 27·4%).

An excess of methyl iodide was refluxed with 3-chloromethyl-3-hydroxymethylthiacyclobutane (15·3 g.) for 4 hr. and left to cool overnight. The mixture solidified and was recrystallized from ethanol to give the *sulphonium iodide*, m. p. 114—115·5° (Found: C, 20·1; H, 3·5; I, 57·4; S, 7·8. $C_7H_{15}ClI_2OS$ requires C, 19·2; H, 3·5; I, 58·2; S, 7·3%).

"Shell" Research Ltd., Thornton Research Centre,
P.O. Box 1, Chester.

[Present addresses: (J. D. D.) Texaco Trinidad Inc., Pointe-a-Pierre, Trinidad, West Indies.
(J. E. C.) Imperial Chemical Industries, Ltd., Mond Division,
Runcorn Heath, Cheshire.]

[*Received, May 14th*, 1964.]

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277. *Transition Metal–Carbon Bonds. Part III.* Cyclopentadienyltrimethylplatinum*(IV).

By S. D. Robinson and B. L. Shaw.

Platinum forms a large number of organometallic complexes containing σ- and π-bonded organic ligands but no example of platinum(IV) complexes containing π-bonded organic ligands has previously been prepared. We have now found that treatment of trimethylplatinum iodide with cyclopentadienylsodium in tetrahydrofuran gives cyclopentadienyltrimethylplatinum(IV) as very volatile air-stable white prisms, very soluble in organic solvents and readily purified by vacuum sublimation at room temperature. Cryoscopic molecular weight determinations in benzene show cyclopentadienyltrimethylplatinum(IV) to be a monomer, in contrast to trimethylplatinum iodide, which is a tetramer,[1] and acetylacetonatotrimethylplatinum(IV), which is a dimer;[2,3] this suggests that the cyclopentadienyl group is not σ-bonded to the metal but is π-bonded, thus giving the platinum atom an 18-electron configuration. In agreement with this, the compound shows no tendency to form adducts with ligands such as pyridine, unlike other trimethylplatinum(IV) complexes.

Further evidence for the suggested structure is provided by the infrared spectrum,

* Part II, S. D. Robinson and B. L. Shaw, *J.*, 1964, 5002.

[1] Rundle and Sturdivant, *J. Amer. Chem. Soc.*, 1947, **69**, 1561.
[2] Menzies, *J.*, 1928, 565.
[3] Swallow and Truter, *Proc. Roy. Soc.*, 1960, *A*, **254** 205.

Infrared absorption results for cyclopentadienyltrimethylplatinum(IV) (potassium bromide disc.)

Band position ($cm.^{-1}$), and intensity	Assignment	Band position ($cm.^{-1}$), and intensity	Assignment
3100w	C–H stretch, π-C_5H_5	1253s	H–C–H bending, CH_3
2950m	C–H stretch, CH_3	1214s	,, ,,
2890s	,, ,,	1102w	Ring " breathing " π-C_5H_5
2805m	,, ,,	996s	C–H bending ∥, π-C_5H_5
1796vw, 1692vw, 1582vw	Not assigned but often present in π-cyclopentadienyl compounds	862w	H–C–Pt bending, CH_3
		787vs	C–H bending ⊥, π-C_5H_5
		583w	C–Pt valency vibration, CH_3
1420m	C–C stretch, π-C_5H_5	555m	,, ,, ,,

which shows the bands characteristic of a π-cyclopentadienyl group [4] together with those characteristic of the trimethylplatinum group [5] (see Table).

The nuclear magnetic resonance spectrum confirms the structure, showing two main peaks at τ 9·12 (methyl protons) and τ 4·39 (cyclopentadienyl protons), with relative intensities 9 : 5. Each of these two main peaks has two symmetrically placed side peaks due to coupling with the ^{195}Pt nucleus (natural abundance 33%); $J(^{195}Pt–H$, methyl) is 82·5 c./sec., which is slightly higher than the range 71·6—78·9 c./sec. reported for other trimethylplatinum complexes [6] and $J(^{195}Pt–H$, cyclopentadienyl) is 5·8 c./sec., which is much smaller than the value of 10·5 c./sec. for allylcyclopentadienylplatinum(II).[7]

Attempts to prepare π-allyltrimethylplatinum(IV) by the reaction of trimethylplatinum iodide with allylmagnesium bromide have been unsuccessful. A preliminary account of some of this work has been published.[8]

Experimental.—Cyclopentadienyltrimethylplatinum(IV). Trimethylplatinum iodide (0·286 g.) suspended in sodium-dried benzene under nitrogen was treated with a tetrahydrofuran solution of cyclopentadienylsodium (1·95 ml., 0·44M; 1·1 mole per atom of platinum) at 20°. After 10 min. the light brown solution was evaporated to dryness under reduced pressure; the residue was sublimed at 20° and 10^{-2} mm. and then recrystallised from methanol to give volatile *white prisms* (0·075 g.), m. p. 65° (Found: C, 31·65; H, 4·65%; *M*, cryoscopically in 0·97% benzene, 304, in 1·47% solution, 294. $C_8H_{14}Pt$ requires C, 31·45; H, 4·6%, *M*, 305).

Treatment of cyclopentadienyltrimethylplatinum(IV) *with pyridine.* Cyclopentadienyltrimethylplatinum(IV) (0·06 g.) was dissolved in ether (1 ml.), pyridine (0·040 g.) was added, and the mixture set aside overnight. Evaporation under reduced pressure followed by vacuum sublimation of the residue at 25° gave unchanged cyclopentadienyltrimethylplatinum(IV) (0·40 g.), identified by its infrared spectrum.

School of Chemistry, The University, Leeds 2. [*Received, May 22nd,* 1964.]

[4] Cotton in " Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience, 1960.
[5] Gribor, Gel'man, Zakharova, and Orlova, *Russ. J. Inorg. Chem.*, 1960, **5**, 473.
[6] Smith, *J.*, 1962, 4736.
[7] Shaw and Sheppard, *Chem. and Ind.*, 1961, 517.
[8] Robinson and Shaw, *Z. Naturforsch.*, 1963, **18***b*, 507.

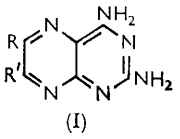
278. 2,4-*Diamino-7-hydroxymethylpteridine and Related Compounds.*

By D. J. Brown and B. T. England.

We have found that tetra-aminopyrimidine undergoes condensation with dihydroxyacetone to give 2,4-diamino-6-methylpteridine (I; R = Me, R′ = H) in place of the hydroxymethyl or dihydrohydroxymethyl analogue. This behaviour is similar to that observed [1,2] when 2,4,5-triamino-6-hydroxypyrimidine was used for analogous condensations, but it differed in that pretreatment of the ketone with hydrazine or sodium hydrogen sulphite affected

[1] Forrest and Walker, *J.*, 1949, 79, 2077; Angier *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3029.
[2] Seeger, Cosulich, Smith, and Hultquist, *J. Amer. Chem. Soc.*, 1949, **71**, 1753.

neither the nature nor the orientation of the product. However, hydroxymethylglyoxal (the aldehyde corresponding to dihydroxyacetone) did give the 7-hydroxymethylpteridine (I; R = H, R′ = CH_2·OH), a result again in no way affected by pretreatment of the ketone. The structures of both products were confirmed by oxidation to 2,4-diamino-6(and 7)-carboxypteridine, respectively. These underwent alkaline hydrolysis to the corresponding 2-amino-6(and 7)-carboxy-4-hydroxypteridine which were already known [3] to be easily distinguishable by their ultraviolet spectra.


(I)

In an attempt to prepare the 6-hydroxymethyl isomer (I; R = CH_2·OH; R′ = H) through a bromomethyl intermediate, the amino-groups of 2,4-diamino-6-methylpteridine were first protected by acetylation. Brief treatment with warm alcoholic sodium ethoxide [4] was a satisfactory method for gently deacylating 2,4-bisacetamidopteridine and its 6-methyl derivative. However, bromination of the latter (even with one mol. of bromine or *N*-bromosuccinimide) afforded only the dibromomethyl derivative (I; R = $CHBr_2$, R′ = H), and partial dehalogenation to the required monobromo-derivative was unsuccessful.

The ionization constants determined for 2,4-diamino-6-carboxypteridine (5·17 and 1·94) differed slightly from those recorded by Dion and Loo.[5] More important, the previous assignment [5] of the higher figure to the acidic group and the lower to the basic centre appeared to be in error on the following grounds. (i) The insertion of four powerful electron-withdrawing ring-nitrogen atoms and only two electron-releasing amino-groups into 2-naphthoic acid [6] (pK_a 4·2) should considerably enhance its acidic strength, not the reverse. Conversely, the addition of an electron-withdrawing carboxyl group to 2,4-diaminopteridine [7] (pK_a 5·3) in the ring remote from the basic centre would be expected only mildly to reduce its basic strength, certainly by less than the 2—3 unit drop observed in passing from pyrimidine (1·2) to 2-carboxypyrimidine [8] (—1·1), or from pyridine (5·2) to 3-carboxypyridine [9] (2·1), each of which had the carboxyl group attached to the same ring as the basic centre. (ii) There was little change of ultraviolet spectrum in passing from cation (pH —1·5) to neutral molecule or zwitterion (pH 3·5), but a considerable bathochromic shift on further passing to anion (pH 7·7). This was reasonable only if the species at pH 3·5 was a zwitterion so that the first change (pK_a 1·9) represented the ionization of the carboxyl group (which leads to little change in a spectrum) and the second (pK_a 5·2) the deprotonation of the basic centre (which, in molecules such as 2,4-diaminopteridine,[7] is accompanied by a general bathochromic shift of the same order). In 2,4-diamino-7-carboxypteridine, the lower pK_a value was similarly assigned to the acidic group and the upper one to the basic centre.

Because 2,4-diaminopteridine is temporarily effective in certain acute leukæmias [10] several of its derivatives above are being tested for activity in leukæmic mice.

Experimental.—Analyses were done by Dr. J. E. Fildes and her staff. Ionization constants were measured spectrometrically [11] at 20°.

2,4-*Diamino-6-methylpteridine.* Tetra-aminopyrimidine sulphate dihydrate [12] (1·6 g.), hydrated sodium sulphite (1·6 g.), and dihydroxyacetone (0·5 g.) were dissolved in hot water (9 ml.). A stream of air was drawn through the solution for 3 days. The solid was removed and thrice reprecipitated from N-acetic acid by adjustment to pH 9. The pure product (20%) did not

[3] Mowat, *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 14.
[4] Cf. Oakes, Rydon, and Undheim, *J.*, 1962, 4678.
[5] Dion and Loo, *J. Org. Chem.*, 1961, **26**, 1857.
[6] Dippy, Hughes, and Laxton, *J.*, 1954, 1470.
[7] Brown and Jacobsen, *J.*, 1961, 4413.
[8] Mason, *J.*, 1959, 1247.
[9] Lumme, *Suomen Kem.*, 1957, **30***B*, 168.
[10] W. Jacobson, personal communication.
[11] Albert and Serjeant, " Ionization Constants of Acids and Bases," Methuen, London, 1962; Ang, *J. Phys. Chem.*, 1958, **62**, 1109.
[12] Sato, Nakajima, and Tanaka, *J. Chem. Soc. Japan*, 1951, **72**, 866.

melt below 300° (Found: C, 47·5; H, 4·7. Calc. for $C_7H_8N_6$: C, 47·7; H, 4·6%). It was identified with authentic material by the acetylation and oxidation of both specimens.

2,4-Diamino-6-carboxypteridine. Potassium permanganate (1·8 g.) was added during 30 min. to a stirred suspension of 2,4-diamino-6-methylpteridine (0·5 g.) in hot water (19 ml.). After heating for 30 min. longer, the solution was decolourized with sodium hydrogen sulphite, filtered, and adjusted to pH 2. The resulting yellow carboxylic acid (0·3 g.) was thrice reprecipitated from N-ammonium hydroxide and had m. p. $<340°$ (cf. $>300°$ for anhydrous material made by another route [5]) (Found: C, 37·6; H, 3·7; N, 37·1. Calc. for $C_7H_6N_6O_2,H_2O$: C, 37·5; H, 3·6; N, 37·5%); pK_a 5·17 ± 0·02, 1·94 ± 0·03 (analyt. λ, 260 mμ); $\lambda_{max.}$ (pH 7·7) 382, 260 mμ (log ε 4·13, 4·26), (pH −1·5) 336, 248 (infl.) (3·96, 4·03). Alkaline hydrolysis, as for the 7-isomer below, gave 2-amino-4-hydroxy-6-carboxypteridine.

Hydroxymethylglyoxal. Of all the described preparations from dihydroxyacetone, that of Evans *et al.*[13] was least unsatisfactory. Modified in the following respects it gave repeatable results. The reaction mixture was continuously stirred for 2 days at *ca.* 28°. Copper was precipitated by addition of oxalic acid dihydrate (10 g.) in water (100 ml.). Evaporation with 10-ml. portions of ethanol was repeated (8—10 times) until the residue became a semi-solid mass. This was then extracted with cold ethanol (6 × 10 ml.) and each extract diluted with ether (80 ml.) to precipitate the product, which was dried *in vacuo* at room temperature. 2-Hydroxymethylquinoxaline prepared from it in 72% yield had m. p. 165°, as recorded by Norrish and Griffiths; [14] Evans *et al.*[13] record 250—251°.

2,4-Diamino-7-hydroxymethylpteridine. Tetra-aminopyrimidine sulphate [12] (3·2 g.) and sodium sulphite heptahydrate (32 g.) were dissolved in warm water (145 ml.). Hydroxymethylglyoxal (0·8 g.) was dissolved in aqueous sodium pyrosulphite solution (saturated at 25°; 33 ml.). The two solutions were mixed and maintained at 30° for 45 min. The yellow solid (0·4 g.) was filtered off at once, and twice reprecipitated from 2N-acetic acid (40°) by adjustment to pH 9. The *hydroxymethyl compound* had m. p. $<300°$ (from water) (Found, when dried at 60°/10 mm.: C, 39·8; H, 4·6; N, 39·8. $C_7H_8N_6O,H_2O$ requires C, 40·0; H, 4·8; N, 40·0%); pK_a 5·44 ± 0·04; $\lambda_{max.}$ (pH 9) 368, 256 mμ (log ε 3·92, 4·34), (pH 3) 334, 287, 243 (4·02, 3·67, 4·02).

2,4-Diamino-7-carboxypteridine. 2,4-Diamino-7-hydroxymethylpteridine was oxidized as above. The yellow *carboxypteridine* (61%) decomposed above 300° (Found: C, 37·4; H, 3·6; N, 37·4. $C_7H_6N_6O_2,H_2O$ requires C, 37·5; H, 3·6; N, 37·5%); pK_a 5·68 ± 0·06, 2·0 ± 0·10 (analyt. λ, 340 mμ); $\lambda_{max.}$ (pH 8·0) 380, 260 mμ (log ε 3·90, 4·25), (pH −1·5) 350, 295 (infl.), 248 (3·98, 3·64, 3·94). A sample heated in N-sodium hydroxide for 15 min. at 100° afforded 2-amino-4-hydroxy-7-carboxypteridine on adjustment to pH 3 (Found: C, 37·6; H, 3·4; N, 31·4. Calc. for $C_7H_5N_5O_3,H_2O$: C, 37·3; H, 3·1; N, 31·1%). Its spectra were identical with those of authentic material.[3]

2,4-Bisacetamidopteridine. 2,4-Diaminopteridine [15] (1 g.) was refluxed for 1 hr. in acetic anhydride (27 ml.). The *diacetyl compound* (60%) was filtered off, m. p. 235° (decomp.) (from methoxyethanol) (Found: C, 48·5; H, 4·2; N, 34·25. $C_{10}H_{10}N_6O_2$ requires C, 48·8; H, 4·1; N, 34·1%). This compound (0·3 g.) was deacetylated by refluxing in ethanolic sodium ethoxide (sodium, 0·3 g.) for 25 min. Addition of the cooled solution to water (30 ml.) gave diaminopteridine (50%), m. p. *ca.* 306° undepressed on admixture with authentic material.

2,4-Bisacetamido-6-dibromomethylpteridine. 2,4-Bisacetamido-6-methylpteridine was prepared as by Seeger *et al.*[2] However, after repeated recrystallization from ethanol it had m. p. 257° (cf. lit.,[2] 235—236°) (Found: C, 50·8; H, 4·65; N, 32·3. Calc. for $C_{11}H_{12}N_6O_2$: C, 50·95; H, 4·95; N, 32·6%); pK_a 1·55 ± 0·03; $\lambda_{max.}$ (pH 4) 339, 251 mμ (log ε 3·94, 4·29), (pH −1) 331, 283, 246 (4·07, 3·82, 4·17).

A stirred solution of this methylpteridine (0·25 g.) in acetic acid (7·0 ml.) at 60° was treated dropwise during 30 min. with a solution of *N*-bromosuccinimide (0·25 g.) in acetic acid (5 ml.) and acetic anhydride (1 ml.). After a further 30 min. at 50° and 12 hr. at room temperature, the solution was evaporated to dryness and the residue was triturated with water (16 ml.) to remove succinimide and bromosuccinimide. The residual *dibromomethylpteridine* (68%), when recrystallized from ethyl acetate–light petroleum, darkened progressively above 250° but did not melt below 300° (Found: C, 31·95; H, 2·6; Br, 37·7. $C_{11}H_{10}Br_2N_6O_2$ requires C, 31·6;

[13] Evans, Carr, and Krantz, *J. Amer. Chem. Soc.*, 1938, **60**, 1628.
[14] Norrish and Griffiths, *J.*, 1928, 2829.
[15] Albert, Brown, and Checseman, *J.*, 1952, 4219.

H, 2·4; Br, 38·1%). Partial hydrogenation of the dibromo-derivative in aqueous sodium acetate over palladium–charcoal was attempted. It gave only bisacetamido-6-methylpteridine (identified by mixed m. p.) and unchanged material.

We thank Dr. W. Jacobson, Strangeways Laboratory, Cambridge, for his kind collaboration in the biological aspects of this work.

DEPARTMENT OF MEDICAL CHEMISTRY, AUSTRALIAN NATIONAL UNIVERSITY,
CANBERRA, AUSTRALIA. [*Received, June 2nd,* 1964.]

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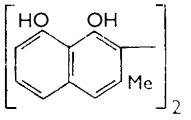
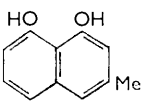
279. 3-*Methylnaphthalene*-1,8-*diol from* Diospyros mollis.

By STANG MONGKOLSUK and CHIRAVAT SDARWONVIVAT.

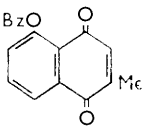
IT is already known [1] that an important phenolic constituent of the berries of *Diospyros mollis* is a dinaphthol, diospyrol (I), which rapidly blackens in air. Because oxidative coupling of phenols is now a recognised mode of biosynthesis of many complex phenols,[2] we searched the berries again and isolated 3-methylnaphthalene-1,8-diol (II), the monomer from which diospyrol can be supposed to arise. The instability of the compound prevented



(I)



(II)



(III)

analytical determinations, but there is no doubt about identity since the compound gave a diacetate and a dibenzoate identical with specimens kindly supplied by Dr. J. W. Morgan, while chromic oxidation of the latter ester afforded plumbagin benzoate (III). Plumbagin itself occurs in various species of *Diospyros*, but attempts to oxidise the naphthol (II) to diospyrol (I) failed.

Experimental.—Fresh berries (600 g.) of *Diospyros mollis* were crushed under ether (1 l.), and 4 hr. later the solvent was decanted, dried (Na_2SO_4), and evaporated under nitrogen to about 50 ml. The crystalline product (diospyrol) was removed and the remaining solution evaporated and the residue sublimed at 220°/0·6 mm. The sublimate (2 g.) crystallised from light petroleum (b. p. 60—70°) giving 3-methylnaphthalene-1,8-diol (II) as needles, m. p. 140—141°. This compound gave a bright green ferric reaction in ethanol, and a blue colour with Gibbs's reagent. The diacetate (acetic anhydride and pyridine) had m. p. and mixed m. p. 117—118°, and the dibenzoate (benzoyl chloride and pyridine) had m. p. and mixed m. p. 192°; both esters were further identified spectroscopically.

The dibenzoate (0·8 g.) in acetic acid (50 ml.) was oxidised by chromic oxide (3 g.) at 90° during 1 hr. Dilution with water supplied a yellow solid which, crystallised from methanol, afforded plumbagin benzoate as yellow prisms (0·4 g.), m. p. 147—148°, identical with an authentic specimen.

We thank the Rockefeller Foundation for financial aid in the course of this work.

FACULTY OF MEDICAL SCIENCE, UNIVERSITY OF MEDICAL SCIENCES,
SRI-AYUTHYA ROAD, BANGKOK, THAILAND. [*Received, June 8th,* 1964.]

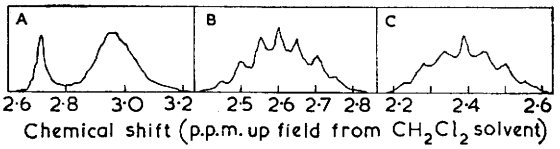
[1] Loder, Mongkolsuk, Robertson, and Whalley, *J.*, 1957, 2233.
[2] Hassall and Scott, "Recent Developments in the Chemistry of Natural Phenolic Compounds," ed. Ollis, Pergamon Press, Oxford, 1961, ch. 5.

280. *Long-range Proton–Boron Coupling in Dimeric Dimethylaminoboron Dihalides.*

By A. J. Banister and N. N. Greenwood.

Long-range coupling between a proton and another atom has been observed in many organic compounds but it is comparatively rare in inorganic and organometallic compounds. Proton–boron coupling *via* one other atom has been observed [1] in the compound $Me_2PH{\cdot}BH_3$ but no example is recorded * where the nuclei are separated by two other atoms. Long-range coupling *via* two other atoms has been reported [2] between cyclopentadienyl protons and phosphorus in *cis*- and *trans*-$[C_5H_5Fe(PMe_2)(CO)]_2$. In these two compounds the phosphorus nuclei which couple with the protons are contained in a four-membered ring.

The proton magnetic resonance spectra are described of the compounds dimethylaminoboron difluoride and the dimers of dimethylaminoboron difluoride, dichloride, and dibromide. Spin–spin coupling between hydrogen and boron nuclei (separated by carbon and nitrogen) resulting in a septet, is observed in the dimer chloride and dimer bromide. Since both boron and nitrogen possess not only a nuclear spin but also an electric quadrupole moment which is capable of broadening multiplet components through its spin-lattice



Proton magnetic resonance spectra: A, $(Me_2N{\cdot}BF_2)_{1,2}$. B, $(Me_2N{\cdot}BCl_2)_2$. C, $(Me_2N{\cdot}BBr_2)_2$.

relaxation, it is perhaps remarkable that such clear long-range proton–boron coupling is observed. The relative intensities of the seven equally spaced lines in both the dimer chloride and the dimer bromide spectra were close to 1 : 2 : 3 : 4 : 3 : 2 : 1; the dimer fluoride gave two peaks. Typical spectra are shown in the Figure and details of chemical shifts, etc., are given in the Table.

Proton magnetic resonance data.[a]

	Chemical shift δ (p.p.m.)[b]	Coupling constant J_{B-H} (c./sec.)	Half-height band width (c./sec.)
$(Me_2N{\cdot}BF_2)_2$ (i)	2·96	—	9·8
(ii)	2·71	—	2·3
$(Me_2N{\cdot}BCl_2)_2$	2·60	3·1	—
$(Me_2N{\cdot}BBr_2)_2$	2·39	3·3	—

[a] Standard deviations were $\delta \not> 0{\cdot}02$ p.p.m., $J \not> 0{\cdot}15$ c./sec., and for the half height band width (i) 0·8 c./sec., (ii) 0·2 c./sec. [b] Methylene chloride solvent as internal standard. In a separate experiment the chemical shift of tetramethylsilane added to a saturated solution of dimer chloride in methylene chloride was found to be 5·33 p.p.m.

Natural boron contains 18·83% of ^{10}B and so the relative abundance of dimer molecules containing (*a*) $^{11}B + {}^{11}B$, (*b*) $^{11}B + {}^{10}B$, and (*c*) $^{10}B + {}^{10}B$ is 18·58 : 4·31 : 1. The contribution by (*c*) to the observed spectrum is weaker than the instrumental background and so can be neglected. In (*a*) and (*b*), proton coupling to the ^{11}B nucleus ($I = 3/2$) results in the splitting of the proton resonance into four lines of equal intensity. In case (*a*)

[1] J. N. Schoolery, *Discuss. Faraday Soc.*, 1955, **19**, 215.
[2] R. G. Hayter, *J. Amer. Chem. Soc.*, 1963, **85**, 3120.

further coupling to the second boron nucleus results in the four ^{11}B–H resonance lines each splitting into four lines which superimpose to give seven equally spaced lines of relative intensities 1 : 2 : 3 : 4 : 3 : 2 : 1. In case (*b*) the ^{10}B isotope ($I = 3$) splits each of the four ^{11}B resonance lines into seven resonances with separation $J(^{10}B–H)$ and equal intensity. The ratio $J(^{11}B–H)/J(^{10}B–H)$ is 2·99, hence some of the expected 28 lines for (*b*) superimpose to give 16 lines of relative intensities 1 : 1 : 1 : 2 : 2 : 2 : 3 : 2 : 2 : 3 : 2 : 2 : 2 : 1 : 1 : 1. Since the relative abundance of structures (*a*) and (*b*) are 4·3 : 1, the sum of the intensities of the seven lines due to (*a*) will be 4·3 times the sum of the intensities of the sixteen lines due to (*b*). The lines due to (*b*) will therefore be superimposed upon and contained within a septet of relative intensities 7·5 : 15 : 22·5 : 30 : 22·5 : 15 : 7·5. The relative peak heights for $(Me_2N·BCl_2)_2$ and $(Me_2N·BBr_2)_2$ were in agreement with this assignment and the contribution by (*b*) was just discernible in some of the recorded spectra. The relative intensities of the peaks eliminated the possibility of proton–proton coupling across the ring since this would give rise to a 1 : 6 : 15 : 20 : 15 : 6 : 1 septet. The spectra for $(Me_2N·BCl_2)_2$ and $(Me_2N·BBr_2)_2$ are consistent with a planar BN ring or with rapidly interconverting puckered forms.

The proton magnetic resonance spectrum of the dimer fluoride consisted of two bands (see Table). The width of the high field band, which is attributed to undissociated dimer, and the absence of fine structure suggests that in addition to H–B coupling further broadening occurs due to the fluorine nuclei. The sharper peak at lower field was attributed to monomer since the infrared spectrum of the dimer fluoride in methylene chloride showed extra bands which could be assigned to the monomer. These infrared bands increased in intensity for the first few hours after the preparation of the solution. The infrared spectra of both monomer and dimer are already known.[3] When the temperature of the dimer chloride solution was raised to 59°, there was some improvement in the resolution of the septet, presumably due to an increase in the relaxation time. The resolution deteriorated on cooling to −40°.

The appearance of proton–boron coupling on dimerisation of dimethylaminoboron dichloride suggests that this occurs only when the hydrogen atoms are spatially close to the boron atoms (a molecular model constructed using published data [4] shows this to be the case) or when the boron atom is sp^3 hybridised (quadrupole broadening is markedly dependent upon hybridisation). If the latter is true, long-range coupling may also occur in some amine complexes of boron trichloride and tribromide. Ohashi *et al.*[5] report that the proton resonance spectrum of trimethylamine–boron trichloride " consisted of four almost equally spaced quartet lines separated by 2·6 c./sec., a line at the highest field being weaker than three others." These authors incline to the view that the splitting is due to H–N coupling (which should in fact give a triplet) but the occurrence of a quartet and and similarity in coupling constant to that observed in the present work suggests that H–B coupling is being observed.*

Experimental.—The preparation of dimeric dimethylaminoboron difluoride and monomeric dimethylaminoboron dichloride and dibromide have already been described.[3] The chloride and bromide dimers deposited spontaneously from the liquid monomers on standing at 60° or more slowly at room temperature. They were purified by washing with a little benzene to remove remaining monomer, followed by sublimation under dynamic vacuum on to a cold-water finger.

The proton magnetic resonance spectra were recorded on spinning samples at 23° by means

* Since this Note was submitted for publication J. M. Miller and M. Onyszchuk (*Canad. J. Chem.*, 1964, **42**, 1518) have reported the proton resonance spectra of $Me_3N·BCl_3$ and $Me_3N·BBr_3$. Their results are consistent with the occurrence of proton–boron coupling.

[3] A. J. Banister, N. N. Greenwood, B. P. Straughan, and J. Walker, *J.*, 1964, 995.
[4] H. Hess, *Z. Krist.*, 1963, **118**, 361.
[5] O. Ohashi, Y. Kurita, T. Totani, H. Watanabe, T. Nakagawa, and M. Kubo, *Bull. Chem. Soc. Japan*, 1962, **35**, 1317.

of an RS2 spectrometer of the Associated Electrical Industries Ltd. operating at 60 Mc/sec. Saturated solutions in dichloromethane of the dimeric aminoboranes $(Me_2N{\cdot}BX_2)_2$ where X = F, Cl, or Br were prepared at room temperature and chemical shifts were evaluated with respect to the solvent as internal standard. Measurements were carried out on solutions that had stood for a few hours. No significant changes in the spectra were observed when week-old solutions were used.

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DEPARTMENT OF INORGANIC CHEMISTRY, THE UNIVERSITY,
NEWCASTLE-UPON-TYNE 1. [*Received, June 12th*, 1964.]

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281. *The Preparation of Dibenzo*[d,f]*dioxepins and Their Use as Synthetic Intermediates.*

By F. R. HEWGILL and D. G. HEWITT.

THE use of isopropylidene or derivatives as protecting groups for 1,2-diols is well known. Being interested in the preparation of 2,2′-dihydroxybiphenyls containing alkoxy-groups, we have examined the possibility of cyclic acetal formation in this series as a means of protecting the 2,2′-hydroxyl groups. Although heterocyclic derivatives of 2,2′-dihydroxybiphenyl containing germanium,[1] phosphorus,[2] silicon,[3] sulphur,[4] and even tin [5] as the heteroatom have been described, curiously there is only one instance in the literature of the preparation of a dibenzo[*d,f*]dioxepin from a 2,2′-dihydroxybiphenyl, this being by condensation of the phenol with dibromoethyl acetate in the presence of sodium hydride.[6] However we have recently shown that this ring system is formed by the oxidative condensation of certain phenols,[7] and is therefore of added interest.

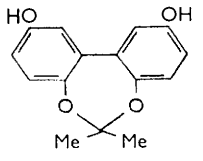
We have found that dibenzo[*d,f*]dioxepins may be prepared by a variety of methods developed for the production of aliphatic acetals. While ketones react with 2,2′-dihydroxybiphenyl under acid catalysis to form cyclic acetals, the yields are considerably improved if trans-ketalisations are utilised. Thus, treatment of the phenol with a dimethyl ketal in the presence of an acid catalyst gives good yields of the dioxepins. The use of dimethoxypropane for the preparation of aliphatic acetals by this method has recently been described by Lorette and Howard.[8] Similarly, tetramethoxysilane, as used by Helferich and Hausen,[9] facilitates acetal formation. Of the methods described, that involving the use of dimethyl ketals is probably preferable.

Aldehydes form acetals more readily than do ketones with aliphatic alcohols. However, we have found that, while 2,2′-dihydroxybiphenyl gives 6,6-diphenyldibenzo[*d,f*]dioxepin when treated with benzophenone, no acetal could be isolated from the reaction with benzaldehyde. This is possibly due to the competing oxidation of the phenol by the aldehyde.

The potential use of these cyclic acetals as protecting groups is illustrated by the

[1] R. Müller and L. Heinrich, *Chem. Ber.*, 1962, **95**, 2276.
[2] L. Anschütz and W. Marquardt, *Chem. Ber.*, 1956, **89**, 1119.
[3] R. Schwarz and W. Kuchen, *Z. anorg. Chem.*, 1955, **279**, 84.
[4] P. B. de la Mare, J. G. Tillett, and H. F. van Woerden, *Chem. and Ind.*, 1961, 1533.
[5] J. J. Zuckerman, *J.*, 1963, 1322.
[6] R. Breslow and E. Mohacsi, *J. Amer. Chem. Soc.*, 1963, **85**, 431.
[7] F. R. Hewgill, *J.*, 1962, 4987; F. R. Hewgill and B. S. Middleton, *J.*, 1965, in the press.
[8] N. B. Lorette and W. L. Howard, *J. Org. Chem.*, 1960, **25**, 521.
[9] B. Helferich and J. Hausen, *Ber.*, 1924, **57**, 795.

following synthesis. The reaction of 2,2′,5,5′-tetrahydroxybiphenyl with 2,2-dimethoxypropane gave the acetal (I), which was then methylated and hydrolysed, giving 2,2′-dihydroxy-5,5′-dimethoxybiphenyl in 30% overall yield; twice that obtained by ferricyanide oxidation of *p*-methoxyphenol.[10] It is not necessary to isolate intermediates and, in view of the difficulty of separating a dihydroxydibenzodioxepin from unchanged tetrahydroxybiphenyl, it is advantageous not to do so. The method is clearly adaptable to the preparation of other 2,2′-dihydroxybiphenyls.



(I)

Unlike the related dioxepins produced by phenol oxidation,[7] and which contain a carbonyl group α to the spiro atom, those now described are not readily susceptible to hydrogenolysis. 6,6-Dimethyldibenzo[*d*,*f*]dioxepin can not be hydrogenolysed over 10% palladium–charcoal, but 6-methyldibenzo[*d*,*f*]dioxepin slowly absorbs hydrogen with the formation of 2,2′-dihydroxybiphenyl. Examination of models suggests that dibenzo[*d*,*f*]dioxepins should be resolvable.

Several workers [11,12] have discussed the infrared absorption of aliphatic acetals and have assigned a number of bands in the 1200—1000 cm.$^{-1}$ region to various stretching modes of the C–O–C–O–C system. The spectra of the dioxepins we have prepared all show a number of strong bands in the region 1250—1150 cm.$^{-1}$ The slightly higher values found here are in accord with the rise in frequency reported for unsaturated cyclic ethers containing the group =C–O–C= as compared to the saturated analogues.[12]

Experimental.—Melting points were determined on a Kofler hot-stage apparatus. Infrared (i.r.) spectra were recorded on Perkin-Elmer Infracords, models 137 and 137G, for carbon disulphide solutions. Nuclear magnetic resonance (n.m.r.) spectra were determined on a Varian Associates A-60 spectrometer at 60 Mc./sec. for 6% carbon tetrachloride solutions unless otherwise stated, with tetramethylsilane as an internal standard.

6,6-*Dimethyldibenzo*[d,f]*dioxepin*. (*a*) A mixture of 2,2′-dihydroxybiphenyl (970 mg.), toluene-*p*-sulphonic acid (10 mg.), acetone (5 ml.), and benzene (5 ml.) was boiled under reflux for 3 hr. The solvent was removed, the residue dissolved in chloroform, and the solution washed with 10% sodium hydroxide solution and water, dried (Na_2SO_4), and evaporated to give the *dioxepin* (220 mg., 20%) which crystallised from methanol as rectangular plates, m. p. 77·5—78·5° [Found: C, 79·4; H, 5·9%; *M*(f.p. depression of cyclohexane), 214. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%; *M*, 226]; $\nu_{max.}$ 1250, 1240, 1210, 1200 cm.$^{-1}$ (C–O); τ 8·38 (CH_3).

(*b*) A solution of 2,2′-dihydroxybiphenyl (1·0 g., 1·1 mol.), 2,2-dimethoxypropane (0·52 g., 1 mol.), and toluene-*p*-sulphonic acid (1 mg.) in benzene was fractionally distilled until all the fraction of b. p. 57—59° had been removed. The residue was cooled, neutralised with sodium methoxide, and poured into 5% potassium hydroxide solution (100 ml.). Ether extracted 6,6-dimethyldibenzo[*d*,*f*]dioxepin (800 mg., 70%), m. p. 77·5—78·5° (from methanol).

The dioxepin, in ethanol, was unaltered by hydrogen in the presence of 10% palladium–charcoal.

6,6-*Diphenyldibenzo*[d,f]*dioxepin*. Procedure (b), with 2,2′-dihydroxybiphenyl (1·0 g.) and dimethoxydiphenylmethane (1·1 g.) gave the *dioxepin* (0·61 g.) as needles (from acetone), m. p. 168—169·5° [Found: C, 85·5; H, 5·1%; *M* (Rast), 306. $C_{25}H_{18}O_2$ requires C, 85·7; H, 5·2%; *M*, 350]; $\nu_{max.}$ 1250, 1245, 1210, and 1200 cm.$^{-1}$ (C–O).

Cyclohexane-1-*spiro*-6′-*dibenzo*[d,f]*dioxepin*. From 1,1-dimethoxy*cyclo*hexane (0·73 g.) and 2,2′-dihydroxybiphenyl (1·0 g.), procedure (b) gave the *dioxepin* (0·71 g.) as prisms (from acetone), m. p. 67—68° [Found: C, 81·0; H, 6·7%; *M* (Rast), 243. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%; *M*, 266]; $\nu_{max.}$ 1245, 1240, 1207, and 1205 cm.$^{-1}$ (C–O).

6-*Methyldibenzo*[d,f]*dioxepin*. A mixture of 2,2′-dihydroxybiphenyl (1·0 g.), paraldehyde (2 ml.), toluene-*p*-sulphonic acid (1 mg.) and anhydrous sodium sulphate (2 g.) was set aside for 6 days. The solution was neutralised with sodium methoxide, poured into 5% potassium hydroxide solution (100 ml.) and extracted with ether. Evaporation of the dried ethereal

[10] C. G. Haynes, A. H. Turner, and W. A. Waters, *J.*, 1956, 2823.
[11] E. D. Bergman and S. Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161.
[12] H. Tschamler and R. Leutner, *Monatsh.*, 1952, **83**, 1502.

solution gave the *dioxepin* (0·515 g.), as prisms (from methanol), m. p. 48—49° [Found: C, 79·0; H, 5·7%; *M*(Rast), 179. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%; *M*, 212]; $\nu_{max.}$ 1280, 1240, 1205, and 1185 cm.$^{-1}$ (C–O); τ 7·40 (doublet, J = 5 c./sec.; CH_3) and 4·31 (quartet, J = 5 c./sec.; CH). The dioxepin (280 mg.) was hydrogenolysed in ethanol over 10% palladium–charcoal to give 2,2′-dihydroxybiphenyl (240 mg.), m. p. alone and mixed with an authentic sample, 110—111°.

2,10-*Dihydroxy*-6,6-*dimethyldibenzo*[d,f]*dioxepin*. A solution of 2,2′,5,5′-tetrahydroxybiphenyl (0·95 g., 1 mol.), tetramethoxysilane (0·80 g., 1·1 mol.) and concentrated sulphuric acid (2 drops) in acetone (4 ml.) was boiled under reflux for 2 hr. The cooled mixture was poured into saturated sodium hydrogen carbonate solution (100 ml.) and extracted with ether. Evaporation of the ether gave a solid which on crystallisation from ethanol–benzene gave the *dihydroxy-dioxepin* (300 mg.) as prisms, m. p. 193—194° [Found: C, 69·5; H, 5·5%; *M*(Rast), 297. $C_{15}H_{14}O_4$ requires C, 69·75; H, 5·5%; *M*, 258]; τ (6% in acetone), 8·47 (CH_3) and 1·98 (OH).

Methylation with dimethyl sulphate gave 2,10-*dimethoxy*-6,6-*dimethyldibenzo*[d,f]*dioxepin*, as prisms (from acetone), m. p. 154—154·5° (Found: C, 71·4; H, 6·3. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%); $\nu_{max.}$ 1245, 1210, 1200, 1185 (C–O), and 2830 cm.$^{-1}$ (OCH_3).

Boiling a solution of the dimethyl ether (13 mg.) in acetone (5 ml.) with 5% sulphuric acid (5 ml.) for 0·5 hr. gave 2,2′-dihydroxy-5,5′-dimethoxybiphenyl (10 mg.), m. p. alone and mixed with an authentic sample [9] 128—129°.

The following procedure gave an improved yield of 2,2′-dihydroxy-5,5′-dimethoxybiphenyl. A solution of 2,2′,5,5′-tetrahydroxybiphenyl (1·0 g.), 2,2-dimethoxypropane (5 ml.), and concentrated sulphuric acid (2 drops) in dry acetone (20 ml.) was fractionally distilled until 5 ml. of solution remained. A further 20 ml. acetone was added and the process repeated. 2,2-Dimethoxypropane (5 ml.) in acetone (20 ml.) was then added and the fractionation repeated. After the addition of two further 20 ml. portions of acetone the b. p. had reached 56·5° and remained constant. The residue was poured into 10% potassium hydroxide solution (100 ml.) and after being shaken for 0·5 hr. with dimethyl sulphate (15 ml.) the orange precipitate (0·79 g.) was collected. This was dissolved in acetone (25 ml.) and boiled with 10% hydrochloric acid (10 ml.) for 2 hr. The cooled solution was poured into 20% potassium hydroxide solution (100 ml.) and extracted with ether giving 2,2′,5,5′-tetramethoxybiphenyl, m. p. 105—107°, alone and mixed with an authentic sample. Ether extraction of the acidified alkaline solution gave 2,2′-dihydroxy-5,5′-dimethoxybiphenyl (0·34 g., 30%), m. p. 128—129°.

2,10-*Dimethoxycyclohexane*-1-*spiro*-6′-*dibenzo*[d,f]*dioxepin*. Heating 2,2′,5,5′-tetrahydroxybiphenyl (1·1 g.) with *cyclo*hexanone (6 ml.) containing tetramethoxysilane (0·79 g.) and concentrated sulphuric acid (2 drops) for 0·5 hr. under reflux and working up in the manner described for the dimethyldihydroxy-dioxepin gave a solid which crystallised as prisms (from methanol or acetone), m. p. 175—218°. Repeated crystallisation failed to improve the purity. Methylation of this product (120 mg.) with dimethyl sulphate gave the *spiran* (85 mg.), as plates (from acetone), m. p. 135—136° (Found: C, 73·4; H, 6·7. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·7%); $\nu_{max.}$ 1240, 1215, 1200, 1185 (C–O), and 2830 cm.$^{-1}$ (OCH_3).

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Department of Chemistry, University of Western Australia,
Nedlands, Western Australia. [*Received, June 12th*, 1964.]

282. *Formylation of Alcohols, Using Catalysts Based on Epoxides.*

By S. Brewis, W. T. Dent, and R. D. Smith.

The alkoxide-catalysed addition of carbon monoxide to alcohols, to give formate esters, is a well-known high-pressure reaction: [1]

$$ROH + CO \xrightarrow{NaOR} HCO_2R \qquad (1)$$

It has now been found that the reaction occurs when a mixture of an epoxide with a salt, or with a Group V tertiary alkyl or aryl, is used as catalyst. Thus, methanol containing sodium acetate and ethylene oxide reacts with carbon monoxide at 200 atm. and 130° to give methyl formate. Table 1 gives the results of experiments where mixtures of an epoxide with a salt were used as catalysts, and it shows that both epoxide and salt are essential for the reaction.

Table 1.

Synthesis of methyl formate from methanol and carbon monoxide, using mixtures of an epoxide with a salt as catalysts (conditions: 200 atm.; 130° for 2·5 hr.).

	Product (wt. %)			Product (wt. %)	
Catalyst (wt. %)	HCO_2Me	MeOH	Catalyst (wt. %)	HCO_2Me	MeOH
$MeCO_2Na$, 1·0	*		$PhCO_2Na$, 0·4; C_2H_4O, 4·0 ...	64	29
C_2H_4O, 23·0	*		Na_2CO_3, 0·5; C_2H_4O, 4·0	59	34
Na, 1·2	63	36	$(PhCO_2)_2Ca$, 0·8; C_2H_4O, 4·0...	22	73
$MeCO_2Na$, 0·4; C_2H_4O, 4·0...	58·5	31	KBr, 0·6; C_2H_4O, 4·0	7	91
HCO_2Na, 1·4; C_2H_4O, 2·0 ...	56	43	$(MeCO_2)_2Mn$, 1·2; C_2H_4O, 4·0	*	
HCO_2Na, 0·4; C_3H_6O, 5·2 ...	59	33	$(MeCO_2)_2Hg$, 1·6; C_2H_4O, 4·0	*	

C_2H_4O = Ethylene oxide. C_3H_6O = Propylene oxide. * No gas absorption.

The gas absorption in the experiment with sodium was very rapid, and the product distribution is therefore believed to represent the equilibrium point in the reaction under the chosen conditions. The results show that sodium salts of weak acids give very nearly the maximum possible reaction within 2·5 hr., but the salts of divalent metals or strong acids are less effective.

The salts in the catalyst mixtures of Table 1 may be replaced by tertiary amines, phosphines, or arsines; some results are given in Table 2.

Table 2.

Synthesis of methyl formate from methanol and carbon monoxide, using mixtures of a group V alkyl or aryl with an epoxide as catalysts (conditions: 200 atm.; 130°; for 2·5 hr.).

	Product (wt. %)			Product (wt. %)	
Catalyst (wt. %)	HCO_2Me	MeOH	Catalyst (wt. %)	HCO_2Me	MeOH
Bu^n_3P, 1·5	*		Et_3N, 0·5; C_2H_4O, 4·0.....	50	47·5
Na, 1·2.....	63	36	Ph_3As, 1·5; C_2H_4O, 4·0	38	51
Bu^n_3P, 1·5; C_2H_4O, 1·0	56·5	43	Bu^n_3P, 1·0; C_3H_6O, 5·2	52	35
Ph_3P, 1·5; C_2H_4O, 4·0	44·5	53	Bu^n_3P, 1·0; C_8H_8O, 10·0	35	42
Bu^n_3N, 0·9; C_2H_4O, 4·0	47	48	Ph_3PO, 1·3; C_2H_4O, 4·0	*	

C_2H_4O = Ethylene oxide. C_3H_6O = Propylene oxide. C_8H_8O = Styrene oxide.
* No gas absorption.

Again, the experiment with sodium indicates the maximum possible degree of reaction. It is clear that both the tertiary base and the olefine oxide are necessary components of the catalyst, and that triphenylphosphine oxide, a minor component of the reaction mixture when triphenylphosphine was used, is ineffective.

The new catalysts, typified by the mixture of tributylphosphine and ethylene oxide, vary in effectiveness for different alcohols (see Table 3).

The failure of tertiary butyl alcohol to react is noteworthy.

The activity of the salt–epoxide catalysts is thought to be due to the formation of

[1] Orchin and Wender, "Catalysis," ed. Emmett, Reinhold, Baltimore, 1957, vol. 5, p. 35.

TABLE 3.

Formylation of some alcohols at 200 atm. and 130° (catalyst: 1·0% Bu^n_3P + 4·0% C_2H_4O).

Reactant	Reaction time (hr.)	Product (wt. %)
EtOH	2·5	HCO_2Et, 51
Bu^nOH	2·5	HCO_2Bu^n, 60
MeCH(OH)Et	2·5	$HCO_2CH(Me)Et$, 38
Bu^tOH	1·5	*
$HOCH_2{\cdot}CH_2{\cdot}OH$	1·5	*

* No gas absorption.

alkoxide ions under the conditions of the reaction. This hypothesis was supported by the observation that a dilute solution of sodium benzoate and ethylene oxide in methanol, left at 35—40° for fourteen days, had a titratable alkalinity, equivalent to a 29% conversion of sodium benzoate. Methyl benzoate was also isolated from this reaction, equivalent to a 16·5% conversion of sodium benzoate to ester. It is suggested that the alkoxide ion and ester arise by the following series of reactions:

$$PhCO_2^- + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow PhCO_2CH_2{\cdot}CH_2O^- \quad (2)$$

$$PhCO_2CH_2{\cdot}CH_2O^- + MeOH \longrightarrow PhCO_2CH_2CH_2OH + MeO^- \quad (3)$$

$$PhCO_2CH_2{\cdot}CH_2OH + MeOH \xrightarrow{MeO^-} PhCO_2Me + HOCH_2{\cdot}CH_2OH \quad (4)$$

The initial step is the rupture of the epoxide ring by the salt anion (reaction 2), as in the established reactions of tertiary bases and epoxides,[2,3] followed by transfer of a proton from methanol to give the methoxide ion and a glycol monoester (reaction 3). Finally, an alkoxide-catalysed transesterification gives methyl benzoate (reaction 4).

A reaction analogous to the generation of methoxide ion from methanol has been observed between aqueous sodium chloride and ethylene oxide, which react to a limited degree to give hydroxyl ions:[4]

$$\underset{\diagdown O \diagup}{CH_2{-}CH_2} + Cl^- + H_2O \rightleftharpoons HOCH_2{\cdot}CH_2Cl + OH^- \quad (5)$$

Similar reactions with some anions other than chloride have been reported.[5,6]

In the catalyst mixtures containing tertiary bases and epoxides, the alkoxide ion is probably generated by the following type of reaction:

$$Ph_3P + \underset{\diagdown O \diagup}{CH_2CH_2} \longrightarrow Ph_3\overset{+}{P}{\cdot}CH_2{\cdot}CH_2O^- \quad (6)$$

$$Ph_3\overset{+}{P}{\cdot}CH_2{\cdot}CH_2O^- + MeOH \longrightarrow Ph_3\overset{+}{P}{\cdot}CH_2{\cdot}CH_2OH + MeO^- \quad (7)$$

The fission of the epoxide ring to give a zwitterionic species (reaction 6) has been postulated as the initial stage of the reaction of trisubstituted phosphines with epoxides to give the phosphine oxide and alkene,[2] and its analogue with trialkylamines is also known.[3] The subsequent abstraction of a proton from methanol, to give a methoxide ion, is a reasonable postulate.

In order to test this hypothesis, the reaction at room temperature between triphenylphosphine, ethylene oxide, and methanol was briefly investigated. As with the epoxide–salt systems, a titratable alkalinity slowly developed, which was ultimately equivalent to 91% of the triphenylphosphine reactant. The phosphonium cation in the product was isolated as its iodide, which was shown to be 2-methoxyethyltriphenylphosphonium iodide, $Ph_3\overset{+}{P}{\cdot}CH_2{\cdot}CH_2{\cdot}OMe\ I^-$, and not the predicted 2-hydroxyethyltriphenylphosphonium iodide, $Ph_3\overset{+}{P}{\cdot}CH_2{\cdot}CH_2{\cdot}OH\ I^-$. Presumably, the latter compound is etherified under the reaction

[2] Boskin and Denney, *Chem. and Ind.*, 1959, 330; Wittig and Haag, *Chem. Ber.*, 1955, **88**, 1654.
[3] Hansson, *Acta Chem. Scand.*, 1954, **8**, 365.
[4] Porret, *Helv. Chim. Acta*, 1944, **27**, 1321.
[5] Brönsted, Kilpatrick, and Kilpatrick, *J. Amer. Chem. Soc.*, 1929, **51**, 428.
[6] Petty and Nichols, *J. Amer. Chem. Soc.*, 1954, **76**, 4385.

conditions. From these observations, we suggest that the true catalysts for the formylation reaction are bases of the type $Ph_3\overset{+}{P}\cdot CH_2\cdot CH_2\cdot OMe\ OMe^-$, generated by reaction between the alcohol, the epoxide, and the tertiary base.

In the sodium-catalysed formylation of alcohols, tertiary butyl alcohol reacts more readily than n-butyl alcohol. With the new catalysts, tertiary butyl alcohol is unreactive. This is presumably due to the failure of the analogue of reaction 7, tertiary butyl alcohol being a relatively weak acid compared with the n-alcohol.

Experimental.—High-pressure reactions. The reactions were carried out in stirred silver-lined autoclaves of 110-ml. capacity. The pressure was maintained between 190 and 210 atm. by successive additions of carbon monoxide and the temperature was held at 130° for 2·5 hr. The products were analysed by means of gas–liquid chromatography. A column of tetraethyleneglycol dimethyl ether on celite was used for the mixtures of methanol and methyl formate, and one of dinonyl phthalate on Celite for the other products.

Reaction of sodium benzoate, ethylene oxide, and methanol. Sodium benzoate (6·0 g.) and ethylene oxide (6·0 g.) were dissolved in methanol (" Fischer reagent quality ") to a total volume of 200 ml., and left at 35—40° for 14 days; 20 ml. of the solution then required 45·2 ml. of 0·022N hydrochloric acid to the phenolphthalein end-point. (The same concentration of sodium benzoate in methanol is neutral to phenolphthalein.) The remaining 180 ml., after partial removal of solvent and extraction with pentane from saturated aqueous sodium chloride, gave methyl benzoate (0·72 g.), b. p. 198—199° (lit., 200°), (Found: C, 70·9; H, 6·0. Calc. for $C_8H_8O_2$, C, 70·6; H, 5·9%).

Reaction of triphenylphosphine, ethylene oxide, and methanol. Triphenylphosphine (3·25 g.), ethylene oxide (10·0 g.), and methanol (to 240 ml.) were mixed and left at 22—25°. Samples (10 ml.) were diluted with 100 ml. water, and titrated with 0·1N hydrochloric acid to the Methyl Orange end-point. The liberation of alkali, expressed as an equivalent of the triphenylphosphine, was: after 5 min., zero; after 6 hr., 50%; after 48 hr., 91%, not rising further.

Triphenylphosphine (10·0 g.), ethylene oxide (24·9 g.), and methanol (244 g.) were mixed and left at room temperature for 16 hr. The mixture was then evaporated under a vacuum at 25—30°. Hydriodic acid (50%) was then added in excess, and the mixture evaporated at 40—50°. Several recrystallizations from a mixture of acetone, methanol, and ethyl acetate gave pale yellow crystals of *2-methoxyethyltriphenylphosphonium iodide* (2·8 g.), m. p. and mixed m. p. 202—204° (Kofler block) (Found: C, 56·1; H, 5·2; I, 28·5; P, 6·8. $C_{21}H_{22}IOP$ requires C, 56·3; H, 4·9; I, 28·3; P, 6·9%). The nuclear magnetic resonance spectrum, in deuterochloroform, showed no OH frequency, and was identical with that of the authentic iodide (see below).

2-Methoxyethyltriphenylphosphonium iodide. Iodo-2-methoxyethane [7] (18·7 g.) was heated with triphenylphosphine (27·0 g.) at 80° for 6 hr. The solid product was ground and digested with ether, and the residual solid crystallized twice from a mixture of methanol and acetone, giving 29·6 g. (66%) of a pale yellow solid. Two further crystallizations gave *material* of m. p. 202—204° (Kofler block) (Found: C, 56·2; H, 5·0; I, 27·9; P, 6·7. $C_{21}H_{22}IOP$ requires C, 56·3; H, 4·9; I, 28·3; P, 6·9%). The nuclear magnetic resonance spectrum, in deuterochloroform, showed a singlet at $6{\cdot}9_7$ τ (CH_3O–), a triplet at $6{\cdot}3_9$ τ (–O–CH_2–CH_2–), a quartet (approx.) at $5{\cdot}9_8$ τ (–CH_2–CH_2–P–), and a multiplet at 2·2 τ (–PC_6H_5). The ratio of the protons in these groups was determined as 3 : 2 : 2 : 15, and the shape of the phenyl group multiplet was characteristic of the C_6H_5P grouping. The infrared spectrum was consistent with the same formulation.

We thank Dr. J. M. Rowe and Dr. A. J. Wilkinson for measuring the spectra, and Mr. B. R. Braithwaite for performing microanalyses.

RESEARCH DEPARTMENT, IMPERIAL CHEMICAL INDUSTRIES LIMITED,
HEAVY ORGANIC CHEMICALS DIVISION, BILLINGHAM,
CO. DURHAM.

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[7] Jones and Powers, *J. Amer. Chem. Soc.*, 1924, **46**, 2531.

283. *Stability of Carbonium Ions. Part II.*[1]

By Roger Bolton.

Previously we reported the rates of solvolysis of a number of derivatives of α-(4-biphenylyl)benzyl chloride, and we have shown that the ease of formation of the carbonium ions in an S_N1 reaction is increased when the biphenyl residue is substantially planar (*e.g.*, 2-fluorenyl), probably owing to the increased extent to which resonance stabilisation can occur.[1]

Two further cases of such systems are now reported, and their rates of solvolysis in 9 : 1 ethanol–acetone (v/v) are discussed.

2-Benzoyl-4,5,9,10-tetrahydropyrene [2] was reduced by lithium aluminium hydride to the alcohol, m. p. 112·5—114·0°. Thionyl chloride then gave α-(4,5,9,10-tetrahydro-2-pyrenyl)benzyl chloride, m. p. 143—144°. By a similar route, α-(9,10-dihydro-2-phenanthryl)benzyl chloride was prepared from 2-benzoyl-9,10-dihydrophenanthrene, m. p. 81—82°. The benzoyldihydrophenanthrene was obtained as an oil, which, after purification through Girard's reagent T, solidified during four months and could then be crystallised from ethanol; the derived alcohol and chloride were similarly obtained as oils and used in this form. There was no evidence of impurity in the chlorides; each gave good first-order rate constants over 75—90% reaction (extreme range: ±1·5% mean deviation from the mean).

The courses of the solvolyses were followed as described previously.[1] The Arrhenius plot comprised six points taken over a range of 30°; least-squares analysis was used to obtain the slope of this line and the probable error (Table 1).

Table 1.

Kinetic results for the solvolysis of the α-arylbenzyl chlorides in 9 : 1 ethanol–acetone (v/v).

Aryl group	E (kcal. mole^{-1})	log A	k_{rel}
9,10-Dihydro-2-phenanthryl	17·2 ± 0·4	10·0	90
4,5,9,10-Tetrahydro-2-pyrenyl	17·4 ± 0·2	10·8	247
2-Fluorenyl	17·5 ± 0·4	10·8	250

E and A are derived from the equation $k = A \exp(-E/RT)$. k_{rel} is the rate of solvolysis of the arylbenzyl chloride, relative to that of diphenylmethyl chloride, at 25°.

The results show two interesting features. First, the tetrahydropyrenyl system is almost as effective as the fluorenyl system in stabilising the incipient carbonium ion. Fluorene is planar [3] and there is strong evidence that 4,5,9,10-tetrahydropyrene is also very near coplanarity so far as the two benzene systems are concerned.[4] The similarity of the rates of solvolysis and of the derived Arrhenius parameters for the corresponding chlorides indicates that both hydrocarbon residues assist in the formation of the carbonium ion to a similar extent. The small difference in the observed rates of solvolysis at 25°, probably reflecting a difference in activation energy of 0·5 kcal. mole^{-1} at the most, may merely reflect the effects of the different bridge systems in each hydrocarbon entity. On these results, there is no need to postulate any strain factor to explain the high reactivity of the fluorenyl derivative.

In contrast, the two phenyl rings in 9,10-dihydrophenanthrene may be twisted to an angle of about 17° relative to each other; accordingly, we find that the dihydrophenanthryl substituent, while not as effective as the fluorene or tetrahydropyrene systems, is more effective than the biphenyl system in promoting the formation of a carbonium ion.

Secondly, there is an approximately linear relation between log(Rate of solvolysis of

[1] Part I, Bolton, Jones, and Tucker, *J.*, 1964, 1464.
[2] Bolton, *J.*, 1964, 4637.
[3] Iball and Burns, *Nature*, 1954, **173**, 635; *Proc. Roy. Soc.*, 1954, *A*, **227**, 200.
[4] Mislow, Glass, Hopps, Simon, and Wahl, *J. Amer. Chem. Soc.*, 1964, **86**, 1710.

TABLE 2.

Comparison of the rates of the reactions PhCHCl(x-Ar) = PhC$\overset{+}{\text{H}}$(x-Ar) and Cl_2 + ArH = x-ClAr.

x	Aryl group (Ar)	k_N	k_E
4	Biphenyl	12·2	$7{\cdot}8 \times 10^2$ [a]
2	9,10-Dihydrophenanthrene	90·1	$2{\cdot}6 \times 10^4$ [b]
2	4,5,9,10-Tetrahydropyrene	247	$2{\cdot}9 \times 10^4$ [c]
2	Fluorene	250	$3{\cdot}1 \times 10^5$ [d]
2	Biphenylene	560	*ca* $1{\cdot}1 \times 10^6$ [e]

k_N is the same as k_{rel} in Table 1 of this Note, and Table 3 of ref. 1; k_E is the partial rate factor for substitution by chlorine in acetic acid at 25° at the x-position.

[a] de la Mare and Hassan, *J.*, 1958, 1519. [b] de la Mare and Lomas, *J.*, 1963, 5973. [c] de la Mare and Lomas, unpublished results. [d] de la Mare, Hall, Harris, and Hassan, *Chem. and Ind.*, 1958, 1086. [e] Bolton, unpublished results.

α-x-arylbenzyl chloride) and log(Rate of chlorination of ArH in the x-position). Such a correlation is by no means usual (cf. the rates of formation of the isomeric phenanthryl-carbonium ions [5] with the almost exclusive attack of chlorine at the 9-position of phenanthrene in acetic acid [6]) but this correlation between electrophilic and nucleophilic reactions has been observed in the present series.[7]

The correlation would imply that similar requirements are made of the hydrocarbon system in each reaction, which may be rationalised since the transition state in either case involves the localisation of a partial positive charge upon the system.

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CHEMISTRY DEPARTMENT, BEDFORD COLLEGE, LONDON N.W.1. [*Received, June 23rd*, 1964.]

[5] Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, 1961.
[6] de la Mare, Klassen, and Koenigsberger, *J.*, 1961, 5285.
[7] Berliner, personal communication; Verbit and Berliner, *J. Amer. Chem. Soc.*, 1964, **86**, 3307.

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284. *Two Crystalline Modifications of* 1,1′-*Binaphthyl.*

By YASMEEN BADAR, CHUA CHEUNG KING LING, ANN S. COOKE, and MARGARET M. HARRIS.

DURING work on optically active and racemic 1,1′-binaphthyl [1-4] we have prepared and purified specimens of this compound by several methods: our findings support the suggestion of Brown, Trotter, and Monteath Robertson [5] that the variety of melting points recorded in the literature for 1,1′-binaphthyl may indicate more than one crystalline form.

Observation of 1,1′-binaphthyl on a Kofler hot-stage apparatus, in polarised light, while taking the temperature up and down between 140 and 165°, reveals at least two distinct interchangeable crystalline types. Crystallisation from acetic acid, or slow crystallisation from light petroleum, (b. p. 40—60°) gives a major deposit of shining white plates, m. p. 144·5—145°; when heated above the melting point these may change to stout rhombic crystals, m. p. 157—159°, or they may remain liquid until they are cooled to 140° again, when they re-crystallise. Quick crystallisation from light petroleum (b. p. 40—60°) gives the form melting at 157—159°.

These two crystalline species show identical pairs of spectra, between 768 and 1212 cm.$^{-1}$, in solution in carbon disulphide, in carbon tetrachloride, and in cyclohexane.

[1] Harris and Mellor, *Chem. and Ind.*, 1961, 1082.
[2] Cooke and Harris, *J.*, 1963, 2365.
[3] Badar and Harris, see ref. 2.
[4] Badar, Cheung King Ling, and Harris, see ref. 2.
[5] Brown, Trotter, and Monteath Robertson, *Proc. Chem. Soc.*, 1961, 115.

In Nujol mull small differences appear near 1206 cm.$^{-1}$ and in the 970—940 cm.$^{-1}$ region, but the most striking difference, immediately diagnostic of the sample, is the major peak at 769 cm.$^{-1}$, which appears in the spectrum of the lower-melting form and not in that of the higher.

Infrared spectra (cm.$^{-1}$; 768—1212 cm.$^{-1}$) of two crystalline forms of 1,1′-binaphthyl: (a) m. p. 144·5—145°; (b) m. p. 157—159°.

Region	768—802 cm.$^{-1}$				941—971 cm.$^{-1}$			1199—1212 cm.$^{-1}$	
CS_2 *solution*									
(*a*)	769m	776s	781s	799s	943m	965m		1203w	
(*b*)	769m	776s	781s	799s	943m	965m			
C_6H_{12} *solution*									
(*a*)	768sh	776s	781s	797s					
(*b*)	768sh	776s	781s	797s					
Nujol mull									
(*a*)	769s	(779, 780)s		802s	941m	952m	968m	1199w	1212w
(*b*)	769sh	779s		798s	942w	952w	971w	1206m	

These differences in the spectra might be due to different arrangements of molecules of like conformation in the crystal,[6] or to different conformations of the molecules, or to both causes. The ultraviolet spectrum[7] and the low-temperature fluorescence spectrum[8] resemble those for naphthalene; the two α-naphthyl units are assumed to be sufficiently removed from planarity for there to be little resonance interaction between them. The preliminary crystallographic experiments[5] on a sample melting at 148—149° which have been reported are considered to indicate a *cis*-disposition of the naphthalene rings with an interplanar angle of 73°.

The biphenyl molecule, non-planar in solution and in the vapour state, is planar in the crystal:[9] there is little likelihood that 1,1′-binaphthyl can have a crystalline modification in which the molecules are planar because the energy barrier between the *R* and the *S* configurations[2] is 22·5 kcal. mole^{-1}, while it is probably less than 4 kcal. mole^{-1} in biphenyl.

Models suggest that, within each *R* or *S* configuration, there would be two conformations of similar ground-state energy; one is that already postulated by the crystallographers, with *cis*-disposed planes, while the other has *trans*-planes at a similar angle. In the *cis*-conformation the 8- and 8′-hydrogen atoms approach each other and also come close to the 8′- and 8-carbon atoms, while the 2- and 2′-hydrogen atoms are free from steric interference. In the *trans*-conformation there would be only one kind of interfering non-bonded hydrogen–hydrogen situation, that of 2′ with 8 and 2 with 8′, and little significant hydrogen–carbon interference. The spectral region in which the most marked difference appears is one in which the C–H out-of-plane vibrations may be detected,[10] and it seems reasonable to suggest that the appearance of the extra band in the *cis*-molecule's spectrum might be due to these two different C–H situations.

The crystalline optically active specimen[1,2] obtained by deamination of (+)-4,4′-naphthidine and purified by chromatography, with benzene–light petroleum as eluent, melted at 157—159°: it showed a spectrum, in Nujol mull, of the higher melting (±)-type, with a very small inflexion at 769 cm.$^{-1}$. Melted and re-solidified, it melted again at 145° and then showed a sharp peak at 769 cm.$^{-1}$.

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BEDFORD COLLEGE, UNIVERSITY OF LONDON,
REGENT'S PARK, LONDON N.W.1.

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[6] Ebert and Gottlieb, *J. Amer. Chem. Soc.*, 1952, **74**, 2806.
[7] Friedel, Orchin, and Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.
[8] Hochstrasser, *Can. J. of Chemistry*, 1961, **39**, 459.
[9] G. B. Robertson, *Nature*, 1961, **191**, 593; Trotter, *Acta Cryst.*, 1961, **14**, 1135; Hargreaves and Rizvi, *ibid.*, 1962, **15**, 365.
[10] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., 1954, pp. 66 and 67.

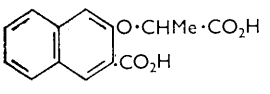
285. *The Synthesis of 2,3-Dihydro-2-methylnaphtho*[2,3-b]*furan, and its 4- and 9-Methoxy-derivatives.*

By D. C. C. Smith and D. E. Steere.

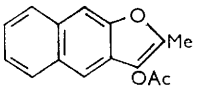
The compounds named in the title were required for spectroscopic comparisons with the natural product xanthorrhoein.[1]

Methyl 3-hydroxy-2-naphthoate was alkylated with ethyl α-bromopropionate, and the resulting diester was saponified giving α-(3-carboxy-2-naphthyloxy)propionic acid (I). Decarboxylative cyclisation in acetic anhydride afforded 3-acetoxy-2-methylnaphtho-[2,3-*b*]furan (II) which, on saponification and reduction, gave two isomeric hydroxy-compounds (III). Hydrogenolysis of these afforded 2,3-dihydro-2-methylnaphtho-[2,3-*b*]furan (IV) in 85% overall yield from methyl 3-hydroxy-2-naphthoate.

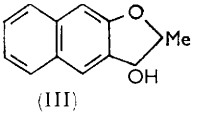
For a parallel synthesis of 2,3-dihydro-9-methoxy-2-methylnaphtho[2,3-*b*]furan (V), 3-hydroxy-4-methoxy-2-naphthoic acid (VI) was required. 3,4-Dihydroxy-2-naphthoic acid (VII) was available from acidic hydrolysis of 4-amino-3-hydroxy-2-naphthoic acid (VIII).[2,3] Addition of zinc dust before hydrolysis has been suggested,[3] but we found this to completely inhibit the reaction, which therefore probably involves adventitious oxidation



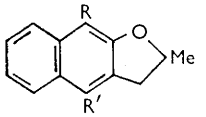
(I)



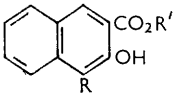
(II)



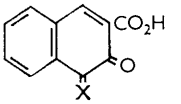
(III)



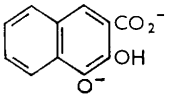
(IV) R = R′ = H
(V) R = OMe, R′ = H
(XIII) R = H, R′ = OMe
(XIV) R = H, R′ = OH



(VI) R = OMe, R′ = H
(VII) R = OH, R′ = H
(VIII) R = NH_2, R′ = H
(XI) R = OH, R′ = Me



(IX) X = NH_2^+
(X) X = O



(XII)

to the quinoneimmonium salt (IX), hydrolysis to the quinone (X), and reduction to the dihydroxy-acid (VII) by the aminohydroxy-acid (VIII). Partial methylation of the dihydroxy-acid (VII) with diazomethane afforded only the dihydroxy-ester (XI), but treatment with methyl iodide in the presence of two equivalents of sodium hydroxide, gave the required 3-hydroxy-4-methoxy-2-naphthoic acid (VI). The good yield in this partial methylation is attributable to the predominance of the dianion (XII), predictable from intramolecular electrostatic repulsion between oxyanion groups. The methoxy-acid (VI) was converted into 2,3-dihydro-9-methoxy-2-methylnaphtho[2,3-*b*]furan (V) by the sequence already described.

2,3-Dihydro-4-methoxy-2-methylnaphtho[2,3-*b*]furan was prepared by methylation of the known [4] 2,3-dihydro-4-hydroxy-2-methylnaphtho[2,3-*b*]furan (XIV).

Experimental.—*α-(3-Carboxy-2-naphthyloxy)propionic acid.* Methyl 3-hydroxy-2-naphthoate (35 g.),[5] acetone (500 c.c.), ethyl α-bromopropionate (45 c.c.), and anhydrous potassium carbonate (300 g.) were stirred for 3 days. The solids were filtered off and washed with acetone; the filtrate and washings were concentrated, mixed with 95% ethanol (100 c.c.) and water (150 c.c.) containing potassium hydroxide (50 g.), and concentrated slowly on a steam-bath for 2 hr. Cooling and acidification with hydrochloric acid precipitated the *diacid*, which slowly crystallised. This was powdered, washed with cold water, and dried (44·4 g.). A

[1] Birch, Salahud-Din, and Smith, *Tetrahedron Letters*, 1964, 1623.
[2] Möhlau and Kriebel, *Ber.*, 1895, **28**, 3092.
[3] Spruit, *Rec. Trav. chim.*, 1948, **67**, 285.
[4] Latif and Soliman, *J.*, 1944, 56.
[5] Strohbach, *Ber.*, 1901, **34**, 4146.

portion recrystallised from aqueous acetic acid had m. p. 166—168° (Found: C, 64·7; H, 4·6. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·65%).

3-Acetoxy-2-methylnaphtho[2,3-b]*furan.* α-(3-Carboxy-2-naphthyloxy)propionic acid (44 g.), potassium acetate (44 g.) and acetate anhydride (0·5 l.) were heated causing a brisk evolution of carbon dioxide. After 30 min., the mixture was boiled briefly, cooled, poured into ice–water (3 l.), and stirred until crystalline. The solids were collected, washed, dried, and recrystallised from ethyl acetate affording the *ester* as colourless prisms (38 g.), m. p. 134—136° (Found: C, 74·8; H, 4·75. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%).

2,3-Dihydro-3-hydroxy-2-methylnaphtho[2,3-b]*furan.* 3-Acetoxy-2-methylnaphtho[2,3-*b*]-furan (9·15 g.), suspended in methanol (100 c.c.), was treated with potassium hydroxide (2 g.) in methanol (5 c.c.) followed immediately by potassium borohydride (2 g.) in water (5 c.c.), warmed to 40° to dissolve the solids, and kept overnight. Dilution with water and ether extraction yielded colourless crystals (6·9 g.) of the *hydroxy-compounds* (III). Fractional crystallisation from benzene–light petroleum yielded one isomer, m. p. 128—130° (Found: C, 77·8; H, 5·9. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%), and another isomer, m. p. 83—84° (Found: C, 77·8; H, 6·0%).

2,3-Dihydro-2-methylnaphtho[2,3-b]*furan.* 2,3-Dihydro-3-hydroxy-2-methylnaphtho[2,3-*b*]-furan (5 g.) and solid palladium chloride (300 mg.) in ethyl acetate (50 c.c.) were shaken with hydrogen until uptake ceased. The solution was freed from catalyst and acid by filtration through a column of alumina, and, on concentration, afforded the *dihydro-compound* (4·7 g.) as a low-melting solid. A sample recrystallised from cold pentane had m. p. 35° (Found: C, 84·9; H, 6·4. $C_{13}H_{12}O$ requires C, 84·8; H, 6·6%). The *picrate* had m. p. 110—112° (from methanol) (Found: C, 55·1; H, 3·7; N, 9·4. $C_{19}H_{15}N_3O_8$ requires C, 55·2; H, 3·7; N, 10·2%).

3-Hydroxy-4-methoxy-2-naphthoic acid. 3,4-Dihydroxy-2-naphthoic acid,[2] (25 g.) was dissolved in warm methanol (1·5 l.), treated with N-sodium hydroxide (250 c.c.) and methyl iodide (50 c.c.), and kept overnight at room temperature. The solution was freed from a precipitate by filtration, concentrated under reduced pressure, acidified with hydrochloric acid, and diluted with water (0·5 l.). The precipitate was collected and washed. The filtrate and washings on extraction with ether gave a further quantity of solid. The combined solids were extracted with hot methanol (70 c.c.), filtered hot to remove impurities, and, on cooling, afforded *3-hydroxy-4-methoxy-2-naphthoic acid* as pink prisms (15·5 g.) m. p. 186—187°. When scratched or heated after drying, the crystals underwent a sudden and spectacular colour change from pink to yellow (Found: C, 66·1; H, 4·7. $C_{12}H_{10}O_4$ requires C, 66·05; H, 4·6%).

3-Acetoxy-9-methoxy-2-methylnaphtho[2,3-b]*furan.* 3-Hydroxy-4-methoxy-2-naphthoic acid (1·23 g.) was converted by ethereal diazomethane into the methyl ester, yellow prisms, m. p. 72—73° (from light petroleum). This whole product (1·02 g.) was treated exactly as the methyl 3-hydroxy-2-naphthoate described above, successively giving α-(3-carboxy-1-methoxy-2-naphthyloxy)propionic acid as a colourless glass (1·30 g.), then *3-acetoxy-9-methoxy-2-methylnaphtho*[2,3-b]*furan,* (0·27 g.), m. p. 112—113° (from ethanol) (Found: C, 70·8; H, 5·1. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%).

2,3-Dihydro-9-methoxy-2-methylnaphtho[2,3-b]*furan.* 3-Acetoxy-9-methoxy-2-methylnaphtho[2,3-*b*]furan (135 mg.) by alkaline hydrolysis, borohydride reduction, then hydrogenolysis as described above, gave the dihydro-naphtho[2,3-*b*]furan as a colourless oil (86 mg.) forming a *picrate* m. p. 102—105°, in methanol (Found: C, 55·0; H, 4·05; N, 10·0. $C_{20}H_{17}N_3O_9$ requires C, 54·2; H, 3·9; N, 9·5%), and a *1,3,5-trinitrobenzene adduct,* m. p. 100—102° in methanol (Found: C, 56·5; H, 4·2; N, 10·3. $C_{20}H_{17}N_3O_8$ requires C, 56·2, H, 4·0; N, 9·8%).

2,3-Dihydro-4-methoxy-2-methylnaphtho[2,3-b]*furan.* 2,3-Dihydro-4-hydroxy-2-methylnaphtho[2,3-*b*]furan (400 mg.) [4] was methylated in acetone, with methyl iodide and potassium carbonate, giving the *dihydro-compound* as a colourless mobile oil (422 mg.), b. p. 200° (bath temp.)/0·1 mm. (Found: C, 77·8; H, 6·7. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%). The red-brown *picrate,* formed in methanol, had m. p. 140—141° (Found: C, 54·1; H, 4·0; N, 9·6. $C_{20}H_{17}N_3O_9$ requires C, 54·2; H, 3·9; N, 9·5%).

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THE UNIVERSITY, MANCHESTER 13. [*Received, July 6th,* 1964.]

286. *Reduction of Substituted Nitrobenzenes. Part II.*[1] *Reduction of Some Aromatic Nitro-compounds with Reducing Sugars.*

By Brian T. Newbold and Raymond P. LeBlanc.

In Part I [1] the reduction of a series of monohalogenated nitrobenzenes with various sugars in alkaline medium and the isolation of the corresponding dihalogenated azoxybenzenes was described. In the present work galactose, fructose, and mannose were employed as reducing agents for 2,5-dichloronitrobenzene and *o*- and *p*-nitrotoluene. The nitrotoluenes were also reduced with maltose. Some results are given in the Table.

Reductions of aromatic nitro-compounds.

Compound (g.)	Sugar (g.)	NaOH (g.)	H_2O (ml.)	Time (min.)	Temp.	Recovered nitro-compound	Products (%) Azoxy-benzene	Amine
			2,5-Dichloronitrobenzene					
20·0	Galactose (14·3)	18·7	184	45	80—82°	7·0	65·1	3·6
20·0	Fructose (14·3)	18·7	184	40	68—72	5·5	74·3	1·8
6·9	Mannose (5·0)	6·5	62	45	68—73	8·6	66·6	0·2
			o-*Nitrotoluene*					
5·8	Galactose (11·7)	7·5	71	45	80—90	19·8	6·9	Nil
5·8	Fructose (11·7)	7·5	71	45	80	39·5	1·8	44·3
5·0	Mannose (5·0)	6·4	73	45	80—86	50·8	10·2	Nil
23·3	Maltose (46·8)	30·0	285	60	80—82	34·9	15·6	16·5
			p-*Nitrotoluene*					
23·3	Galactose (23·0)	30·0	285	40	78—80	22·3	53·1	0·1
5·0	Mannose (5·0)	6·4	73	45	75—80	33·3	12·1	Nil
13·7	Dextrose (53·1)	20·0	180	150	60	Nil	Nil	63·5
23·3	Maltose (46·8)	30·0	285	40	81	17·2	18·2	19·2

Reduction of 2,5-dichloronitrobenzene with magnesium and methyl alcohol was reported [2] to give 2,2′,5,5′-tetrachloroazoxybenzene in 35% yield. This azoxybenzene was also prepared in 25% yield by oxidation of 2,2′,5,5′-tetrachloroazobenzene with hydrogen peroxide in glacial acetic acid,[3] and in 35% yield from the hydrazobenzene using the same oxidizing agent.[4] Reduction of 2,5-dichloronitrobenzene with galactose, fructose, or mannose gave 2,2′,5,5′-tetrachloroazoxybenzene in good yield. There was little tar formation and some 2,5-dichloroaniline was also isolated. It is generally accepted that azoxybenzenes are formed during the reduction of nitrobenzenes by the condensation of the nitrosobenzene with the phenylhydroxylamine under the influence of alkali. This condensation should be subject to steric hindrance, although in the case of 2,5-dichloronitrobenzene this effect does not seriously impede the formation of the azoxybenzene, probably because of the relatively small size of the chlorine atom.

Galbraith *et al.*[5] reduced the isomeric nitrotoluenes with glucose in alkaline medium and obtained dimethylazoxybenzenes as the main products. We found that reduction of *o*-nitrotoluene with galactose, fructose, or mannose caused conversion into the 2,2′-dimethylazoxybenzene and some tar was also formed. In a few experiments, a large excess of reducing sugar was employed and in every case there was less conversion into the azoxy-compound, though *o*-toluidine was obtained in fair yield. The reduction to the amine may be due to the fact that the nitro-group in *o*-nitrotoluene is sterically hindered. Amine formation increases with increasing steric hindrance around the nitro-group for reductions of aromatic nitro-compounds with lithium aluminium hydride, and *o*-nitrotoluene gives

[1] Part I, Newbold and LeBlanc, *J. Org. Chem.*, 1962, **27**, 312.
[2] Keirstead, *Canad. J. Chem.*, 1953, **31**, 1064.
[3] Gagnon and Newbold, *Canad. J. Chem.*, 1959, **37**, 366.
[4] Newbold, *J. Org. Chem.*, 1962, **27**, 3919.
[5] Galbraith, Degering, and Hitch, *J. Amer. Chem. Soc.*, 1951, **73**, 1323.

o-toluidine in 26% yield when reduced with this agent.[6] We also reduced *o*-nitrotoluene with maltose and obtained 2,2′-dimethylazoxybenzene, together with *o*-toluidine (17%). The latter result is surprising because a weak reducing agent such as maltose is not expected to reduce *o*-nitrotoluene to the amine. However, it was shown [1] that reduction of some halogenated nitrobenzenes with lactose or maltose gives substantial yields of the corresponding amines. Furthermore, *m*-nitrotoluene is converted into *m*-toluidine (10%) by maltose in alkaline medium.[7]

Reduction of *p*-nitrotoluene with an equimolar amount of galactose or mannose gave 4,4′-dimethylazoxybenzene. On the other hand, when *p*-nitrotoluene was reduced with an excess of monosaccharide the amine was formed in good yield, *e.g.*, when a large excess of glucose was employed and the reaction time increased to 2½ hours, the only product was *p*-toluidine (64%). Reduction with maltose also gave *p*-toluidine in significant yield, together with 4,4′-dimethylazoxybenzene.

In some reductions of the nitrotoluenes the temperature was slowly raised over the range 40—85°, and in each case there was less tar formation, less reaction occurred, and the toluidine rather than the azoxybenzene was formed. We also found that rapid stirring was essential in order to achieve reduction.

Experimental.—The 2,5-dichloronitrobenzene and *o*- and *p*-nitrotoluenes used were commercially available samples. M. p.s were determined on a calibrated Fisher–Johns apparatus. Since essentially the same method was employed for all the reductions, only one procedure is described. Products were identified by mixed m. p., and by infrared spectroscopy with a Perkin-Elmer Infracord 137B spectrophotometer.

Reduction of 2,5-dichloronitrobenzene with fructose. To 2,5-dichloronitrobenzene (20·0 g.) as added a solution of sodium hydroxide (18·7 g.) in water (184 ml.). The mixture was heated to 55° and fructose (14·3 g.) added in small portions. The mixture was vigorously stirred at 66—72° for 40 min. and then steam-distilled. The distillate, which contained a yellow solid, was acidified with hydrochloric acid and filtered to give 2,5-dichloronitrobenzene (5·5%). The filtrate was made alkaline with sodium hydroxide and set aside overnight, after which 2,5-dichloroaniline (1·8%) separated out, colourless needles, m. p. 48·5—49·5° (from ethanol). Treatment with acetic anhydride gave 2,5-dichloroacetanilide m. p. 134°. The mixture from steam-distillation was filtered to give a brownish-yellow residue of 2,2′,5,5′-tetrachloroazoxybenzene (74·3%), which was recrystallised from ethanol as yellow needles, m. p. and mixed m. p. 145—146° (lit.,[8] 147°).

Reductions of nitrotoluenes. In the reductions of *o*-nitrotoluene, the acidified steam-distillate was extracted with ether to recover unreacted *o*-nitrotoluene. Ether extraction of the alkaline steam-distillate sometimes yielded *o*-toluidine, which on acetylation gave *N*-acetyl-*o*-toluidine, m. p. 108—109° (from ethanol). Reductions of *p*-nitrotoluene gave recovered *p*-nitrotoluene, m. p. 50—52° and in some cases, *p*-toluidine was formed, m. p. 41—43°. Acetylation of the latter gave *N*-acetyl-*p*-toluidine, m. p. 147—147·5°. The dimethylazoxybenzenes were purified by recrystallisation from ethanol. 2,2′-Dimethylazoxybenzene was obtained as deep yellow needles, m. p. 57—58° (lit.,[9] 58·5°), and 4,4′-dimethylazoxybenzene as yellow needles, m. p. 71—72° (lit.,[9] 70°).

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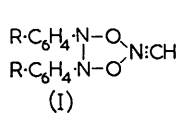
Department of Chemistry, University of Moncton,
Moncton, New Brunswick, Canada. [*Received, July 6th*, 1964.]

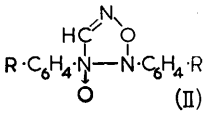
[6] Anet and Muchowski, *Canad. J. Chem.*, 1960, **38**, 2526.
[7] Newbold and LeBlanc, unpublished results.
[8] De Crauw, *Rec. Trav. chim.*, 1931, **50**, 768.
[9] Zechmeister and Rom, *Annalen*, 1929, **468**, 117.

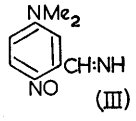
287. *The Interaction of* p-*Nitrosoanilines with Potassium Cyanide.*

By F. Bell and K. R. Buck.

By the interaction of *NN*-dialkyl-*p*-nitrosoanilines with potassium cyanide Lippmann and Fleissner,[1] and Mandl [2] obtained bright red compounds to which they ascribed formulæ of type (I). Although this method of formulation expresses the fact that one nitrogen can be eliminated as ammonia by reduction, it is clearly no longer acceptable. The attractive hypothesis that these red compounds are produced by the addition of hydrogen

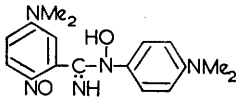

(I)

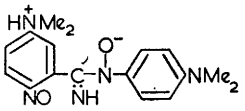

(II)

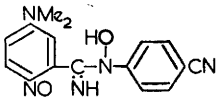

(III)

cyanide to the nitrosodimers to give products such as (II) we reject for two reasons. The first is that the reaction goes most readily with dimethyl-*p*-nitrosoaniline, which is negligibly dimerised, and not at all with nitrosobenzene, which is mainly dimerised. The second that the n.m.r. spectrum shows that the two aromatic residues are not identically substituted as they are in (II).

These and other considerations make it probable that the first step in the interaction is analogous to the reaction with phenols and leads to the formation of (III), which by


(IV)


(V)


(VI)

interaction with a further molecule of dimethyl-*p*-nitrosoaniline gives (IV). Structure (IV) has many alternative methods of representation, and of these (V) agrees best with the i.r. and n.m.r. spectra, which, however, are limited by the sparing solubility of the compound.

Proton magnetic resonance of (V) in $CDCl_3$.

(60 mc./sec.; tetramethylsilane as internal standard)

Protons	τ (p.p.m.)	Relative peak area
NMe_2 and $\overset{+}{N}Me_2$	6·90, 6·93	12
o to NMe_2 and $\overset{+}{N}Me_2$	3·3 complex band, main component has J = 10 cps.	3
m to NMe_2	2·0 doublet, J = 10 (*z*)	2
o to NO	1·0 doublet, J = 10	1
o to >C:NH	2·43 doublet, J = 3	1
C:NH	3·7 (broad band) *	1
$\overset{+}{N}H$	~2 (broad band) * (superimposed on *z*)	1

* Eliminated by deuteration with heavy water.

The diethyl analogue, from *NN*-diethyl-*p*-nitrosoaniline, showed the above features and in addition

CH_3	8·8 triplet, J = 7 c./sec.	12
CH_2	6·55 quartet, J = 7 (with secondary splitting 3 c./sec.)	8

The analogue from *N*-ethyl-*N*-methyl-*p*-nitrosoaniline showed the above features below τ 6 and in addition

NMe and $\overset{+}{N}$Me	7·03 and 6·98	6
NEt and $\overset{+}{N}$Et.....	8·85 triplet, J = 7 c./sec.	6 (methyl H)
	6·5 quartet, J = 7 (with secondary splitting 3 c./sec.)	4 (methylene H)

[1] Lippmann and Fleissner, *Monatsh.*, 1885, **6**, 537.
[2] Mandl, *Monatsh.*, 1886, **7**, 99.

Infrared spectrum (KBr disc) C:NH 1660, 3400; NH_2^+ 1880, 2770 (not well-established correlation); NMe_2 2850; *p*-disubstituted ring 818; 1,2,4-trisubstituted ring 865, 825sh cm.$^{-1}$.

Further we believe that dimethyl-*p*-nitrosoaniline undergoes nucleophilic attack by the cyanide ion to yield *p*-nitrosobenzonitrile, which is mainly converted into 4,4'-dicyanoazoxybenzene. Part, however, gives rise to (VI), which has all the significant structural features of (III). The presence of small amounts of compounds of this type is, we think, responsible for the difficulty of purification, commented upon by the original workers.

As all the red compounds had melting points over 200° and decomposition points not much higher the properties were not favourable for mass-spectrometer measurements. The *m/e* values measured by using an inlet temperature of 245° were, in order of diminishing intensity (down to one fifth of the initial mass-number intensity):

Red compound from	*M*	*m/e* values
ON·C_6H_4·NEt_2	383	149, 216, 164, 120, 175, 188, 231, 29, 43, 44, 119, 136
ON·C_6H_4·NMeEt	355	135, 150, 188, 107, 202, 119, 93, 44, 122, 65

*Experimental.—Interaction of dimethyl-*p*-nitrosoaniline with hydrogen cyanide.* Hydrogen cyanide, from potassium ferrocyanide (30 g.), was passed into a boiling solution of the compound (10 g.) in ethanol (75 c.c.). The solution on cooling deposited a first crop (1·8 g.) and after some days a second crop (1·5 g.). This material was taken up in chloroform, and the filtered solution chromatographed on alumina. The first chloroform eluates yielded 4,4'-dicyanoazoxybenzene, needles, m. p. 220—222°, from acetic acid (Found: C, 67·3; H, 3·2; N, 21·7. Calc. for $C_{14}H_8N_4O$: C, 67·7; H, 3·2; N, 22·5%). Its identity was confirmed by comparison with 4,4'-dicyanoazoxybenzene [3] prepared from 4-cyano-1-nitrobenzene [4] (mixed m. p. and infrared spectrum, $\nu_{max.}$ 730w, 845s, 856sh, 912, 1012, 1286, 1302w, 1322w, 1400, 1458vs, 1485s, and 2220 cm.$^{-1}$). The later eluates furnished a basic, orange-red compound (VI) which formed needles, m. p. 234° (decomp.) from chloroform or ethanol (Found: C, 62·2; H, 4·8; N, 22·0. $C_{16}H_{15}O_2N_5$ requires C, 62·2; H, 4·8; N, 22·6%); $\nu_{max.}$ 690w, 720w, 781, 819, 858, 866, 912, 968, 1063, 1160, 1180, 1235, 1250, 1275, 1328, 1370, 1432, 1460, 1510, 1590vs, 1635, 1675, and 2220 cm.$^{-1}$. This compound could be recrystallised without change from acetic anhydride.

When diethyl-*p*-nitrosoaniline was submitted to the same treatment it was essentially unchanged.

*Interaction of dimethyl-*p*-nitrosoaniline with potassium cyanide.* Potassium cyanide (5 g.) in water (7 c.c.) was added to a boiling solution of the compound (5 g.) in ethanol (60 c.c.) and the boiling continued for 2 hr. The mixture was cooled and filtered. Further boiling of the filtrate gave further crops, making a total of 1·7 g., m. p. *ca.* 200°. This material was dissolved in chloroform and the filtered solution poured on a column of alumina and eluted with chloroform. The first fraction was 4,4'-bisdimethylaminoazoxybenzene, identified by comparison (mixed m. p. and infrared spectrum) with an authentic sample,[5] m. p. 243—245° ($\nu_{max.}$ 812s, 824s, 904, 946, 1090w, 1160s, 1188, 1226, 1256, 1360vs, 1438, 1520vs, and 1600vs cm.$^{-1}$), followed by rather sticky material and then by the main red compound (IV or V), m. p. 234—238° unchanged after recrystallisation from acetic anhydride; $\nu_{max.}$ 693w, 750w, 818, 865, 945, 967, 1060, 1100, 1175, 1225, 1275, 1350s, 1440, 1510, 1590vs, 1660, 1880w, 2850w, and 3400 cm.$^{-1}$ (Found: C, 62·2; H, 6·3; N, 21·1; O, 10·4. Calc. for $C_{17}H_{21}O_2N_5$: C, 62·4; H, 6·5; N, 21·4; O, 9·7%). (Lippmann and Fleissner give m. p. 221—222°.) The final washings yielded a small amount of a red varnish.

The red compound gave a crimson solution in concentrated hydrochloric acid; when this solution was kept overnight only about a quarter of the material could be recovered.

*Interaction of diethyl-*p*-nitrosoaniline with potassium cyanide.* Under the same conditions diethyl-*p*-nitrosoaniline (5 g.) gave material (1·5 g.), which on elution from alumina by chloroform gave successively brownish, sticky material, then red crops, m. p. 185—197°, m. p. 185—195°, m. p. 176—190°, m. p. 200—210°, and m. p. 200—215°, and finally a red varnish. The first two crops on recrystallisation from boiling ethanol gave red-blue prisms, m. p. 200—202° (Found: C, 66·5; H, 7·7; N, 18·4. Calc. for $C_{21}H_{29}N_5O_2$: C, 65·8; H, 7·6; N, 18·3%)

[3] Nisbet, *J.*, 1927, 2081.
[4] Sandmeyer, *Ber.*, 1885, **18**, 1492.
[5] Schraube, *Ber.*, 1875, **8**, 619.

(Lippmann and Fleissner [1] give m. p. 169—171°); $\nu_{max.}$ 718w, 733w, 786, 820, 885, 1012, 1075, 1100, 1160, 1185, 1265, 1350, 1390, 1440, 1510, 1590vs, 1655, 2650w, 2850, 2950, and 3350 cm.$^{-1}$. The small, later crops gave an unidentified orange, crystalline powder, m. p. 220—222° (Found: C, 64·4; H, 6·7; N, 20·0%); $\nu_{max.}$ 782w, 812w, 825w, 1015w, 1080, 1160w, 1195, 1235sh, 1260, 1350, 1370w, 1390w, 1442, 1500, 1590vs, 1660, 2220w. After solution in acetic anhydride this gave rise to red prisms, m. p. 254°.

Interaction of ethylmethyl-p-*nitrosoaniline with potassium cyanide.* By the above method this base gave a *compound* which crystallised from benzene in red-blue prisms, m. p. 181—184° (Found: C, 64·6; H, 6·9. $C_{19}H_{25}N_5O_2$ requires C, 64·2; H, 7·0%); $\nu_{max.}$ 718, 741, 820vs, 850, 885, 915, 950, 990, 1060, 1075, 1100, 1160, 1190, 1220, 1250, 1265, 1360, 1445, 1510, 1595, and 1660 cm.$^{-1}$. It was unchanged by boiling acetic anhydride.

The authors are indebted to Mr. B. Semple, B.Sc., for the n.m.r. spectra and to Mr. J. M. Philp, A. H-W. C., for the mass spectra.

HERIOT-WATT COLLEGE, EDINBURGH. [*Received, July 7th,* 1964.]

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288. *Propionyloxydifluoroborane.*

By A. K. HOLLIDAY, G. N. JESSOP, and F. B. TAYLOR.

THE reaction of anhydrous acetic acid with trimethylborane gives acetoxydimethylborane which is polymerised through carboxylate-group bridges in the solid state but monomeric in the vapour phase.[1] Although the reaction of propionic acid with methyldichloroborane gives the expected yield of methane,[2] the isolation of the other product, propionyloxydichloroborane, has not been reported, and the only similar fluoroborane known is the rather ill-defined $(MeCO_2 \cdot BF)_2$.[3] We have prepared propionyloxydifluoroborane in almost quantitative yield by reaction of propionic acid with diboron tetrafluoride:

$$B_2F_4 + 2EtCO_2H \longrightarrow 2EtCO_2 \cdot BF_2 + H_2$$

The white crystalline product had m. p. 117° and could be sublimed below 100° without change; it was rapidly hydrolysed by water. Molecular weight determination in benzene showed it to be monomeric, and the solid, when warmed with trimethylamine, gave a white solid 1 : 1 adduct. However, the infrared spectrum of the solid $EtCO_2 \cdot BF_2$ showed a carbonyl stretching frequency at 1612 cm.$^{-1}$, a shift of 115 from the value (1727) for the normal carboxylate C=O stretching. This shift is close to the value of 119 cm.$^{-1}$ observed in the C=O stretching of ethyl acetate co-ordinated to boron trifluoride,[4] and implies either intermolecular bridging or intramolecular chelation by the $EtCO_2$ group. The shift was completely removed when the solid $EtCO_2 \cdot BF_2$ was dissolved in a donor solvent (*e.g.*, ether) or converted into the 1 : 1 trimethylamine adduct. These latter observations, and the resemblance in physical properties (high m. p. and low volatility) to the bridged acetoxydimethylborane,[1] favour a polymeric bridge structure rather than a chelated monomer for which low m. p. and appreciable volatility might be expected.

Experimental.—Diboron tetrafluoride was prepared by fluorination of diboron tetrachloride; the propionic acid was dried over phosphorus(v) oxide for several days. Molecular weight measurements were carried out by determination of the vapour-pressure lowering of benzene, in an apparatus designed for air- and moisture-sensitive materials.[5] Reactions were carried out *in vacuo* using millimole quantities. In a typical reaction, diboron tetrafluoride 0·86 mmole) and propionic acid (4·93 mmoles) were mixed at −196° and warmed slowly to 20°; when the vigorous reaction ceased, propionic acid (3·28 mmoles) was recovered and a

[1] J. Goubeau and H. Lehmann, *Z. anorg. Chem.*, 1963, **322**, 224.
[2] A. G. Massey, *J.*, 1960, 5264.
[3] J. W. Kroeger, F. J. Sowa, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1937, **59**, 965.
[4] M. F. Lappert, *J.*, 1962, 542.
[5] D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, 1963, **59**, 2058.

white crystalline solid remained; the only volatile products were hydrogen and a small amount of silicon tetrafluoride. The solid *product* (0·200 g. = 1·64 mmoles of $EtCO_2 \cdot BF_2$) had *M* 125; hydrolysis gave boric acid (1·69 mmoles), propionic acid (1·67 mmoles), and fluoride (3·14 mmoles) (*M* for $EtCO_2 \cdot BF_2$, 122). In a reaction with trimethylamine (4·36 mmoles) the propionyloxyborane (3·66 moles) and amine were warmed to 80°; on cooling, trimethylamine (0·56 mmole) and propionic acid (0·02 mmole) were the only volatile materials, and the solid product had $EtCO_2 \cdot BF_2/NMe_3 = 1·04$.

DONNAN CHEMISTRY LABORATORIES,
THE UNIVERSITY OF LIVERPOOL.

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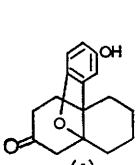
289. *Hydroaromatic Steroid Hormones. Part XI.* A Steroid with an Angular Aromatic Ring.*

By A. J. BIRCH and J. B. SIDDALL.

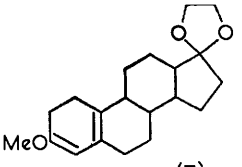
REPLACEMENT of 10β-Me by 10β-H in the steroid hormone series leads to interesting alterations in biological properties.[1] Accordingly, it would be of interest to replace it by other groupings to examine the effects on biological activities. The oxidation of the 10β-Me recently accomplished [2] makes this possible in the case of aliphatic groups. We report an attempt to introduce an aromatic ring of undefined stereochemistry.

We have reported [3] a series of reactions involving a Diels–Alder reaction of a benzoquinone and a 1-methoxycyclohexa-1,3-diene and reaction of the product with acid to form a compound containing only one new carbon–carbon bond. In appropriate cases a quaternary carbon atom results: 1,2,3,4,7,8-hexahydro-6-methoxynaphthalene and benzoquinone yield eventually (I) in about 30% yield.

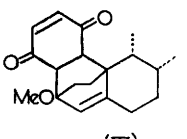
Compound (II) is available [4] by base-catalysed conjugation of the corresponding 1,4-dihydro-œstrone derivative. The main product of its reaction with benzoquinone was œstrone methyl ether 17-ethylene ketal. From the residue by chromatography was



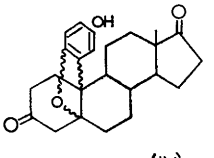
(I)



(II)



(III)



(IV)

obtained unchanged (II) and a yellow gum (8% yield) which appeared to contain the desired (III) since it had $\lambda_{max.}$ 221 mμ (ε 6300), and $\nu_{max.}$ 1630 and 1665 cm.$^{-1}$ due to the enedione system.[3] Additional bands at 1730 and 1752 cm.$^{-1}$ were probably due to the presence of some cage-compound formed readily in such cases by daylight. Since it could not be crystallised it was submitted to acidic rearrangement conditions and chromatographed to give a crystalline phenolic compound $C_{24}H_{28}O_4$ (2% overall yield) with the properties expected for (IV); $\lambda_{max.}$ 304 mμ (ε 5420), $\nu_{max.}$ 1697, 1732, and 3250 cm.$^{-1}$. Because of the very poor yield of adduct due to oxidation of the dihydrobenzene ring by the quinone, the reaction was not further pursued.

Experimental.—The diene (II) (990 mg.) was refluxed with resublimed benzoquinone (486 mg.) in benzene (10 c.c.) for 8 hr. The cooled solution was placed on a column of alumina (Spence H; 50 g.) after filtration. Elution with benzene gave œstrone methyl ether 17-ethylene ketal

* Part X, Birch, Siddall, and G. S. Subba Rao, *J.*, 1964, 3309.

[1] Fieser and Fieser, "Steroids," Reinhold, New York, 1959.
[2] Bowers, Ibanez, Cabezan, Ringold, *Chem. and Ind.*, 1960, 1299; Heusler, Kalvoda, Meystre, Ueberwasswer, Wieland, Anner, and Wettstein, *Experientia*, 1962, **18**, B464.
[3] Birch, Butler, and Siddall, *J.*, 1964, 2932, 2941.
[4] Birch, Graves, and Siddall, *J.*, 1963, 4234.

(823 mg.), followed by unchanged (II) (74 mg.). Elution with 10—20% ether in benzene gave a yellow gum (71 mg.) (spectra above). Acid rearrangement under the usual conditions [3] gave a gum which was chromatographed on alumina (Spence H). Elution with ether containing methanol (10%) gave a gum (24 mg.) which crystallised from methanol to give the *phenol* (IV), m. p. 287—298° (decomp.) (Found: C, 75·8; H, 7·25. $C_{24}H_{28}O_4$ requires C, 75·8; H, 7·4%). Variation of conditions in the original diene reaction: varying periods of time and the use of acetone as solvent, gave lower yields.

We are indebted to the D.S.I.R. for a scholarship (to J. B. S.) and to Syntex S.A. for gifts for œstrone.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANCHESTER. [*Received, July 22nd,* 1964.]

290. *Glycerol* 1,2-*Carbonate.*

By JILL CUNNINGHAM and ROY GIGG.

GLYCEROL 1,2-CARBONATE was required as an intermediate for synthetic studies in connection with the plasmalogens. The only reported synthesis of a monomeric glycerol carbonate (by a trans-esterification reaction between glycerol and ethylene carbonate) is in the patent literature.[1] Previous attempts to prepare a monomeric glycerol carbonate by trans-esterification reactions between glycerol and organic carbonates had led to the formation of the crystalline di(glycerol 1,2-carbonate) 3,3′-carbonate and of more highly polymerised materials.[2] In order to characterise the material prepared by the patent procedure,[1] a further synthesis via 3-*O*-benzylglycerol was undertaken. 3-*O*-Benzylglycerol 1,2-carbonate was prepared by a reaction between 3-*O*-benzylglycerol and diethyl carbonate. The benzyl group was removed by catalytic hydrogenation to give glycerol 1,2-carbonate which had properties identical with those of the material prepared by the trans-esterification reaction between glycerol and ethylene carbonate, and which gave identical α-naphthylurethane and triphenylmethyl ether derivatives. The triphenylmethyl ether derivative gave 1-*O*-triphenylmethylglycerol on alkaline hydrolysis, proving the position of the carbonate ring. Previous studies [3] have distinguished between the structures of 1-*O*-triphenylmethylglycerol (m. p. 109—110°) and 2-*O*-triphenylmethylglycerol (m. p. 143—144°).

Glycerol 1,2-carbonate is a hygroscopic liquid immiscible with ether, benzene, and chloroform but miscible with water, ethyl acetate, and other polar solvents.

Experimental.—3-O-*Benzylglycerol* 1,2-*carbonate.* 3-*O*-Benzylglycerol [4] (50 g.), ethyl carbonate (100 ml.), and sodium hydrogen carbonate (500 mg.) were heated under reflux in a flask fitted with a fractionating column. Ethanol (30 ml.) was collected from the top of the column over a period of 8 hr. The mixture was washed with saturated potassium chloride solution, dried, and distilled. After removal of the excess ethyl carbonate, distillation gave 3-O-*benzylglycerol* 1,2-*carbonate,* b. p. 150°/0·08 mm. (46 g., 80%), $\nu_{max.}$ 1790 cm.$^{-1}$ (C=O) (Found: C, 63·4; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%).

Glycerol 1,2-*carbonate.* 3-*O*-Benzylglycerol 1,2-carbonate (12 g.) in acetic acid (40 ml.) was treated with hydrogen at atmospheric pressure in the presence of 10% palladium on charcoal (500 mg.) until uptake was complete (20 hr.). Removal of the catalyst and the solvent and distillation of the residue gave glycerol 1,2-carbonate, b. p. 130°/0·08 mm. (6·1 g., 90%), $\nu_{max.}$ 1760—1800br cm.$^{-1}$ (C=O) (Found: C, 40·3; H, 5·4. Calc. for $C_4H_6O_4$: C, 40·7; H, 5·1%). The α-*naphthylurethane* (prepared in pyridine and recrystallised from ethanol), m. p. 130—132° (decomp.) (Found: C, 62·8; H, 4·6; N, 5·0. $C_{15}H_{13}NO_5$ requires C, 62·7; H, 4·6; N, 4·9%).

3-O-*Triphenylmethylglycerol* 1,2-*carbonate.* A solution of glycerol 1,2-carbonate (1 g.) and

[1] J. B. Bell, V. A. Currier, and J. D. Malkemus, U.S.P. 2,915,529/1959 (*Chem. Abs.*, 1960, **54**, 6552.)
[2] L. Hough, J. E. Priddle, and R. S. Theobald, *Adv. Carbohydrate Chem.*, 1960, **15**, 91; L. Hough and J. E. Priddle, *J.*, 1961, 581.
[3] P. E. Verkade, *Rec. Trav. chim.*, 1938, **57**, 824.
[4] R. J. Howe and T. Malkin, *J.*, 1951, 2663.

triphenylmethyl chloride (2·4 g.) in pyridine (10 ml.) was heated on the steam-bath for 1 hr. The cooled solution was poured into a mixture of ice–water (200 ml.) and ether (100 ml.) and the precipitated solid (2·2 g.) was collected, washed with water and ether, and dried. Recrystallisation from ethanol–chloroform (3 : 1) gave needles of 3-O-*triphenylmethylglycerol* 1,2-*carbonate*, (1·9 g., 62%), m. p. 224—226°, $\nu_{max.}$ 1785 cm.$^{-1}$ (Found: C, 76·5; H, 5·5. $C_{23}H_{20}O_4$ requires C, 76·6; H, 5·6%).

1-O-*Triphenylmethylglycerol*. 3-*O*-Triphenylmethylglycerol 1,2-carbonate (1 g.) in ethanol (25 ml.) and N-sodium hydroxide solution (8 ml.) was heated on the steam-bath for 15 min. Solid carbon dioxide was added to destroy the excess hydroxide and the ethanol was evaporated under reduced pressure. The residue was extracted with ether and the extract dried over magnesium sulphate. Evaporation of the ether and crystallisation of the residue from cyclohexane gave 1-*O*-triphenylmethylglycerol as needles (0·71 g., 77%), m. p. 110—112° (Found: C, 78·8; H, 6·8. Calc. for $C_{22}H_{22}O_3$: C, 79·0; H, 6·6%) (lit.,[3] m. p. 109—110°).

NATIONAL INSTITUTE FOR MEDICAL RESEARCH, LONDON N.W.7. [*Received, July 23rd*, 1964.]

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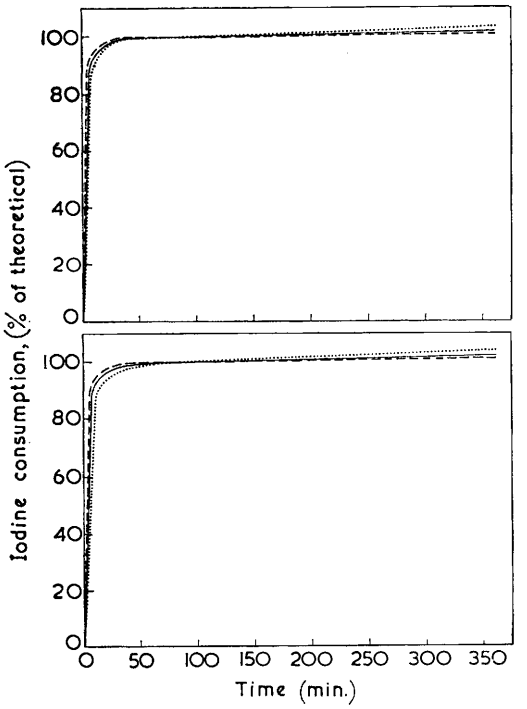
291. *Determination of Reducing Oligosaccharides with Alkaline Iodine.*

By K. SELBY.

SATISFACTORY methods are available for the determination of individual reducing oligosaccharides although their empirical nature precludes their application to mixtures.[1] Contrary to the opinions of some authors [1,2] Colbran and Nevell [3,4] have shown that stoicheiometric determination of glucose by the so-called hypoidite method is possible if the composition of the reagent is chosen with care. The two most-quoted disadvantages are overoxidation and lack of sensitivity because the loss of available iodine by disproportionation of hypoiodite to iodide and iodate demands a large excess of oxidant. Addition of potassium iodide to the reaction mixture was known to retard disproportionation, but Colbran and Nevell showed that it also increased the rate of overoxidation. With glucose, a satisfactory compromise was reached by ensuring that the reaction mixture was 0·01M in iodine and contained 8 g./l. of potassium iodide. The oxidation was done at 20° in a sodium carbonate : sodium hydrogen carbonate buffer. The method has now been extended to some simple reducing oligosaccharides and in each case, under Colbran and Nevell's conditions, the main reaction, oxidation of the hemiacetal group, is complete within 60 minutes (Figure). The proportion of oxidant consumed by side-reactions is related to the number of glucose residues in the molecule; after 5 hours it is 1% for glucose, 2% for maltose or cellobiose, 3% for maltotriose, and 4% for cellotetraose. If, as a standard procedure, the iodine consumed is measured after 80 minutes, it differs from the stoicheiometric amount by less than 0·5%. Colbran and Nevell found that if oxidation was slow, much of the iodine initially available was lost by disproportionation. The oxidation of the hemiacetal group in simple oligosaccharides is rapid so that in our experience a 100% excess of iodine is adequate allowance for that lost by disproportionation. Should the iodine colour disappear within 80 minutes, however, it is possible that oxidation is incomplete and the assay should be repeated using a less concentrated solution of the oligosaccharide.

Another criticism made of the alkaline iodine reagent is that the optimum pH is too high for some alkali-sensitive sugars,[1] but we have shown that treatment of cellobiose with the carbonate : hydrogen carbonate buffer solution for 20 hours at 20° did not change the extent of oxidation when iodine was subsequently added. We conclude that under the

[1] J. E. Hodge and B. T. Hofreiter, in "Methods in Carbohydrate Chemistry," ed. R. L. Whistler and M. L. Wolfrom, Academic Press, New York, 1962, Vol. 1, p. 380.
[2] H. F. Launer and Y. Tomimatsu, *Analyt. Chem.*, 1961, **33**, 79.
[3] R. L. Colbran and T. P. Nevell, *J.*, 1957, 2427.
[4] R. L. Colbran and T. P. Nevell, *J. Textile Inst.*, 1958, **49**, T333.



Rate of oxidation of several reducing oligosaccharides by alkaline iodine.

conditions outlined, simple reducing oligosaccharides can be quickly and accurately determined. Values for the average chain-length of mixtures of these substances can thus be obtained.

Experimental.—To the aldose solution (3 ml. containing up to 24 mequiv.) at 20° were added, also at 20°, buffer solution (1 ml.; 0·75M in sodium carbonate and 0·05M in sodium hydrogen carbonate; pH 10·8) and 0·05N-iodine solution (1 ml.) containing potassium iodide (40 g./l.). The reaction vessel was stoppered and kept at 20° for 80 min. An excess of 2N-sulphuric acid (2 ml.) was then added and the liberated iodine was titrated with 0·01N-sodium thiosulphate using sodium starch glycollate as internal indicator. The titration could be reproduced in duplicate experiments to within 0·01 ml. If a potentiometric endpoint was used the sensitivity could be further increased by titrating with 0·002N-sodium thiosulphate.

The maltotriose and cellotetraose were a gift from Dr. J. R. Turvey. This work was supported by a grant from Glaxo Laboratories Ltd., to whom grateful acknowledgment is made.

SHIRLEY INSTITUTE, DIDSBURY, MANCHESTER 20. [*Received, July 27th*, 1964.]

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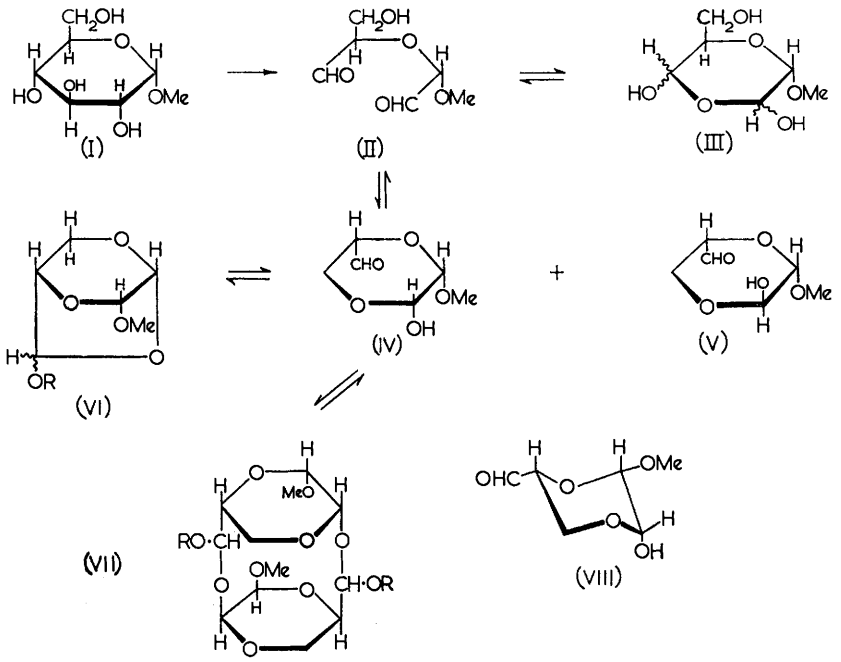
292. *A Dimeric Hemiacetal from the Periodate Oxidation of Methyl α-D-Glucopyranoside.*

By M. CANTLEY, J. R. HOLKER, and L. HOUGH.

OXIDATION of methyl α-D-glucopyranoside (I) with periodate normally yields a syrup, from which Guernet and his co-workers [1] have recently isolated a solid compound, believed to be the hemialdal (III) analogous to the crystalline products prepared from methyl β-L-arabinopyranoside and methyl 6-deoxy-α-L-mannopyranoside.[2] We have now isolated a crystalline compound in 30% yield from this syrupy reaction product. Its elementary

[1] M. Guernet, A. Jurado-Soler, and P. Malangeau, *Bull. Soc. chim. France*, 1963, 1188.
[2] I. J. Goldstein, B. A. Lewis, and F. Smith, *J. Amer. Chem. Soc.*, 1958, **80**, 939.

composition, $C_6H_{10}O_5$, excludes the hemialdal structure (III), whilst absence of C=O absorption in its infrared spectrum shows that it is neither the acyclic derivative (II) nor the aldehydo-hemiacetal (IV), which hydrogenation studies [3] suggest may be present in the syrup. Methylation of our compound with Purdie's reagent gave an ether with m. p. and solubility characteristics in good agreement with those reported by Goldstein and Smith [4] for a derivative obtained by direct methylation of the syrupy oxidation product of methyl α-D-glucopyranoside, to which they assigned the bicyclic structure (VI; R = Me). Molecular weight determinations, however, show this ether to be dimeric and we now suggest that it is the di-intermolecular acetal (VII; R = Me); a dimeric di-*p*-nitrobenzoate (VII; R = CO·C_6H_4·NO_2-*p*) and diacetate (VII; R = Ac) have also been



prepared. The optical rotation of the parent compound in water rose from +102 to +120° in 20 hr., the latter value corresponding to that quoted by Hudson and Jackson [5] for the syrupy "dialdehyde," and whilst the molecular weight in water agreed with a monomeric structure, solubility difficulties precluded measurements in organic solvents. However, a mass spectrum revealed weak ions of mass 324 and 322, corresponding to the dimer (VII; R = H) and a dehydrogenation product, as well as ions of mass 162 and 144, corresponding to a monomer and a dehydration product thereof. Furthermore, an infrared spectrum of the solid in Nujol exhibits two strong bands in the O–H region (3440 and 3550 $cm.^{-1}$; Δν about 100 $cm.^{-1}$), which, considered with the absence of C=O absorption, is inconsistent with any monomeric structure containing less than two OH groups. We suggest, therefore, that our crystalline compound is the dimer (VII; R = H) and that this can dissociate thermally or on dissolution in water. The dimer can arise by intermolecular hemiacetal formation between two molecules of the 5-formyl-1-hydroxy-3-methoxy-1,4-dioxan (IV or V). Molecular models reveal that the D-*ribo*-form (IV) can retain its stable chair conformation (VIII) in the dimer, whereas the D-*arabino*-analogue (V)

[3] J. E. Cadotte, G. G. S. Dutton, I. J. Goldstein, B. A. Lewis, F. Smith, and J. W. van Cleve, *J. Amer. Chem. Soc.*, 1957, **79**, 691.
[4] I. J. Goldstein and F. Smith, *J. Amer. Chem. Soc.*, 1960, **82**, 3421.
[5] C. S. Hudson and E. L. Jackson, *J. Amer. Chem. Soc.*, 1937, **59**, 994.

requires a boat conformation. The intramolecular hemiacetal (VI) also requires a bridged boat conformation and hence the formation of the dimer (VII; R = H) from (IV) will be the more favourable process.

Experimental.—Methyl α-D-glucopyranoside (19·2 g.) was oxidised with sodium metaperiodate (45 g.) in water (1 l.) for 48 hr. at 20° in the dark. Most of the iodate and residual periodate was then precipitated with barium chloride (22 g.) in water (100 ml.). The filtered solution was concentrated under reduced pressure at 50° to a thick syrup (*A*), which was extracted with cold acetonitrile to leave residual inorganic salts. The extract was again evaporated under reduced pressure, finally at 70° for 2 hr., and the residue dissolved in hot acetonitrile. The solution deposited a white solid on cooling. Repeated evaporation of the mother-liquors, finally at 70°, and extraction with fresh acetonitrile, afforded more of the same material (total yield, 4·5 g.). Recrystallisation of the solid from acetic acid, *NN*-dimethylformamide, or a large volume of light petroleum (b. p. 40—60°) gave the *dimeric hemiacetal* (VII; R = H) of D-*ribo*-5-formyl-2-hydroxy-3-methoxy-1,4-dioxan (IV) as fine white needles, m. p. 168—169°, $[\alpha]_D$ +102° (*c* 1·27 in water; 20 min.) ⟶ +120° (equilibrium value; 20 hr.) [Found: C, 44·25; H, 6·1; OMe, 19·1; active H, 0·7%; *M* (Rast), 143 (v. p. osmometer), 151, 155 (Ramsay [6]), 167, 173. $C_{12}H_{20}O_{10}$ requires C, 44·4; H, 6·2; OMe, 19·1; active H, 0·6%; *M*, 324].

Extracts of the syrup *A* with ethyl acetate and with acetone also gave crystals of dimer when left for several months. Paper chromatography on Whatman No. 1 paper, using butan-1-ol–ethanol–water (40 : 11 : 19 v/v) gave a single spot, R_F 0·81, detected with ammoniacal silver nitrate.

A suspension of the dimer (0·5 g.) and silver oxide (1·4 g.) in methyl iodide (10 ml.) was boiled under reflux overnight with a second addition of oxide (1 g.) after 2 hr. The mixture, containing a crystalline solid, was then evaporated to dryness and extracted with hot chloroform (20 ml.). Crystallisation of the extracted material from ethanol (50 ml.) gave the *di*-O-*methyl ether* (VII; R = Me) as colourless needles, m. p. 251—253·5° (sublimes) [Found: C, 47·8; H, 6·7; OMe, 35·0%; *M* (v.p. osmometer), 355. $C_{14}H_{24}O_{10}$ requires C, 47·6; H, 6·8; OMe, 35·2%; *M*, 352]. The same product, which is soluble in acetone, but only sparingly soluble in methanol and ethanol, was obtained on methylation at 20° for 24 hr.

The dimer (1 g.) was acetylated with acetic anhydride (3 ml.) in pyridine (3 ml.) for 24 hr. at 20° and finally for 1 hr. at 100°, to give the *di*-O-*acetyl* derivative (VII; R = Ac), isolated as a *hydrate*, m. p. 196—198° after crystallisation from benzene [Found: C, 45·2; H, 6·0%; *M* (v.p. osmometer), 396, 387. $C_{16}H_{24}O_{12},H_2O$ requires C, 45·1; H, 6·1%; *M*, 426].

Treatment of the dimer (0·5 g.) with *p*-nitrobenzoyl chloride (1 g.) in pyridine (5 ml.) for 16 hr. at 20° afforded the *di*-p-*nitrobenzoate* (VII; R = CO·$C_6H_4NO_2$-*p*), m. p. 213—217° after three crystallisations from acetonitrile [Found: C, 49·5; H, 4·5; N, 4·7%; *M* (ebullioscopic in acetone), 569. $C_{26}H_{26}N_2O_{16}$ requires C, 50·2; H, 4·2; N, 4·5%; *M*, 622].

We thank Dr. D. Ball for determining molecular weights by vapour-pressure osmometry and Dr. A. E. Williams for the mass spectrum. The work in Manchester (J. R. H.) was supported by the U.S. Department of Army, through its European Office, and one of us (M. C.) thanks the D.S.I.R. for a maintenance grant.

THE UNIVERSITY, BRISTOL.
SHIRLEY INSTITUTE, MANCHESTER 20.

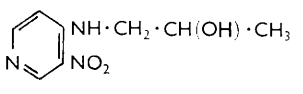
[*Received, July 30th*, 1964.]

[6] J. A. Ramsay, *J. Exp. Biol.*, 1949, **26**, 57.

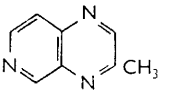
293. *An Unambiguous Synthesis of 3-Methyl-1,4,6-triazanaphthalene.*

By J. D. Hepworth and E. Tittensor.

Recent interest [1,2] in the synthesis of unsymmetrically substituted 1,4,6-triazanaphthalenes prompts us to report some of our findings. As part of a study of the condensations between diaminopyridines and unsymmetrical *o*-dicarbonyl compounds, 3-hydroxy-, 3-hydroxy-2-methyl-, and 3-hydroxy-2-phenyl-1,4,6-triazanaphthalene have been prepared by unequivocal routes. The properties of the first two compounds were identical with those reported.[2]



(I)



(II)

In addition, 3-methyl-1,4,6-triazanaphthalene (II) has been synthesised by the reaction of 4-chloro-3-nitropyridine with 2-hydroxypropylamine to give 4-2′-hydroxypropylamino-3-nitropyridine (I), which was then reduced to the 3-amino-derivative. Cyclisation, followed by oxidation of the resulting tetrahydrotriazanaphthalene gave the required triazanaphthalene.

Experimental.—Melting points were taken on a Kofler hot-stage apparatus.

4-2′-*Hydroxypropylamino*-3-*nitropyridine.* 4-Chloro-3-nitropyridine (7·9 g.) was added to a solution of 2-hydroxypropylamine (7·5 g.) in ether (150 ml.) by means of a Soxhlet extractor, and the mixture refluxed for 3 hr. Removal of solvent and crystallisation from benzene gave 4-2′-*hydroxypropylamino*-3-*nitropyridine* (71%), m. p. 138—139°, as lemon-yellow needles (Found: C, 48·4; H, 5·4; N, 21·7. $C_8H_{11}N_3O_3$ requires C, 48·7; H, 5·6; N, 21·3%).

3-*Amino*-4-2′-*hydroxypropylaminopyridine.* 4-2′-Hydroxypropylamino-3-nitropyridine (7·0 g.), palladium–charcoal (1 g.; 10%), and ethanol (50 ml.) were shaken in hydrogen at room temperature and pressure. Filtration, evaporation, and crystallisation from ethanol gave 3-*amino*-4-2′-*hydroxypropylaminopyridine* (93%), m. p. 169—170° (Found: C, 57·0; H, 7·8; N, 25·4. $C_8H_{13}N_3O$ requires C, 57·5; H, 7·8; N, 25·2%). The *benzoate*, m. p. 206—207°, formed needles from methylated spirits (Found: C, 66·5; H, 6·2. $C_{15}H_{17}N_3O_2$ requires C, 66·4; H, 6·3%); the *picrate*, prepared in alcohol, had m. p. 150—151° (Found: C, 41·9; H, 4·1; N, 21·4. $C_{14}H_{16}N_6O_8$ requires C, 42·4; H, 4·0; N, 21·2%).

1,2,3,4-*Tetrahydro*-3-*methyl*-1,4,6-*triazanaphthalene.* 3-Amino-4-2′-hydroxypropylaminopyridine (1·4 g.) was boiled for 9 hr. with hydrobromic acid (3 ml.; *d* 1·5). Evaporation and crystallisation from ethanol gave the *hydrobromide* as needles, m. p. 185—186° (Found: C, 41·9; H, 5·7; Br, 34·3; N, 18·1. $C_8H_{12}BrN_3$ requires C, 41·7; H, 5·2; Br, 34·8; N, 18·3%). The hydrobromide, in the minimum of cold water, was basified with saturated potassium carbonate. Extraction with chloroform (5 × 5 ml.), followed by drying (Na_2SO_4) and removal of the solvent gave an oil, whose *picrate*, m. p. 168—169°, was crystallised from ethanol (Found: C, 44·5; H, 3·9; N, 22·2. $C_{14}H_{14}N_6O_7$ requires C, 44·4; H, 3·7; N, 22·2%).

3-*Methyl*-1,4,6-*triazanaphthalene.* 1,2,3,4-Tetrahydro-3-methyl-1,4,6-triazanaphthalene (1·0 g.) and palladium–charcoal (0·2 g.; 30%) were heated at 180—190° for 1 hr. Extraction of the residue with light petroleum (b. p. 80—100°) gave a solid which, after sublimation and crystallisation from light petroleum, yielded 3-*methyl*-1,4,6-*triazanaphthalene*, m. p. 84·5—85°, as needles which slowly darkened on exposure to air (Found: C, 66·2; H, 5·0; N, 28·8. $C_8H_7N_3$ requires C, 66·2; H, 4·9; N, 28·9%); $\lambda_{max.}$ 231 (ε 24,550), 309 (ε 4,100), and 317 (ε 3,900) in 99% ethanol.

We thank Imperial Chemical Industries Limited for a research scholarship (to J. D. H.) and for a grant.

Department of Chemistry, Colour Chemistry and Dyeing, College of Technology, Huddersfield. [*Received, July 29th,* 1964.]

[1] J. W. Clark-Lewis and R. P. Singh, *J.*, 1962, 3162.
[2] A. Albert and G. B. Barlin, *J.*, 1963, 5156.

294. *The Lattice Types of Some* Na_2MF_6 *Complexes.*

By D. H. Brown, K. R. Dixon, R. D. W. Kemmitt, and D. W. A. Sharp.

The lattice types of complex fluorides of stoicheiometry $Na_2M^{IV}F_6$ have previously been discussed in terms of the hexagonal sodium hexafluorosilicate structure.[1] Complete structural determinations have been carried out on sodium hexafluorosilicate(IV) and hexafluorogermanate(IV), and the co-ordination about the silicon or germanium atoms is an octahedral arrangement of fluorine atoms.[2] These complexes are isomorphous with lithium hexafluorozirconate, Li_2ZrF_6.[3] The γ-forms of sodium hexafluorouranate(IV) [4] and sodium hexafluoropraseodymate(IV) [5] are, however, orthorhombic, the co-ordination number about the uranium atom being eight.[6] Such structures would be expected to be more stable with larger atoms, M, in the Na_2MF_6 lattice.

Results of a study of the structures of a larger range of Na_2MF_6 complexes are given in the Table, where it is shown that there is a clear relation between the structure adopted

Complex	Radius of M^{4+} ion (Å) [a]	Lattice type	Lattice parameters (Å) a	c	Complex	Radius of M^{4+} ion (Å) [a]	Lattice type	Lattice parameters (Å) a	b	c
Na_2SiF_6 [c]	0·41	H	8·86	5·02	Na_2OsF_6 [b]		O	5·80	4·50	10·14
Na_2GeF_6 [c]	0·53	H	9·10	5·13	Na_2ReF_6 [b]		O	5·81	4·49	10·1
Na_2MnF_6 [c]	0·54	H	9·03	5·15	Na_2MoF_6 [b]		O	5·76	4·48	10·14
Na_2CrF_6 [b]	0·56	H	9·14	5·15	Na_2SnF_6 [b]	0·71	O	5·80	4·50	10·1
Na_2TiF_6 [c]	0·68	H	9·21	5·15	Na_2PbF_6 [b]	0·84	O	5·85	4·55	10·1
Na_2PdF_6 [d]		H	9·23	5·25	Na_2PrF_6 [f]	0·92	O	5·54	3·97	11·57
Na_2RhF_6 [d]		H	9·32	5·32	γ-Na_2UF_6 [g]	0·97	O	5·56	4·01	11·64
Na_2RuF_6 [b]		H	9·32	5·15						
Na_2PtF_6 [e]		H	9·41	5·16						
Na_2IrF_6 [e]		H	9·34	5·11						
Na_2OsF_6 [b]		H	9·36	5·11						

H = hexagonal. O = orthorhombic. [a] L. Pauling, "The Nature of the Chemical Bond," 3rd edn., Oxford University Press, London, 1960. [b] Present work. [c] Ref. 1. [d] B. Cox, D. W. A. Sharp, and A. G. Sharpe, *J.*, 1956, 1242. [e] M. A. Hepworth, P. L. Robinson, and G. J. Westland, *J.*, 1958, 611. [f] Ref. 5. [g] Ref. 4.

and the radius of the M^{4+} ion. The ionic radii of several of the heavier elements are not known, and the order adopted in the Table is that which would be expected from a consideration of the position of the atom in the Periodic Table. This convention gives a consistent structural series, with a change from the hexagonal sodium hexafluorosilicate(IV) structure to the orthorhombic γ-sodium hexafluorouranate(IV) structure at sodium hexafluoro-osmate(IV), which exists in both crystalline forms. There appears to be a slight departure from the expected order of lattice parameters for sodium hexafluoroplatinate(IV).

It has thus been established that the lattice adopted by $Na_2M^{IV}F_6$ complexes depends upon the size of the M^{4+} ion. The major omission from the Table is that of the unknown sodium hexafluorotechnetate(IV), Na_2TcF_6, which should be very similar to sodium hexafluoro-osmate(IV), and would possibly exist in both lattice forms.

Experimental.—*X*-Ray powder photographs were obtained by using Cu K_α-radiation. Lindemann glass capillary tubes were filled with the samples in the dry-box, and the tubes were sealed with warm picein wax. Photographs were taken in a 9-cm. powder-camera and were indexed on a Ferranti Sirius computer.

Analytical results were obtained for all compounds by standard text-book and literature methods.

Sodium hexafluorochromate(IV). This complex was obtained by passing fluorine over a 2 : 1 molar mixture of sodium chloride and chromium(III) chloride at 375°. Some chromium

[1] B. Cox, *J.*, 1954, 3251.
[2] C. Cipriani, *Rend. Soc. Mineral. Ital.*, 1955, **11**, 58.
[3] R. Hoppe and W. Dahne, *Naturwiss.*, 1960, **17**, 397.
[4] W. H. Zachariasen, *J. Amer. Chem. Soc.*, 1948, **70**, 2147.
[5] L. B. Asprey and T. K. Keenan, *J. Inorg. Nuclear Chem.*, 1961, **16**, 260.
[6] W. H. Zachariasen, *Acta Cryst.*, 1948, **1**, 265.

sublimed out of the mixture as one of the higher fluorides, and it was not possible to obtain consistent analytical data; however, the *X*-ray powder photograph clearly showed the presence of sodium hexafluorochromate(IV), isomorphous with sodium hexafluorosilicate.

Sodium hexafluororuthenate(IV) and *hexafluoro-osmate*(IV) resulted from the action of water on sodium hexafluororuthenate(V) and hexafluoro-osmate(V), respectively. The latter two complexes were prepared by the action of bromine trifluoride on an equimolar mixture of sodium chloride and ruthenium trichloride or osmium tetrabromide. The tetrapositive complexes were precipitated from aqueous solution with ethanol (Found: Ru, 37·4; Na_2RuF_6 requires Ru, 38·7%. Found: Os, 53·8. Na_2OsF_6 requires Os, 54·3%). In the case of sodium hexafluoro-osmate(IV), the hexagonal form was produced by this method, while slow crystallisation at 0° gave the orthorhombic form. On standing, the hexagonal form went slowly over to the orthorhombic form, and precipitation with ethanol frequently gave a mixture of the two phases.

Sodium hexafluororhenate(IV) has been previously indexed on a tetragonal unit-cell [7] and sodium hexafluoromolybdate(IV) on a cubic unit-cell.[8] We are greatly indebted to Drs. A. J. Edwards and R. D. Peacock for allowing us to have access to their *X*-ray powder data, which were re-indexed as shown in the Table.

Sodium hexafluorostannate(IV) *and hexafluoroplumbate*(IV) were prepared by the action of excess of sulphur tetrafluoride on a 2 : 1 molar mixture of sodium chloride and the metal dioxide contained in a stainless-steel bomb. The reaction was carried out at 350° over a period of 12 hr. (Found: Sn, 42·9. Na_2SnF_6 requires Sn, 42·6%. Found: Pb, 56·0. Na_2PbF_6 requires Pb, 56·4%).

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DEPARTMENT OF CHEMISTRY, UNIVERSITY OF STRATHCLYDE,
GLASGOW C.1. [*Received, July* 31*st*, 1964.]

[7] R. D. Peacock, *J.*, 1956, 1291.
[8] A. J. Edwards and R. D. Peacock, *Chem. and Ind.*, 1960, 1441.

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295. *The Synthesis of Some Divinyl Ethers.*

By D. M. JONES and N. F. WOOD.

DIVINYL ETHERS cannot be prepared by many of the methods used for synthesising monovinyl ethers.[1] We have found that pyrolysis of the acetal EtO·CHMe·CH_2·O·CH_2·O·CHMe·OEt, reaction of vinyl chloride with the disodium alcoholates of several diols in an autoclave at 150°, and dehydrochlorination of di-1-chloroalkyl ethers with *NN*-diethylaniline all failed to give the required products. The last reagent converted 1,5-di-(1-chloropropoxy)-pentane into 2-ethyl-1,3-dioxacyclo-octane, which is possibly formed by the splitting from the precursor of one of the chloropropoxy-groups, followed by cyclisation of the monovinyl ether subsequently produced. Hurd and Botteron [2] noted cyclic acetal formation in the dehydrochlorination of some di-1-chloroalkyl ethers with quinoline.

Transvinylation by vinyl acetate in the presence of mercuric sulphate,[3] which is unsuitable [4] for the conversion of alcohols into the corresponding ethers, gave cyclic acetals similar to 2-ethyl-1,3-dioxacyclo-octane with some alkane-αω-diols.[5] The alkali-catalysed reaction of diols with acetylene at atmospheric pressure [6] was extremely slow, whilst dehydrochlorination of di-2-chloroalkyl ethers with potassium hydroxide gave low yields. Vinyl interchange between an alkyl vinyl ether and an alcohol, widely used in the synthesis

[1] O. Wichterle, J. Stepek, and V. Brajko, *Coll. Czech. Chem. Comm.*, 1961, **26**, 1099; W. Reppe, U.S.P. 1,941,108/1933; H. Böhme and H. Bentler, *Chem. Ber.*, 1956, **89**, 1468.
[2] C. D. Hurd and D. G. Botteron, *J. Amer. Chem. Soc.*, 1946, **68**, 1200.
[3] R. L. Adelman, U.S.P. 2,579,411/1951; *J. Amer. Chem. Soc.*, 1953, **75**, 2678.
[4] U. Wyss, *Promotionsarb. Zurich*, 1960, No. 3083.
[5] D. M. Jones and N. F. Wood, unpublished results.
[6] H. M. Teeter, E. J. Dufek, C. B. Coleman, C. A. Glass, E. H. Melvin, and J. C. Cowan, *J. Amer. Oil Chemists' Soc.*, 1956, **33**, 399.

of vinyl ethers [7,8] but hitherto applied to only two diols,[8,9a] has now been extended to the preparation of several divinyl ethers which were required for studies into the cross-linking of cotton cellulose.[10]

Experimental.—*2-Methyl-1,3-dioxacyclo-octane.* Pentane-1,5-diol (52 g.), vinyl acetate (258 g.) containing copper resinate inhibitor, mercuric acetate (0·9 g.), and concentrated sulphuric acid (0·1 g.) were added in that order, with stirring, to a flask at −25°. After 7 hr., the mixture was poured into 5% aqueous sodium carbonate and shaken well. The organic layer was separated, dried (Na_2SO_4), and fractionally distilled, to give the *acetal* (20 g.), b. p. 44—46°/6 mm., n_D^{19} 1·4385 (Found: C, 64·5; H, 10·6. $C_7H_{14}O_2$ requires C, 64·6; H, 10·8%).

2-Ethyl-1,3-dioxacyclo-octane. 1,5-Di-(1-chloropropoxy)pentane was prepared by passing hydrogen chloride gas through propionaldehyde (348 g.) and pentane-1,5-diol (312 g.) at 0°. The crude product was separated, dried ($CaCl_2$), and used without purification since it decomposed when distilled at 105—120°/0·2 mm. Its infrared spectrum was free from O–H stretching

Properties of divinyl ethers.

Ether	Yield (%)	B. p. (°c)	n_D^t	d_4^t	Found (%) C	Found (%) H	Formula	Calc. or Reqd. (%) C	Calc. or Reqd. (%) H	Purity (%)
1,3-*Divinyloxypropane*	20	143	1·4532[20]	0·8998[20]	64·9	9·5	$C_7H_{12}O_2$	65·6	9·4	96 *
1,5-*Divinyloxypentane*	24	75—77/11 mm.	1·4410[25]	0·8850[25]	69·1	10·4	$C_9H_{16}O_2$	69·0	10·4	98·5 †
1,10-Divinyloxydecane	50	144/4 mm.	1·4503[25]	0·8729[25]	73·6	11·5	$C_{14}H_{26}O_2$	74·3	11·6	97 *
1,4-*Divinyloxycyclohexane* §	13·5	81—83/2 mm.	—	—	71·9	9·5	$C_{10}H_{16}O_2$	71·4	9·6	100 ‡
	—	—	—	—	71·7	9·4	$C_{10}H_{16}O_2$	71·4	9·6	94 ‡
Di-2-vinyloxyethyl ether	16	85—87/14 mm.	1·4430[20]	0·9631[20]	60·6	9·0	$C_8H_{14}O_2$	60·7	8·9	97 *
Di-2-vinyloxypropyl ether	12	82—84/7 mm.	1·4314[20]	0·9040[20]	65·3	10·2	$C_{10}H_{18}O_2$	64·5	9·7	96 *
Di-2-vinyloxyethyl sulphide	14	112—113/12 mm.	1·4897[25]	1·0126[25]	54·6	7·9	$C_8H_{14}O_2S$	55·1	8·1	99 *
Di-(2-vinyloxyethoxy)ethane	12	136—138/19 mm.	1·4518[25]	0·9962[25]	59·4	9·0	$C_{10}H_{18}O_4$	59·4	8·7	95 ‡

* Acetaldehyde produced by hydrolysis.[11] † Iodometric titration.[9b] ‡ Gas chromatography. § Two isomers separated by gas chromatography.

absorption and consistent with what would be expected for a di-1-chloroalkyl ether. The chloro-ether was treated with *NN*-diethylaniline in a method analogous to that of Böhme and Bentler.[1] Yield of the *acetal* 100 g., b. p. 54—56°/5 mm., n_D^{25} 1·4389, d_4^{25} 0·9420 [Found: C, 66·8; H, 11·1%; *M* (cryoscopic in benzene), 146; aldehyde yield [11] 40·6%. $C_8H_{16}O_2$ requires C, 66·6; H, 11·2%; *M*, 144; aldehyde yield, 40·3%].

Preparation of divinyl ethers. The diol (1 mole) was heated under reflux with n-butyl vinyl ether (8 moles) and pure mercuric acetate (12 g.) for 18 hr. Sodium carbonate (20 g.) was then added, and the excess of n-butyl vinyl ether removed by distillation. The remaining liquid was washed three times with 1% sodium hydroxide solution, dried (K_2CO_3), and fractionally distilled several times from sodium wire until an infrared spectrum of the main fraction was free from O–H stretching absorption. The infrared spectra of the products showed all the principal characteristics noted by Mikawa.[12]

Properties of the divinyl ethers synthesised in this way are given in the Table.

We thank Mr. B. F. Sagar for gas chromatography determinations.

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SHIRLEY INSTITUTE, DIDSBURY, MANCHESTER 20. [*Received, August 5th*, 1964.]

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296. *Constituents of* Megoura viciae *Buckton.*

By A. F. G. Dixon, M. Martin-Smith, and G. Subramanian.

The observation[1] that the aphid *Megoura viciae* Buckton is highly poisonous to the larvæ of the predatory insect *Adalia decempunctata* L. (inducing obvious distress within 2 minutes and so seemingly eliminating viral transmission [2] or polypeptides [3] as the factors responsible) prompted an investigation into the possible presence of physiologically active compounds. Previous studies [4,5] had indicated the inability of *Megoura viciae* to synthesise and excrete melezitose, a trisaccharide believed to be toxic to certain insects,[6] and, in the present work, paper chromatography confirmed the absence of this compound from the honeydew obtained from our cultures. In contrast to the earlier results,[4,5] however, sucrose was the only sugar detectable in the honeydew, indicating the absence of invertase and transglucosidase activity (known to be influenced by factors such as temperature [4,7]) in the aphid and simple excretion of plant phloem sugar in excess of nutritional requirements under the conditions of culture. Unlike certain other aphids,[8] *Megoura viciae* appeared harmless to mammals as shown by the absence of any discernible effect in mice or guinea pigs after oral administration of the whole dried carcasses or of the unfractionated extractives separately obtained from the aphid with the solvents chloroform, acetone, ethanol, and water.

Application of the standard tests [9] to living specimens of *Megoura viciae* showed the presence of aphin pigments, known to be without pronounced toxic properties.[10] In view of the difficulties in making positive identification of individual aphins [11] these compounds were not further investigated. No organic bases or sterols were detected in the extractives from the aphid—this last observation being of interest since insects are believed unable to synthesise cholesterol [12] although the insect hormone ecdysone [13] would appear to be derived from a trimethyl-steroid precursor. Steam distillation of freshly killed specimens revealed the absence of volatile components.

The chloroform-soluble extractives of *Megoura viciae* consisted mainly of alkanes and fatty acid esters. The paraffin hydrocarbons were analysed by g.l.c. following the procedure of Eglinton *et al.*[14] and compared with the hydrocarbon fraction of the leaves of the host plant, *Vicia faba* L. The two alkane distribution patterns, which are portrayed in the Figure, were distinctly different, thus paralleling the observations of Schreiber [15] with respect to the alkanes present in the larvæ of the potato beetle, *Leptinotarsa decemlineata* Say and in the leaves of the potato plants on which they were feeding—although in his case the paraffins of the beetle larvæ proved to be of surprisingly high molecular weights. It is perhaps noteworthy that branched-chain alkanes were present in *Megoura viciae* but absent from the leaves of *Vicia faba*, especially as isoparaffins are also absent from the leaf wax of the string bean, *Phaseolus aureus* Roxb.[16] Saponification of the mixed fatty acid esters gave seven fatty acids identified through g.l.c. analysis of the derived methyl esters as

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[3] Cf. Kazda, *Experientia*, 1962, **18**, 270.
[4] von Dehn, *Z. Vergleich. Physiol.*, 1961, **45**, 88.
[5] Ehrhardt, *Z. Vergleich. Physiol.*, 1962, **46**, 169.
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[7] Auclair, *Ann. Rev. Entomol.*, 1963, **8**, 439.
[8] Völker, " Fröhner's Lehrbuch der Toxikologie für Tierärzte," 6th edn., Stuttgart, Ferdinand Enke Verlag, 1950, p. 386, and refs. cited.
[9] Duewell, Human, Johnson, MacDonald, and Todd, *J.*, 1950, 3304.
[10] Lord Todd, personal communication.
[11] Human, Johnson, MacDonald, and Todd, *J.*, 1950, 477.
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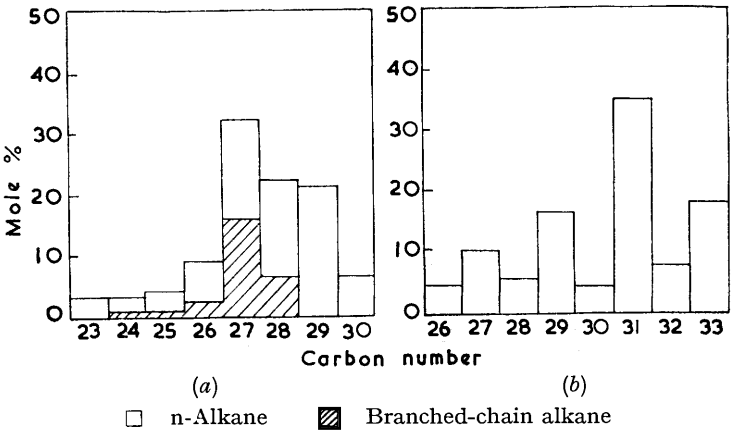
[13] Karlson, Hoffmeister, Hoppe, and Huber, *Annalen*, 1963, **662**, 1.
[14] Eglinton, Gonzalez, Hamilton, and Raphael, *Phytochemistry*, 1962, **1**, 89.
[15] K. Schreiber, personal communication.
[16] Wanless, King, and Ritter, *Biochem. J.*, 1955, **59**, 684.

myristic, pentadecylic, palmitic, margaric, stearic, oleic, and linoleic acids. Acetylation of the long-chain alcohols liberated in the saponification and application of g.l.c. employing authentic samples, showed the three alcohols present to be octan-1-ol, decan-1-ol, and myristyl alcohol.

The water-soluble and ethanol-soluble extractives consisted mainly of amino-acids. peptides, and the two sugars D-glucose and D-ribose (identified by paper chromatography).



Distribution in mole-percentage of n- and branched-chain alkanes C_{23}—C_{33} in the hydrocarbon fractions of (a) *Megoura viciae* and (b) the leaf surface wax of *Vicia faba*, where the mole-percentage is calculated on the basis employed previously.[17]

The presence of D-glucose was further confirmed by conversion into the penta-acetate, identical with an authentic sample.

Experimental.—The light petroleum employed had b. p. 60—80°.

Megoura viciae was cultured on young *Vicia faba* plants in a glasshouse and harvested at intervals. Honeydew was collected by micropipette. For solvent extraction specimens stored in chloroform (150 ml.) until 160 g. had accumulated, were homogenised in a blender. Celite (5 g.) was added and the suspension filtered. The residue was kept for further extraction with ethanol, acetone, and water and the filtrate taken to dryness *in vacuo* at room temperature. The chloroform extractives (6·06 g.) proved virtually completely soluble in light petroleum (5·91 g.).

Alkanes. Removal of esters and traces of carbonyl compounds from the crude light petroleum extractives (200 mg.) through treatment with alcoholic sodium hydroxide and 2,4-dinitrophenylhydrazine by the procedure described earlier [17] afforded, after chromatography over alumina (Brockmann grade I), 9 mg. of alkanes uncontaminated with other compounds as evidenced by infrared spectroscopy. G.l.c. of the alkane fraction dissolved in chloroform on a Pye argon instrument with 0·5% Apiezon L on Embacel (80—100 mesh) in a column 130 × 0·4 cm. at 225° employing authentic n-alkanes and isoalkanes for identification showed the constituent alkanes to be as summarised in the Figure. Analysis of the hydrocarbons in the leaf surface wax of *Vicia faba* was performed following the procedure described previously.[14]

Esters. The crude light-petroleum extractives (200 mg.) were refluxed for 18 hr. with 4 g. of sodium hydroxide in 30 ml. of ethanol and 14 ml. of water. After removal of the solvents under reduced pressure the residue was separated into water soluble and ether soluble fractions. The ether soluble material (62 mg.) was acetylated by refluxing with acetic anhydride to give the acetates of octan-1-ol, decan-1-ol, and myristyl alcohol as shown by g.l.c. with an Apiezon L (0·5%) on Embacel column at 175° employing authentic acetates for comparison.

The basic aqueous solution on acidification with 6N-hydrochloric acid and extraction with ether yielded a mixture of carboxylic acids (115 mg.) which after conversion into the methyl esters by means of excess of diazomethane in ether was subjected to g.l.c. on a butane-1,4-diol

[17] Eglinton, Hamilton, and Martin-Smith, *Phytochemistry*, 1962, **1**, 137.

succinate poly-ester column at 175°. Five of the seven esters so resolved were identified as methyl myristate, methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate (major constituent) by intensification of the appropriate peaks on addition of authentic material, while the linear plot of carbon atom number against log retention time for the saturated esters indicated the remaining two to be methyl pentadecylate and methyl margarate.

Sugars. Both the ethanolic and aqueous extractions of the carcasses of *Megoura viciae* contained D-glucose and D-ribose as shown by ascending paper chromatography on Whatman No. 1 sheet employing butanol–acetone–water (2 : 7 : 1) as solvent system [18] and aniline–diphenylamine phosphate as detecting reagent.[19]

Water-soluble extractives (1 g.) were acetylated by refluxing in acetic anhydride (25 ml.) in the presence of zinc chloride (1 g.) for 3 hr., and the reaction mixture poured into 250 ml. of water at 0°. The crystalline deposit formed after 12 hr. (0·8 g.) was collected and chromatographed in benzene over alumina (Woelm, acid; 15 g.). Crystallisation of the residue from the benzene eluants from methanol gave D-glucose penta-acetate, m. p. 109° (lit.,[20] 110°) identical with that of authentic material (mixed m. p.; infrared spectrum).

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DEPARTMENT OF ZOOLOGY, THE UNIVERSITY, GLASGOW W.2.
DEPARTMENT OF PHARMACY, UNIVERSITY OF STRATHCLYDE, GLASGOW C.1.

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297. *A Convenient One-step Conversion of Aldehydes into Nitriles.*

By T. VAN ES.

RECENTLY several methods have been described whereby nitriles can be prepared directly from aldehydes.[1] It is now found that, by refluxing a solution of an aldehyde in formic acid with hydroxylamine hydrochloride and sodium formate, excellent yields of nitriles are obtained, particularly in the aromatic series.

The author has examined the use of various bases (sodium acetate, pyridine), various strengths of formic acid, and various proportions of hydroxylamine, and has arrived at a recommended, standard process.

The formation of the nitrile probably occurs *via* the oxime formate which loses formic acid in the presence of base.[2] In confirmation, *o*-nitrobenzaldoxime (*anti*) gave the nitrile when refluxed with formic acid in the presence of either sodium formate (about 10% by weight of the oxime) or a somewhat larger amount of hydroxylamine hydrochloride.

The following aldehydes were converted into nitriles, the percentage yields being indicated: Ph, 89; *p*-Cl·C_6H_4, 97; *p*-Br·C_6H_4, 84; *o*-O_2N·C_6H_4, 83; *m*-O_2N·C_6H_4, 90; *p*-O_2N·C_6H_4, 90; *p*-Me_2N·C_6H_4, 84; *p*-MeO·C_6H_4, 81; *p*-NC·C_6H_4, 96; Vanillin, 95; Piperonal, 83; o-HO·C_6H_4, 87; α-$C_{10}H_7$, 93; n-C_3H_7, 30; n-C_6H_{13}, 42.

Experimental.—The aldehyde (0·01 mole), hydroxylamine hydrochloride (0·80 g.; 0·01 mole + 15%), sodium formate (1·25 g.; excess), and formic acid (15 c.c.; 98—100%) were refluxed for 1 hr. The nitriles were obtained by dilution with water or if necessary by ether extraction. The m. p.s or b. p.s of the nitriles so obtained agreed with reported values.

UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG, SOUTH AFRICA.

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