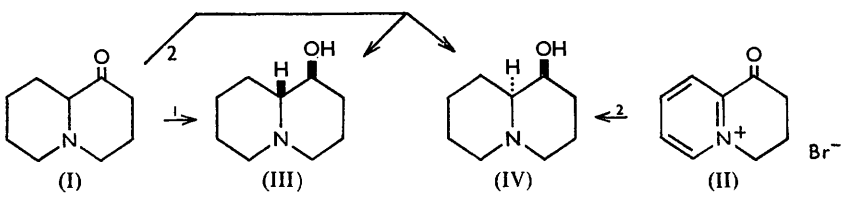
NOTES.

414. *Stereoisomeric* 1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*Octahydro*-1-*hydroxypyridocolines.*

By G. A. SWAN.

CLEMO and RAMAGE [1] reduced 1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-octahydro-1-oxopyridocoline (I) with sodium amalgam to 1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-octahydro-1-hydroxypyridocoline, m. p. 65—68°. In our hands this gave a product (III), m. p. 72°. 1 : 2 : 3 : 4-Tetrahydro-1-oxopyridocolinium bromide [2] (II) in acetic acid solution absorbed 4 mols. of hydrogen in the presence of Adams catalyst, giving the isomer (IV), m. p. 80°. Catalytic hydrogenation of the octahydro-ketone (I) gave a mixture of these alcohols.



1, Na–Hg. 2, H_2–Pt–AcOH.

The structures assigned rest on the following arguments: The more thermodynamically stable isomer (III), with the hydroxyl group equatorial, will be formed by sodium amalgam. Catalytic hydrogenation of the tetrahydro-ketone does not proceed *via* the octahydro-ketone since the former gives a single and the latter a mixed product. If then hydrogenation of the carbonyl group of (II) is the first step, the bridge-head hydrogen atom will enter on the opposite side of the rings to the hydroxyl group, leading to structure (IV). The keto-group of the octahydro-compound (I) is enolisable, so the hydrogenation product is a mixture.

Experimental.—Reduction of 1 : 2 : 3 : 4-*tetrahydro*-1-*oxopyridocolinium bromide* (II). The bromide (137 mg.) in acetic acid (10 ml.) absorbed 54·9 ml. of hydrogen at 18°/760 mm. during 40 min. in the presence of freshly reduced Adams catalyst (50 mg.) which was then removed immediately by filtration. The filtrate was evaporated to dryness (water-bath/reduced pressure). A solution of the residue in hot methanol was filtered and evaporated, giving a gum,

[1] Clemo and Ramage, *J.*, 1931, 437.
[2] Prasad and Swan, *J.*, 1958, 2024.

which was dissolved in a little hot acetone. Diluting the solution with ether gave a hydrobromide (90 mg.), m. p. 216° (from ethanol–acetone). When its solution in a little water was treated with 40% sodium hydroxide solution an oil separated, but soon solidified, giving 1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*octahydro*-1-*hydroxypyridocoline B* (IV), separating from light petroleum (b. p. 40—60°) as prisms, m. p. 80° (Found: C, 70·1; H, 11·1. $C_9H_{17}ON$ requires C, 69·65; H. 11·0%). This gave a *picrate*, prisms (from ethyl acetate), m. p. 152—153° (for analysis dried for 1 hr. at 90°/0·1 mm.) (Found: C, 46·35; H, 4·9. $C_9H_{17}ON,C_6H_3O_7N_3$ requires C, 46·75; H, 5·2%).

Reduction of 1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*octahydro*-1-*oxopyridocoline* (I). (*a*) Reduction with sodium amalgam was as described by Clemo and Ramage [1] and the distilled product yielded 1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*octahydro*-1-*hydroxypyridocoline A hydrobromide*, prisms, m. p. 243—244° (from ethanol) (Found: C, 45·25; H, 7·95. $C_9H_{18}ONBr$ requires C, 45·75, H, 7·65%). Basification yielded *base A* (III), separating from light petroleum (b. p. 40—60°) as needles, m. p. 72° (Found: C, 69·7; H, 10·8%).

(*b*) The ketone (0·137 g.) in acetic acid absorbed 20·9 ml. of hydrogen at 18°/760 mm. during 35 min. in the presence of Adams catalyst (60 mg.). The resulting hydrobromide, on fractional crystallisation from ethanol, yielded the less soluble salt of base A, together with the more soluble *salt* of base B; the latter had m. p. 232—233° (from ethanol–acetone) (Found: C, 45·95; H, 7·9%) and yielded base B, prisms, m. p. 81° [from light petroleum (b. p. 40—60°)] (Found: C, 69·1; H, 10·65%).

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415. *The Depolymerisation of Paraldehyde in the Solvent System* $ZnCl_2$–$CH_3{\cdot}CO_2H$.

By D. P. N. SATCHELL.

IN the solvent system zinc chloride–acetic acid, the exchange of " aromatic " hydrogen shows the same parallelism with the ionisation of Brønsted indicator bases as it does in systems where only Brønsted acids are involved.[1] It was therefore concluded that the zinc chloride does not directly affect the ionisation of such indicators. The solvent system appears to behave analogously to the hydrochloric acid– or sulphuric acid–acetic acid systems, the addition of zinc chloride simply producing an increasing amount of a complex Brønsted acid, formulated as $H_2ZnCl_2(OAc)_2$, with acetic acid.

Because of the high acidity necessary to effect exchange, the correlation between the exchange rates and the ionisation data was necessarily observed at rather large zinc chloride concentrations. In order to demonstrate that this solvent system behaves like the conventional Brønsted acidic systems at low zinc chloride concentrations also, we must study another reaction whose rate runs parallel with indicator ionisation in the presence of Brønsted acids, but which proceeds measurably at low acidities. Such a reaction is the depolymerisation of paraldehyde,[2] one of particular interest in connection with this type of solvent system in that it is catalysed by both Lewis and Brønsted acids.[3] Some free zinc chloride will doubtless be in equilibrium with $H_2ZnCl_2(OAc)_2$ (though the quantity may be very small) and therefore if the behaviour of the zinc chloride–acetic acid system at low zinc chloride concentrations *is* similar to that at higher concentrations, the depolymerisation rates would be expected either to run parallel with the indicator ionisation data or to increase somewhat faster. The latter circumstance would arise if the free zinc chloride appreciably catalysed the depolymerisation.

The rate of depolymerization for stoicheiometric zinc chloride concentrations between 0·016M and 0·212M at 25° was studied; the indicator ionisation data for this composition

[1] Satchell, *J.*, 1927.
[2] Bell and Brown, *J.*, 1954, 774; Satchell, *J.*, 1957, 3524.
[3] Bell and Skinner, *J.*, 1952, 2955.

range for *o*-nitroaniline have been given previously.[4] The Table contains the values of the first-order depolymerisation rate constants (k), together with the appropriate values of the logarithm of the indicator ionisation ratio (I). If log k is plotted against log I a good

Depolymerisation of paraldehyde in the zinc chloride–acetic acid solvent system at 25°.

$ZnCl_2$ (M)	0·016	0·027	0·053	0·106	0·159	0·212
$-\log I$	2·07	1·83	1·49	1·08	0·80	0·56
10^4k (sec.$^{-1}$)	0·46	0·86	2·20	6·51	14·0	29·9

straight line of slope 1·15 is obtained. The observed correlation between rates and ionisation is thus, as for the exchange reactions at higher zinc chloride concentrations, of the kind found in systems containing only Brønsted acids. The value of the slope is also very similar to that found in such systems.[2] Hence it seems very likely (*a*) that at low, as well as high, zinc chloride concentrations, the addition of this compound to anhydrous acetic acid produces an acidic system which behaves analogously to systems such as hydrochloric–acetic acid, from the viewpoints of both ionisation equilibria and acid catalysis, and (*b*) that free zinc chloride plays no significant part in the depolymerisation of paraldehyde in the zinc chloride–acetic acid system. This may be because its concentration is very low and/or because its catalytic power is small compared with that possessed by the medium due to its Brønsted acidity.

Experimental.—Materials. These were prepared as previously described.[2,5]

Depolymerisation rates. The titration method[2] was found suitable. The paraldehyde concentration was *ca.* 0·03M, and " infinity " titres showed the reaction to proceed to *ca.* 97% completion. The rate of depolymerisation was studied at six different zinc chloride concentrations, and in all cases the first-order plot was linear over at least the first 70% of reaction. The rate constants were reproducible to ±5%.

Fresh and aged zinc chloride–acetic acid mixtures possessed the same catalytic power. Hence there is no slow reaction occurring in the solvent system itself which affects its acidic properties.

KING'S COLLEGE, STRAND, LONDON, W.C.2. [*Received, November 7th*, 1957.]

[4] Bethell, Gold, and Satchell, *J.*, 1918.
[5] Satchell, *J.*, 1916.

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416. *The Heat of Formation of Nickel Carbonyl from Combustion Calorimetry.*

By K. W. SYKES.

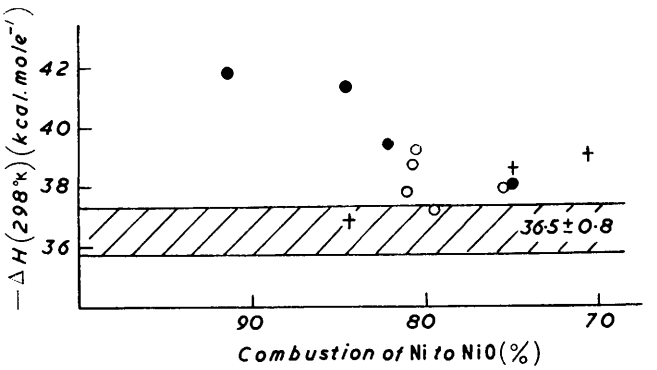
THE apparent difference[1] of 8 kcal. mole^{-1} between the two most recent calorimetric measurements of the heat of formation of nickel carbonyl is largely due to discrepancies in the interpretation of the results. Fischer, Cotton, and Wilkinson[1] assumed that Smagina and Ormont's result[2] for liquid carbonyl (47·3 kcal. mole^{-1}) referred to gaseous carbonyl, while the latter authors used different auxiliary data of unspecified origin. Smagina and Ormont[2] took the heat of combustion of 4 moles of carbon monoxide at constant volume at 25° C to be 270·5 kcal., which is the figure given by standard tables[3] for constant pressure; it should be replaced by $-\Delta E = -\Delta H - 2\boldsymbol{R}T = 269{\cdot}3$ kcal. They also assumed that the heat of combustion of one mole of nickel at constant volume at 25° was 58·9 kcal., whereas a more recent value[4] which Fischer, Cotton, and Wilkinson

[1] Fischer, Cotton, and Wilkinson, *J. Amer. Chem. Soc.*, 1957, **79**, 2044.
[2] Smagina and Ormont, *J. Gen. Chem. U.S.S.R.*, 1955, **25**, 207 (English translation by Consultants Bureau, Inc., New York).
[3] " Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Standards. Circular 500, Washington, 1952.
[4] Boyle, King, and Conway, *J. Amer. Chem. Soc.*, 1954, **76**, 3835.

used gives $-\Delta E = -\Delta H - \frac{1}{2}RT = 57{\cdot}0$ kcal. With these corrections and a heat of vaporisation of 6·5 kcal. mole^{-1},[1,5] Smagina and Ormont's three results for the heat of formation of gaseous carbonyl become $-\Delta H$ (298° K) = (i) 36·9, (ii) 39·0, (iii) 38·6 kcal. mole^{-1}, as compared with Fischer, Cotton, and Wilkinson's estimate of 39·1 kcal. mole^{-1}.

The individual values of $-\Delta H$ (298° K), calculated as above for gaseous carbonyl, vary systematically over a range of several kcal. mole^{-1} with the percentage combustion of nickel to nickel oxide (Figure), but this variation runs in different directions in the two investigations. No appreciable trend is to be expected because the heat of combustion of nickel powder is constant to within 0·05 kcal. mole^{-1} over the range 87—93% combustion.[4]

Heat of formation of gaseous nickel carbonyl.



Fischer, Cotton, and Wilkinson [1]: ● internal ignition; ○ external ignition.
Smagina and Ormont [2]: +
Sykes and Townshend [6] (from equilibrium constant): shaded band.

The spread of the experimental values is thus probably due to errors in the measurement of the percentage combustion, a 1% deviation in which affects ΔH by 0·6 kcal. mole^{-1}. Fischer, Cotton, and Wilkinson's distinction between runs with external and internal ignition, attributed to hydration or further oxidation of nickel oxide in the former, does not appear to be valid since the results agree when the percentage combustion is the same. All the points in the Figure give a mean and standard deviation of 38·8 $\pm$ 1·5 kcal. mole^{-1}, which is the best estimate to be derived from the calorimetric data. In view of the uncertainties involved, the agreement with the figure of 36·5 $\pm$ 0·8 kcal. mole^{-1} calculated by Sykes and Townshend [6] from the equilibrium constant is as close as can be expected.* It now seems unlikely that the true value lies outside the range 36—40 kcal. mole^{-1}, but greater precision could only be obtained by more accurate experiments.

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* Fischer, Cotton, and Wilkinson misquote this value in their Table III, but are correct in stating that Sykes and Townshend omitted from the denominator of the expression for C a factor 4 which is necessary and which was included in the calculation.

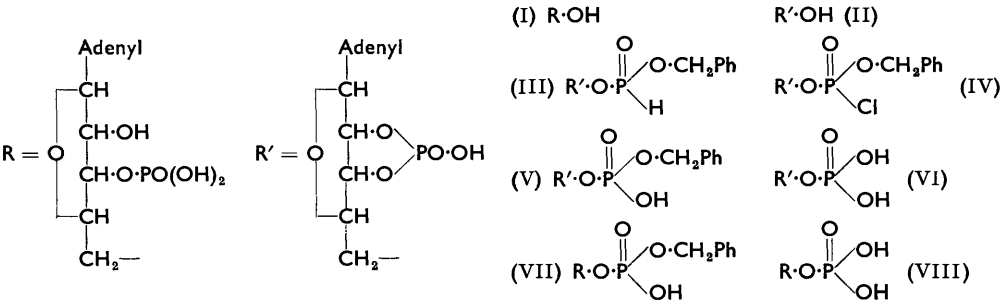
[5] Spice, Staveley, and Harrow, *J.*, 1955, 100.
[6] Sykes and Townshend, *J.*, 1955, 2528.

417. *An Alternative Synthesis of Adenosine-2′(3′) : 5′ Diphosphate.*

By A. M. Michelson.

Todd and his co-workers [1] have described the synthesis of a mixture of adenosine-2′ : 5′ and -3′ : 5′ diphosphate wherein adenosine is phosphorylated directly with dibenzyl phosphorochloridate and the benzyl groups are later removed. An alternative synthesis from adenosine-2′(3′) phosphate has been developed: while the overall yield is not high, some of the intermediates are of possible use for the synthesis of certain co-enzymes.

A solution of the anhydrous mono(tri-*n*-decylamine) salt of adenosine-2′(3′) phosphate (I) (commercial yeast adenylic acid) in dioxan was treated with diphenyl phosphorochloridate,[2] giving adenosine-2′ : 3′ cyclic phosphate (II) quantitatively.[3] This with



O-benzylphosphorous di-*O*-phenylphosphoric anhydride [4] gave a 50% yield of adenosine 2′ : 3′-(cyclic phosphate) 5′-(benzyl phosphite) (III) which was separated from the concomitant polymers.[5] Treatment of the crude phosphite in the usual way [6] with *N*-chlorosuccinimide gave the phosphorochloridate (IV), which with aqueous lutidine yielded an intermediate, presumably adenosine 2′ : 3′-(cyclic phosphate) 5′-(benzyl phosphate) (V). Hydrogenation then gave adenosine 2′ : 3′-(cyclic phosphate) 5′-phosphate (VI), converted by alkali into a mixture of the 2′ : 5′- and the 3′ : 5′-diphosphate (VIII) of adenosine. Alternatively, treatment of adenosine 2′ : 3′-(cyclic phosphate) 5′-(benzyl phosphate) with alkali produced the 2′(3′)-phosphate 5′-(benzyl phosphate) (VII) which was readily hydrogenated to adenosine-2′(3′) : 5′ diphosphate.

Experimental.—Adenosine 2′ : 3′-(cyclic phosphate) 5′-(benzyl phosphite). Diphenyl phosphorochloridate (1·56 c.c.) was added to a solution of mono(tri-*n*-decylammonium)adenosine-2′(3′) phosphate (from 2 g. fo the nucleotide) in dry dioxan (20 c.c.), and the solution left at room temperature for 1 hr. with occasional shaking. *O*-Benzylphosphorous di-*O*-phenylphosphoric anhydride (from 3 g. of benzyl dihydrogen phosphite [4]) in dioxan (20 c.c.) was then added, followed dropwise by a solution of 2 : 6-lutidine (1·85 g.) in dioxan (5 c.c.) with stirring under anhydrous conditions. The clear solution was set aside at room temperature overnight. Solvent was removed under reduced pressure and a mixture of ether (50 c.c.) and *cyclo*hexane (50 c.c.) added to the residue with vigorous shaking. The precipitated solids were dissolved in a little dioxan, tri-*n*-butylamine being added to neutrality. Methyl cyanide (50 c.c.) was then added and the precipitated polymer material [5] centrifuged off. The supernatant liquids were concentrated to small volume, dry benzene (50 c.c.) was added, and the resultant precipitate of phosphate phosphite washed with small quantities of ether and dried to a white solid foam (1·975 g.). Although analyses were unsatisfactory, possibly owing to the indeterminate amount

[1] Cramer, Kenner, Hughes, and Todd, *J.*, 1957, 3297.
[2] Brigl and Müller, *Ber.*, 1939, **72**, 2121.
[3] Michelson, *Chem. and Ind.*, 1958, 70.
[4] Corby, Kenner, and Todd, *J.*, 1952, 3669.
[5] Michelson, unpublished work.
[6] Kenner, Todd, and Weymouth, *J.*, 1952, 3675.

of base held by the compound, the material was almost homogeneous, running as a single spot in paper chromatography, free from other nucleotide and phosphorus compounds.

Adenosine 2′(3′)-phosphate 5′-(benzyl phosphate). The above phosphate phosphite (0·478 g.) in methyl cyanide (2·5 c.c.) and dioxan (2·5 c.c.), with sufficient tri-*n*-butylamine to ensure solution, was added to *N*-chlorosuccinimide (0·15 g.). After 1 hr. at room temperature aqueous N-lithium hydroxide (5 c.c.) was added, the mixture left at room temperature overnight, neutralised with N-hydrochloric acid, and evaporated under reduced pressure, and alcohol (10 c.c.) was added to the residue. A trace of water was added to dissolve precipitated matter, followed by ethanolic calcium chloride (250 mg. in 25 c.c.). The precipitated *calcium salt* of adenosine 2′(3′)-phosphate 5′-(benzyl phosphate) was centrifuged off, washed with alcohol, and ether, and dried (0·414 g.) [Found, in material dried at 50°/10^{-3} mm. for 12 hr.: P, 10·6. $(C_{17}H_{18}O_{10}N_5P_2)_2Ca_3$ requires P, 10·8%].

Adenosine-2′(3′) : 5′ diphosphate. Hydrogenation of the preceding ester in water with a palladium catalyst at atmospheric pressure gave a mixture of adenosine 2′ : 5- and 3′ : 5′-diphosphate, isolated as the calcium salt in the usual way (Found, in material dried at 50°/10^{-3} mm. for 12 hr.: N, 13·5; P, 12·6. Calc. for $C_{10}H_{11}O_{10}N_5P_2Ca_2$: N, 13·9; P, 12·3%).

Adenosine 2′ : 3′-(cyclic phosphate) 5′-phosphate. A solution of adenosine 2′ : 3′-cyclic phosphate 5′-(benzyl phosphite) (0·63 g.) in dioxan (8 c.c.) was treated in the usual way with *N*-chlorosuccinimide (0·198 g.), and the crude phosphorochloridate treated with 50% aqueous lutidine (5 c.c.) overnight. Solvent was removed under reduced pressure, the residue dissolved in ethanol (15 c.c.), and ethanolic calcium chloride added. The precipitated calcium salt was centrifuged off, washed with alcohol, and ether, and dried. This fine white powder was hydrogenated in water in the normal way and the resultant *calcium adenosine 2′ : 3′-(cyclic phosphate) 5′-phosphate* isolated as its calcium salt (0·31 g.) [Found, in material dried at 50°/10^{-3} mm. for 12 hr.: N, 14·6; P, 13·4. $(C_{10}H_{10}O_9N_5P_2)_2Ca_3$ requires N, 15·0; P, 13·3%].

Treatment with 0·1 N-sodium hydroxide at room temperature gave a mixture of adenosine-2′ : 5′ and -3′ : 5′ diphosphate.

Paper chromatography. R_F values, for ascending chromatograms on Whatman No. 1 paper with 95% ethanol–M-ammonium acetate (75 : 30) as the solvent, were: adenosine 0·58; (II) 0·49; (III) 0·62; (V) 0·45; (VII) 0·24; (I) 0·15; adenosine-5′ phosphate 0·13; (VI) 0·09; (VIII) 0·02; adenosine-5′ pyrophosphate 0·05.

Paper electrophoresis. Movements towards the anode on Whatman No. 1 paper, 30 cm. in length, (*a*) in M/50-KH_2PO_4 at 500 V for 60 minutes, and (*b*) in M/50-Na_2HPO_4 at 400 V for 90 min., respectively are: (I) 5·5, 9·2; (II) 5·3, 5·8; (V) 7·6, 9·3; (VII) 8·3, 11·3; (VI) 8·8, 11·4; (VIII) 8·8, 12·5; adenosine-5′ pyrophosphate 7·0, 9·2.

Thanks are offered to Dr. A. K. Mills for interest and encouragement and to the directors of Arthur Guinness Son & Co. (Dublin) Ltd. for permission to publish this work.

ARTHUR GUINNESS SON & CO. (DUBLIN) LTD.,
DUBLIN, EIRE.

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418. *Properties and Reactions of Free Alkyl Radicals in Solution. Part X.* Further Studies of Tertiary Hydroxylamines.*

By A. N. BOYD, P. F. SOUTHERN, and WILLIAM A. WATERS.

THE preparation of tri-(2-cyano-2-propyl)hydroxylamine from nitric oxide and 2-cyano-2-propyl radicals was described in Part VII.[1] We have now extended this work and have established that the addition of 2-methoxycarbonyl-2-propyl radicals to nitric oxide occurs in stages, for the intermediate methyl α-nitroso*iso*butyrate can be removed by distillation and converted with nitrogen dioxide (as in Part IX [2]) into methyl α-nitro-*iso*butyrate.

Alkaline hydrolysis of *ON*-di-(2-methoxycarbonyl-2-propyl)-*N*-phenylhydroxylamine

* Part IX, *J.*, 1957, 3129.

[1] Gingras and Waters, *J.*, 1954, 1920.
[2] Tilney-Bassett and Waters, *J.*, 1957, 3129.

yields the corresponding dibasic acid which is easily converted into a stable anhydride that must contain a seven-membered ring. Bouveault–Blanc reduction of the above ester gives aniline and α-hydroxy*iso*butyric acid whilst reduction with lithium aluminium hydride yields *ON*-di-(2-hydroxy-1 : 1-dimethylethyl)-*N*-phenylhydroxylamine. Boiling 2N-hydrochloric acid decomposes the latter, giving some *iso*butyraldehyde and a basic residue which, after benzoylation yields some benzanilide and a small amount of a product that appears to be *N*-(2-benzoyloxy-1 : 1-dimethylethyl)-*p*-chloroaniline. The mechanism of formation of *p*-chloroaniline from *N*-phenylhydroxylamine [3] serves to indicate how the latter could have been formed: aldehydes have previously been reported as products of acid hydrolysis of tertiary hydroxylamines.[4]

Experimental

ONN-(*Tri*-1-*cyano*cyclo*hexyl*)*hydroxylamine*.—After air had been displaced with nitrogen, nitric oxide was passed slowly for 7 hr. through a refluxing solution of 1 : 1′-azobis-1-cyano-*cyclo*hexane (9 g.) in dry toluene (100 ml.). The toluene was removed and the product, in light petroleum–benzene, was separated through alumina into 1 : 1′-dicyanodi*cyclo*hexyl (1·1 g.; m. p. 222°) and ONN-*tri*-(1-*cyano*cyclo*hexyl*)*hydroxylamine* (4·6 g.), m. p. 144° (from methanol) (Found: C, 71·0; H, 8·5; N, 16·1. $C_{21}H_{30}ON_4$ requires C, 71·1; H, 8·5; N, 15·8%). Hydrolysis with dilute sodium hydroxide solution yielded a little *cyclo*hexanone (dinitrophenylhydrazone, m. p. and mixed m. p. 154°); cold concentrated hydrochloric acid did not effect hydrolysis.

ONN-*Tri*-(2-*methoxycarbonyl*-2-*propyl*)*hydroxylamine*.—Nitric oxide diluted with nitrogen was passed slowly for 6 hr. into a refluxing solution of dimethyl αα′-azo*iso*butyrate (13·8 g.) in dry benzene (150 ml.). After the solution had been flushed with nitrogen the benzene was removed under diminished pressure, and the residue in a little light petroleum (b. p. under 40°) was cooled (methanol–solid carbon dioxide) until it crystallised. Recrystallisation gave ONN-*tri*-(2-*methoxycarbonyl*-2-*propyl*)*hydroxylamine*, m. p. 55°, additional material being obtained by chromatographic separation of mother liquors that contained also dimethyl tetramethylsuccinate (total yield 5·9 g., 44%) (Found: C, 54·5; H, 8·1; N, 3·9. $C_{15}H_{27}O_7N$ requires C, 54·0; H, 8·2; N, 4·2%). In a similar experiment with less solvent volatile materials were distilled away as the reaction proceeded whilst fresh benzene was added dropwise at a corresponding rate. The green distillate was warmed with nitrogen dioxide, benzene was removed, and the residue was distilled giving methyl α-nitro*iso*butyrate (2 g.), b. p. 85—95°/19 mm., which was identified, after crystallisation at low temperature, by its refractive index and infrared spectrum.[2]

Alkaline hydrolysis of *ONN*-tri-(2-methoxycarbonyl-2-propyl)hydroxylamine caused extensive decomposition. Reduction in ether with lithium aluminium hydride gave ONN-*tri*-(2-*hydroxy*-1 : 1-*dimethylethyl*)*hydroxylamine* (72%), needles, m. p. 74° [from light petroleum (b. p. 60—80°)] (Found: C, 58·0; H, 10·7; N, 5·3. $C_{12}H_{27}O_4N$ requires C, 57·8; H, 10·9; N, 5·6%). This was basic enough to dissolve in dilute mineral acid.

ON-*Di*-(2-*methoxycarbonyl*-2-*propyl*)-N-*phenylhydroxylamine*.—Prepared from nitrosobenzene and dimethyl αα′-azo*iso*butyrate in boiling toluene (compare Part VII) in 66% yield, this *hydroxylamine* had m. p. 69° [from light petroleum (b. p. 40—60°)] (Found: C, 62·0; H, 7·6; N, 4·5. $C_{16}H_{23}O_5N$ requires C, 62·1; H, 7·4; N, 4·5%). Reaction in benzene gave a much lower yield whilst use of boiling xylene led to decomposition of the nitrosobenzene. The isomeric chloronitrosobenzenes decomposed too quickly in boiling toluene for effective reaction with 2-methoxycarbonyl-2-propyl free radicals: small amounts of nitro- and azoxy-compounds were isolated. Alkaline hydrolysis of the above ester in aqueous alcohol yielded ON-*di*-(2-*carboxy*-2-*propyl*)-N-*phenylhydroxylamine* which had m. p. 154° (decomp.) when heated rapidly, but when slowly heated decomposed at 129—130° (Found: C, 59·8; H, 6·9; N, 4·9. $C_{14}H_{19}O_5N$ requires C, 59·7; H, 6·8; N, 5·0%). It evolved carbon monoxide when heated with concentrated sulphuric acid. With boiling acetic anhydride it yielded the *cyclic anhydride*, m. p. 135° (from methanol) (Found: C, 63·9; H, 6·5; N, 5·25. $C_{14}H_{17}O_4N$ requires C, 63·9; H, 6·5; N, 5·3%). The infrared spectrum of this was typical of acid anhydrides, with absorption bands

[3] Hughes and Ingold, *Quart. Rev.*, 1952, **6**, 34.
[4] Jones and Major, *J. Amer. Chem. Soc.*, 1928, **50**, 2742; Kleinschmidt and Cope, *ibid.*, 1944, **66**, 1929; Meisenheimer, *Ber.*, 1919, **52**, 1667.

at 1760 and 1800 cm.$^{-1}$. The anhydride, which was easily hydrolysed to the original acid by treatment with aqueous sodium hydroxide, condensed with resorcinol to an alkali-soluble product having a green fluorescence. A *monoamide*, m. p. 141°, of *ON*-di-(2-carboxy-2-propyl)-*N*-phenylhydroxylamine was obtained by treating the anhydride in dioxan with ammonia (Found: C, 59·6; H, 7·2; N, 10·1. $C_{14}H_{20}O_4N_2$ requires C, 60·0; H, 7·2; N, 10·0%). Hydrolysis of *ON*-di-(2-cyano-2-propyl)-*N*-phenylhydroxylamine with 6% sodium hydroxide in aqueous alcohol gave a cyano-amide, m. p. 220—221° (decomp.) (Found: C, 64·6; H, 7·5; N, 15·9. $C_{14}H_{19}O_2N_3$ requires C, 64·3; H, 7·3; N, 16·1%), whose infrared spectrum showed absorption due to the carbamoyl but not that due to the cyano-group. Since the latter absorption is often suppressed in nitriles having strongly polar α-substituents [2] the substance is probably N-(2-*carbamoyl*-2-*propyl*)-O-(2-*cyano*-2-*propyl*)-N-*phenylhydroxylamine*.

Reduction of *ON*-di-(2-methoxycarbonyl-2-propyl)-*N*-phenylhydroxylamine (2·1 g.) with sodium metal (8 g.) and ethanol (50 ml.) gave an alkaline solution from which a little aniline could be extracted. Acidification yielded, besides *ON*-di-(2-carboxy-2-propyl)-*N*-phenylhydroxylamine, α-hydroxy*iso*butyric acid (20 mg.), m. p. 77°, unchanged after admixture with an authentic specimen prepared as described by Hepworth.[5] Reduction of the above ester (3 g.) with lithium aluminium hydride (0·75 g.) in ether (50 ml.) followed by treatment with alkali to dissolve alumina gave the basic product ON-*di*-(2-*hydroxy*-1 : 1-*dimethylethyl*)-N-*phenylhydroxylamine* (2 g.), m. p. 69° (from light petroleum) (Found: C, 66·2; H, 9·1; N, 5·5. $C_{14}H_{23}O_3N$ requires C, 66·4; H, 9·2; N, 5·5%) [*diphenylurethane*, m. p. 130° (Found: C, 68·7; H, 7·0; N, 8·1. $C_{28}H_{33}O_5N_3$ requires C, 68·4; H, 6·8; N, 8·5%)]. Hydrolysis of this hydroxy-compound (2 g.) with boiling 2N-hydrochloric acid under nitrogen gave a little *iso*butyraldehyde (dinitrophenylhydrazone, m. p. 178°, mixed m. p. 180°) and, after benzoylation, benzanilide (0·19 g.), and a product (0·49 g.), m. p. 72°, which, from its infrared spectrum, appears to be N-(2-*benzoyloxy*-1 : 1-*dimethylethyl*)-p-*chloroaniline* (Found: C, 67·8; H, 6·3; N, 4·8; Cl, 11·5. $C_{17}H_{18}O_2NCl$ requires C, 67·2; H, 6·0; N, 4·6; Cl, 11·7%). The infrared spectrum had peaks at 2·96 μ (NH), 5·86, 7·78, and 8·95 μ (Ph·CO·O), 7·18 and 7·29 μ (CMe_2), and 12·30 μ (*para*-substituted phenyl).

All the trisubstituted hydroxylamines described show distinct infrared absorptions in the same 8 wave-bands listed in Part VII, *i.e.*, 7·6—7·9 μ; 8·25—8·5 μ, 2 or 3 bands; 8·6—8·7 μ; 9·35 μ; 9·5—9·95 μ, 2 bands; 10·1 and 10·3—10·4 μ; 10·8—10·9 μ; and 11·1—11·9 μ, 2 bands.

THE DYSON PERRINS LABORATORY, OXFORD. [*Received, December 23rd*, 1957.]

[5] Hepworth, *J.*, 1919, 1207.

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419. *Some New Sulphur-containing Diacids.*

By W. A. W. CUMMINGS.

SINCE the literature contains few examples of the use of sulphur-containing acids in polyamides,[1] a number of acids of the following types have been used as monomers. Some of these compounds and their derivatives are new, and their synthesis is described.

(I) $HO_2C{\cdot}[CH_2]_x{\cdot}S{\cdot}[CH_2]_y{\cdot}S{\cdot}[CH_2]_x{\cdot}CO_2H$ $HO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4(p){\cdot}S{\cdot}CH_2{\cdot}CO_2H$ (II)

$HO_2C{\cdot}[CH_2]_x{\cdot}C_6H_4(p){\cdot}S{\cdot}[CH_2]_y{\cdot}S{\cdot}C_6H_4(p){\cdot}[CH_2]_x{\cdot}CO_2H$ (III)

Four known examples of series (I) were prepared: $x = 1$, $y = 1$ (ref. 2); $x = 1$, $y = 2$ (ref. 3); $x = 1$, $y = 3$ (ref. 4); $x = 2$, $y = 3$ (ref. 5). All except the third were oxidised by hydrogen peroxide in acetic acid to the disulphones, this method being better than the permanganate oxidation used by Tiberg [7] for one case. The sulphones which contain the $\cdot SO_2{\cdot}CH_2{\cdot}CO_2H$ group are decarboxylated above 200°.

[1] B.P. 571,708; 670,177.
[2] Holmberg and Mattison, *Annalen*, 1907, **353**, 123.
[3] Ramberg and Tiberg, *Ber.*, 1914, **47**, 730.
[4] Rothstein, *Ber.*, 1925, **58**, 53.
[5] Larsson, Hernäss, and Torssell, *Trans. Chalmers Univ. Technol. Gothenburg, Sweden*, 1945, **47**, 13.
[6] Reuterskiöld, *Chem. Abs.*, 1940, **34**, 2791.
[7] Tiberg, *Ber.*, 1916, **49**, 2024.

β-(*p*-Carboxymethylthiophenyl)propionic acid (II) was prepared by the following route:

$$p\text{-}NH_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H \longrightarrow HS\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H \longrightarrow (II)$$
(IV)

β-*p*-Nitrophenylpropionic acid was prepared by Manske and Kulka's method [8] and on catalytic reduction gave the amino-acid. Treatment of the diazonium solution with potassium ethyl xanthate and decomposition with potassium hydroxide then gave the thiol-acid (IV), which with chloroacetic acid gave acid (II) in 44% overall yield from the amino-acid.

Two acids of series (III) were prepared: 1 : 3-di-(-*p*-carboxyphenylthio)propane (III; $x = 0, y = 3$) was made from *p*-mercaptobenzoic acid [9] and trimethylene dibromide, and 1 : 3-di-(*p*-2-carboxyethylphenylthio)propane (III; $x = 2$, $y = 3$) similarly from the acid (IV).

Some of these compounds gave fibre-forming polymers with hexamethylenediamine but none had useful textile properties.

Experimental.—Methylenebis-sulphonylacetic acid. Methylenebisthioglycollic acid [2] (10 g.), acetic acid (200 ml.), and 30% hydrogen peroxide (60 ml.) were heated under reflux for 3 hr. at 70°. The solution was concentrated to about 60 ml. and cooled. The precipitate recrystallised from ethyl acetate–benzene, giving *methylenebis-sulphonylacetic acid* (10·5 g., 40%), m. p. 209—210° (decomp.) (Found: C, 22·7; H, 2·9%; equiv., 131. $C_5H_8O_8S_2$ requires C, 23·1; H, 3·1%; equiv., 130) [*diethyl ester*, needles (from ethanol), m. p. 72—74° (Found: C, 34·6; H, 5·2; S, 20·3. $C_9H_{16}O_8S_2$ requires C, 34·2; H, 5·1; S, 20·4%)].

Ethylenebis-sulphonylacetic acid, similarly prepared (75% yield) from ethylenebisthioglycollic acid,[3] crystallised from water as plates, m. p. 230—232° (lit.,[6] 228—230°) (Found: equiv., 139. Calc. for $C_6H_{10}O_8S_2$: equiv., 137), and gave a diethyl ester, m. p. 80—81° (lit.,[7] 81°).

The acid (I; $x = 2, y = 3$) (5·5 g.), acetic acid (50 ml.), and 30% hydrogen peroxide (17 ml.) were heated for 1 hr. at 100°. The product which separated was recrystallised from water, giving 1 : 3-*di*-(2-*carboxyethylsulphonyl*)*propane* (6·65 g., 96%) as plates, m. p. 247—250° (decomp.) (Found: C, 34·4; H, 5·1. $C_9H_{16}O_8S_2$ requires C, 34·2; H, 5·1%) [*dimethyl ester*, plates (from acetone), m. p. 159·5—160° (Found: C, 38·25; H, 5·6; S, 18·35. $C_{11}H_{20}O_8S_2$ requires C, 38·4; H, 5·8; S, 18·6%)].

β-p-*Aminophenylpropionic acid.* β-*p*-Nitrophenylpropionic acid [8] (82 g.), alcohol (500 ml.), and 10% palladised charcoal (20 g.) were shaken with hydrogen until no further absorption occurred. After removal of the catalyst and excess of solvent the amino-acid, m. p. 130—131° (lit.,[8] 131—132°), crystallised.

β-p-*Mercaptophenylpropionic acid* (IV). The diazonium solution from the above amino-acid (69 g.), concentrated hydrochloric acid (89 ml.), water (160 ml.), and ice (400 g.), with sodium nitrite (33 g.) in water (80 ml.), was poured into a solution of potassium ethyl xanthate (140 g.) and sodium acetate (57 g.) in water (270 ml.). The yellow precipitate decomposed on a steam-bath. The resulting brown oil was extracted with ether and after removal of solvent was heated with potassium hydroxide (56 g.), water (50 ml.), and ethanol (300 ml.) in a stream of nitrogen. The solvent was removed and the mixture acidified with 10% sulphuric acid, giving a yellow oil which rapidly solidified. This was dissolved in ammonium carbonate solution, and filtered from small amounts of sulphur, and the mercapto-acid (35 g., 58%), m. p. *ca.* 100—105°, was reprecipitated with dilute sulphuric acid.

β-(p-*Carboxymethylthiophenyl*)*propionic acid* (II). The acid (IV) (20·7 g.), chloroacetic acid (10·5 g.), sodium dithionite (5 g.), and ethanol (150 ml.) were warmed together on the steam-bath. Sodium hydroxide (13·5 g.) in water (40 ml.) was added and the mixture heated under reflux for 4 hr. The product was filtered off and dissolved in warm water (charcoal), and the solution acidified with hydrochloric acid. The precipitate (20·9 g., 76%) recrystallised from ethanol, giving the *acid*, m. p. 203—205° (Found: C, 55·0; H, 4·7; S, 13·2%; equiv., 120. $C_{11}H_{12}O_4S$ requires C, 55·0; H, 5·0; S, 13·3%; equiv., 120). Its *hexamethylenediammonium salt* formed needles, m. p. 215—217° (decomp.) (Found: C, 57·4; H, 8·2; N, 7·9; S, 9·3%;

[8] Manske and Kulka, *Canad. J. Res.*, 1947, **25**, *B*, 376.
[9] Thompson, *J. Soc. Chem. Ind.*, 1925, **44**, 196T.

amine equiv., 183; carboxyl equiv., 179. $C_{11}H_{12}O_4S,C_6H_{16}N_2$ requires C, 57·3; H, 7·9; N, 7·9; S, 9·0%; amine and carboxyl equiv., 178).

p-*Mercaptobenzoic acid.* Diazotised *p*-aminobenzoic acid was converted into the thiol-acid (52%), m. p. 216—218° (lit.,[9] 219°), by the method described for β-*p*-aminophenylpropionic acid.

1 : 3-*Di*-(p-*carboxyphenylthio*)*propane.* *p*-Mercaptobenzoic acid (50 g.), sodium hydroxide (53 g.), sodium dithionite (15 g.), water (220 ml.), and absolute ethanol (320 ml.) were heated under reflux on a steam-bath. Trimethylene dibromide (29 ml.) was added during 12 min. and heating continued for 16 hr. Ethanol was removed, the residue dissolved in sodium carbonate solution (charcoal), and the solution acidified. The product was recrystallised 4 times from acetic acid, giving the *acid* (7·2 g., 13%), m. p. 256—258° (Found: C, 58·4; H, 5·0; S, 17·9. $C_{17}H_{16}O_4S_2$ requires C, 58·6; H, 4·6; S, 18·4%).

1 : 3-*Di*-(p-2′-*carboxyethylphenylthio*)*propane.* This was prepared in a similar manner from the acid (IV) (20 g.), sodium dithionite (5 g.), water (150 ml.), ethanol (200 ml.), and sodium hydroxide (14 g.). Trimethylene dibromide (12 ml.) was added during 4 hr., and heating continued overnight. Three recrystallisations of the product from acetic acid gave the *acid* (5 g., 22%), m. p. 143—144° (Found: C, 62·1; H, 5·8; S, 15·6. $C_{21}H_{24}O_4S_2$ requires C, 62·4; H, 5·9; S, 15·8%).

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420. *Some Derivatives of* iso*Pentylbenzene.*

By W. E. HARVEY.

WE have prepared several derivatives of *iso*pentylbenzene, which are either new or have been obtained by routes superior to those previously described.

*iso*Pentylbenzene was most conveniently prepared from α-*iso*butylbenzyl alcohol which was smoothly dehydrated to β-*iso*propylstyrene by treatment with boiling 33% sulphuric acid (w/w), although more dilute acid was ineffective and more concentrated acid led to an excessive amount of polymer. Hydrogenation of β-*iso*propylstyrene gave very pure *iso*pentylbenzene in good yield.

Nitration of *iso*pentylbenzene gave approximately equal amounts of the *ortho*- and *para*-nitro-compounds which were converted into the corresponding bromo-compounds, amines, and carboxylic acids by standard methods. Nitration of *o-iso*pentylaniline [1] in concentrated sulphuric acid gave 5-nitro-2-*iso*pentylaniline whose structure follows from its method of preparation and its conversion into 2 : 4-diacetamido*iso*pentylbenzene.[2,3] Attempts to convert the nitro-amine into the corresponding nitro-nitrile by the Sandmeyer method with either copper or nickel [4] salts yielded only intractable gums.

Experimental.—Amides, anilides, and *p*-bromophenacyl esters were prepared by standard methods and crystallised from aqueous ethanol.

iso*Pentylbenzene.* α-*iso*Butylbenzyl alcohol (100 g.) and 33% sulphuric acid (w/w) (250 ml.) were refluxed with vigorous stirring for 3 hr. The product was taken up in ether, and the ethereal solution was washed with water until neutral, dried (Na_2SO_4), and distilled from 2 : 5-di-*tert.*-butylquinol (2 g.), finally under reduced pressure, giving 3-methyl-1-phenylbutene (64 g., 72%), b. p. 100—102°/24 mm., n_D^{25} 1·5270 (Klages [5] gives b. p. 102—103°/26 mm., n_D^{20} 1·5248). The olefin, in absolute ethanol (80 ml.), was hydrogenated at 60°/50 atm. in presence

[1] Lauer and Lockwood, *J. Amer. Chem. Soc.*, 1954, **76**, 3974.
[2] Ipatieff and Schmerling, *ibid.*, 1938, **60**, 1476.
[3] Hass and Bender, *ibid.*, 1949, **71**, 3482.
[4] Storrie, *J.*, 1937, 1746.
[5] Klages, *Ber.*, 1904, **37**, 2301.

of Raney nickel (10 g.), giving *iso*pentylbenzene (51 g., 80%), b. p. 86—88°/16 mm., n_D^{25} 1·4850. Hass and Bender [3] give b. p. 83—84°/16 mm., n_D^{20} 1·4862.

o- *and* p-*Nitro*iso*pentylbenzenes*. An ice-cold mixture of concentrated nitric acid (135 g., 1·5 mol.) and concentrated sulphuric acid (250 g., 2·5 mol.) was added dropwise with stirring and cooling to *iso*pentylbenzene (150 g.), at such a rate that the temperature did not exceed 10°. Stirring was continued for a further 1 hr., during which the mixture was allowed to reach room temperature. The product, isolated with ether, yielded on fractionation o-*nitro*iso*pentylbenzene* (81 g., 41%), b. p. 94—96°/0·5 mm., n_D^{25} 1·5158 (Found: C, 68·6; H, 7·5; N, 6·95. $C_{11}H_{15}O_2N$ requires C, 68·4; H, 7·8; N, 7·25%), and p-*nitro*iso*pentylbenzene* (90 g., 45%), b. p. 110°/0·5 mm., n_D^{25} 1·5222 (Found: C, 68·6; H, 7·5; N, 7·3%). Oxidation of the two nitro-compounds with 25% nitric acid overnight at 175—180° gave *o*- and *p*-nitrobenzoic acids respectively.

o-iso*Pentylaniline*. Concentrated hydrochloric acid (3 ml.) was added at intervals of 2 hr. to a boiling, vigorously stirred mixture of iron powder (65 g.) and *o*-nitro*iso*pentylbenzene (75 g.) in ethanol (500 ml.). After 12 hr. the mixture was basified and steam-distilled, and the product was isolated with ether, giving the amine (56 g., 90%), b. p. 90°/1 mm., n_D^{25} 1·5257 (Found: C, 80·9; H, 10·0; N, 8·2. Calc. for $C_{11}H_{17}N$: C, 80·9; H, 10·5; N, 8·6%). Lauer and Lockwood [1] give b. p. 128—131°/15 mm., n_D^{25} 1·5310. The *acetyl derivative* formed needles (from aqueous ethanol), m. p. 93—94° (Found: C, 76·0; H, 9·4; N, 7·0. $C_{13}H_{19}ON$ requires C, 76·05; H, 9·3; N, 6·8%). The benzoyl derivative formed needles (from ethanol), m. p. 151—152° (Found: C, 81·3; H, 7·8; N, 5·3. Calc. for $C_{18}H_{21}ON$: C, 80·9; H, 7·9; N, 5·2%) Lauer and Lockwood [1] give m. p. 154—154·5°.

p-iso*Pentylaniline*. The amine, prepared in 93% yield analogously to the *ortho*-isomer, had b. p. 96°/1 mm., n_D^{25} 1·5251. The acetyl derivative formed plates (from alcohol), m. p. 115—116° (Found: C, 75·9; H, 9·5; N, 7·1%), and the benzoyl derivative formed plates (from alcohol), m. p. 150—151° (Found: C, 80·6; H, 7·8; N, 5·4%). Hickinbottom [6] records m. p. 115—115·5° and m. p. 151—153° respectively for these derivatives. The m. p. of the benzoyl derivative was depressed on admixture with *o*-benzamido*iso*pentylbenzene.

4-*Acetamido*-3-*bromo*iso*pentylbenzene*. Bromine (10·3 g.) in acetic acid (10 ml.) was added dropwise to a solution of *p*-acetamido*iso*pentylbenzene (11 g.) in acetic acid (20 ml.) at 40°. The temperature rose and was kept at 50—55° for 1 hr. Isolation in the usual way gave the 3-*bromo-compound* (13·4 g., 88%) as colourless plates (from aqueous ethanol), m. p. 83·5—84° (Found: C, 55·0; H, 6·1; N, 4·8. $C_{13}H_{18}ONBr$ requires C, 54·9; H, 6·4; N, 4·9%).

2-*Bromo*-4-iso*pentylaniline*. The above acetamido-derivative (13 g.) was refluxed with ethanol (20 ml.) and concentrated hydrochloric acid (20 ml.) for 2 hr. The resulting *bromo-amine* (9·75 g., 88%), n_D^{25} 1·5504, was distilled in high vacuum in a short-path still at 100° (bath temp.) (Found: N, 5·6. $C_{11}H_{16}NBr$ requires N, 5·8%).

5-*Nitro*-2-iso*pentylaniline*. An ice-cold mixture of concentrated nitric acid (6·35 g., 1 mol.) and concentrated sulphuric acid (30 g.) was added dropwise with stirring to a solution of *o*-*iso*pentylaniline (11·5 g.) in concentrated sulphuric acid (170 g.) at 0°. The mixture was stirred for 3 hr., then poured on powdered ice (300 g.). Treatment with alkali gave the *nitro-amine* (7·8 g., 50%) which crystallised from aqueous methanol as orange-yellow prisms, m. p. 70—71° (Found: C, 63·3; H, 7·6; N, 13·4. $C_{11}H_{16}O_2N_2$ requires C, 63·4; H, 7·7; N, 13·45%).

Reduction with tin and hydrochloric acid in ethanol, followed by acetylation as usual, gave 2 : 4-diacetamido*iso*pentylbenzene,[2,3] m. p. and mixed m. p. 219—219·5°.

p-iso*Pentylbenzoic acid*. Sodium nitrite (7·6 g.) in water (15 ml.) was added dropwise to a cooled suspension of *p-iso*pentylaniline (16·3 g.) in 46% hydrobromic acid (70 g.) and water (10 ml.), the flask being stoppered and well shaken after each addition of the nitrite solution. Copper bronze (2 g.) was added and the mixture was warmed gently until a vigorous reaction set in. When this subsided the mixture was heated at 100° for 1 hr. and then steam-distilled. The resulting bromo-compound (11·6 g., 51%), b. p. 96—98°/0·7 mm., n_D^{25} 1·5210, was converted into the Grignard reagent in the usual manner and poured on an excess of powdered solid carbon dioxide. The syrupy product was treated with hydrochloric acid, and the ethereal layer was separated and extracted with sodium carbonate solution. Acidification of the extract gave p-iso*pentylbenzoic acid* (5 g.) which crystallised from hexane as needles, m. p. 128·5—129° (Found: C, 75·4; H, 8·15. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%). The p-*bromophenacyl ester* formed plates, m. p. 124—124·5° (Found: C, 62·0; H, 5·7. $C_{20}H_{21}O_3Br$ requires C, 61·7; H, 5·4%); the *amide*, plates, m. p. 136—137° (Found: C, 75·2; H, 8·5; N, 7·0. $C_{12}H_{17}ON$

[6] Hickinbottom, *J.*, 1932, 2396.

requires C, 75·35; H, 9·0; N, 7·3%); and the *anilide*, plates, m. p. 137·5—138° (Found: C, 81·1; H, 7·5; N, 5·2. $C_{18}H_{21}ON$ requires C, 80·9; H, 7·9; N, 5·2%).

o-iso*Pentylbenzoic acid*. This *acid*, prepared from *o-iso*pentylaniline analogously to the *para*-isomer, was distilled *in vacuo* forming a wax-like solid, m. p. 45·5—46° (Found: C, 75·1; H, 8·3%). The p-*bromophenacyl ester* formed needles, m. p. 59·5—60° (Found: C, 61·7; H, 5·5%), and the *anilide* formed plates, m. p. 102—103° (Found: C, 81·5; H, 7·6; N, 5·2%).

m-iso*Pentylbenzoic acid*. 2-Bromo-4-*iso*pentylaniline (9·7 g.) in concentrated hydrochloric acid (12·5 ml.) and water (25 ml.) was diazotised, at 5°, by the slow addition of sodium nitrite (3 g.) in water (15 ml.). Hypophosphorous acid (50%, 100 ml.) was added, and the mixture was set aside overnight at 0°. The oil which separated was isolated with ether, distilled *in vacuo* in a short-path still and converted into the Grignard reagent. Carbonation, as before, yielded m-iso*pentylbenzoic acid* (3 g.) which crystallised from hexane as prisms, m. p. 59—60° (Found: C, 75·0; H, 8·2%). The p-*bromophenacyl ester* formed woolly needles, m. p. 64—64·5° (Found: C, 62·1; H, 5·5%); the *amide*, needles, m. p. 105—106° (Found: C, 76·0; H, 8·7; N, 7·2%); and the *anilide*, needles, m. p. 78—78·5° (Found: C, 81·4; H, 7·7%).

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421. *Some Reactions of* 1 : 2-*Epithio-octane.*

By C. G. MOORE and M. PORTER.

RECENT examination [1] of the polysulphide obtained from sulphur and oct-1-ene at 140° necessitated a study of the reactivity of the epithio-group in 1 : 2-epithio-octane (I) towards heat and the nucleophilic reagents AlH_4^- and HS^-. The episulphide (I) was prepared by reaction of 1 : 2-epoxyoctane [2] with thiourea, the procedure used [3] being designed to minimise alkali-catalysed polymerization of the product.

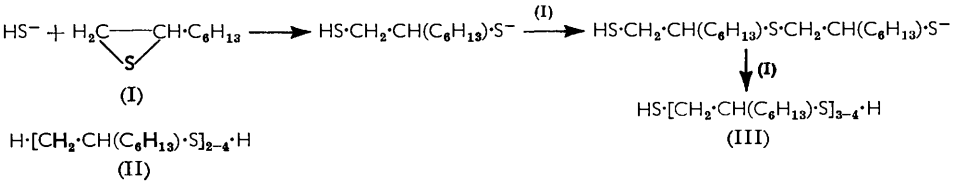
The susceptibility of episulphides to polymerization becomes less marked in the higher members of the series; [4] thus the epithio-octane (I) is stable at room temperature in the absence of acids or alkalis and is little changed after 1 hr. *in vacuo* at 140°. Heating for 5 hr. at 140° causes appreciable increase in molecular weight, but spectral evidence suggests that this is due to decomposition into oct-1-ene and sulphur followed by reaction of these to form a polysulphide. Thermal decomposition into olefin and sulphur has been observed similarly with 1 : 2-epithio-1-phenylethane [5] and with 1 : 2-epithio*cyclo*hexane.[6]

Reduction of episulphides with lithium aluminium hydride gives [7] thiols in about 75% yield, the sulphur atom remaining bound to the more substituted carbon atom. Contrary to this finding, reduction of the epithio-octane (I) gave only a small amount of the expected octane-2-thiol, the major product being a polymer (II), probably formed by anionic polymerization initiated by attack of the AlH_4^- ion on the episulphide. This polymer was similar in structure to that formed by action of alkali; the latter polymer is only slightly attacked by lithium aluminium hydride. There was no evidence for any anomalous hydrogenolysis involving removal of sulphur and formation of oct-1-ene in the manner in which butyl- or phenyl-lithium removes the sulphur atom from episulphides [7] or lithium aluminium hydride removes the oxygen atom from oxazirans.[8]

Culvenor, Davies, and Heath [4] found that attack of HS^- and RS^- ions on episulphides

[1] Bateman, Glazebrook, Moore, Porter, Ross, and Saville, *J.*, in the press.
[2] Swern, Billen, and Scanlan, *J. Amer. Chem. Soc.*, 1946, **68**, 1504.
[3] Bordwell and Andersen, *ibid.*, 1953, **75**, 4959.
[4] Culvenor, Davies, and Heath, *J.*, 1949, 282.
[5] Guss and Chamberlain, *J. Amer. Chem. Soc.*, 1952, **74**, 1342.
[6] Mousseron *et al.*, *Bull. Soc. chim. France*, 1948, 84.
[7] Bordwell, Andersen, and Pitt, *J. Amer. Chem. Soc.*, 1954, **76**, 1082.
[8] Emmons, *ibid.*, 1957, **79**, 5739.

produces vicinal dithiols and mercapto-sulphides, respectively, together with polymeric material. In corroboration of this, reaction of potassium hydrogen sulphide with the episulphide (I) gave a small yield of octane-1 : 2-dithiol and considerable polymer (III) formed by the process: [9]



Experimental.—1 : 2-*Epithio-octane* (I). The episulphide was prepared by reaction of 1 : 2-epoxyoctane (from oct-1-ene by perbenzoic acid oxidation [10]) with thiourea as described by Bordwell and Andersen.[3] Fractionation of the product gave unchanged epoxide (7%), episulphide (I) contaminated with some epoxide (78%) (Found: C, 68·5; H, 11·3; S, 18·1%), and residual pale yellow polymer (15%) (Found: C, 67·35; H, 11·35; S, 20·5%; *M*,* 2000—3000). Refractionation afforded pure 1 : 2-*epithio-octane*, b. p. 83°/5 mm., n_D^{20} 1·4702 (Found: C, 66·95; H, 10·9; S, 22·2%; *M*,* 142. $C_8H_{16}S$ requires C, 66·6; H, 11·2; S, 22·2%; *M*, 144), showing principal infrared bands (measured on the Hilger H. 800 double-beam instrument as a 100μ-thick film) at ~1445, 1371, 1296, 1263, 1107, 1030, 905, 716 cm.$^{-1}$.

Thermal stability of episulphide (I). The episulphide (I) was indefinitely stable at room temperature but after 1 hr. *in vacuo* at 140° it had become yellow (Found: S, 21·9%; *M*,* 148, 151). Similar treatment for 5 hr. gave a red-brown product (Found: S, 21·7%; *M*,* 218, 214) which did not react with lead acetate. The infrared spectra of both products were similar to that of pure episulphide (I) but additional bands due to vinylic unsaturation were present. Estimates, as oct-1-ene, gave results of 1% and 8%, respectively. Another band at 970 cm.$^{-1}$ was ascribed to a skeletal vibration of a sulphurated octane grouping, since octane-1- and -2-thiol and octane-1 : 2-dithiol all show this absorption.[1] The ultraviolet absorption spectra indicated the presence of elemental sulphur or polysulphide groups.

Reduction of episulphide (I). The compound (1·425 g.) was reduced with lithium aluminium hydride (0·9 g.) as described by Bateman *et al.*[1] No hydrogen sulphide was evolved and fractionation of the product gave: (i) mainly octane-2-thiol (0·28 g.), b. p. 66—69°/23 mm. (Found: C, 67·3; H, 12·35; S, 20·15. Calc. for $C_8H_{18}S$: C, 65·7; H, 12·4; S, 21·9%), identified as 2 : 4-dinitrophenyl 1-methylheptyl sulphide, m. p. and mixed m. p. 49—49·5° (after 3 recrystallisations from ethanol) (Found: C, 53·9; H, 6·5; N, 8·9. Calc. for $C_{14}H_{20}O_4N_2S$: C, 53·8; H, 6·45; N, 9·0%); (ii) a liquid (0·33 g.), b. p. 105—108°/0·05 mm. (Found: C, 66·2; H, 11·7; S, 21·8%; *M*,* 307, 286. Calc. for $C_{16}H_{34}S_2$: C, 66·1; H, 11·8; S, 22·1%; *M*, 289), containing thiol groups (infrared spectrum); (iii) a yellow residue (0·44 g.) [Found: C, 66·9; H, 11·6; S, 21·5%; *M*,* 466, 448. This corresponds to $(C_8H_{16\cdot5}S_{1\cdot0})_{3\cdot2}$], whose infrared spectrum was similar to that of the episulphide polymer isolated during the preparation of the monomer (I); thiol groups were also present.

Action of potassium hydrogen sulphide on episulphide (I). The episulphide (1·367 g.) was shaken for 3 days with a solution of potassium hydrogen sulphide in ethanol [prepared by saturating a solution of potassium hydroxide (0·94 g.) in ethanol (10 ml.) at 0° with hydrogen sulphide]. The bulk of the ethanol was removed at low pressure and excess of aqueous sodium hydroxide was added to the residue, which was then extracted with light petroleum (b. p. <40°; 3 × 30 ml.), washed with water, and dried (Na_2SO_4). Removal of the solvent gave an oil (1·20 g.) [Found: C, 63·8; H, 11·0; S, 25·1%; *M*,* 559, 560. This corresponds to $(C_8H_{16\cdot4}S_{1\cdot2})_{3\cdot7}$]. The infrared spectrum showed the presence of ~1—2 thiol groups per molecule. The alkaline solution was worked up in the same way to give impure octane-1 : 2-dithiol (0·05 g.) (Found: C, 56·0, 56·2; H, 9·7, 9·6; S, 33·0. Calc. for $C_8H_{18}S_2$: C, 53·9; H, 10·2; S, 36·0%), identified by its infrared spectrum.

Stability of the polymer towards lithium aluminium hydride. The polymer (0·885 g.) obtained

* All molecular weights thus recorded were obtained ebullioscopically in benzene.

[9] Cf. Meade and Woodward, *J.*, 1948, 1894.

[10] Swern, in " Organic Reactions," Vol. VII, John Wiley, London, 1953, p. 396.

as by-product in the preparation of episulphide (I) was treated with lithium aluminium hydride (1·73 g.) in tetrahydrofuran (20 ml.) for 5 hr. in the usual way. The product (0·744 g.) was a viscous liquid, not distillable below 120°/17 mm. (Found: C, 67·45; H, 11·3; S, 19·3%; *M*,* 1220, 1540).

We thank Mr. G. M. C. Higgins and Mr. M. B. Evans for the spectroscopic data.

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48—56, TEWIN ROAD, WELWYN GARDEN CITY, HERTS. [*Received, January 1st*, 1958.]

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422. *The Solubility of Arsenious Oxide in Aqueous Hydrochloric Acid at 25°.*

By I. A. MENZIES and L. W. OWEN.

THE solubility of arsenious oxide in hydrochloric acid solutions at 15° was determined by Wood [1] and at 25° by Ghiron and Mangili.[2] More extensive studies were made of this system (0—8m-hydrochloric acid) and of the system arsenious oxide–sodium hydroxide–water by Garrett, Holmes, and Laube,[3] whose data have now been extended to 15m-hydrochloric acid.

The results (expressed in moles per kg. of water; see Table) are in good agreement with those of Garrett, Holmes, and Laube. Comparison of the present values with those of Wood indicate the lower solubility at 15°.

HCl ...	$0{\cdot}286_1$	$1{\cdot}25_4$	$2{\cdot}50_4$	$3{\cdot}45_3$	$5{\cdot}27_4$	$6{\cdot}70_4$	$7{\cdot}17_1$	$9{\cdot}14_7$	$10{\cdot}4_9$	$12{\cdot}6_7$	$14{\cdot}7_2$
As_2O_3	$0{\cdot}083_6$	$0{\cdot}081_5$	$0{\cdot}075_5$	$0{\cdot}076_0$	$0{\cdot}120_2$	$0{\cdot}254_9$	$0{\cdot}317_6$	$0{\cdot}734_2$	$1{\cdot}03_5$	$1{\cdot}58_4$	$2{\cdot}04_1$

The minimum in the solubility curve occurs at a hydrochloric acid molality of 2·5—3·5 and is understandable on the basis of interaction between (*a*) chemical and physical salting-out and (*b*) formation of arsenious oxide–hydrochloric acid compounds. Chemical salting-out is the result of repression of dissociations of the type $As_2O_3,xH_2O \rightleftharpoons [AsO_3^{3-}][3H^+] + As_2O_3,yH_2O$ by hydrochloric acid: physical salting-out results from the lowering of the activity of the water by hydrochloric acid.

The rapid increase in solubility at higher hydrochloric acid concentrations is undoubtedy caused by compound formation between arsenious oxide and hydrochloric acid. The formation of arsenious chlorides and oxychlorides is most probable and arsenic trichloride has been isolated from such solutions by distillation.[4]

Experimental.—" AnalaR " chemicals were used, arsenious oxide being recrystallised from hydrochloric acid as described by previous authors.[1,5] Redistilled water was used.

The concentration of each hydrochloric acid solution was determined by titration against a solution of sodium hydroxide previously standardised by titration with a solution of hydrochloric acid prepared from constant-boiling hydrochloric acid. Excess of arsenious oxide was added to each acid solution in a conical borosilicate glass flask at 25° ± 0·01°. The suspension was stirred until no further increase in arsenic concentration of the solution was detectable over two periods of 6 hr. each. Then the excess of arsenious oxide was filtered off and the solution neutralised with sodium carbonate. The solution was then made slightly acid. 2·5 g. of sodium

[1] Wood, *J.*, 1908, 411.
[2] Ghiron and Mangili, *Gazzetta*, 1935, **65**, 1244.
[3] Garrett, Holmes, and Laube, *J. Amer. Chem. Soc.*, 1940, **62**, 2024.
[4] Partington, " General and Inorganic Chemistry," MacMillan & Co., London, 1951.
[5] Garrett and Howell, *J. Amer. Chem. Soc.*, 1939, **61**, 1730.

hydrogen carbonate were added and the solution was titrated with 0·1N-iodine with starch as indicator.

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UNITED KINGDOM ATOMIC ENERGY AUTHORITY, MATERIALS RESEARCH DIVISION,
A.W.R.E., ALDERMASTON, BERKS. [*Received, January 6th,* 1958.]

423. *Non-ionic Surface-active Agents. Part II.* The Synthesis of Some Polyoxyethylene Glycol Monohexyl Ethers.*

By B. A. MULLEY.

FOR a study of non-ionic surface-active agents a range of pure compounds was required with lipophilic and hydrophilic properties. This Note describes the preparation of polyoxyethylene glycol monohexyl ethers with two to six ethylene oxide units per molecule. The compounds with two and three ethylene oxide units severally are almost insoluble in water at 20°. Higher members are soluble in water at this temperature and have a hydrophilic nature which increases with the number of oxide units per molecule.

A few reports[1] have previously appeared describing homogeneous compounds of this type although in the first two cases no experimental details were given. The Williamson ether synthesis was chosen as a synthetic route in the present work: $C_6H_{13}Br + NaO\cdot[CH_2\cdot CH_2O]_n\cdot H \longrightarrow C_6H_{13}\cdot O\cdot[CH_2\cdot CH_2\cdot O]_n\cdot H \rightleftharpoons C_6H_{13}\cdot O\cdot[CH_2\cdot CH_2\cdot O]_{n-1}\cdot CH_2\cdot CH_2Cl$. To minimise the formation of dialkyl ethers approximately eight equivalents of the glycol were used to one of sodium, so that mainly monosodium derivatives were obtained. Small amounts of the diethers were probably still produced but these were not isolated. The monoethers with $n = 2$ and 3 were prepared in this way from di- and tri-ethylene glycol and with thionyl chloride in the presence of pyridine gave the derived chloro-compounds. These condensed readily with the appropriate monosodium derivative of diethylene or triethylene glycol to give the monoethers with $n = 4$, 5, and 6.

The cooling curves of the compounds showed a constant temperature at the f. p. and the sudden drop as the solids started to cool, which is characteristic of pure substances.

Experimental.—Microanalyses were by Mr. G. S. Crouch, School of Pharmacy, University of London. Hydroxyl groups were determined by the method given by Curme and Johnston.[2] *n*-Hexyl bromide was obtained from Eastman Kodak Co.

3 : 6-*Dioxadodecan*-1-*ol* ($n = 2$). Sodium (20·9 g.) was dissolved in diethylene glycol (385·6 g.), and the solution heated with *n*-hexyl bromide (150 g.) at ~200° for several hours. Benzene (750 ml.) was added and the mixture extracted with water (3 × 100 ml.). The theoretical quantity of sodium bromide was found in the water fractions. Evaporation of the benzene from the organic layer and fractional distillation of the residue gave 3 : 6-dioxadodecan-1-ol (93 g.), b. p. 140—141°/16 mm., f. p. −33·6° (Found: C, 62·2; H, 11·9; OH, 9·25. Calc. for $C_{10}H_{22}O_3$: C, 63·1; H, 11·6; OH, 8·9%). Chakhovskoy, Martin, and Van Nechel [1] give b. p. 115—115·6°/2 mm., f. p. −40·2°.

1-*Chloro*-3 : 6-*dioxadodecane* ($n = 2$). To the above alcohol (60 g.) and pyridine (20·5 g.), thionyl chloride (75 g.) was added in portions and the whole refluxed for 1½ hr. Excess of

* Part I, *J. Pharm. Pharmacol.*, 1956, 8, 774.

[1] Brandner, Lockwood, Nagel, and Russell, F.I.A.T. Final Report, No. 1141, p. 11; Goto, Sugano, and Koizumi, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1953, **31**, 305; Chakhovskoy, Martin, and Van Nechel, *Bull. Soc. chim. belges*, 1956, **65**, 453, and references there cited; Gingras and Bayley, *Canad. J. Chem.*, 1957, **35**, 599.

[2] Curme and Johnston, "Glycols," Reinhold Pub. Corp., New York, 1952, p. 333.

thionyl chloride was destroyed with water (40 ml.), and benzene (100 ml.) was added. The organic layer was washed with sodium hydrogen carbonate solution and with water, dried ($MgSO_4$), and evaporated. Distillation then gave 1-*chloro*-3 : 6-*dioxadodecane* (49 g.), b. p. 126°/14 mm. (Found: C, 57·1; H, 10·0; Cl, 17·5. $C_{10}H_{21}O_2Cl$ requires C, 57·5; H, 10·1; Cl, 17·0%).

3 : 6 : 9-*Trioxapentadecan*-1-*ol* ($n = 3$).—A solution from sodium (7 g.) and triethylene glycol (182 g.) was treated with *n*-hexyl bromide (50 g.) as described above. Water (250 ml.) and light petroleum (b. p. 100—120°; 200 ml.) were added, and the two-phase mixture heated to 70°. The organic layer was then washed with water (50 ml.) at 70°. Distillation, after removal of the solvent, gave 3 : 6 : 9-trioxapentadecan-1-ol (34 g.), b. p. 152—153°/5 mm., f. p. −26·1° (Found: C, 62·2; H, 11·5; OH, 7·1. Calc. for $C_{12}H_{26}O_4$: C, 61·5; H, 11·2; OH, 7·3%). Chakhovskoy and his co-workers [1] gave b. p. 150—150·4°/2 mm., f. p. −34·5°. Sodium bromide (25·2 g.) was found in the water-fractions obtained from the extraction procedure.

1-*Chloro*-3 : 6 : 9-*trioxapentadecane* ($n = 3$). The alcohol ($n = 3$) (20 g.) with thionyl chloride (15·3 g.) in the presence of pyridine (6·75 g.) gave the *chloride* (16·2 g.), b. p. 137—141°/3·5 mm. (Found: C, 56·6; H, 10·1; Cl, 14·0. $C_{12}H_{25}O_3Cl$ requires C, 57·0; H, 10·0; Cl, 14·0%).

3 : 6 : 9 : 12-*Tetraoxaoctadecan*-1-*ol* ($n = 4$). 1-Chloro-3 : 6-dioxadodecane ($n = 2$) (50 g.) was heated with the derivative made by dissolving sodium (5·5 g.) in diethylene glycol (101·5 g.), and the precipitated sodium chloride was removed. Distillation of the filtrate gave 3 : 6 : 9 : 12-tetraoxaoctadecan-1-ol (36·6 g.), b. p. 158—159°/1·5 mm., f. p. −11·9° (Found: C, 60·1; H, 11·1; OH, 6·2. Calc. for $C_{14}H_{30}O_5$: C, 60·4; H, 10·8; OH, 6·1%). Chakhovskoy *et al.*[1] gave b. p. 134—134·2°/0·005 mm., f. p. −18·1°. The sodium chloride filtered from the reaction mixture, together with that found in the residue after distillation, was in theoretical yield.

3 : 6 : 9 : 12 : 15-*Pentaoxaheneicosan*-1-*ol* ($n = 5$) (30·5 g.) was obtained from 1-chloro-3 : 6-dioxadodecane ($n = 2$) (40 g.), triethylene glycol (114·8 g.), and sodium (4·4 g.) and had b. p. 163—165°/0·15 mm., f. p. −3·3° (Found: C, 59·7; H, 10·5; OH, 5·35. $C_{16}H_{34}O_6$ requires C, 59·6; H, 10·6; OH, 5·3%) [with sodium chloride (11·06 g.)].

3 : 6 : 9 : 12 : 15 : 18-*Hexaoxatetracosan*-1-ol ($n = 6$) prepared (12 g.) as in the last two cases, from the chloride ($n = 3$) (15·2 g.), triethylene glycol (36 g.), and sodium (1·8 g.), had b. p. 192—194°/0·15 mm., f. p. 1·2° (Found: C, 58·9; H, 10·7; OH, 4·9. $C_{18}H_{38}O_7$ requires C, 59·0; H, 10·4; OH, 4·6%); the sodium chloride amounted to 3·33 g.

Cooling curves. About 5 g. of the compounds were used in a lagged tube immersed in a bath maintained about 10° below the f. p.

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424. *Acidity-dependence of Decomposition of Cumene Hydroperoxide.*

By A. W. DE RUYTER VAN STEVENINCK.

THE acid-catalyzed decomposition of cumene hydroperoxide has been reported to be of first-order with respect to the concentration of both hydroperoxide and acid when the reaction is carried out in 50% (w/w) acetic acid with toluene-*p*-sulphonic acid as the catalyst and the ionic strength is maintained constant by the addition of lithium chloride.[1] Using the same solvent and sulphuric acid as the catalyst, Wichterle and Cefelin [2] established the same relation for the reaction in absence of neutral salts.

When carrying out the reaction in 50% (w/w) ethanol, the catalyst being perchloric acid of various concentrations, the author found that the second-order rate constant

[1] Seubold and Vaughan, *J. Amer. Chem. Soc.*, 1953, **75**, 3790.
[2] Wichterle and Cefelin, *Chem. Listy*, 1957, **51**, 747.

k_{II}, defined by $-d[R{\cdot}O{\cdot}OH]/dt = k_{II}[R{\cdot}O{\cdot}OH][HClO_4]$, increases with increasing acid concentration, as shown by the data in Table 1.

TABLE 1. *Influence of acid concentration on the second-order rate constant of cumene hydroperoxide decomposition, in* 50% *(w/w) ethanol, at* 50°. $[R{\cdot}O{\cdot}OH] = 0{\cdot}20$M.

$HClO_4$ (moles/l.)	0·048	0·098	0·196	0·283	0·382
$k_{II} \times 10^5$ (l. mole^{-1} sec.$^{-1}$)	4·9	5·5	6·9	7·7	9·4

In order to obtain more information on this effect, a series of rate measurements was carried out in which the concentration of perchloric acid was kept constant, whilst increasing quantities of lithium perchlorate were added. Determination of the acetone and phenol produced showed that the addition of this salt has no influence on the composition of the product and only enhances the reaction velocity (Table 2).

TABLE 2. *Influence of addition of salt on the second-order rate constant of cumene hydroperoxide decomposition, in* 50% *(w/w) ethanol, at* 50°. $[R{\cdot}O{\cdot}OH] = 0{\cdot}12$M, $[HClO_4] = 0{\cdot}19$N.

$[ClO_4^-]$ (g.-ions/l.)	0·19	0·30	0·50	0·70	0·90	1·10	1·30	1·54	1·75	2·00
$k_{II} \times 10^5$ (l. mole^{-1} sec.$^{-1}$)	6·9	8·2	11·4	14·3	19·0	25·1	33·7	47·5	63·5	88·0

Examination of the results given in Table 2 shows a linear dependence of log k_{II} on the total electrolyte concentration. Similarly, a determination of the values of Hammett's acidity function [3] H_0 under the conditions of the kinetic experiments, *p*-nitroaniline being used as the indicator base, demonstrated that H_0 depends linearly on the total electrolyte

TABLE 3. *Influence of the electrolyte concentration on acidity function* H_0.

$[ClO_4^-]$ (g.-ions/l.)	0·190	0·689	1·186	1·686	2·184
H_0	1·72	1·53	1·31	1·10	0·89

concentration (Table 3). From this result, in combination with the above-mentioned linear dependence of log k_{II} on the total electrolyte concentration, it follows that log k_{II} depends linearly on H_0, a plot showing a straight line with slope −1·45. According to Zucker and Hammett [4] such a linear dependency on H_0 rather than on $-\log [H_3O^+]$ suggests that the formation of the transition state is a unimolecular rather than a bimolecular process involving a solvent (water) molecule.

In order to investigate whether this relationship is specific for the $HClO_4$–$LiClO_4$ system, the same experiments were carried out with two other acid–salt pairs, *viz.*, HCl–LiCl and *p*-$CH_3{\cdot}C_6H_4{\cdot}SO_3H$–*p*-$CH_3{\cdot}C_6H_4{\cdot}SO_3Li$. Here, too, straight lines were obtained on plotting log k_{II} against H_0, the slopes being −1·01 and −0·76, respectively. Deviations from a slope of unity—predicted by Zucker and Hammett—are probably caused by the use of an only partially aqueous solvent.

The apparent difference in behaviour between the acid-catalyzed cumene hydroperoxide decomposition in aqueous acetic acid and that in aqueous ethanol—the former showing correlation with acid concentration and the latter with acidity function—does not imply a difference in reaction mechanism. Wichterle and Cefelin [2] have established a proportionality between H_0 and $-\log [H_3O^+]$ on determining H_0 in solutions of sulphuric acid in 50% (w/w) acetic acid. Very probably the greater proton affinity of ethanol than of acetic acid causes deviations to occur between H_0 and $-\log [H_3O^+]$ at much lower acid concentrations.

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(N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ). [*Received, November* 29*th*, 1957.]

[3] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 267.
[4] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

425. *Decamethylene Dibromide.*

By E. P. Taylor.

Kaluszyner [1] has described an easy and inexpensive preparation of tetramethylene dibromide by reaction of sodium bromide and concentrated sulphuric acid with tetrahydrofuran. Published preparations of decamethylene dibromide include reaction of decamethylene glycol with fuming hydrobromic acid in a sealed tube [2] (yield 98%), with dry hydrogen bromide [3, 4] (yield 85—90%), or with hydrobromic–sulphuric acid [5] (yield 67%). We have found the simplest preparation to be reaction of the glycol with sodium bromide and concentrated sulphuric acid, giving yields of the order of 80%.

Experimental.—Concentrated sulphuric acid (194 g.) was added dropwise to a well-stirred mixture of sodium bromide (150 g., 1·45 moles), water (130 ml.), and decamethylene glycol (63 g., 0·36 mole). The stirred mixture was then gently refluxed for 6 hr. and then allowed to cool, an equal volume of water added, and the solution extracted with ether. The extract was washed with water, sodium hydrogen carbonate solution, sodium thiosulphate solution, and water, and dried (Na_2SO_4), the solvent removed, and the residue distilled *in vacuo*, giving decamethylene dibromide (88 g., 81%), b. p. 166—168°/12 mm., plates, m. p. 28°.

I thank the Directors of Allen and Hanburys Ltd. for permission to publish this note.

Research Division, Allen & Hanburys Ltd.,
Ware, Herts. [*Received, December 2nd,* 1957.]

[1] Kaluszyner, *J. Org. Chem.*, 1957, **22**, 834.
[2] Franke and Hankam, *Monatsh.*, 1910, **31**, 177.
[3] Chuit, *Helv. Chim. Acta*, 1926, **9**, 264.
[4] Carothers, Hill, Kirby, and Jacobson, *J. Amer. Chem. Soc.*, 1930, **52**, 5279.
[5] Price, Guthrie, Herbrandson, and Peel, *J. Org. Chem.*, 1946, **11**, 281.