NOTES.

939. *The Spontaneous Decomposition of Aryl Thiolsulphinates.*

By D. BARNARD.

BACKER and KLOOSTERZIEL [1] have reported the occasional spontaneous disproportionation of thiolsulphinates into thiolsulphonates and disulphides:

$$2R{\cdot}SO{\cdot}S{\cdot}R \longrightarrow R{\cdot}SO_2{\cdot}S{\cdot}R + R{\cdot}S{\cdot}S{\cdot}R$$

A number of aryl thiolsulphinates have been prepared by the method of these authors and found to be stable for several months under normal atmospheric conditions but to undergo rapid decomposition *in vacuo*. Thus *p*-tolyl benzenethiolsulphinate, which was particularly sensitive in this respect, decomposed after five minutes at 10^{-5} mm. and after one hour at 10^{-2} mm.; the corresponding times for *p*-chlorophenyl benzenethiolsulphinate were one and eight hours. The decomposition was made evident by sudden melting of the sample; no detectable loss in weight occurred and the rise in temperature was small (*ca.* 20°). Similar decomposition took place after longer periods of storage over phosphoric oxide, suggesting that in each case the stringent drying was responsible. An explanation might be that the destabilising effect of the highly polar $S\rightarrow O$ group on the thiolsulphinate molecule (the yellow colour of aryl thiolsulphinates suggesting charge separation within the molecule) is lessened by strong intermolecular bonding in the crystal lattice, the boundary molecules partially satisfying their bonding requirements by hydrogen-bond formation with absorbed water. On removal of the latter the decomposition of the surface molecules, possibly initiated photochemically, is propagated throughout the crystal either by a free-radical or ionic chain process or simply by the destabilisation of successive layers of molecules.

Thiolsulphinates carrying unlike aryl groups did not give an equimolar yield of disulphide and thiolsulphonate, and a third substance, isolated in the examples studied as benzenesulphonic acid, was a minor product. The disulphide and acid contents shown in the Table are considered accurate to ± 1%, but separation of thiolsulphonate was complicated by the presence of acidic material and no effort was made to improve the

Products of decomposition of thiolsulphinate Ph·SO·S·Ar′.

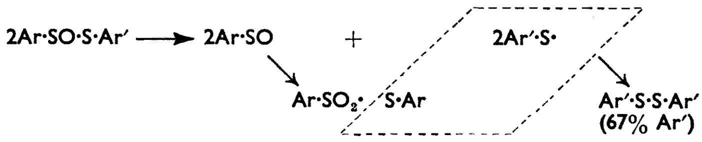
	Products (mole %)			
Ar′	Disulphide	Thiolsulphonate	Sulphonic acid	Ar′ group in disulphide (mole %)
Ph	51	46	—	—
p-Tolyl	57	43	7	64
p-$Cl{\cdot}C_6H_4$	62·5	30	16	67

---

[1] Backer and Kloosterziel, *Rec. Trav. chim.*, 1954, **73**, 129.

accuracy of recovery beyond ± 10%. It is difficult to visualise the formation of free benzenesulphonic acid and the infrared spectra of freshly decomposed thiolsulphinates confirmed the absence of hydroxyl groups. It must be assumed, therefore, that the sulphonic acid is formed by hydrolysis of an anhydride during the isolation procedure.

Now it has been shown that exchange of sulphenyl groups between disulphides and thiolsulphonates does not occur under the experimental conditions,[2] so the composition of the disulphides suggests that disproportionation of the thiolsulphinates does not involve



a simple oxygen transfer and that breaking of the S–S bond is an essential step. If this is assumed to be a homolytic cleavage to sulphinyl and sulphenyl radicals, then thiolsulphonate would be derived from the former radicals [2] and a mixed disulphide from the sulphenyl radicals after their equilibration with the sulphenyl group of the thiolsulphonate.

Experimental.—The thiolsulphinates were prepared by the method of Backer and Kloosterziel [1] and crystallised to constant m. p. by cooling solutions in chloroform–light petroleum (b. p. 30—40°) (1 : 30), saturated at room temperature, to −10°. Phenyl benzenethiolsulphinate had m. p. 69—70° (Found: C, 61·4; H, 4·2; S, 27·3. Calc. for $C_{12}H_{10}OS_2$: C, 61·5; H, 4·3; S, 27·4%). *p*-Tolyl benzenethiolsulphinate had m. p. 70·0—70·2° (Found: C, 62·7; H, 5·0; S, 25·7. Calc. for $C_{13}H_{12}OS_2$: C, 62·9; H, 4·8; S, 25·8%). p-*Chlorophenyl benzenethiolsulphinate* had m. p. 61—62° (Found: C, 53·8; H, 3·5. $C_{12}H_9OS_2Cl$ requires C, 53·6; H, 3·4%).

Isolation of the products of decomposition. The following procedure was typical. *p*-Tolyl benzenethiolsulphinate (1·1935 g.) was kept at 10^{-5} mm. until decomposition occurred (5 min.), to give a yellow oil (1·1933 g.), a portion of which (0·6277 g.), dissolved in carbon tetrachloride (50 ml.), was absorbed on a silica gel column (20 × 1 cm.; 20 g.; 100—120 mesh). Elution with carbon tetrachloride (150 ml.) and then chloroform (200 ml.) gave respectively, after removal of the solvents, disulphide (0·3407 g.) [Found: C, 67·5; H, 5·4; S, 27·1. Calc. for $C_{14}H_{14}S_2$ (64 mole %) + $C_{12}H_{10}S_2$ (36 mole %): C, 67·5; H, 5·3; S, 27·1%)] and thiolsulphonate (0·2870 g.; purity by infrared spectroscopy 96%) contaminated with acidic material. The original material (0·5395 g.) required 8·0 ml. of 0·0213N-sodium hydroxide for neutrality to screened methyl-red. A larger quantity of the thiolsulphinate (10·41 g.) was similarly decomposed and the products extracted with water. The aqueous solution was neutralised and evaporated to small volume (2 ml.). Addition of benzyl*iso*thiuronium chloride (0·3 g.) in water (1 ml.) gave an immediate precipitate (0·24 g.), m. p. 140—142·5°, which after one crystallisation from light petroleum (b. p. 60—80°)–ethanol had m. p. and mixed m. p. with authentic benzyl*iso*thiuronium benzenesulphonate 145·5—146·5°.

British Rubber Producers' Research Association,
48–56, Tewin Road, Welwyn Garden City, Herts.

[*Received, June 28th,* 1957.]

---

[2] Barnard, preceding paper.

940. *The Resolution of* 3 : 5-*Dimethylhex*-1-*yn*-3-*ol. The Reduction of its* (+)-*Isomeride to* (—)-3 : 5-*Dimethylhexan*-3-*ol.*

By J. R. Hickman and J. Kenyon.

ALTHOUGH the brucine salt of (+)-3 : 5-dimethylhex-1-yn-3-yl hydrogen phthalate is much less soluble than its diastereoisomeride, their separation by fractional crystallisation proved slower than expected—owing, possible, to adsorption of the more soluble salt on the crystals of the less soluble. This behaviour was not encountered in the resolution of 3-methylpent-1-yn-3-ol.[1]

The specific rotatory powers of the (+)-hydrogen phthalate have been determined in a number of solvents (see Table 1); the values are all of the same sign and, for a given wavelength, cover a relatively restricted range.

TABLE 1.

Specific rotatory powers of (+)-3 : 5-*dimethylhex*-1-*yn*-3-*yl hydrogen phthalate in various solvents* (*l*, 1; *c*, 10·00).

Solvent	Temp.	$[\alpha]_{4358}$	$[\alpha]_{4800}$	$[\alpha]_{5086}$	$[\alpha]_{5461}$	$[\alpha]_{5780}$	$[\alpha]_{5893}$
EtOH	24°	+106°	+75·3°	+65·4°	+54·4°	+47·1°	+45·5°
Et_2O	24	82·5	60·0	51·6	41·8	37·3	34·0
Dioxan	23	53·1	38·8	33·2	27·4	24·8	22·2
Acetone ...	24	80·4	58·6	50·9	40·8	35·6	34·8
Pyridine ...	23	66·2	46·4	42·5	33·8	30·7	26·3
$CHCl_3$	23	67·3	48·8	44·3	35·6	32·1	29·5
C_6H_6	24	47·0	43·9	36·5	30·0	27·2	25·5
EtOAc	23	78·6	58·0	50·2	40·5	36·5	33·1

Specific rotatory powers of (—)-3 : 5-*dimethylhex*-1-*yn*-3-*yl* p-*nitrobenzoate* (*l*, 1; *c*, 7·9).

		$[\alpha]_{4800}$	$[\alpha]_{5086}$	$[\alpha]_{5461}$	$[\alpha]_{5780}$	$[\alpha]_{5893}$	$[\alpha]_{5438}$
Benzene......	21°	—71·0°	—60·4°	—41·1°	—40·9°	—36·1°	—37·7°

Despite this uniformity of optical behaviour, the (—)-hydrogen phthalate yielded, on hydrolysis, the (+)-alcohol, which in turn gave a (—)-*p*-nitrobenzoate. This acetylenic alcohol was readily hydrogenated to the saturated lævorotatory alcohol.

The rotatory power of the saturated alcohols obtained (*a*) by direct resolution[2] (α_{5893}^{21} —2·26°) and (*b*) (α_{5893}^{20} —2·65°) by reduction of the acetylenic alcohol are in close agreement, suggesting that both the saturated and the unsaturated alcohol have been obtained virtually optically pure. Further evidence for this is provided by an independent resolution of the saturated alcohol in this laboratory by Salamé[3] which gave the value α_{5893}^{20} —2·72°.

TABLE 2.

Observed rotatory powers of (—)-3 : 5-*dimethylhex*-1-*yn*-3-*ol at* 20° (*l*, 1).

α_{4358}	α_{4800}	α_{5086}	α_{5461}	α_{5780}	α_{5893}	α_{6438}
—2·22°	—1·58°	—1·47°	—1·44°	—1·19°	—1·26°	—1·08°

Observed rotatory powers of (—)-3 : 5-*dimethylhexan*-3-*ol* (*optical purity* 40%) *at* 19° (*l*, 1)

α_{4358}	α_{4800}	α_{5086}	α_{5461}	α_{5780}	α_{5893}
—2·46°	—1·79°	—1·52°	—1·41°	—1·24°	—0·99°

---

[1] Hickman and Kenyon, *J.*, 1955, 2051.

[2] Doering and Zeiss, *J. Amer. Chem. Soc.*, 1948, **70**, 3966.

[3] Salamé, Ph.D. Thesis, London, 1955.

Experimental.—(±)-3 : 5-Dimethylhex-1-yn-3-ol was obtained by distillation of a commercial sample, the middle fraction of b. p. 150—151°, d_{20}^{20} 0·8597, n_{D}^{20} 1·4350, being used (Found: C, 76·1; H, 11·2. Calc. for $C_8H_{14}O$: C, 76·2; H, 11·1%).

(±)-3 : 5-*Dimethylhex*-1-*yn*-3-*yl hydrogen phthalate.* The alcohol (35 g.), phthalic anhydride (40 g.), and triethylamine (20 g.) were heated at 90° for 2 hr., then treated with cold dilute hydrochloric acid and extracted with ether. The extract was washed with dilute acid, then with aqueous sodium carbonate; the sodium carbonate extracts were shaken with ether, then acidified, and the liberated *ester* extracted with chloroform. This, after drying and removal of the solvent, yielded the crude ester (59 g., 79%) which separated from aqueous ethanol (charcoal) in rhombs, m. p. 111—112° [Found: C, 70·1; H, 6·6%; *M* (by titration with KOH), 274. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·6%; *M*, 274].

Resolution. The (±)-phthalate (50 g.) and anhydrous brucine (73·5 g.) were dissolved in the minimum quantity (750 c.c.) of boiling acetone, and the solution allowed to cool. The crystals which had separated during 2 days were recrystallised thrice from acetone, thus becoming almost insoluble in the boiling solvent. They were then heated under reflux with acetone and the procedure repeated four times with fresh solvent. The resulting crystals were recrystallised from benzene in which they were appreciably more soluble. The last two crops of brucine salt, rhombs, m. p. 183—184°, after decomposition with acid, yielded (+)-3 : 5-*dimethylhex*-1-*yn*-3-*yl hydrogen phthalate* of identical rotatory powers. The last ester (17·5 g.) separated from aqueous ethanol in rhombs, m. p. 61—62° (Found: *M*, 273). Rotatory powers are in Table 1.

A mixture of the more soluble fractions of brucine salt produced as above was decomposed with dilute hydrochloric acid, and the liberated acid ester extracted with ether. After removal of the ether, this had m. p. 102—104° and $[\alpha]_{5893}^{20}$ −11·2° (*c*, 10·00; *l*, 1) in C_6H_6: after seven recrystallisations from benzene–light petroleum, the (−)-*hydrogen phthalate* was optically pure, forming rhombs, m. p. 63—65°, $[\alpha]_{5893}^{20}$ −24·9° (*c*, 10·00; *l*, 1) in C_6H_6 (Found: *M*, 272).

(−)-3 : 5-*Dimethylhex*-1-*yn*-3-*ol.* The (+)-hydrogen phthalate (16·0 g.) was heated with a slight excess of methanolic potassium hydroxide, and the liberated alcohol removed in steam; the distillate was saturated with salt and extracted with ether. The resulting (−)-3 : 5-*dimethylhex*-1-*yn*-3-*ol* (5·2 g.) had b. p. 150—151°/760 mm., 56—57°/19 mm., d_{20}^{20} 0·8594, n_{D}^{20} 1·4348 (Found: C, 76·1; H, 11·0%). Rotatory powers are in Table 2.

(±)-3 : 5-*Dimethylhex*-1-*yn*-3-*yl* p-*nitrobenzoate.* The (±)-alcohol (1·4 g.), *p*-nitrobenzoyl chloride (1·9 g.), and pyridine (3 g.), after 5 min. on the steam bath, gave this *ester*, needles (1·2 g.) (from aqueous ethanol), m. p. 52—53° (Found: C, 65·5; H, 6·4; N, 5·1. $C_{15}H_{17}O_4N$ requires C, 65·0; H, 6·8; N, 5·1%).

The (−)-*ester*, similarly prepared from the (+)-alcohol, formed needles (from aqueous ethanol), m. p. 53—54° (Found: C, 65·4; H, 6·2; N, 5·1%). Rotatory powers are in Table 1.

(±)-2-(3 : 5-*Dimethylhex*-1-*yn*-3-*yl*) 1-*hydrogen* 3-*nitrophthalate.* The (±)-alcohol (2 g.), 3-nitrophthalic anhydride (2·8 g.), and pyridine (3 g.), after 1 hr. on the steam-bath, were worked up as above. The resulting *ester* (2·3 g.) separated from aqueous ethanol in rhombs, m. p. 145—146° [Found: C, 60·0; H, 5·2; N, 4·4%; *M* (by titration), 316. $C_{16}H_{17}O_6N$ requires C, 60·2; H, 5·3; N, 4·4%; *M*, 319]. The structure of this ester is based on the usual behaviour of 3-nitrophthalic anhydride when heated with alcohols.

Reduction of (+)-3 : 5-*dimethylhex*-1-*yn*-3-*ol to* (−)-3 : 5-*dimethylhexan*-3-*ol.* (+)-3 : 5-Dimethylhex-1-yn-3-ol, α_{5893}^{20} +0·50° (*l*, 1) (optical purity 40%) (5 g.), in ether (100 c.c.) was shaken with hydrogen (palladium–charcoal) until no more was absorbed. After filtration and distillation, the resulting (−)-3 : 5-dimethylhexan-3-ol (2·1 g.) had b. p. 150—151°/760 mm., d_{20}^{20} 0·8344, n_{D}^{18} 1·4271 (Found: C, 73·0; H, 13·6. Calc. for $C_8H_{18}O$: C, 73·8; H, 13·8%). Rotatory powers are in Table 2.

Thanks are expressed to the Central Research Fund Committee of London University for a Grant.

BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, April* 30*th*, 1957.]

941. *Relative Rates of Mutarotation of Tetra-O-methyl-α-D-glucose in H_2O and D_2O and the Mechanism of the Reaction.*

By B. C. CHALLIS, F. A. LONG, and Y. POCKER.

THE most probable mechanism for the acid catalysed mutarotation of glucose and similar sugars involves protonation of the ether-oxygen atom, followed by attack of a base on the alcohol proton with simultaneous ring opening.[1] This is, of course, a case of general acid-catalysis. A somewhat similar mechanism presumably holds for the observed general base-catalysis.

A frequent test for the existence of a pre-equilibrium proton transfer of the type of step (1) is a study of the relative rates of reaction in the solvents deuterium oxide and water. Data for such studies with glucose are listed in Table 1. The $(k_H/k_D)_{H^+}$ ratio for catalysis by strong acids is greater than unity, considerably larger than is usually observed for reactions with a pre-equilibrium proton transfer. This fact has frequently led to the suggestion that the reaction does not involve a pre-equilibrium but goes by a one-step slow protonation.[2] However, an alternative explanation for the observed large ratio is that there is indeed a pre-equilibrium proton transfer, with as a consequence a relatively larger concentration of conjugate acid for the D_2O case, but that the rate of step (2) (for reaction with water as the base) is so much slower in the solvent D_2O that the effect of step (1) is more than counterbalanced. Such a large isotope effect on the slow step does not appear to occur in other pre-equilibrium mechanisms but it is imaginable that the glucose reaction is special, possibly because glucose has five hydroxyl groups with exchangeable hydrogen atoms. To see if this last aspect of glucose is of importance we

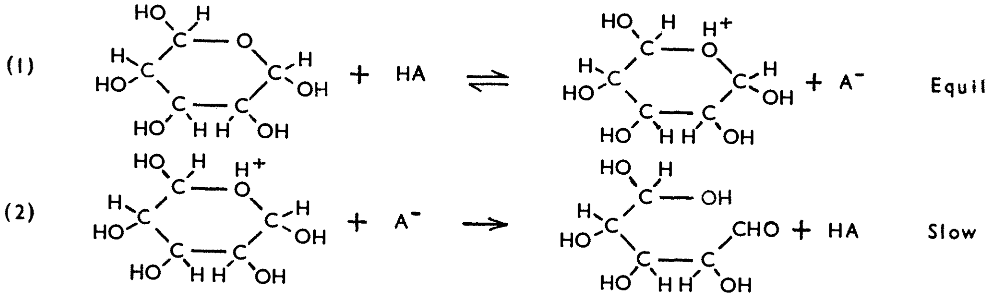


TABLE 1. *Relative rates of mutarotation* (k_H/k_D) *in* H_2O *and* D_2O *at* 25°.

Catalyst	Glucose	Ref.	Tetramethylglucose
H^+	1·37	[a]	1·31
H_2O	3·80 or 3·16	[a, b]	3·2
AcOH	2·6	[a]	
AcO^-	2·38		

[a] Hamill and LaMer, *J. Chem. Phys.*, 1936, **4**, 395. [b] Moelwyn-Hughes, Klar, and Bonhoeffer, *Z. Electrochem.*, 1934, **40**, 469.

---

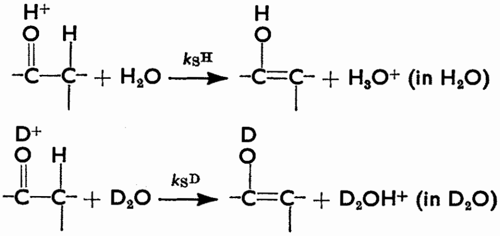
[1] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, Chap. XI; Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N.Y., 1953, Chap. X.

[2] Bonhoeffer, *Trans. Faraday Soc.*, 1938, **34**, 252; Bell, " Acid–Base Catalysis," Oxford Univ. Press, 1941.

have studied the uncatalysed and the acid-catalysed mutarotation of tetra-*O*-methyl-α-D-glucose in the solvents D_2O and H_2O. Table 1 summarises the results.

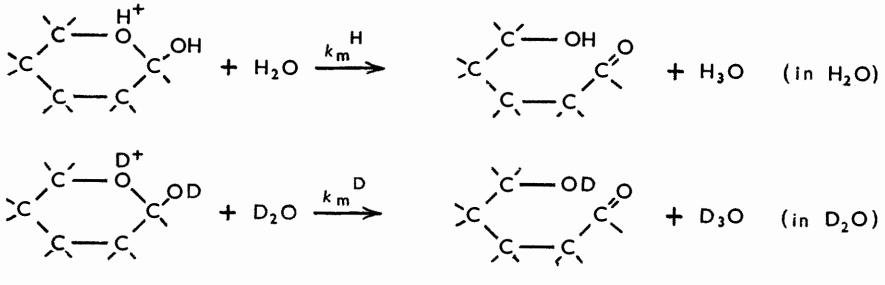
Since the results for tetramethylglucose are so similar to those for ordinary glucose, it is reasonable to conclude that the large value of k_H/k_D for catalysis by strong acids is a characteristic property of the mutarotation. The question then remains: if a pre-equilibrium proton transfer is involved, why the uniquely high $(k_H/k_D)_{H^+}$ ratio? We believe that there is a plausible answer to this question and hence that the pre-equilibrium mechanism is very probably correct.

Almost all of the many acid-catalysed reactions studied in H_2O and D_2O involve specific hydrogen-ion catalysis, not general acid-catalysis. The slow step for these reactions thus does not involve a proton transfer. Other than the glucose mutarotation, the only reaction studied which certainly shows general acid-catalysis and hence involves a slow proton transfer is the enolisation of acetone (normally studied by halogen absorption). In this case the observed $(k_H/k_D)_{H^+}$ ratio is 0·47, *i.e.*, the acid-catalysed reaction is faster in D_2O.[3] This is the expected result since it is well established from other evidence that the reaction involves a pre-equilibrium proton transfer.[4] The important thing is that here the proton which is attacked in the slow step remains unchanged for reaction in the solvents D_2O and H_2O. The rate-determining reactions for water as the base, are:



Since a C–H bond is broken in the rate step for both reactions, a value of $k_S^H/k_S^D = 1$ is reasonable. Hence the observed $(k_H/k_D)_{H^+}$ of 0·47 is a straightforward reflection of the different amounts of conjugate acid formed in the pre-equilibrium step. However, if the reaction in D_2O had involved fission of a C–D rather than of a C–H bond the rate would have been decreased enough to make the $(k_H/k_D)_{H^+}$ ratio considerably greater than unity. This follows from the fact that the acid-catalysed enolisation of [$^2H_6$]acetone in either H_2O or D_2O is slower [5] than that of ordinary acetone by a factor of 7·7.

The reason for the large $(k_D/k_H)_{H^+}$ ratio for mutarotation (on the pre-equilibrium mechanism) is now evident. The protons of hydroxyl groups are known to equilibrate instantaneously with an aqueous solvent.[6] Hence for mutarotation the slow step involves rupture of an O–H bond for reaction in H_2O and an O–D bond in D_2O, with simultaneous ring opening in both cases:



---

[3] Reitz, *Z. phys. Chem.*, 1937, **179**, *A*, 119.
[4] Ref. 1, chap. VIII.
[5] Reitz and Kopp, *Z. phys. Chem.*, 1939, **184**, *A*, 429.
[6] Ref. 5 gives data on this point for glucose itself.

One can thus expect a slower rate-determining step in D_2O. Even noting that much of the energy of activation for this step must come from the simultaneous ring opening, a factor of k_m^H/k_m^D of around 3 is not unreasonable. This is enough to counterbalance the effect of the pre-equilibrium and explain the observed $(k_H/k_D)_{H^+}$ ratio.[*]

If this explanation is valid it can be predicted that $(k_H/k_D)_{H^+}$ values for aqueous reactions which exhibit general acid-catalysis along with pre-equilibrium proton transfer will separate fairly sharply into two groups: values of about $\frac{1}{2}$ to $\frac{1}{3}$ for cases where the proton which is attacked in the slow step does not exchange with the solvent and values of 1 or larger where the proton which is attacked exchanges rapidly with the solvent.

Experimental.—2 : 3 : 4 : 6-Tetra-*O*-methyl-D-glucose was prepared in the usual manner,[7] and the α-form was recovered by repeated recrystallisation from anhydrous " pentane " (b. p. 26—40°) containing 0·5% of ether. The rate of mutarotation was followed polarimetrically in a jacketed 20 cm. polarimeter tube. The solutions contained 0·0936 g. of tetramethylglucose per ml. Rate coefficients were determined by the Guggenheim procedure.

Studies were made at 25° and at a constant ionic strength of 0·2. The spontaneous rate was measured at pH 4·7, at which contributions from terms in H^+ and OH^- are negligible; the solutions were 0·005M in sodium acetate, 0·0025M in acetic acid, and 0·195M in sodium chloride. The acid-catalysed mutarotation was studied with solutions of hydrochloric acid containing sodium chloride to give an ionic strength of 0·2. The experimental results are in Table 2.

TABLE 2.

Solvent	[HCl] (M)	$10^4k_{exp.}$ (sec.$^{-1}$)	$10^4k_{exp.}$ (average)	$k_{H^+} = (k_{exp.} - k_{H_2O})/C_{H^+}$
H_2O	(pH = 4·7)	3·42; 3·44; 3·46	3·44	—
D_2O	(pH = 4·7)	1·07; 1·06	1·065	—
H_2O	0·0585	6·22; 6·24	6·23	47·7
D_2O	0·0538	2·99	2·99	35·8
H_2O	0·115	9·06; 9·14	9·10	49·2
D_2O	0·100	4·88; 4·76	4·82	37·6
H_2O	0·173	11·74	11·74	48·0
D_2O	0·165	7·11	7·11	36·6

From the average values the ratios are $(k_H/k_D)_{H_2O} = 3·23$ and $(k_H/k_D)_{H^+} = 1·31$.

The original deuterium oxide contained 99·8 atoms % of D. There was some isotopic dilution from the added tetramethylglucose, acetic acid, and hydrochloric acid, and the extent of this differed slightly in the various runs. However, to a good approximation the quoted ratios can be taken to be for the solvents water and 99% deuterium oxide.

One of the authors (F. A. L.) is indebted to the National Science Fundation (U.S.A.) for a Fellowship during 1956—1957.

F. A. LONG: Permanent address, DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N.Y.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE,
GOWER STREET, LONDON, W.C.1. [*Received, June 24th*, 1957.]

---

[*] A fairly straightforward argument can be made to show that the observed $(k_H/k_D)_{H^+}$ ratio for mutarotation is semi-quantitatively in accord with the pre-equilibrium mechanism. From the Bigeleisen procedure for treating isotope effects (*J. Chem. Phys.*, 1949, **17**, 324) one can express the ratio of rate coefficients for the slow step as $(k_m^H/k_m^D) = F\nu_*^H/\nu_*^D$, where F is a function which involves zero-point energies of reactants and transition state and ν_* is the frequency with which the transition state species moves across the barrier to give products. Since movement of H *versus* D is involved, ν_*^H/ν_*^D should be $\sqrt{2}$. The observed $(k_H/k_D)_{H^+}$ value will be the product of the above ratio and a term which expresses the different concentrations of the conjugate acids formed in the pre-equilibrium step. However, the latter also depends on the different zero-point energies and can be written $1/F'$ where, because for both step (1) and (2) the important change is from an OH to an OD group, $F' \approx F$. Hence the observed ratio should be $(k_H/k_D)_{H^+} \approx \sqrt{2}$.

[7] *Org. Synth.*, 1940, **20**, 100.

942. *The Organic Chemistry of Phosphorus. Part VI.** *Some Phosphorus-containing Derivatives of 2 : 2 : 2-Trichloroethanol and* N-*Methylaniline.*

By H. N. RYDON and B. L. TONGE.

THE experiments described below were carried out in an unsuccessful attempt to find reagents which might, in certain cases, advantageously replace triphenyl phosphite in the preparation of alkyl [1] and aryl [2] halides.

One such reagent is tris-2 : 2 : 2-trichloroethyl phosphite (I), which is readily prepared by the action of phosphorus trichloride on 2 : 2 : 2-trichloroethanol in the presence of a tertiary amine.[3] In our hands, contrary to the experience of Gerrard, Green, and Phillips,[3] omission of the base led to the formation of the phosphonate (II); the most obvious mechanism for the formation of this ester (II) is by an intramolecular Arbuzov reaction of the ester (I), but such reactions are generally slow [4] and ester (I) has been shown to be stable to hydrogen chloride under the reaction conditions; some more direct mechanism may, therefore, obtain. Gerrard, Green, and Phillips [3] state that the action of chlorine on the phosphite (I) yields the phosphate (IV), directly, " by a mechanism still obscure." Stoicheiometric considerations alone seem to preclude direct formation of a phosphate from a phosphite; the maximum possible yield in such a reaction, without intervention of any other oxygen-containing reagent, is 75%, which is the yield of phosphate actually isolated by Gerrard, Green, and Phillips, while even higher yields of phosphate from tris-1 : 1 : 1 : 3 : 3 : 3-hexachloro*iso*propyl phosphite are recorded.[5] Re-investigation of the reaction between the phosphite (I) and chlorine has shown that the first product is a dichloride, (III), or some ionic form of this,[6] which yields 1 : 1 : 1 : 2-tetrachloroethane on pyrolysis; this dichloride, which is the first trialkyl phosphite dihalide to have been isolated, gave a good yield of the phosphate (IV) on treatment with water. The dichloride (III) resembles the analogous aryl compounds [6] in being extremely susceptible to the action of moisture, mere traces of which suffice to convert it into the phosphate; there seems little doubt that the earlier workers underestimated the sensitivity of the dichloride towards moisture and were thus led to believe that the phosphate was formed directly.

(I) $(CCl_3{\cdot}CH_2{\cdot}O)_3P$ $(CCl_3{\cdot}CH_2{\cdot}O)_2P(O){\cdot}CCl_2{\cdot}CH_2Cl$ (II)

(III) $(CCl_3{\cdot}CH_2{\cdot}O)_3PCl_2$ $(CCl_3{\cdot}CH_2{\cdot}O)_3PO$ (IV)

Another reagent which might replace triphenyl phosphite in some of its preparative applications is phosphorous tri-(*N*-methylanilide) † $P(NMePh)_3$, which is readily prepared from phosphorus trichloride and *N*-methylaniline; it forms an addition compound with chlorine, which gives phosphoric tri-(*N*-methylanilide) $PO(NMePh)_3$ with water but is insufficiently reactive towards alcohols to be of preparative value.

---

* Part V, Ayres and Rydon, *J.*, 1957, 1109.

† Since our work was completed this compound has been prepared, but not purified, by Abramovitch, Hey, and Long.[7]

[1] Landauer and Rydon, *J.*, 1953, 2224; Coe, Landauer, and Rydon, *J.*, 1954, 2281.

[2] Coe, Rydon, and Tonge, *J.*, 1957, 323.

[3] Gerrard, Green, and Phillips, *J.*, 1954, 1148.

[4] Kabachnik and Rossiiskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1946, 295, 403, 515.

[5] Gerrard and Howe, *J.*, 1955, 505.

[6] Rydon and Tonge, *J.*, 1956, 3043.

[7] Abramovitch, Hey, and Long, *J.*, 1957, 1781.

Experimental.—Tris-2 : 2 : 2-*trichloroethyl phosphite* (I). Phosphorus trichloride (13·8 g.) was added slowly, with stirring, to 2 : 2 : 2-trichloroethanol (45 g.) and diethylaniline (45 g.) in ether (200 ml.) at 0°. After 2 hr. dimethylaniline hydrochloride (52 g., 93%) was filtered off and the filtrate distilled, affording the phosphite (33·7 g., 71%), b. p. 127—131°/0·1 mm., n_D^{20} 1·5174.

The phosphite (3 g.), containing chloral (10 mg.), was warmed to 60° while dry hydrogen chloride was passed through it for an hour. Distillation gave unchanged phosphite (2·75 g., 92%), b. p. 150—153°/3 mm., n_D^{20} 1·5173.

Bis-2 : 2 : 2-*trichloroethyl* 1 : 1 : 2-*trichloroethyl phosphonate* (II). Phosphorus trichloride (13·8 g.) was added slowly during an hour to cooled, stirred 2 : 2 : 2-trichloroethanol (45 g.). Stirring was continued for a further hour, the mixture solidifying. The product was treated with light petroleum (b. p. 40—60°) and filtered; recrystallisation of the solid (31 g., 65%), m. p. 144—146°, from chloroform–light petroleum (b. p. 40—60°) gave the *phosphonate* in fine needles, m. p. 153—154° [Found: C, 15·0; H, 1·6; P, 6·4%; *M* (Rast), 450 ± 25. $C_6H_6O_3PCl_9$ requires C, 15·2; H, 1·3; P, 6·5%; *M*, 476·5]. The compound was unchanged after treatment with chlorine or bromine in chloroform solution; hydrolysis by 4 hours' refluxing with 2N-sodium hydroxide yielded 2 : 2 : 2-trichloroethanol (1·85 mol.), characterised as its 1-naphthylurethane, m. p. and mixed m. p. 120°.

Action of chlorine on tris-2 : 2 : 2-*trichloroethyl phosphite*. (*a*) Chlorine was passed, with stirring, into a solution of the phosphite (9·5 g.) in anhydrous ether (50 ml.) until a faint permanent green colour appeared. The product was evaporated under reduced pressure and the solid, hygroscopic residue was treated with water. The resulting solid was recrystallised from aqueous ethanol, affording tris-2 : 2 : 2-trichloroethyl phosphate (7·3 g., 74%), m. p. 71° (lit.,[3] m. p. 72°).

(*b*) The phosphite (23·8 g.) was similarly treated with chlorine (3·6 g.); after a further hour's stirring, the bulk of the ether was removed by decantation and the residue dried *in vacuo*. The product was heated in a bath at 150°; redistillation of the volatile product gave 1 : 1 : 1 : 2-tetrachloroethane (4·5 g., 54%), b. p. 130—134° (lit.,[8] b. p. 135°).

Phosphorous tri-(N-*methylanilide*). Phosphorus trichloride (13·75 g.) was added, with stirring and ice-cooling, to *N*-methylaniline (64·2 g.) in ether (500 ml.). After refluxing for 2 hr., the mixture was cooled and base hydrochloride removed by filtration. Evaporation of the filtrate to dryness gave a deliquescent solid which, on recrystallisation from benzene, gave *phosphorous tri*-(N-*methylanilide*) (30 g., 86%) as prisms, m. p. 208—209° (Found: N, 11·9. $C_{21}H_{24}N_3P$ requires N, 12·0%).

This anilide (11·4 g.), dissolved in a little anhydrous chloroform, was treated with chlorine (2·33 g.). The solution was evaporated under reduced pressure and the solid residue treated with butan-1-ol (2·5 g.); there was no reaction. Water (100 ml.) was then added and the mixture heated on a steam-bath for an hour. After cooling, the solid product was washed with 2N-hydrochloric acid and water; recrystallisation from ethanol gave phosphoric tri-(*N*-methylanilide) (10·9 g., 92%), m. p. 162° (lit.,[9] m. p. 162°).

We thank Mr. V. Manohin for the microanalyses.

MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY,
MANCHESTER, 1.

[*Received, July* 1*st*, 1957.]

---

[8] Kokatnur, *J. Amer. Chem. Soc.*, 1919, **41**, 120.
[9] Michaelis, *Annalen*, 1903, **326**, 129.

943. *Potassium Fluoromanganate*(III).

By R. D. PEACOCK.

ALTHOUGH potassium aquopentafluoromanganate(III) is sometimes prepared in the laboratory as a student exercise, the existence of the anhydrous complex fluoride K_3MnF_6 appears to have been overlooked, perhaps because it cannot be made from aqueous solution. We have prepared it by a method similar to that used to isolate potassium fluororhodate(III) and potassium fluororuthenate(III), *viz.*, the treatment of a suitable salt, in this case the complex aquofluoride, with anhydrous potassium hydrogen difluoride.

Potassium fluoromanganate(III) is a bluish-violet powder, stable indefinitely in the atmosphere at ordinary temperatures. It dissolves in dilute hydrofluoric acid re-forming the aquo-complex, but is decomposed by warm water to hydrated manganese sesquioxide Mn_2O_3,nH_2O. The magnetic moment ($\mu = 4{\cdot}95$ B.M.) indicates the four unpaired spins expected for Mn^{3+}. *X*-Ray photographs show the unit cell to be tetragonal (Table) with a large unit cell; the stronger lines can, however, be indexed on a smaller tetragonal pseudo-cell related to that of other cryolites.

In view of discrepancies in the literature regarding cryolite structures, the compounds K_3CrF_6 and K_3FeF_6 have also been made by the same technique; they then show a very slight tetragonal modification of their cubic structures reported by Bode and Voss.[2] However, small distortions of this kind have been noticed for several other cryolites at the ordinary temperature; they have been variously explained as being due to changes of composition[1] or to temperature effects causing rotation of the MF_6^{3-} octahedra about one axis.[2]

The distortion of potassium fluoromanganate(III) is obviously of a different kind, since the c/a axis ratio is reversed. Furthermore, in other cryolite structures the MF_6^{3-} octahedra can be regarded as approximately regular, but in K_3MnF_6 the distortion is so great that this is unlikely to be true. Crystal-field theory predicts[3] that a large Jahn–Teller distortion should occur for the d^4 electronic configuration attained in tervalent manganese, and this has recently been observed in manganese trifluoride[4] where two of the Mn–F bonds in each MnF_6 octahedron are considerably longer than the other four.

It is tempting to assume that in K_3MnF_6 the cell dimensions indicate the alternative distortion whereby two bonds in each MnF_6^{3-} octahedron are *shorter* than the other four. If, however, it is assumed that there are two *longer* bonds in each octahedron, it is still possible to have a unit cell with the required c/a ratio provided the cell edges are at least doubled. The available data therefore agree with either explanation.

The observed molecular volumes (Table) are important inasmuch as they suggest that in this kind of distortion the lengthening of some bonds is exactly compensated for by the shortening of others.

Experimental.—*Potassium fluoromanganate*(III). The aquo-salt K_2MnF_5,H_2O was prepared by Palmer's method[5] (Found: Mn, 22·0. Calc. for K_2MnF_5,H_2O: Mn, 22·3%). Potassium hydrogen difluoride was prepared from "AnalaR" reagents and dried at 100° before use.

Unit cells of potassium fluorochromate(III), *fluoromanganate*(III), *and fluoroferrate*(III) (Å).

CrF_6^{3-}	a_0 8·56,	c_0 8·62,	Molecular volume 631·6
MnF_6^{3-} *	a_0 8·75,	c_0 8·30,	Molecular volume 635·5
FeF_6^{3-}	a_0 8·59,	c_0 8·66,	Molecular volume 639·0

* Pseudo-cell. True cell has $a_0 = 17{\cdot}50$; $c_0 = 16{\cdot}60$ A.

---

[1] Brosset, *Arkiv Kemi, Min., Geol.*, 1946, **21**, *A*, 142.

[2] Bode and Voss, *Z. anorg. Chem.*, 1957, **290**, 1.

[3] Orgel, *J.*, 1952, 4756.

[4] Hepworth, Jack, and Nyholm, *Nature*, 1957, **179**, 211.

[5] Palmer, "Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954, p. 479.

The aquo-salt was added little by little to a large excess of molten potassium hydrogen difluoride to form a deep bluish-purple melt. After being heated at 400° for some time all the hydrogen fluoride was evolved and the melt solidified. The solid cake was allowed to cool and potassium fluoride leached out of it with formamide. The resulting *powder* was washed with acetone and ether and air-dried (Found: Mn, 18·8; F, 40·0. K_3MnF_6 requires Mn, 19·2; F, 39·8%).

Potassium fluorochromate(III) *and fluoroferrate*(III). With the aquo-salts K_2CrF_5,H_2O and K_2FeF_5,nH_2O as starting materials, the same technique as used for the fluoromanganate(III) gave the *salts* [Found: Cr, 18·7; F, 40·0. K_3CrF_6 requires Cr, 18·4; F, 40·2%. Found: Fe, 20·1; F, 39·7. K_3FeF_6 requires Fe, 19·5; F, 39·7%.]

Analysis. Manganese(III) was estimated iodometrically with thiosulphate; iron and chromium gravimetrically after precipitation of the hydroxides, and fluorine gravimetrically as lead chlorofluoride.

X-*Ray photographs.* Powder photographs were obtained on 19-cm. cameras with Co-$K\alpha$, Fe-$K\alpha$, or Cr-$K\alpha$ radiation as was most suitable. The magnetic moment of K_3MnF_6 at 25° was determined by the Gouy method.

I am indebted to Dr. J. D. Dunitz for valuable discussion of the interpretation of the experimental results.

Department of Chemistry, Imperial College,
London, S.W.7.

[*Received, July 26th,* 1957.]

944. *The Oxidation of Hydrazine by Iron*(III) *in Acid Aqueous Solution.*

By D. R. Rosseinsky.

Recent investigations of the oxidation of hydrazine by iron(III) in acid solution have led to two similar suggestions for the mechanism of reaction. The main difference is that the back reaction (—1) is omitted by Cahn and Powell[1] but is included by Higginson and Wright.[2]

$$\mathrm{Fe^{III} + N_2H_4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe^{II} + N_2H_3} \qquad \ldots\ldots \quad (1), (-1)$$

$$\mathrm{2N_2H_3} \xrightarrow{k_2} \mathrm{N_4H_6} \qquad \ldots\ldots \quad (2)$$

followed by

$$\mathrm{N_4H_6} \longrightarrow \mathrm{N_2 + 2NH_3}\ (\text{fast})$$

$$\mathrm{2N_2H_3} \xrightarrow{k_3} \mathrm{N_2H_2 + N_2H_4} \qquad \ldots\ldots \quad (3)$$

followed by

$$\mathrm{N_2H_2 - 2e} \longrightarrow \mathrm{N_2}\ (\text{fast})$$

$$\mathrm{Fe^{III} + N_2H_3} \xrightarrow{k_4} \mathrm{N_2H_2 + Fe^{II}} \qquad \ldots\ldots \quad (4)$$

followed by

$$\mathrm{N_2H_2 - 2e} \longrightarrow \mathrm{N_2}\ (\text{fast})$$

The values obtained for k_3/k_2 from measurements following the two mechanisms are 0·15 and <0·02 respectively. Cahn and Powell state " Although cupric ion does not react at an appreciable rate with hydrazine in acid solution, nor change the rate of oxidation of hydrazine by ferric ion, its presence greatly increases the relative amount of four-electron oxidation " [*i.e.*, by catalysis of reaction (4)]. Actually according to their mechanism a small increase, not greater than 7%, in the rate of disappearance of hydrazine would be

---

[1] Cahn and Powell, *J. Amer. Chem. Soc.*, 1954, **76**, 2568.
[2] Higginson and Wright, *J.*, 1955, 1551.

expected in the presence of copper(II), as reaction (3) becomes less important. If the mechanism favoured by Higginson and Wright were correct, copper(II) should increase $d[N_2H_4]/dt$ greatly by reducing the extent of the back reaction (—1). We have now measured $d[N_2H_4]/dt$ in the absence of copper(II) and with different amounts of it.

The results are shown in the Table together with (Calc.) the maximum rate (values from Expt. 1 plus 7%) expected in the presence of copper(II), if $k_{-1} = 0$. These results provide clear evidence for a large catalytic effect and hence the back reaction (—1) must be appreciable since, in similar experiments in the absence of iron(III), copper(II) alone did not oxidise hydrazine. Initial rates are similar in all experiments since the back reaction (—1) is negligible in the early stages when the concentration of iron(II) is small. (This allowed the evaluation of k_1 in these conditions as 0·48 l. mole^{-1} hr.$^{-1}$.) As the reaction proceeds and iron(II) accumulates, the difference in rates in the presence and absence of copper(II) increases in accordance with expectations based on Higginson and Wright's mechanism.

Values of the rate, $10^4 d[N_2H_4]/dt$ *(mole l.$^{-1}$ hr.$^{-1}$), at various molar concentrations of reagents.*

$[H_2SO_4]$ = 0·75M; initial $[N_2H_4]$ = 0·014M; initial $[Fe^{III}]$ = 0·12M; Temp. = 50°.

Expt.	$[CuSO_4]$	$10^3[N_2H_4]$ =	13	11	9	6	4	3·5	3·0	2·5	2·0
1	0	Rate =	41	35	21	10	5·4	4·1	3·0	2·6	1·2
2	0·025		41	35	22	12	7·2	5·8	4·3	3·7	3·2
3	0·05		41	35	22	13	8·1	7·1	5·8	4·4	3·5
4	0·075		41	35	24	14	9·1	7·5	6·0	4·8	3·7
Calc.	Maximum		—	—	22	11	5·8	4·4	3·2	2·8	1·3

Experimental.—The stock solution prepared from " AnalaR " hydrazine sulphate was standardised by Andrews's method and kept in the dark under nitrogen. Iron(III) sulphate stock solution, standardised iodometrically by titration with sodium thiosulphate, was prepared by dissolving Hilger H.P. iron in " AnalaR " sulphuric acid, followed by oxidation with inhibitor-free hydrogen peroxide, the excess of which was removed by gentle heating. 0·5M-Copper(II) sulphate and 0·5M-magnesium sulphate stock solutions were prepared from " AnalaR " reagents.

The kinetic experiments were conducted in conditions similar to those of Cahn and Powell. Magnesium sulphate was used to maintain the same total sulphate concentration, when the concentration of copper(II) sulphate was varied, by keeping $[MgSO_4] + [CuSO_4]$ = 0·10M. Higginson and Wright's procedure was followed, except that hydrazine concentrations were measured. Samples were withdrawn for analysis at the start of the experiment, and then at intervals increasing from 15 min. to 1 hr.; final readings were taken after 24 hr.

After the samples were quenched in potassium iodate solution, the iodine liberated was twice extracted with carbon tetrachloride and estimated by optical density measurements at 510 mμ on a Unicam S.P. 500 spectrophotometer. The optimum iodate concentration for the quantitative production of iodine was 0·05M, the slow reaction between iron(II) and iodate being negligible, during the short extraction period, at that concentration. Copper(II), magnesium, and iron(III) at the experimental concentrations did not affect the determination, the accuracy of which was ±4%.

Plots of hydrazine concentration against time were drawn and gradients obtained at the hydrazine concentrations quoted in the Table. These are considered to be accurate to ±8%.

The residual reaction solutions of experiments 1 and 4 were heated to 90° for 1 hr. to complete reaction, and titration of the iron(II) with potassium permanganate showed the stoicheiometries in the absence and presence of copper(II) to be 1·27 and 3·83 equiv. of oxidant per mole of hydrazine, respectively, in accord with Cahn and Powell's results.

The author thanks Dr. W. C. E. Higginson for helpful discussion, and Rhodes University for a Union Scholarship.

THE UNIVERSITY, MANCHESTER, 13.

[*Received, July 4th,* 1957.]

945. *The Urea–Formaldehyde Polycondensation. Part II.* The Alkaline Hydrolysis of Alkoxymethylureas.*

By A. S. DUNN.

USING the technique described in Part I,* we have investigated the rates of alkaline hydrolysis of other alkoxymethylureas, $R{\cdot}O{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$. At 25° and ionic strength 1·0 the catalytic coefficients for hydroxyl ions, k_{OH^-}, are: R = Et, $1{\cdot}23 \times 10^{-4}$; R = Bu^n, $1{\cdot}22 \times 10^{-4}$; R = Bu^i, $2{\cdot}0 \times 10^{-4}$ l. $mole^{-1}$ $sec.^{-1}$. Under the same conditions the value for methoxymethylurea * was $3{\cdot}05 \times 10^{-4}$ l. $mole^{-1}$ $sec.^{-1}$.

For ethoxymethylurea the rate of hydrolysis at a sodium hydroxide concentration of 0·5N decreased linearly as the ionic strength was increased to 2·5; at a lower hydroxide concentration, 0·1N, this effect was much less marked. The temperature dependence of the catalytic constant is given by $k_{OH^-} = 2{\cdot}34 \times 10^9 \exp(-18{,}100/\boldsymbol{R}T)$; this energy of activation is 2 kcal./mole higher than that for methoxymethylurea.*

BRITISH RAYON RESEARCH ASSOCIATION,
HEALD GREEN LABORATORIES, WYTHENSHAWE, MANCHESTER, 22. [*Received, July 4th*, 1957.]

---

* Part I, *J.*, 1957, 1446.

---

946. 1-*Ethyl-2-methyl-5-nitrobenziminazole.*

By R. FOSTER.

RECENTLY 1-ethyl-2-methyl-6-methylaminobenziminazole was prepared[1] by a sequence of reactions involving ethylation of 2-methyl-5(6)-nitrobenziminazole to a pair of isomers, in the proportion of 8 : 1 by weight. By analogy with Philips's work,[2] we assumed that the more abundant isomer (m. p. 142°) was 1-ethyl-2-methyl-6- and the other (m. p. 176°) was 1-ethyl-2-methyl-5-nitrobenziminazole.

1-Ethyl-2-methyl-5-nitrobenziminazole has now been synthesised unambiguously. *N*-Ethyl-2 : 4-dinitroaniline was reduced to *N*-ethyl-4-nitro-*o*-phenylenediamine by ammonium sulphide in pyridine. This with acetic acid gave 1-ethyl-2-methyl-5-nitrobenziminazole, identical with the above isomer, m. p. 176°.

Catalytic reduction of 1-ethyl-2-methyl-5-nitrobenziminazole gave the 5-amino-compound, and reduction of the formyl derivative gave the 5-methylamino-compound. The latter was prepared as a possible antagonist of 5-hydroxytryptamine.[1]

Experimental.—1-*Ethyl-2-methyl-5-nitrobenziminazole.* 1-Chloro-2 : 4-dinitrobenzene (76 g.) was added slowly to 30% w/w alcoholic ethylamine (100 ml.) and anhydrous cupric chloride (2 g.). Much heat was evolved. The mixture was cooled to room temperature and the solid removed. After repeated washing with water, *N*-ethyl-2 : 4-dinitroaniline (91%) had m. p. 113·5° (Stoermer[3] gives m. p. 114°). This was reduced without further purification, by ammonium sulphide in pyridine.[4] N-*Ethyl-4-nitro*-o-*phenylenediamine* was recrystallised twice from methanol, to give dark red plates (50%), m. p. 140° (Found: C, 53·3; H, 6·0; N, 23·5. $C_8H_{11}O_2N_3$ requires C, 53·0; H, 6·1; N, 23·2%). This diamine (12 g.), 4N-hydrochloric acid (180 ml.), and acetic acid (30 ml.) were refluxed for 8 hr. The product was precipitated by an

---

[1] Foster, Ing, and Rogers, *J.*, 1957, 1671.
[2] Philips, *J.*, 1931, 1143.
[3] Stoermer, *Ber.*, 1898, **31**, 2531.
[4] Brady, Day, and Reynolds, *J.*, 1929, 2264.

excess of ammonia and twice recrystallised from aqueous ethanol (50% v/v). 1-*Ethyl*-2-*methyl*-5-*nitrobenziminazole* was obtained as pale yellow needles, m. p. 176° (92%) alone or mixed with the higher-melting isomer mentioned above (Found: C, 58·9; H, 5·5; N, 20·7. $C_{10}H_{11}O_2N_3$ requires C, 58·5; H, 5·4; N, 20·5%). This material and the previous sample had absorption max. at 307 (ε 9500—9700) and 241 mμ (ε 25,000) in MeOH at 20°. The isomer, m. p. 142°, had max. at 310 (ε 10,100) and 240 mμ (ε 19,000) in MeOH at 20° and, mixed with the 5-nitro-compound, melted at 139—140°.

1-*Ethyl*-2-*methyl*-5-*methylaminobenziminazole*. 1-Ethyl-2-methyl-5-nitrobenziminazole was hydrogenated in alcohol over Raney nickel at 7 atm. for 1 hr. The amine (95%) did not crystallise. The *picrate* formed orange needles, decomp. *ca.* 210°, from aqueous methanol (30% v/v) (Found: C, 48·1; H, 4·4; N, 20·7. $C_{10}H_{13}N_3,C_6H_3O_7N_3$ requires C, 47·5; H, 4·0; N, 20·8%). The amine (10 g.), 98—100% formic acid (100 ml.), and toluene (200 ml.) were slowly distilled on a steam-bath. After 6 hr., when 280 ml. of liquid had distilled, the remainder was evaporated *in vacuo*, and the residual solid dissolved in the minimum of water, basified with solid sodium hydrogen carbonate, and extracted with chloroform. The solution gave, on evaporation, 1-*ethyl*-5-*formamido*-2-*methylbenziminazole* which, crystallised from ethyl methyl ketone, had m. p. 217° (yield 60%) (Found: C, 65·0; H, 6·4; N, 20·2. $C_{11}H_{13}ON_3$ requires C, 65·0; H, 6·4; N, 20·7%). The formyl compound (5 g.) was added slowly to a solution of lithium aluminium hydride (5 g.) in dry ether. Then the mixture was refluxed with vigorous stirring for 2 hr. The excess of hydride was decomposed by wet ether, and finally water. The ethereal solution was decanted and on evaporation gave 1-*ethyl*-2-*methyl*-5-*methylaminobenziminazole* which was recrystallised three times from ethyl acetate, forming prisms (60%), m. p. 134·5° (Found: C, 69·3; H, 7·7; N, 22·2. $C_{11}H_{15}N_3$ requires C, 69·8; H, 7·9; N, 22·2%).

This work was carried out during the tenure of an Edward A. Deeds Fellowship of the University of St. Andrews.

QUEEN'S COLLEGE, DUNDEE,
UNIVERSITY OF ST. ANDREWS.

[*Received, July 4th*, 1957.]