707. *The Racemisation of 9 : 10-Dihydro-3 : 4-5 : 6-dibenzophenanthrene.*

By D. Muriel Hall.

The rates of racemisation of this hydrocarbon were previously [1] determined in boiling ethylbenzene and in boiling toluene; from the values found ($k = 3{\cdot}18 \times 10^{-3}$ min.$^{-1}$ and $5{\cdot}3 \times 10^{-2}$ min.$^{-1}$, respectively) the activation energy was calculated as 34 kcal./mole. This appeared to be rather high and a reinvestigation has given the value of 31 kcal./mole.

The boiling point of toluene is particularly sensitive to small changes in pressure. The racemisation has now been repeated in toluene which had been carefully fractionated and had b. p. 110·5°/760·5 mm.; heating was restricted to times when the atmospheric pressure was 760 ± 3 mm. The value of k so obtained is $4{\cdot}4 \times 10^{-3}$ min.$^{-1}$; half-life, 158 min. The racemisation has also been carried out in boiling dioxan, b. p. 101·0°/762 mm., giving k, $1{\cdot}53 \times 10^{-3}$ min.$^{-1}$; half-life, 453 min.

These rates, together with that in ethylbenzene, give an activation energy of 31 kcal./mole. (The change of solvent is unlikely to have much effect on the rate of racemisation of such a hydrocarbon.) The activation energy for the racemisation of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene is thus the same as that for the racemisation of 4 : 6 : 4′ : 6′-tetramethyldiphenyl-2 : 2′-thiolsulphonate,[2] although the latter is about twice as stable optically.

Experimental.—Racemisations were carried out as previously described,[1] *viz.*, by heating the solution rapidly to the boiling point and, after a suitable interval, cooling it quickly in ice–water. Polarimetric readings were then made at room temperature, the solution returned to the flask, and re-heated for a further period. The main sources of error (apart from fluctuations in pressure) are thus uncertainties in the times and the small increases in concentration resulting from loss of solvent by evaporation.

Bedford College, University of London. [*Received, May 28th*, 1956.]

[1] Hall and Turner, *J.*, 1955, 1242.
[2] Armarego and Turner, preceding paper.

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708. *The Mechanism of the Pinacol–Pinacone Rearrangement. Part III.*[1] *Evidence on General Acid Catalysis.*

By J. F. Duncan and K. R. Lynn.

It has previously been established that the pinacol–pinacone rearrangement in aqueous acid solution is strongly catalysed by the H_3O^+ ion, but the only other acidic species besides H_3O^+ which has been discussed is the bisulphate ion, which does not appear to catalyse the reaction.[1]

We have now studied the reaction in aqueous solutions of a number of weak acids, and it has been found that the reaction does not proceed at a measurable rate except by catalysis by the H_3O^+ ion.

Results.—Catalysing acids. The reaction rate was determined with oxalic acid and phosphoric acid. The results are given in the Table.

The hydrogen-ion concentrations in the various solutions are shown in the Table. These have been calculated by using a value of $5{\cdot}7 \times 10^{-2}$ for the acidity constant for oxalic acid [2] (value at 18°) and of $1{\cdot}59 \times 10^{-2}$ for phosphoric acid. The latter value (for 113·5°) was calculated from values at lower temperatures by using Everett and Wynne-Jones's technique,[3] but acidity constants are not available over a sufficiently wide temperature range to permit similar calculation for oxalic acid. With both acids the ionic strength was always less than

[1] Parts I and II, Duncan and Lynn, *J.*, 1956, 3512, 3519.
[2] Bell, "Acid–base Catalysis," Oxford Univ. Press, 1941; Parton and Nicholson, *Trans. Faraday Soc.*, 1939, **35**, 546.
[3] *Ibid.*, p. 1340. For a discussion on the validity of the method, see Dippy, and Jenkins, *ibid.*, 1941, **37**, 366, and Everett and Wynne-Jones, *ibid.*, p. 373.

Calculated ionic composition of catalysing solutions at 113·5° (*concentrations in g.-ions/l.*; k_{exp} *in* 10^5 *sec.*$^{-1}$).

Oxalic acid				*Phosphoric acid*			
Concn.				Concn.			
$[(CO_2H)_2]$	$[H^+]$ and $[HO_2C{\cdot}CO_2^-]$	k_{exp}	k_{exp}*	$[H_3PO_4]$	$[H^+]$ and $[H_2PO_4^-]$	k_{exp}	k_{exp}*
0·228	0·089	22·80	39·0	0·428	0·075	16·08	33·0
0·308	0·107	31·23	49·0	0·597	0·089	21·04	39·0
0·418	0·128	43·05	58·0	0·733	0·103	29·70	47·0
0·511	0·144	44·60	66·0	0·877	0·111	33·30	51·0

k_{exp}* is interpolated from the plot of $[H^+]$ against k_{exp} for monobasic acids.[1]

0·15 and there was no significant concentration of bivalent ions. We should, therefore, expect that the reaction rate would be identical with that obtained with strong monobasic acids at the same concentration of hydrogen ions, if the hydrogen ion were the sole catalysing species. It will be seen from the Table that systematically low values of k_{exp} are obtained. Agreement would be close if the acidity constants used in the calculation were about twofold too large. Such a discrepancy is quite possible, with phosphoric acid because of the large extrapolation (from 50° to 113·5°) and the method of calculation; and with oxalic acid owing to the use of an acidity constant quoted at 18° for calculation of hydrogen-ion concentrations at 113·5°. We conclude, therefore, that the observed reaction rates can be adequately explained by catalysis by hydrogen ions.

Non-catalysing acids. At 113·5° no reaction was detected with saturated ammonium chloride during 2 days; or with M-sodium dihydrogen phosphate or 0·1M-sodium hydrogen oxalate after 5 hr. From these results and those for phosphoric and oxalic acid it is clear that none of the species NH_4^+, $H_2PO_4^-$, HPO_4^{2-}, or $HO_2C{\cdot}CO_2^-$ catalyses the reaction significantly. It has also been shown that the bisulphate ion does not catalyse the reaction.[1] It would seem reasonable therefore to conclude that the pinacol–pinacone rearrangement is not subject to general acid catalysis.

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[*Received, July 19th,* 1955.]

709. *Absorption Spectra of Ketones. Part V.* γ-Substituted αβ-Unsaturated Ketones.*

By C. W. BIRD, R. C. COOKSON, and S. H. DANDEGAONKER.

THE difference in absorption of light by equatorial and by axial 2-substituted *cyclo*hexanones in both the infrared [1,2] and the ultraviolet [3,4] region of the spectrum aroused our interest in the spectroscopic properties of geometrically analogous γ-substituted αβ-unsaturated ketones, typified by the epimeric 6-substituted cholest-4-en-3-ones (I).

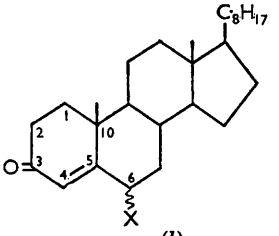
In the stable conformation of structure (I), C-1 lies below the plane occupied by C-2, C-3, C-4, C-5, C-6, C-10, and the oxygen atom. The relation of a 6α- and a 6β-substituent to the 4 : 5-double bond is then the same as that of an equatorial and an axial substituent to the carbonyl group of a 2-substituted *cyclo*hexanone [see partial formula (II)].

The increase in frequency of the carbonyl stretching vibration of a *cyclo*hexanone produced by introduction of an equatorial 2-bromine atom was attributed by Jones and his colleagues [1] to the reduction in the single-bond character of the C=O bond by the adjacent, almost co-planar, C→–Br dipole, an effect that would be almost at a minimum for an axial bromine atom, which in fact has little influence on the frequency. Consistently with Jones's electrostatic field effect, introduction of a 6-bromine atom into cholestenone in either configuration only slightly affects the carbonyl frequency (Table 1). The slight increase in frequency produced by a 6-bromine atom may arise from its inductive pull

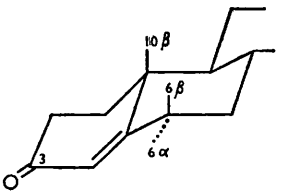
* Part IV, *J.*, 1956, 2302.

[1] Jones, Ramsay, Herling, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 2828.
[2] Corey, *ibid.*, 1953, **75**, 2301, 3297; 1954, **76**, 175.
[3] Cookson, *J.*, 1954, 282.
[4] Cookson and Dandegaonker, *J.*, 1955, 352.

through the carbon chain. 6-Hydroxy- and 6-acetoxy-cholestenone absorb very near 1670 cm.$^{-1}$ regardless of the configuration of the oxygen atom.[5,6,7]



(I)



(II)

In carbon disulphide solution (potassium bromide prism) the 6α-bromide shows bands at 788 and 726 cm.$^{-1}$, and the 6β-bromide at 700 and 649 cm.$^{-1}$. Dr. J. E. Page tentatively assigns the first pair of bands to stretching of the equatorial C–Br bond and the second pair to the vibrations of the axial C–Br bond.[8]

Table 2 records the ultraviolet spectra of the ketones. The bathochromic effect of

TABLE 1.

	$\nu_{max.}$ (CS_2) (cm.$^{-1}$)		$\nu_{max.}$ (CS_2) (cm.$^{-1}$)
Cholest-4-en-3-one	1674	6α-Bromocholest-4-en-3-one...	1680
		6β-Bromo- „ ...	1678

TABLE 2. *Absorption maxima.* (Wavelengths in mμ; ε in parentheses.)

	K-band (EtOH)	*E*	*R*-band (*n*-hexane) *D*	*C*	*B*	*A*
Cholest-4-en-3-one	241 (18,000)	314 (45)	323·5 (49)	336 (47)	349 (34)	367 (14)
6α-Chloro-	239 (19,000)	317 (45)	327 (45)	339 (41)	352 (31)	368 (15)
6β-Chloro-	241 (15,100)	327 (54)	338 (53)	350 (51)	364 [a] (40)	382 [a] (22)
6α-Bromo-	238 (15,800)	319 [a] (31)	329·5 (36)	340·5 (36)	352 [a] (28)	372 [a] (11·5)
6β-Bromo-	244 (13,700)	—	344 (64·5)	355 (62)	371 [a] (46·5)	391 [a] (20)
6α-Hydroxy-	240 (16,200)	314 [a] (30)	325·5 (36)	338 (36)	348·5 (26)	368·5 (9)
6β-Hydroxy-	236 (13,500)	—	331 (34)	342 (35)	356 (26)	375 (10·5)
6α-Acetoxy-	236 (16,600)	314 [a] (33)	325·5 (39)	338 (39)	350 (30)	370 (13)
6β-Acetoxy-	237 (12,600)	324 [a] (24)	334 (40)	346·5 (40)	361 (29)	380 (13)

[a] Inflection.

6β-bromine has been commented on previously,[9,10] and can be attributed to the axial nature of the C–Br bond, which is almost ideally situated for interaction in the excited state, either by hyperconjugation of its σ-electrons, or by involvement of the *p*-electrons on the bromine atom with the π-electron system. For the equatorial 6α-epimer the possibility of interaction of both sorts is nearly at a minimum.

In ethanol the long-wavelength, $n \longrightarrow \pi$ band of the cholestenones appeared only as a broad, ill-defined maximum or inflection, that was unsuitable for analysis. But in hexane (Table 2) the band was easily resolved, and showed typical [11] vibrational fine structure. Substitution of an equatorial 6α-halogen atom into cholestenone moves the entire $n \longrightarrow \pi$ band to the red by only a few mμ. An axial 6β-halogen atom produces a much larger shift in the same direction. Each bromide absorbs more intensely than the corresponding chloride, and the absorption of the axial halide is stronger, and shows rather less fine structure, than that of the equatorial epimer.

The shapes of the extinction curves of all four 6-oxygenated ketones are very similar. Again, an equatorial substituent causes only a slight shift in wavelength, whereas an axial one causes a substantial shift to the red.

[5] Sondheimer, Kaufmann, Romo, Martinez, and Rosenkranz, *J. Amer. Chem. Soc.*, 1953, **75**, 4712.
[6] Romo, Rosenkranz, Djerassi, and Sondheimer, *J. Org. Chem.*, 1954, **19**, 1509.
[7] Fieser, *J. Amer. Chem. Soc.*, 1953, **75**, 4377.
[8] Cf. Barton, Page, and Shoppee, *J.*, 1956, 331.
[9] Barton and Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 1066; Djerassi, Rosenkranz, Romo, Kaufmann, and Pataki, *ibid.*, p. 4534.
[10] Dorfman, *Chem. Rev.*, 1953, **53**, 71.
[11] Cookson and Dandegaonker, *J.*, 1955, 1651.

Table 3 shows the average shift in wavelength of corresponding vibrational maxima produced by substitution of cholestenone at position 6 by various groups, and, for

TABLE 3. $\Delta\lambda$ (mμ) *for ketones.*

Substituent	γ-Subst. αβ-unsat.		α-Subst. sat.[3,4]	
	e	a	e	a
Cl	+3	+14	− 5	+15 *
Br	+5	+20	− 5	+28
OH	+2	+ 7	−12	+17
OAc	+2	+10	− 5	+10

* 2-Chloro*cyclo*hexanone, with an axial chlorine atom, has $\lambda_{max.}$ 294 mμ (ε 24) in EtOH. Comparison with *cyclo*hexanone, $\lambda_{max.}$ 283 mμ (ε 16), gives a value of +11 mμ for $\Delta\lambda$, agreeing perfectly with that reported by Corey and Burke (*J. Amer. Chem. Soc.*, 1955, **77**, 5418), but rather less than $\Delta\lambda$ found recently [4] for two axial α-chloro*cyclo*hexanones in ring A of the steroids.

comparison, the shift in the maximum of a *cyclo*hexanone produced by the same substituents on the α-carbon atom. The figures do not run exactly parallel: one of the most striking contrasts is the reversal in the relative order of hydroxyl and acetoxyl in the two series.

Experimental.—Ultraviolet spectra were measured as before.[11] Infrared spectra were kindly determined by Glaxo Laboratories Ltd., Greenford, on a Perkin–Elmer 21, double-beam spectrophotometer with a potassium bromide prism. Rotations were measured at about 1—2% concentration in $CHCl_3$.

Cholest-4-en-3-one [12] had m. p. 80—81° $[\alpha]_D$ 92°; 6α-chlorocholest-4-en-3-one,[13] m. p. 121—122°, $[\alpha]_D$ 60°; 6α-bromocholest-4-en-3-one,[9] m. p. 113°, $[\alpha]_D$ 54°; the 6β-epimer,[9,14] m. p. 131°, $[\alpha]_D$ 7°; 6α-hydroxycholest-4-en-3-one,[5,7] m. p. 162°, $[\alpha]_D$ 87·5°; 6β-epimer,[5,6] m. p. 189—190°, $[\alpha]_D$ 31°; 6β-acetoxycholest-4-en-3-one,[5,6] m. p. 102—103°, $[\alpha]_D$ 38°. Samples of the other compounds were generously given by Professor D. H. R. Barton, F.R.S., Professor C. Djerassi, Professor L. F. Fieser, and Dr. F. Sondheimer.

BIRKBECK COLLEGE, LONDON, W.C.1. [*Received, March 19th*, 1956.]

[12] *Organic Syntheses*, 1941, **21**, 18.
[13] Barton and Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 370.
[14] Fieser, *ibid.*, 1953, **75**, 5421.

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710. *Synthesis of Tetramethylhydrazine by Photolysis and Pyrolysis of Tetramethyltetrazen.*

By J. S. WATSON.

TETRAMETHYLHYDRAZINE has proved difficult to prepare [1] and was only recently made by Aston and his co-workers [2] in somewhat small yield by the reduction of *sym.*-diformyldimethylhydrazine with lithium aluminium hydride. The method described below involves photolysis or pyrolysis of tetramethyltetrazen $(NMe_2{\cdot}N{:})_2$ which under favourable conditions yields as much as 40% of tetramethylhydrazine.

Previous work [3,4] has shown that tetra-arylhydrazines may be prepared by the thermal decomposition of the corresponding tetrazens. Wieland and Fresnel,[4] however, found products other than hydrazines when alkyl-aryl-substituted tetrazens were decomposed and from tetraethyltetrazen obtained only nitrogen, diethylamine, and a Schiff base. All these reactions were carried out in solution or in the liquid state. The only information [5] available on the thermal decomposition of tetramethyltetrazen is that it explodes at its boiling point, 130°/760 mm.

The present work describes a method whereby the vapour of tetramethyltetrazen at a pressure of 4 mm. and with a contact time of 10 sec. may be passed safely through a glass

[1] Klages, Naher, Kircher, and Bock, *Annalen*, 1941, **547**, 1.
[2] Class, Aston, and Oakwood, *J. Amer. Chem. Soc.*, 1953, **75**, 2937.
[3] Sidgwick, Taylor, and Baker, "The Organic Chemistry of Nitrogen," Oxford Univ. Press, 1949, pp. 390, 450.
[4] Wieland and Fresnel, *Annalen*, 1912, **392**, 135.
[5] Renouf, *Ber.*, 1880, **13**, 2173.

tube heated to about 300°, decomposing smoothly to nitrogen, tetramethylhydrazine, dimethylamine, and tris(methylmethyleneamine) $(CH_2{:}NMe)_3$, referred to below as "trimer." At 200° no decomposition takes place under these conditions. Photolysis of tetramethyltetrazen in liquid phase, in solution, or in the gas phase at 25° produces the same products. The quantum yield for production of nitrogen is about 0·9. Tetramethylhydrazine (b. p. 73°/760 mm.) may be easily separated by distillation from dimethylamine (b. p. 7°/760 mm.) and the " trimer " (b. p. 63°/25 mm.).

The above products lead one to believe that the reaction involves the production of free dimethylamino-radicals, some of which combine to form hydrazine while others disproportionate. The methylmethyleneamine subsequently polymerises to trimer.

$$Me_2N{\cdot}N{:}N{\cdot}NMe_2 \xrightarrow{h\nu} N_2 + 2Me_2N{\cdot}$$

$$2Me_2N{\cdot} \longrightarrow Me_2N{\cdot}NMe_2$$

$$2Me_2N{\cdot} \longrightarrow NHMe_2 + CH_2{:}NMe$$

It is possible that the trimer and dimethylamine may arise by abstraction of a hydrogen atom from the substrate, *e.g.*:

$$Me_2N{\cdot} + Me_2N{\cdot}N{:}N{\cdot}NMe_2 \longrightarrow NHMe_2 + {\cdot}CH_2{\cdot}NMe{\cdot}N{:}N{\cdot}NMe_2$$

$${\cdot}CH_2{\cdot}NMe{\cdot}N{:}N{\cdot}NMe_2 \longrightarrow CH_2{:}NMe + N_2 + NMe_2{\cdot}$$

but this seems unlikely, at least in photolysis, since a chain would be involved and the quantum yield is less than 1·0.

In addition to the products mentioned, there was a very small amount (1%, detected by the mass spectrometer) of *NNN'N'*-tetramethylmethylenediamine $Me_2N{\cdot}CH_2{\cdot}NMe_2$. This material boils at 83—85°/760 mm. and thus is difficult to separate from the hydrazine. Its origin is obscure, but it is of interest that it has also been found in the mercury-photosensitised decomposition of dimethylamine.[6]

Experimental.—Tetramethyltetrazen was prepared from unsymmetrical dimethylhydrazine by Renouf's method.[5] The hydrazine (10 g.) (dried over solid potassium hydroxide) in anhydrous ether (100 ml.) was treated under reflux with small quantities of mercuric oxide (either the yellow or the red variety is satisfactory). The ether boiled and a black precipitate, presumably mercury, was formed. When further addition of mercuric oxide caused no further reaction, the mixture was heated on a water-bath for 15 min., then cooled and filtered. The light yellow liquid was dried (K_2CO_3), evaporated, and distilled, yielding tetramethyltetrazen (5·5 g.), b. p. 44°/30 mm., $\lambda_{max.}$ 2800 Å (ε 14,000). A deep yellow residue remained.

Pyrolysis in flow system. Tetramethyltetrazen was stored as a liquid in a tube attached *via* a stopcock to a horizontal glass reaction vessel, 30 cm. long, 2·5 cm. in diameter, heated electrically to about 300°. The temperature was measured by a thermometer inserted in a well in the centre of the tube, and the pressure by a mercury manometer. The apparatus was evacuated continuously. The tetrazen was admitted as a vapour, at about 4 mm. After reaction the products flowed through a restricting capillary to two traps, one at −80° (solid carbon dioxide–acetone) and the other at −195° (liquid nitrogen). Uncondensable gas was removed continuously by the vacuum-pump. By weighing the storage tube before and after each experiment the weight of material passed, and consequently the contact time were obtained. The sample collected was weighed and fractionally distilled. Fractions obtained were as follows :

Uncondensable gas : A sample was examined mass spectroscopically and found to be pure nitrogen.

Liquid fractions : Fraction (1), condensable at −195°, but volatile at 25°, was shown by mass spectroscopy to be largely dimethylamine, but occasionally small amounts of monomethylamine were found. Dimethylamine was further characterised by its v. p. (2·8 mm. at 78°), b. p. (7°/760 mm.), picrate (m. p. 158°), and molecular weight (45). Fraction (2), b. p. 70—75°/760 mm., consisted of tetramethylhydrazine with small amounts of *NNN'N'*-tetramethylmethylenediamine and was analysed mass-spectroscopically. Two or three further fractionations gave pure tetramethylhydrazine, with a penetrating fish-like odour, b. p. 73°/760 mm.,

[6] Watson and Darwent, unpublished work.

n_D^{25} 1·4040 [Found : C, 53·5; H, 13·7; N, 31·8. Calc. for $C_4H_{12}N_2$: C, 54·5; H, 13·6; N, 31·8%, *M* (vapour), 87; parent peak from mass spectrum, 88], giving a carbon disulphide complex, m. p. 130°. Fraction (3), b. p. 63—66°/25 mm., essentially the " trimer " $(CH_2{\cdot}NMe)_3$, was identified by comparing it with an authentic specimen, and by its b. p. 64—65°/25 mm., n_D^{25} 1·4600, carbon disulphide complex, m. p. 102°, picrate, m. p. 118°, and the parent peak (129) from the mass spectrum.

In a typical experiment 4·15 g. of tetramethyltetrazen, pyrolysed at 300° at a flow rate of 0·65 g. per hr., gave dimethylamine 0·7 g., " trimer " 0·55 g., tetramethylhydrazine 1·3 g., residue 0·54 g., and no unchanged tetramethyltetrazen. In an experiment at 200° all the tetrazen was recovered unchanged in the traps.

Photolysis of liquid in a static system. Tetramethyltetrazen was placed in a quartz cell, of 35 ml. capacity, 5·6 cm. in diameter, and 2·5 cm. deep, illuminated on each side by two quartz low-pressure mercury lamps about 1 cm. from the cell faces. The whole was placed in water at about 25°. Attached to the cell was a condenser, which led by a tube to a trap containing N-hydrochloric acid to collect the dimethylamine produced, and thence to a trough, etc., tc collect and measure the uncondensable gas.

In a typical experiment 27 g. of the tetrazen were photolysed, nitrogen being evolved at the rate of about 20 ml./hr. After 10 days 4·7 l. had been produced, the light was then switched off. The acid solution was titrated and the contents of the cell fractionated as above. Products were nitrogen 5·9 g., dimethylamine 4·3 g., tetramethylhydrazine 6·0 g., " trimer " 4·0 g., unchanged tetramethyltetrazen 2·4 g., and residue 2·5 g. The quantum yield, measured by photolysing 0·5M-chloroacetic acid [7] at 25°, was 0·09 ± 0·05 for production of nitrogen. Experiments with a solution of the tetrazen in ether gave similar results except that fractionation was more difficult.

In a few experiments the pyrolysis and photolysis of the vapour of tetramethyltetrazen were investigated in a static system. At 25° the v. p. of tetramethyltetrazen is about 8 mm. and reactions were carried out at this pressure. Both the photochemical and the thermal decomposition were investigated in a quartz cell of 200 ml. capacity, enclosed in a furnace, and, for photolysis, illuminated by a quartz mercury lamp. Owing to the small quantities of material in these experiments, the products were analysed mass-spectroscopically. Photochemical decomposition was rapid at 25°, the pressure rising to over double its initial figure when all tetramethyltetrazen had reacted. Pyrolysis of the vapour was very slow at 150°; after 15 hr. the tetrazen had not completely decomposed; but at 280° the reaction was very rapid and was complete in a few minutes. In both cases the products were nitrogen, dimethylamine, tetramethylhydrazine, " trimer, " and traces of tetramethylmethylenediamine.

General Research Organisation, Olin Mathieson Chemical Corporation,
New Haven, Connecticut, U.S.A. [*Received, April 3rd*, 1956.]

[7] Smith, Leighton, P. A., and Leighton, W. G., *J. Amer. Chem. Soc.*, 1939, **61**, 2299.

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711. *The Preparation of the Half Esters of Phthalic Acid and of 3-Nitrophthalic Acid.*

By M. K. Hargreaves.

In the course of other work it became necessary to prepare the pentyl hydrogen 3-nitrophthalates. The original procedure [1] involved heating the neat alcohol with 3-nitrophthalic anhydride for some hours. Pickard and Kenyon prepared many hydrogen phthalates by a similar method,[2] which was later improved by carrying out the reaction in pyridine solution.[3] Balfe, Doughty, and Kenyon [4] found, however, that heating mixtures of 3-nitrophthalic anhydride and an alcohol in pyridine eliminates nitrogen dioxide with the production of a betaine derivative, but that 10% of dioxan inhibited this reaction.

Gerrard, Madden, and Tolcher [5] have shown that dioxan and pyridine have rather

[1] McKenzie, *J.*, 1901, **79**, 1135.
[2] Pickard and Kenyon, *J.*, 1907, **91**, 2058.
[3] Levene and Mikeska, *J. Biol. Chem.*, 1927, **75**, 594.
[4] Balfe, Doughty, and Kenyon, *J.*, 1953, 2470.
[5] Gerrard, Madden, and Tolcher, *J. Appl. Chem.*, 1955, **5**, 31

similar properties in other reactions. It is now found that dioxan can be substituted advantageously for pyridine in the preparation of esters of 2-methylbutanol; with secondary alcohols the advantage of a cleaner product is offset by the slower reaction. The function of the pyridine or dioxan may not be specific since in certain cases an improved product can be obtained by carrying out the reaction in equal parts of pyridine and toluene,[6] whilst in others the product can be obtained by refluxing in a low-boiling solvent such as chloroform;[7] it seems unlikely, however, to be merely that of solvent. Where effective, the substitution of dioxan for pyridine results in an improved product.

2-Methylbutyl hydrogen 3-nitrophthalate is readily formed during 2 hr. on the steam-bath, though longer heating increases the yield somewhat. On the other hand 2-methylbutyl hydrogen phthalate is less readily formed, and the *sec.*-butyl half-ester even less readily still.

Experimental.—2-(±)-2′-*Methylbutyl* 1-*hydrogen* 3-*nitrophthalate.*[8] (±)-2-Methylbutanol (4·4 g., 1 mol.), 3-nitrophthalic anhydride (9·7 g., 1 mol.), and dioxan (13·2 g., 3 mols.) were heated on the steam-bath for 2 hr. after solution was complete. After 2 days at room temperature the mixture was poured on ice–dilute hydrochloric acid. The pale buff crystals, which crystallised from the lower layer, were partly dried at the pump (yield, 14·6 g.) then dissolved in ether and extracted therefrom into saturated sodium hydrogen carbonate solution. The aqueous solution was poured on ice–dilute hydrochloric acid. The crystals (9·4 g., 67%) after two crystallisations from benzene had m. p. 156—156·5° (Found, by rapid titration with 0·1N-sodium hydroxide: *M*, 282. Calc. for $C_{13}H_{15}O_6N$: *M*, 281). 1-(±)-2′-Methylbutyl 2-hydrogen 3-nitrophthalate (10—20%) remained in the benzene mother-liquors.

(±)-2-*Methylbutyl hydrogen phthalate.* (±)-2-Methylbutanol (4·4 g.), phthalic anhydride (7·4 g., 1 mol.), and dioxan (13·2 g., 3 mols.) were treated as above except that the mixture was kept on the steam-bath for 2 days. The mixture was worked up as before but at each stage a liquid was obtained. The liquid ester after reprecipitation from the bicarbonate solution was dissolved in ether, the solution dried ($CaCl_2$), and the ether then removed. The remaining liquid crystallised after being cooled on solid carbon dioxide and worked up in light petroleum. The product (10·2 g., 86%) had m. p. 1—2°. After being reworked in cold petroleum 3·5 g. of material were obtained which remained solid overnight in a desiccator. Recrystallised twice from light petroleum the small rhombs had m. p. 36—37° (Found, by rapid titration with 0·1N-sodium hydroxide: *M*, 238. Calc. for $C_{13}H_{16}O_4$: *M*, 236).

iso*Pentyl hydrogen phthalate.* *iso*Pentanol (8·8 g., 1 mol.), phthalic anhydride (14·8 g., 1 mol.), and dioxan (26·4 g., 3 mols.) were heated and the product worked up as described above. The crystals (7·6 g., 56%) had m. p. 36·5—37·5° after two recrystallisations from light petroleum (Found, by rapid titration with 0·1N-sodium hydroxide: *M*, 239. Calc. for $C_{13}H_{16}O_4$: *M*, 236).

sec.-*Butyl hydrogen phthalate.* A warm mixture of (±)-*sec.*-butyl alcohol (18·5 g.), phthalic anhydride (37 g., 1 mol.), and dioxan (66 g., 3 mols.) was shaken until solution was complete and then heated overnight. On cooling crystals formed and heating was therefore continued for a further 2 days; crystals did not then appear on cooling. The mixture was worked up as before. After the dried ethereal solution had been treated with petroleum the product was recrystallised from light petroleum and then had m. p. 59—60° (corr.) (yield: 31 g., 56%) (Found, by rapid titration with 0·1N-sodium hydroxide: *M*, 221. Calc. for $C_{12}H_{14}O_4$: *M*, 222). Pickard and Kenyon[9] give m. p. 56—57°.

The alcohols used were commercial products dried over fresh quick-lime, and distilled. Dioxan was refluxed over sodium for several days and then distilled. Phthalic anhydride was a commercial product which was free from phthalic acid.

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LONDON, W.8.

[*Received, April 5th,* 1956.]

[6] Balfe, Hargreaves, and Kenyon, *J.*, 1951, 584.
[7] Pickard and Kenyon, *J.*, 1914, **105**, 1115.
[8] Cohen, Marshall, and Woodman, *J.*, 1915, **107**, 887.
[9] Pickard and Kenyon, *J.*, 1911, **99**, 63.

712. *The Viscosities of Iodine Pentafluoride and Ditellurium Decafluoride.*

By G. Hetherington and P. L. Robinson.

To the relatively few viscosities of inorganic fluorides available (those of hydrogen fluoride,[1] arsenious and antimonic fluorides,[2] uranium hexafluoride,[3] chlorine trifluoride,[4] and nitryl fluoride [5]) we now add those of iodine pentafluoride and ditellurium decafluoride.

The method was essentially that used in our nitryl fluoride determination [5] except for a slight modification of the Ostwald-type viscometer. The viscosities of iodine pentafluoride (Table 1) cover a temperature range from 14·55° and 69·30° and by solving the

Table 1. *Viscosities, η(mP), of iodine pentafluoride.*

Temp.	η, Obs.	η, Calc.	Δη	100(Δη)²	Temp.	η, Obs.	η, Calc.	Δη	100(Δη)²
14·55°	26·66	26·82	−0·16	2·56	48·75°	14·30	14·28	+0·02	0·04
25·00	21·11	21·11	0·00	0·00	62·75	12·01	12·01	0·00	0·00
34·30	17·84	17·80	+0·04	0·16	69·30	11·17	11·19	−0·02	0·04

Table 2. *Viscosities of ditellurium decafluoride.*

−30·0°	2·542	2·513	+0·029	0·08	18·2°	1·209	1·215	−0·006	0·00
−23·0	2·210	2·192	+0·018	0·03	25·0	1·140	1·127	+0·013	0·02
−11·0	1·791	1·786	+0·005	0·00	32·2	1·053	1·045	+0·008	0·01
0·0	1·533	1·524	+0·009	0·01	44·9	0·930	0·925	+0·005	0·00

equation of the absolute viscosity–temperature curve, $\eta_t = \eta_0/(1 + At + Bt^2)$ with values from the smoothed curve, it was found that $A = 0{\cdot}04231$, $B = -0{\cdot}000014$, and $\eta_0 = 0{\cdot}04325$ P. The temperature range for ditellurium decafluoride (Table) is from −30·0° to 44·9° and the constants for the above equation are $A = 0{\cdot}01365$, $B = 0{\cdot}0000175$, and $\eta_0 = 0{\cdot}01524$ P.

Experimental.—The apparatus was a slightly modified form of the viscometer previously used by us for nitryl fluoride.[5] The diagram of the viscometer in that communication being referred to, the socket *P* and tap *Q* were replaced by a Y-piece carrying a " break-seal " joint, and a " run-through " joint connected to the sample under investigation. These were for emptying and filling the viscometer, respectively, and were preferred to the original arrangement since they enable contact between the fluoride and fluorocarbon grease to be avoided throughout. After being charged, the apparatus was sealed below the " run-through " joint and the filling device removed. Apart from this change in the mode of introducing the weighed sample of the fluoride, the previous procedure was followed. No difficulty attended the weighing of the fluoride specimens as both are liquids at the ordinary temperature.

The iodine pentafluoride was prepared by burning iodine in a stream of fluorine diluted with nitrogen and purified by bulb-to-bulb distillation in vacuum with rejection of adequate head and tail fractions. The ditellurium decafluoride had been prepared by Campbell and Robinson [6] whose work also furnished the density data used.

The authors thank Imperial Chemical Industries Limited, General Chemicals Division, Widnes, for the use of the fluorine cell. This work was carried out during the tenure of a Salters' Fellowship (G. H.).

King's College, Newcastle upon Tyne, 1. [*Received, April 9th*, 1956.]

[1] Simons and Dresdner, *J. Amer. Chem. Soc.*, 1944, **66**, 1070.
[2] Woolf and Greenwood, *J.*, 1949, 2861.
[3] Llewellyn, *J.*, 1953, 28.
[4] Banks, Davies, and Rudge, *J.*, 1953, 732.
[5] Hetherington and Robinson, *J.*, 1955, 2230.
[6] Campbell and Robinson, *J.*, in the press.

713. *Bitter Principles of the Cucurbitaceae. Part IV.* Dehydrogenation of Cucurbitacin A.*

By P. R. Enslin and D. E. A. Rivett.

Recently a group of related crystalline bitter principles, the cucurbitacins A, B, C, and D, has been isolated in these laboratories from various Cucurbitaceae.[1] They all possess an αβ-unsaturated keto-group. Cucurbitacin A, $C_{28}H_{40}O_8$, also contains two further keto-groups, an acetoxy- and three hydroxy-groups. We now report the dehydrogenation of cucurbitacin A which has been reduced with lithium aluminium hydride.

Zinc dust distillation and selenium dehydrogenation of the closely related elaterin, $C_{28}H_{38}O_7$, were both reported to give 1 : 4-dimethylnaphthalene [2,3] which, however, was insufficiently characterised. From the dehydrogenation of reduced cucurbitacin A, we failed to obtain any simple alkylnaphthalenes but isolated 1 : 2 : 8-trimethylphenanthrene and an unidentified phenanthrene. This indicates a possible structural relation to the diterpenes and tetracyclic triterpenes.

For the separation of the dehydrogenation mixture, we used adsorption on alumina followed by reversed-phase partition chromatography.[4] We believe this technique to be of wide applicability in the separation of the complicated mixtures obtained on dehydrogenation of natural products.

Experimental.—Unless otherwise stated, ultraviolet absorption spectra were measured in 96% EtOH with a Beckman D.U. spectrophotometer. The infrared spectrum was measured on a Perkin–Elmer Model 21 spectrophotometer. M. p.s are corrected.

Reduction of cucurbitacin A with lithium aluminium hydride. Cucurbitacin A (10 g.), dissolved in tetrahydrofuran (40 ml.), was reduced by lithium aluminium hydride (5 g.) in ether (1 l.) for 5 hr. under reflux. Decomposition with absolute ethanol (500 ml.) and 8N-sulphuric acid (65 ml.) precipitated most of the salts. The supernatant solution was dried and neutralised over anhydrous potassium carbonate. Evaporation afforded a white foam (9 g.) which showed no specific ultraviolet absorption.

Dehydrogenation of reduced cucurbitacin A. Reduced cucurbitacin A (18 g.) and selenium powder (18 g.) were heated together in four sealed tubes at 330° for 60 hr. Ether-extraction of the product gave a brown gum (4·5 g.). The pentane-soluble portion of this (2·9 g.) was chromatographed on alumina (Peter Spence, 100 g.) to give : (*a*) pentane eluate (0·67 g.), (*b*) pentane–benzene (9 : 1) eluate (0·29 g.), and (*c*) pentane–benzene (1 : 1) eluate (0·55 g.).

Fractions (*a*), (*b*), and (*c*) were separately rechromatographed and all fractions with similar ultraviolet spectra were combined. In this manner the following three fractions were obtained : (I) benzenoid fraction (0·26 g.), $\lambda_{max.}$ 269 and 277 mμ (in octane); (II) naphthenoid fraction (0·36 g.), $\lambda_{max.}$ 232 and 282 mμ (in octane); (III) phenanthrenoid fraction (0·27 g.), $\lambda_{max.}$ 259—262, 301—308, and 336—340 mμ.

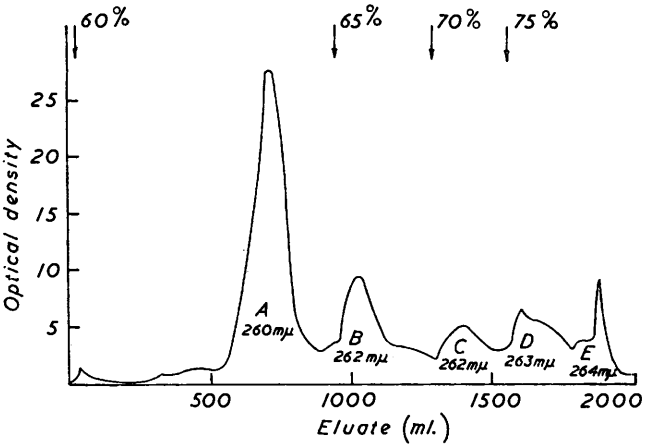
Fraction (III) was rechromatographed and a middle semi-solid fraction (IV) collected, having $\lambda_{max.}$ 261—262, 283, 294, 306—308, and 338—340 mμ. From the general shape of the ultraviolet absorption curve, it was clear that fraction (IV) was still a mixture and further separation was effected by reversed-phase partition chromatography.

Fraction (IV) (0·06 g.) was deposited on non-wetting kieselguhr and packed on top of a column (0·9 × 60 cm.) of non-wetting kieselguhr, impregnated with heptane (9 ml./8 g.), and the column was eluted with aqueous-ethanolic solutions (saturated with heptane) of increasing alcoholic strength.[4] The results are presented in the Figure. Fractions *A* and *B* were diluted with water and extracted with pentane. The crystalline residue (17·6 mg.), m. p. 119—131°, from fraction *A* was recrystallised from 96% ethanol to afford plates (9·4 mg.), m. p. 132—138°, which gave a 1 : 3 : 5-trinitrobenzene adduct, m. p. 189—190° (Found : C, 63·4; H, 4·4. Calc. for $C_{23}H_{19}O_6N_3$: C, 63·7; H, 4·4%) undepressed by authentic 1 : 2 : 8-trimethylphenanthrene 1 : 3 : 5-trinitrobenzene derivative. This material was decomposed on alumina to give 1 : 2 : 8-trimethylphenanthrene, m. p. and mixed m. p. 143—144° after two recrystallisations from methanol, $\lambda_{max.}$ 255, 261, 283, 294, 306, 322, 338, and 354 mμ (ε 43,800, 53,000, 10,800, 10,200, 12,100, 400, 370, and 150 respectively). The residue (9·6 mg.) from fraction B gave, after

* Part III, *J. Sci. Food Agric.*, 1956, **7**, in the press.

[1] Enslin, *J. Sci. Food Agric.*, 1954, **5**, 410.
[2] Moore, *J.*, 1910, **97**, 1801.
[3] Reichel and Eisenlöhr, *Annalen*, 1937, **531**, 287.
[4] Enslin and Rivett, *Chem. and Ind.*, 1956, 23.

another application of reversed-phase partition chromatography one main peak from which a partially crystalline substance (6·7 mg.) was isolated. This material on distillation at 100—110°/10^{-2} mm. afforded an oil, $\lambda_{max.}$ 261, 284, 296, 308, and 340 mμ (ε 50,900, 9900, 8700, 9700, and 860 respectively) which gave a 1 : 3 : 5-trinitrobenzene adduct, m. p. 196—198°. On decomposition of the trinitrobenzene derivative on alumina a crystalline hydrocarbon, m. p. 115—118°, was obtained after two recrystallisations from methanol. The infrared spectrum (in CS_2) showed strong bands at 853, 822, 809, and 776 $cm.^{-1}$. From its ultraviolet spectrum and position on the chromatogram this product appears to be a tetrasubstituted phenanthrene.[4,5] The physical properties of this phenanthrene and of its trinitrobenzene adduct do not correspond to those of any known tetra-alkylphenanthrene.



Separation of fraction (IV) *by reversed-phase partition chromatography. Changes of solvent* (% *v/v of aqueous ethanol*) *are indicated by arrows. Optical densities were measured at the wavelengths indicated.*

No pure substances could be obtained from fraction (II) by reversed-phase partition chromatography. The main chromatographic fractions ($\lambda_{max.}$ 234 and 284 mμ in octane) failed to form crystalline picrates and are considered to consist of incompletely dehydrogenated material. Fractions (I) and (II) were therefore combined and again dehydrogenated, this time at 400° for 48 hr. From the resulting mixture of phenanthrenes no identifiable substances could be isolated.

We thank Dr. O. Jeger and Mr. W. Manser (E.T.H., Zürich) for mixed m. p. determinations with their authentic phenanthrene derivatives, and for microanalyses, and Mr. P. K. Faure for the infrared spectrum. This Note is published with the permission of the South African Council for Scientific and Industrial Research.

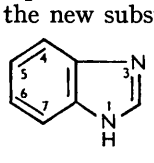
National Chemical Research Laboratory,
South African Council for Scientific and Industrial Research,
Pretoria, South Africa. [*Received, April 30th*, 1956.]

[5] Heilbronner, Däniker, and Plattner, *Helv. Chim. Acta*, 1949, **32**, 1723.

714. *Further Substitution in 5-Substituted Benziminazoles.*

By R. D. Brown and M. L. Heffernan.

Electrophilic reagents attack the benziminazole molecule (I) preferentially in the 5-position.[1] If then a $C_{(5)}$-substituent does not influence the course of further substitution, the new substituent would be expected to enter at the 6-position. In some cases this is the observed position of attack by electrophilic reagents, *e.g.* in nitration of 5-methyl-[2] and 5-methoxy-benziminazole.[3] However, when the substituent at the 5-position is the amino- or hydroxy-group the position of preferential attack is $C_{(4)}$.[4] It thus appears that an electron-releasing substituent at $C_{(5)}$ activates the 4-position to a greater extent than the 6-position. The order of electron release from the substituents mentioned above is [5] $NH_2 > OH > MeO > Me$ and apparently the *ortho*-activating effect of the first two



(I)

[1] Brown and Heffernan, *J.*, in the press.
[2] Fischer and Hess, *Ber.*, 1903, **36**, 3971.
[3] Ochiai and Kataga, *J. Pharm. Soc. Japan*, 1940, **60**, 543.
[4] Fries, *Annalen*, 1927, **454**, 121
[5] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell U.P., 1953, p. 805.

substituents is so great that the preferential activation of the 4-position as compared with the 6-position is sufficient to outweigh the inherent greater reactivity at the 6-position in unsubstituted benziminazole.

In the molecular-orbital theory the extent of transmission of electronic effects from one position, μ, to another, ν, in a conjugated system is measured by the magnitude of the mutual polarizability, $\pi_{\mu,\nu}$. To test theoretically this hypothesis of preferential transmission to the 4-position we have calculated the mutual polarizabilities for benziminazole. The results are given in the accompanying table for two different values of the nitrogen electronegativity parameter, h, which cover the range of values likely to be appropriate for the molecule in various environments.[1,6] For both values of h and doubtless therefore for intermediate values, $\pi_{5,4}$ is greater in magnitude than $\pi_{5,6}$ thus providing theoretical evidence for our hypothesis.

Mutual Polarizabilities for Benziminazole.

ν	1	2	3	4	5	6	7	8	9
$\pi_{5,\nu}$ [a] ...	+0·0092	−0·0200	+0·0036	−0·1780	+0·4028	−0·1244	+0·0216	−0·0840	−0·0272
$\pi_{5,\nu}$ [b] ...	−0·0420	−0·0804	−0·0824	−0·1324	+0·4356	−0·0688	+0·0296	−0·0028	−0·0572

[a] For $h = +1$. [b] For $h = -1$. Both in units of $1/\beta$.

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UNIVERSITY OF MELBOURNE, CARLTON, N.3,
VICTORIA, AUSTRALIA. [*Received, May 7th*, 1956.]

[6] Brown and Penfold, *Trans. Faraday Soc.*, in the press.

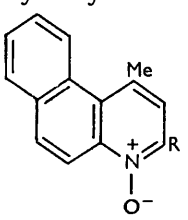
715. *Some Derivatives of 4-Propylpyridine and 5 : 6-Benzoquinoline.*

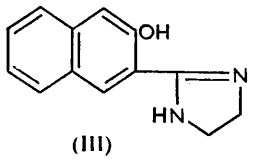
By C. W. REES.

8-HYDROXYQUINOLINE exerts its antibacterial action by combining with iron present in the medium, and the chelate is the true bactericidal agent.[1,2] Another powerful antibacterial, 2-mercaptopyridine 1-oxide,[3] is also a chelating agent. To demonstrate that its mode of action is similar to that of 8-hydroxyquinoline,[4] other lipophilic analogues have been prepared.

2-Chloro-4-methyl-5 : 6-benzoquinoline [5] was converted into the *N*-oxide, and the chlorine atom replaced by a hydroxy- or a mercapto-group, giving compounds (I) and (II)

(I): R = OH
(II): R = SH





(III)

respectively. Likewise 2-mercapto-4-*n*-propylpyridine 1-oxide was prepared from 2-bromo-4-propylpyridine. 4-*n*-Propylpicolinhydrazide was obtained from the acid [6] by way of the ethyl ester. 4 : 5-Dihydro-2-(3-hydroxy-2-naphthyl)glyoxaline (III) was also synthesized.

Experimental.—*5 : 6-Benzoquinolines.* 2-Chloro-4-methyl-5 : 6-benzoquinoline [5] (7·8 g.) and a solution of perbenzoic acid (1·2 equiv.) in chloroform (150 ml.) were set aside at 20° for 9 days. After extraction with 2N-sodium carbonate (3 × 50 ml.) the organic solution was evaporated to dryness and the residue was extracted continuously with light petroleum (b. p. 80—100°) to remove starting material. The residue of *2-chloro-4-methyl-5 : 6-benzoquinoline 1-oxide* gave colourless crystals (3·3 g., 40%), m. p. 208°, from ethanol (200 ml.; then concentrated) (Found : C, 69·4; H, 4·4; Cl, 14·85. $C_{14}H_{10}ONCl$ requires C, 69·0; H, 4·1; Cl, 14·55%).

[1] Albert, Gibson, and Rubbo, *Brit. J. Exp. Path.*, 1953, **34**, 119.
[2] Albert, Hampton, Selbie, and Simon, *ibid.*, 1954, **35**, 75.
[3] Shaw, Bernstein, Losee, and Lott, *J. Amer. Chem. Soc.*, 1950, **72**, 4362.
[4] Albert, Rees, and Tomlinson, unpublished work.
[5] Albert, Brown, and Duewell, *J.*, 1948, 1288.
[6] Solomon, *J.*, 1946, 934.

This oxide (1·4 g.) and 5N-sodium hydroxide were triturated together, then heated under reflux for 8 hr., diluted with boiling water to 250 ml. and filtered immediately, to remove starting material. Trishydroxymethyl-aminomethane (2 g.) was added as a buffer and the pH adjusted to 8·5 with sulphuric acid. After chilling, the precipitate of 2-hydroxy-4-methyl-5 : 6-benzoquinoline was filtered off and discarded. The filtrate, adjusted to pH 2, gave *2-hydroxy-4-methyl-5 : 6-benzoquinoline 1-oxide* (I) (0·4 g.) which, recrystallized from butan-1-ol, had m. p. 248° (Found : C, 74·7; H, 5·2; N, 6·1. $C_{14}H_{11}O_2N$ requires C, 74·7; H, 4·9; N, 6·2%). The product gives a deep red colour with aqueous ferric chloride; its solubility in boiling water is 10^{-4} mole/l.

A freshly prepared 4N-aqueous sodium hydrogen sulphide (1 equiv.) was added, during 1 hr., to 2-chloro-4-methyl-5 : 6-benzoquinoline 1-oxide (2 g.) in boiling ethanol (40 ml.), with stirring. After a further 30 min. the ethanol was recovered, and the residue triturated with a little water and adjusted to pH 2 with sulphuric acid. The precipitate was removed and extracted with cold N-sodium hydroxide (100 ml.; in portions) and precipitated at pH 2 (sulphuric acid). The precipitate was then extracted with 2% sodium hydrogen carbonate solution (4 × 50 ml.), and the extract adjusted to pH 2. This precipitate, recrystallized from acetone (concentrated), gave yellow *2-mercapto-4-methyl-5 : 6-benzoquinoline 1-oxide* (II) (0·2 g.), m. p. 173°, which oxidizes readily when moist (Found : C, 68·8; H, 4·5; N, 5·8; S, 13·5. $C_{14}H_{11}ONS$ requires C, 69·7; H, 4·6; N, 5·8; S, 13·3%). The product gives a deep green colour with aqueous ferric chloride; its solubility in boiling water is $<10^{-4}$ mole/l.

2-Mercapto-4-n-propylpyridine 1-oxide. 2-Bromo-4-propylpyridine [6] (10 g.) and a solution of perbenzoic acid (1·2 equiv.) in chloroform (127 ml.) were set aside at 20° for 5 days. The solution was extracted with 6N-hydrochloric acid (4 × 50 ml.), and the combined acid layers were taken to dryness at 90°/20 mm. The residual oil (10·8 g.) was dissolved in water (25 ml.) and adjusted to pH 6. To this solution, stirred on a steam-bath, freshly prepared 4N-aqueous sodium hydrogen sulphide (23·5 ml.) was added during 45 min., and the whole stirred for a further 45 min. The solution was cooled, taken to pH 2 (H_2SO_4), and extracted with chloroform. Recovery of the solvent left an oil which was extracted with 0·2N-sodium hydroxide, leaving undissolved sulphur. Chloroform-extraction at pH 2 yielded an oil, which was distilled under nitrogen at 110—140°/0·08 mm., and then fractionated to give pale yellow *2-mercapto-4-n-propylpyridine 1-oxide*, b. p. 94—96°/0·01 mm., n_D^{23} 1·6090 (Found : C, 57·2; H, 6·45; N, 8·3. $C_8H_{11}ONS$ requires C, 56·8; H, 6·55; N, 8·3%). It gives a deep purple colour with ferric chloride.

4-n-Propylpicolinhydrazide. 4-Propylpicolinic acid [6] (1·5 g.), fresh silver oxide (1·05 g.), ethyl iodide (1·42 g.), and dry xylene (8 ml.) were heated under reflux gently for 30 min. The mixture was filtered and the solid extracted with xylene. The xylene was recovered from the combined filtrates, and part of the residual *ethyl 4-n-propylpicolinate* (an oil; 1·6 g.) was converted in water into the *picrate*, which, recrystallized from 1 : 1 benzene–light petroleum, had m. p. 80° (Found : C, 48·5; H, 4·2; N, 13·35. $C_{17}H_{18}O_9N_4$ requires C, 48·35; H, 4·3; N, 13·3%). Hydrazine hydrate (90%; 0·8 g.) was added to the above ester (1·35 g.) in ethanol (15 ml.), and the whole set aside for 4 days at 20°. The volatile materials were distilled and the residual oil dried *in vacuo* at 20°, giving *4-n*-propylpicolinhydrazide (1·24 g.) which formed a *picrate* [made in water and recrystallized from benzene (70 parts)], m. p. 111° (Found : C, 44·1; H, 3·8; N, 20·6. $C_{15}H_{16}O_8N_6$ requires C, 44·1; H, 3·95; N, 20·6%), and a *hydrochloride* (dry acid in ethanol, followed by ether; recrystallized from 1 : 1 ethanol–ether), m. p. 200—201° (Found, for material dried at 60°/0·005 mm. over phosphoric oxide : C, 46·1; H, 6·0; O, 7·2; N, 18·1; Cl, 22·4. $C_9H_{13}ON_3,1{\cdot}5HCl$ requires C, 46·2; H, 6·2; O, 6·8; N, 18·0; Cl, 22·7%).

4 : 5-Dihydro-2-(3-hydroxy-2-naphthyl)glyoxaline (III). 3-Hydroxy-2-naphthamide [7] (4·5 g.) and ethylenediamine (1·6 ml., 1 mol.) were heated at 140° for 1·5 hr. and then at 180° for 1·5 hr. Ammonia and water were evolved and the mixture slowly reddened and set solid. The volatile fractions were removed at 180°/20 mm., and the remaining solid (5·0 g.) was crystallized twice from ethanol (60 parts), giving bright yellow crystals of the *naphthol* (3·0 g.), m. p. 222°, sublimed at 150°/0·01 mm. (Found : C, 73·5; H, 5·7; N, 12·9. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·7; N, 13·2%). The product gives a green colour with aqueous ferric chloride; it is readily soluble in N-hydrochloric acid, difficultly soluble in N-sodium hydroxide, and its solubility in water is 5×10^{-4} mole/l. at 20°.

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[7] Lesser, *Ber.*, 1925, **58**, 210.

716. *The Janovsky Reaction.*

By M. J. Newlands and F. Wild.

Development of colour in the well-known reaction [1] between sodium hydroxide and an acetone solution of *m*-dinitrobenzene or of 3 : 5-dinitrobenzoic acid is considered to be limited [2] to derivatives of the former. The wavelength of maximum absorption of the colours produced by a group of *m*-dinitrobenzene derivatives has been measured; other polynitro-aromatic compounds have also been investigated. The results (see Table) suggest that the production of a colour is not restricted to *m*-dinitrobenzene derivatives.

Experimental.—The polynitro-aromatic compounds were dissolved in acetone and their absorption curves determined with a Unicam SP.350 spectrophotometer. 10% Aqueous sodium hydroxide was then added to the acetone solution; the mixture was well shaken and the new absorption curve investigated.

Compound	Colour	$\lambda_{max.}$ (mμ)
1-Fluoro-2 : 4-dinitrobenzene	Greenish-blue	430 and 550
1 : 3-Difluoro-4 : 6-dinitrobenzene	Deep blue	420 and 580
1 : 3-Dichloro-4 : 6-dinitrobenzene	Deep blue	640
1 : 3-Dibromo-4 : 6-dinitrobenzene	Deep blue	615
2 : 4-Dinitrophenetole	Reddish violet	560
2 : 4-Dinitrobenzenesulphonic acid	Rose	490
2 : 4-Dinitroaniline	Red	560
2 : 4-Dinitrodiphenylamine	Red	590
N-2′-Hydroxyethyl-2 : 4-dinitroaniline	Red	—
2 : 4-Dinitrophenylhydrazine	Blood red	570
2-Chloro-1 : 6-dinitronaphthalene	Red	510
2 : 7-Dinitrofluorenone	Red-violet	485
4 : 5-Benzothiazol-2-yl 4 : 8-dinitronaphthyl sulphide	Red	425 and 535
N-Methylimide of 3 : 6-dinitronaphthalene-1 : 8-dicarboxylic acid	Red violet	450 and 570

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[1] Mann and Saunders, "Practical Organic Chemistry," Longmans, Green and Co., London, 1952, 3rd Edn., pp. 216, 261, 293.
[2] Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1948, 2nd Edn., p. 353.

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717. *The Effect of Solvent on the Rates of Solvolysis of* 1 : 2-*Dichloro*-2-*methylpropane and of* 3-*Chloro*-2-*methylpropene, and the Rearrangement of the Latter Chloride in Formic Acid.*

By P. B. D. de la Mare, K. Leffek, and Adib Salama.

In unimolecular solvolysis of alkyl halides, change in solvent from ethanol towards water accelerates substitution, often by a factor of 10^5 or more over the extremes of the range. In bimolecular substitution this factor is usually much smaller. Very few measurements have been recorded which define with certainty the rates of hydrolysis in water of halides which are known to react unimolecularly. A value for *tert.*-butyl chloride has been estimated [1] by extrapolation of data obtained in mixtures of acetone and water; and an approximate kinetic measurement has been made for the solvolysis in water of 3-chlorobut-1-ene.[1] These are included in Table 1, together with values from the literature for methyl bromide [2] and *n*-propyl chloride,[3] typical of compounds which react bimolecularly in aqueous ethanolic solvents. Relative rates [2,3] for solvolysis in slightly aqueous formic acid are also included.

[1] Grunwald and Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 847.
[2] Winstein, Grunwald, and Jones, *ibid.*, 1951, **73**, 2700.
[3] Vernon, *J.*, 1954, 423, 4462.

In an earlier paper, a value was recorded [4] for the solvolysis of 1 : 2-dichloro-2-methylpropane in water. Values are now recorded for mixtures of ethanol and water, and for formic acid, as solvents; and the hydrolysis of 3-chloro-2-methylpropene has also been studied in water. These values are given in Table 2 as initial first-order rate-coefficients

TABLE 1. *Relative rates for the solvolysis of some halides.*

Compound :	MeBr	Pr^{n}Cl	Bu^{t}Cl	Me·CHCl·CH:CH$_2$
Temperature :	50°	101·6°	25°	25°
Rel. k_1 (EtOH)	0·07	0·04	0·00026	0·0008
Rel. k_1 (80% EtOH)	0·39	—	0·025	—
Rel. k_1 (50% EtOH) *	1·0	1·0	1·0	1·0
Rel. k_1 (H_2O)	1·8	—	90	71
Rel. k_1 (H·CO_2H)	—	0·05	3·0	1·5

* For each compound the rate of solvolysis in 50% EtOH is taken as standard.

TABLE 2. *Relative* rates of solvolysis of 1 : 2-dichloro-2-methylpropane, and of 3-chloro-2-methylpropene.*

Compound :	$CMe_2Cl·CH_2Cl$	CH_2:$CMe·CH_2Cl$
Temperature :	45°	45°
Rel. k_1 (EtOH)	—	0·032
Rel. k_1 (80% EtOH)	0·12	—
Rel. k_1 (50% EtOH)	1·0	1·0
Rel. k_1 (H_2O)	56	5·3
Rel. k_1 (H·CO_2H)	1·9	0·0067

* See footnote to Table 1.

(k_1), calculated for the liberation of one mole of chloride ion per mole of dichloride. Included also are values recorded by Vernon [3] for the solvolysis of the latter compound in ethanol, mixtures of ethanol and water, and formic acid.

With regard, first, to the solvolysis of 1 : 2-dichloro-2-methylpropane, bimolecular (S_N2) substitution in this compound under any of the conditions used in this work is highly improbable for steric reasons. Bimolecular elimination would be expected to yield 1-chloro-2-methylpropene, with liberation of one equivalent of chloride ion per mole of dichloride. Unimolecular substitution has been shown [4] to be the dominant mechanism in water, and is the probable mechanism even in 80% ethanol, in view of the liberation, as in water, of a few per cent. of additional chloride per mole of starting material, as established by Brown, Kharasch, and Chao.[5] It is presumed, therefore, that in the intermediate solvents, and in formic acid, the solvolysis of 1 : 2-dichloro-2-methylpropane is unimolecular.

From related considerations, Vernon [3] deduced that solvolysis of 3-chloro-2-methylpropene in ethanol and in mixtures of ethanol and water is substantially bimolecular. The same is almost certainly true for the solvent water (Table 2), in which the reaction is enormously faster than the solvolysis, presumed to be unimolecular,[3] in formic acid. The marked contrast, shown in Table 1, in the effect of solvent on the rate of solvolysis of compounds reacting by unimolecular (S_N1) and bimolecular (S_N2) mechanisms, is maintained in the new results recorded in Table 2, and it is possible that for relatively unreactive halides, such as those now investigated, comparisons involving the more aqueous media may sometimes be convenient, in that they bring the reactivities into a region accessible at moderate temperatures.

The olefinic products formed in the solvolysis of 1 : 2-dichloro-2-methylpropane in slightly aqueous formic acid were found to contain a ratio of allylic to vinylic chloride of 0·1, the former being estimated by reaction with aqueous-ethanolic silver nitrate. This result, at first sight surprising in view of the quite different ratio found for reactions in water,[4] can be understood, since we have also shown that the allylic chloride, if formed, would isomerise under the conditions used in the solvolysis, giving the equilibrium mixture :

$$CH_2{:}CMe{\cdot}CH_2Cl + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3{\cdot}\overset{+}{C}Me{\cdot}CH_2Cl \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} H^+ + CH_3{\cdot}CMe{:}CHCl \qquad (1)$$

[4] de la Mare and Salama, *J.*, 1956, 3337.
[5] Brown, Kharasch, and Chao, *J. Amer. Chem. Soc.*, 1940, **62**, 3435.

This isomerisation, which is well known to occur in various aqueous acidic media,[6] and can be accompanied by hydration of the double bond, proceeds presumably through such a carbonium ionic intermediate as is indicated in reaction (1).

The final position of equilbrium is determined largely by the conjugation, in the vinylic chloride, of the chlorine atom with the double bond; both chlorides are stabilised also by the hyperconjugation of two approximately equivalent alkyl groups.

Added, July 31st, 1956.—More accurate results for the hydrolysis in water of *tert.*-butyl chloride and 3-chlorobut-1-ene have recently been given and discussed.[7]

Experimental.—Kinetic measurements were made by conventional techniques, described in other papers [3,4] where methods of specifying solvents and of calculating rate-coefficients are also described. For product analysis, 1 : 2-dichloro-2-methylpropane (200 g.) was refluxed with formic acid (1400 ml.) and water (50 ml.) for *ca.* 6 hr., while a slow stream of nitrogen was bubbled through the solution. The volatile products were collected in traps cooled to −80°, and added to pentane. The mixture was washed with water, with sodium carbonate till neutral, with water again, dried ($CaCl_2$), and fractionally distilled. The following fractions were obtained :

Fraction	Wt. (g.)	B. p.	n_D^{25}	Total Cl (%)	Hydrolysable Cl (%)
1	2·3	37·1—50·1°	1·3584	—	—
2	0·9	50·1—65·1	1·3869	—	0·6
3	1·6	65·1—68·1	1·4090	28·5	2·0
4	3·8	68·1—68·6	1·4203	28·7	2·6
5	1·1	68·6—71·1	1·4204	35·5	3·5
6	0·2	71·7—76·1	1·4204	—	—

The values under the heading " total Cl " were determined by Mr. A. V. Winter of this Department. Those for " hydrolysable Cl " were obtained in the following way. Known weights of the compound were heated in sealed tubes containing excess of alcoholic silver nitrate at 45° for three days; then the remaining silver nitrate was determined by Volhard's method.

The recovered chlorine-containing material clearly contained very little hydrolysable chlorine. The ratio of hydrolysable to total chlorine in fractions 3—5 is 0·09, a value which approximates closely to the equilibrium [5] value of 0·1.

To show that 3-chloro-2-methylpropene, if it had been formed in excess of the equilibrium amount, would not have survived the experimental conditions, 3-chloro-2-methylpropene (25 g.; b. p. 71·5°/760 mm., n_D^{25} 1·4270; hydrolysable Cl, 39·7%) was dissolved in formic acid (950 ml.) and water (50 ml.). The mixture was heated at 66° for 115 hr. These conditions were chosen because it was necessary to ensure that the chloride remained dissolved in the formic acid, and if the reaction mixture had been sealed up and heated at 100°, dangerous pressure would have developed through the acid-catalysed decomposition of formic acid to give carbon monoxide. After this period of heating, which was considered to be fairly equivalent to 6 hr. at 100°, nitrogen was bubbled through the solution, and the volatile products were collected and worked up as before, giving the following fractions :

Fraction	Wt. (g.)	B. p.	n_D^{25}	Total Cl	Hydrolysable Cl
1′	1·3	66·8—68°	1·4126	33·2	2·9
2′	1·4	68	1·4171	33·2	3·6
3′	3·0	Residue	1·4241	39·6	8·2

Under these conditions, isomerisation is clearly almost complete; the ratio of hydrolysable to total Cl is 0·15.

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[6] Burgin, Hearne, and Rust, *Ind. Eng. Chem.*, 1941, **33**, 385.
[7] Wilputte-Skinert and Fierens, *Bull. Soc. chim. belges*, 1955, **64**, 308.