NOTES.

208. *Anionic Polymerisation. Part III.* The Polymerisation of Styrene in Liquid Ammonia Catalysed by Potassium.*

By N. S. Wooding and W. C. E. Higginson.

Recent copolymerisation studies (Landler, *Compt. rend.*, 1950, **230**, 539; Mayo and Walling, *Chem. Reviews*, 1950, **46**, 191; Walling, Briggs, Cummings, and Mayo, *J. Amer. Chem. Soc.*, 1950, **72**, 48) have indicated that the mechanism of polymerisation by alkali metals, both in liquid ammonia and in the absence of solvent, differs from that obtaining with acid (Friedel–Crafts) catalysts or with free-radical initiators. It seems probable that the polymerisation reaction takes place by an anionic chain mechanism, and comparison of the results obtained in the alkali metal–liquid ammonia system with those using known anionic catalysts supports this view (Beaman, *ibid.*, 1948, **70**, 3115).

The polymerisation of styrene in liquid ammonia by the amide ion, NH_2^-, has been studied by us (*J.*, 1952, 760) and the dependence of the rate of monomer disappearance and of the molecular weight upon reactant concentrations and upon temperatures has been established. A few experiments have also been done with potassium as catalyst in place of potassium amide. Styrene was again used as monomer. The results of rate experiments at −33·5° are shown below.

$[C_8H_8]$, mole/l.	[K], mole/l.	Rate $= d(1/[C_8H_8])/dt$, l. mole^{-1}, min.$^{-1}$	k, l.$^{1\frac{1}{2}}$ mole$^{-1\frac{1}{2}}$ min.$^{-1}$
0·197	0·0075	0·153	1·77
0·190	0·0340	0·318	1·72

As in the previous work, good second-order plots were obtained for the rate of disappearance of monomer (M), and the rate was proportional to the square root of the initial potassium concentration, as shown by the two similar values of the overall reaction velocity constant k, calculated from the expression $-d[M]/dt = k[M]^2[K]^{\frac{1}{2}}$. The average value for k, 1·75, compares with the average value, 2·81, obtained for k' ($-d[M]/dt = k'[M]^2[KNH_2]^{\frac{1}{2}}$) for the potassium amide-catalysed polymerisation at the same temperature, −33·5° (see Higginson and Wooding, *loc. cit.*).

The molecular weight of polymer formed in experiments with initial monomer concentration 0·190 mole/l., the reaction being stopped after 32% of the styrene had reacted, was 4450 (intrinsic viscosity, $[\eta] = 0·160$). The polymer was found to contain nitrogen, and one nitrogen atom being assumed per polymer molecule, as in the amide-ion catalysed polymerisation of styrene, the number-average molecular weight obtained from the nitrogen

* Part II, *J.*, 1951, 774.

content was 3080 and 2980 in two determinations. The discrepancy between the molecular weight values obtained by these two methods is little greater than was found previously in some instances in the experiments using potassium amide. The viscosity molecular weight of polystyrene produced from a reaction mixture of the same initial styrene concentration with potassium amide as catalyst is *ca.* 3500 at 32% reaction (approximately 60% higher than the value obtained at 100% reaction).

There is thus considerable similarity between the experimental findings for the potassium amide- and the potassium-catalysed polymerisation of styrene in liquid ammonia. In both cases there is a second-order dependence of the rate of disappearance of styrene on the styrene concentration. The rate of disappearance of styrene is proportional to $[KNH_2]^{\frac{1}{2}}$ in the first case, and to $[K]^{\frac{1}{2}}$ in the second. The overall rate constants k' and k are numerically similar in the two cases. The viscosity molecular weight of polystyrene prepared with potassium as catalyst is similar to that expected from the potassium amide-catalysed polymerisation under otherwise identical conditions. This overall similarity makes it probable that the mechanism of the potassium-catalysed polymerisation is the same as that established for the potassium amide-catalysed reaction, *i.e.*, as shown by the three equations (with R = Ph) in Part I (*J.*, 1952, 760).

In the potassium-catalysed polymerisation, we suggest that the amide (NH_2^-) ion, which is the true catalyst, is formed in the reduction of styrene by potassium :

$$(O)\quad 2K + CH_2{:}CHPh + 2NH_3 \longrightarrow 2K^+ + CH_3{\cdot}CH_2Ph + 2NH_2^-$$

Wooster and Ryan (*J. Amer. Chem. Soc.*, 1934, **56**, 1133) have prepared ethylbenzene in 50% yield by mixing approximately equivalent quantities of sodium and styrene in liquid ammonia solution.

Reaction (*O*) must be rapid to account for the similarity between the rates of the potassium- and the potassium amide-catalysed polymerisations. This is borne out by (*a*) the almost instantaneous disappearance of the blue colour of potassium in liquid ammonia on admixture with the styrene solution, though the half-life of the polymerisation reaction is of the order 15—30 minutes, and (*b*) the absence of any red colour in the solution characteristic of carbanions of the type $Ph - \overset{(-)}{C}\!<$ which might be formed as intermediates in significant concentration. It is possible that such carbanion intermediates, if formed, would act as initiating species in addition to the amide ion. However, as the nitrogen content of the polymer is close to that expected for amide-ion initiation alone (carbanion initiation would not introduce nitrogen into the polymer), it seems probable that such side reactions are relatively insignificant, if they occur at all. The detailed steps by which reaction (*O*) takes place are at present unknown, but this is unimportant if, as appears probable, the overall reaction occurs rapidly and reactions of intermediates with styrene can be neglected.

The reaction scheme suggested above, *i.e.*, the rapid reduction of monomer by potassium leading to the formation of amide ions which can initiate an anionic polymerisation, is also likely to hold with other vinyl monomers. In certain cases the potassium may reduce groups other than the ethylenic double bond, but as such reduction will usually result in the formation of amide ions, *e.g.*, $2K + 2NH_3 + X \longrightarrow 2K^+ + 2NH_2^- + XH_2$, similarities are in general to be expected between the potassium amide- and potassium-catalysed polymerisations of other monomers in liquid ammonia as solvent. If XH_2 is comparatively acid, so that by reaction with the amide ion the reduction leads to the formation of anions which are weaker bases, and which in many cases (cf. Wooding and Higginson, *J.*, 1952, 774) are ineffective as anionic initiators, alkali metal-catalysed polymerisation is unlikely to occur, provided that the amide ions have been completely removed.

Experimental.—Experiments were carried out in absence of air at −33·5° in the apparatus described by Higginson and Wooding (*loc. cit.*). The rate of monomer disappearance was determined by the sampling method used in the potassium amide-catalysed polymerisation studies. Polymer was purified as before by precipitation from ethyl methyl ketone solution with methanol and was dried in a vacuum (P_2O_5). The viscosity of a polymer solution in benzene was determined at 25° in an Ostwald viscometer, and the molecular weight calculated

from the intrinsic viscosity by Kemp and Peters's equation (*Ind. Eng. Chem.*, 1942, **34**, 1097). Though the use of this particular molecular weight–intrinsic viscosity relation may be questioned, comparison of molecular weights found by using this relation in each case is essentially a comparison of intrinsic viscosities, and so the similarity between molecular weights found in otherwise identical conditions in the potassium amide- and potassium-catalysed polymerisations is legitimately established. Nitrogen determinations were made by using the Kjeldahl method as before.

Our thanks are offered to Messrs. Courtaulds Ltd. for a grant to one of us (N. S. W.).

THE CHEMISTRY DEPARTMENT,
THE UNIVERSITY, MANCHESTER. [*Received, September 25th*, 1951.]

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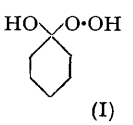
209. *The Structure of a Peroxide from* cyclo*Hexanone and Hydrogen Peroxide.*

By W. COOPER and W. H. T. DAVISON.

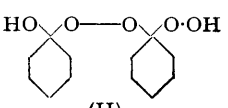
THE peroxide, m. p. 78—79°, obtained from equimolar amounts of *cyclo*hexanone and hydrogen peroxide was considered by Milas, Harris, and Panagiotakos (*J. Amer. Chem. Soc.*, 1939, **61**, 2430) to be 1-hydroxy*cyclo*hexyl hydroperoxide (I). Recently Criegee, Schnorrenberg, and Becke (*Annalen*, 1949, **565**, 7) have stated that it is actually 1-hydroperoxy*cyclo*hexyl 1-hydroxy*cyclo*hexyl peroxide (II) which can be regarded as a dehydration product of (I). They also consider that in solution (II) breaks down to give *cyclo*hexanone and 1 : 1-dihydroperoxy*cyclo*hexane.* Structure (I) was assumed by Cooper (*loc. cit.*) in a study of its thermal decomposition products, but it was pointed out that the results were not inconsistent with the view that other peroxides could also participate in the breakdown. It is, however, of considerable importance to decide between the alternative structures. The facts now reported support in general the structure and reactions proposed by Criegee *et al.* and give further information on the unusual properties of this compound.

The instability of the hydroperoxide caused difficulty in its purification and analyses of many samples were in agreement with structure (I); but repeated recrystallisation from light petroleum, followed by careful drying *in vacuo*, gave a compound analysis of which was correct for structure (II).

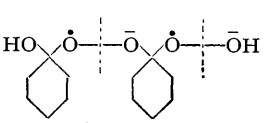
Reduction of the *solid* peroxide with aqueous ferrous sulphate gave mainly hexanoic and dodecane-1 : 12-dioic acid. These compounds would be formed from either structure, (II) forming a radical and an ion radical by one-electron addition to each of the peroxide links (cf. II*a*).



(I)



(II)



(II*a*)

On treatment with aqueous 2 : 4-dinitrophenylhydrazine hydrochloride complete decomposition occurred with the formation of one mole of the 2 : 4-dinitrophenylhydrazone per equivalent of the peroxide.

As the rival structures (I) and (II) have the same functional groups, direct elucidation of the structure from the infra-red spectrum would be difficult, other than by the use of molar extinction coefficients to determine the numbers of hydroxyl and hydroperoxyl groups. This was not attempted because of the additional complication of dissociation

* In the paper by Cooper (*J.*, 1951, 1340) the fact that these workers had described the dibenzoyl and di-*p*-nitrobenzoyl esters of this compound was overlooked.

in solution. The solid, in a mull with paraffin, showed not more than a trace of *cyclo*hexanone. In solution, however, dissociation occurred rapidly and the formation of *cyclo*hexanone was followed spectroscopically and shown to reach equilibrium after several hours (Table 1). The formation of *cyclo*hexanone in this way was observed in carbon

TABLE 1.

Time (hours)	0·25	0·50	0·75	1·75	2·75	3·75
$[C]/[P_0]$	0·12	0·30	0·37	0·57	0·62	0·60

$[P_0] = 0{\cdot}0390$ mole/l.

tetrachloride, styrene, *cyclo*hexane, and benzene. During this dissociation no change was apparent in the 3000—3800-cm.$^{-1}$ region, there being two hydroxyl absorptions only at 3370 and 3540 cm.$^{-1}$, the latter being stronger at greater dilutions (the 3370-cm.$^{-1}$ band is presumably that of hydrogen-bonded hydroxyl). Hydroxyl frequencies for hydroperoxides and alcohols are very similar (Shreve, Heether, Knight, and Swern, *Analyt. Chem.*, 1951, **23**, 282) but water has an absorption at 3450 cm.$^{-1}$ and the absence of this band is evidence against the bimolecular decomposition of (I) with the formation of (III), *cyclo*hexanone, and water.

The dissociation (at 30° in carbon tetrachloride) was increased by dilution (see Table 2) and this further supports structure (II). No displacement of the equilibrium was observed when the temperature was raised to 60°.

TABLE 2.

$[P_0]$	$[C_\infty]$	$[C_\infty]/[P_0]$	$[P_0]$	$[C_\infty]$	$[C_\infty]/[P_0]$	$[P_0]$	$[C_\infty]$	$[C_\infty]/[P_0]$
2·02	—	0	0·0336	0·0192	0·57 ± 0·02	0·00134	0·00135	1·01 ± 0·04
0·0840	0·0417	0·50 ± 0·02	0·0067	0·0053	0·79 ± 0·03	0·00027	0·000297	1·10 ± 0·04

$[P_0]$ is the initial concentration of peroxide. $[C_\infty]$ is the equilibrium concentration of *cyclo*hexanone (mole/l.).

That it was a reversible reaction was shown by the isolation of unchanged hydroperoxide by removal of the solvent at room temperature; there was no appreciable loss of peroxide-oxygen.

The new peroxide was apparently very stable in solution since at 70° it decomposed only very slowly in pure carbon tetrachloride or benzene; in impure solvents it decomposed autocatalytically with the formation of adipic acid.

The correct interpretation of these facts, and the formation of *cyclo*hexyl 1 : 1-diper-esters on treatment with acyl chlorides, would seem to be that suggested by Criegee *et al.* (*loc. cit.*) :

$$HO{\cdot}O{\cdot}C_6H_{10}{\cdot}O{\cdot}O{\cdot}C_6H_{10}{\cdot}OH \rightleftharpoons C_6H_{10}O + C_6H_{10}(O{\cdot}OH)_2$$

This equilibrium would lead to the relation $[C_\infty]^2 = K([P_0] - [C_\infty])$, but its validity was not checked because the experimental results were insufficiently refined for accurate measurement of the small differences in the right-hand side of the equation.

Experimental.—1-*Hydroperoxy*cyclo*hexyl* 1-*hydroxy*cyclo*hexyl peroxide.* The peroxide was recrystallised from light petroleum (b. p. 60—80°) four times. The final slow recrystallisation from the solution of peroxide saturated at 30—40° gave long transparent needles which were dried in air and then in a vacuum at room temperature [Found : C, 58·4, 58·3; H, 9·2, 9·0; active O, 13·2 (iodometric determination with a solution of the peroxide in acetic acid and saturated aqueous potassium iodide). Calc. for $C_{12}H_{22}O_5$: C, 58·5; H, 9·0; active O, 13·0%].

Reduction of 1-*hydroperoxy*cyclo*hexyl* 1-*hydroxy*cyclo*hexyl peroxide with ferrous sulphate.* The peroxide (12 g.) was shaken with ferrous sulphate (60 g.) in water (500 ml.). The mixture became warm and dark brown ferric salts of the carboxylic acids separated. Shaking with acid gave an organic layer (8 g.) consisting of *cyclo*hexanone, hexanoic acid, and dodecane-1 : 12-dioic acid (m. p. 125°; diamide m. p. 186°).

Infra-red measurements were made with a Grubb Parsons single-beam spectrometer with a sodium chloride prism.

*cyclo*Hexanone in solution was determined from the intensity of the carbonyl stretching absorption at 1718 cm.$^{-1}$, at which frequency the other components did not interfere. To

check on the possible effect of hydrogen bonding from (II) and (III) a carbon tetrachloride solution, 0·04M. with respect to both *cyclo*hexanone and methyl alcohol, was examined. No anomalous absorption was observed, from which it was concluded that 1718 cm.$^{-1}$ was a satisfactory analytical frequency for the range of concentrations used. No attempt was made to increase the accuracy beyond about 2%.

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CHEMICAL RESEARCH DIVISION,
RESEARCH CENTRE, FORT DUNLOP. [*Received, October 6th*, 1951.]

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210. *Action of Acrylonitrile on Ethyl Aminomalonate and Ethyl Aminoacetate.*

By WESLEY COCKER, B. E. CROSS, and (MISS) JOAN MCCORMICK.

DURING another investigation, acrylonitrile was treated with ethyl aminomalonate. When potassium hydroxide was used as catalyst, the product isolated in fair yield (47%) was ethyl (2-cyanoethyl)aminomalonate (I). Its isomer (II) was not isolated from other unidentifiable products. That the product was substantially (I) follows from the fact that it gave a pure *p*-toluenesulphonyl derivative after one crystallisation, and on hydrolysis yielded glutamic acid which was substantially pure without crystallisation.

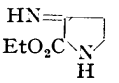
(I) $H_2N{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$ $(EtO_2C)_2{\cdot}CH{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CN$ (II)

Glycine ester condensed with acrylonitrile in presence of potassium hydroxide or sodium ethoxide, the latter giving the larger yields of the product, ethyl N-2-cyanoethylaminoacetate (III; R = H). Its structure was determined by hydrolysis to β-(carboxymethylamino)propionic acid (IV) which was also obtained by the hydrolysis of its ester (V), prepared from ethyl aminoacetate and methyl β-chloropropionate. Although cyclisation

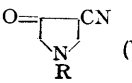
$EtO_2C{\cdot}CH_2{\cdot}NR{\cdot}CH_2{\cdot}CH_2{\cdot}CN$ (III)

$HO_2C{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ (IV)

$EtO_2C{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me$ (V)



(VI)



(VII)

of (III; R = H) could yield either the substituted proline (VI), or 3-cyano-4-pyrrolidone (VII; R = H), the latter was expected since Cook and Reed (*J.*, 1945, 399) have shown that (III; R = Me) cyclises to give (VII; R = Me). That our product was (VII; R = H) is supported by the analytical results.

Experimental.—Ethyl (2-cyanoethyl)aminomalonate. A mixture of aminomalonic ester (2·8 c.c.), potassium hydroxide (0·7 g.), and benzene (5 c.c.) was slowly treated with acrylonitrile (1·14 c.c.). The yellow solution was stirred at room temperature for 4 hours and then refluxed for 1·25 hours. The *product* consisted of an oil (1·86 g.), b. p. 150—154°/18 mm. (Found: C, 52·6; H, 7·1. $C_{10}H_{16}O_4N_2$ requires C, 52·6; H, 7·0%). Its p-*toluenesulphonyl* derivative, once crystallised from alcohol, formed prisms, m. p. 153° unchanged by further crystallisation (Found: C, 54·0; H, 5·8. $C_{17}H_{22}O_6N_2S$ requires C, 53·4; H, 5·8%).

Hydrolysis. The above ester (I) (1·5 g.) was refluxed with 60% sulphuric acid (4 c.c.) for 4 hours. The product was isolated through its lead salt (cf. Cocker and Lapworth, *J.*, 1931, 1391), giving a solution, which on concentration deposited glutamic acid (0·11 g.), m. p. 192—194° (the literature gives figures varying from 190—200°). Its *p*-toluenesulphonyl derivative was obtained with m. p. 169—170° (undepressed by an authentic specimen) without purification.

Ethyl β-(cyanoethylamino)acetate (III; R = H) was obtained as an oil (2·94 g.), b. p. 150—152°/19 mm. (Found: C, 54·2; H, 8·2. $C_7H_{12}O_2N_2$ requires C, 53·8; H, 7·7%), from glycine ester (5 g.), acrylonitrile (3·2 c.c.), benzene (10 c.c.), and sodium ethoxide (sodium, 0·1 g., in

alcohol, 7 c.c.). Its p-*toluenesulphonyl* derivative crystallised from dilute alcohol as prisms, m. p. 71° (Found : C, 54·6; H, 5·7. $C_{14}H_{18}O_4N_2S$ requires C, 54·2; H, 5·8%).

β-(*Carboxymethylamino*)*propionic Acid.* The preceding compound (1·62 g.) was refluxed with concentrated hydrochloric acid (6 c.c.) for 6 hours, yielding the required acid (0·12 g.), m. p. 185—186°, undepressed by a specimen prepared as below.

Methyl β-(*carbethoxymethylamino*)*propionate.* Ethyl aminoacetate (8·4 g.) was allowed to react with methyl β-chloropropionate (10 g.) for 3 days at room temperature, and then warmed on the water-bath for 2·5 hours. Sodium hydroxide solution (11·5 c.c.; 33%), water (14 c.c.), and ether (17·5 c.c.) were added, and the mixture was cooled to −10°. Anhydrous potassium carbonate was added until a thick paste was obtained; the ether was separated, dried and distilled, giving the required *ester* (5·0 g.), b. p. 153—154°/20 mm. (Found : C, 51·4; H, 8·1. $C_8H_{15}O_4N$ requires C, 50·8; H, 7·9%).

Hydrolysis. The ester (5 g.) was refluxed with concentrated hydrochloric acid (15 c.c.) for 1·5 hours, and the product was isolated through its lead salt (cf. Cocker and Lapworth, *loc. cit.*). The *amino-acid* was rubbed with alcohol, and crystallised from dilute alcohol as needles (1 g.), m. p. 184—186° (Found : C, 38·7; H, 6·9. $C_5H_9O_4N,\frac{1}{2}H_2O$ requires C, 38·5; H, 6·4%). Its p-*toluenesulphonyl* derivative gave m. p. 163°, undepressed when the sample was mixed with one prepared by the above alternative method (Found : C, 47·8; H, 5·1. $C_{12}H_{15}O_6NS$ requires C, 47·9; H, 5·0%).

3-*Cyano*-4-*pyrrolidone.* Powdered sodium (0·78 g.) was dissolved in a mixture of benzene (10 c.c.) and alcohol (2 c.c.). On cooling, the ester cyanide (III; R = H) (5·3 g.) was slowly added. The mixture was refluxed for 1 hour, cooled, and poured on ice. The calculated quantity (33·9 c.c.) of N-hydrochloric acid was added, and the aqueous layer was separated and evaporated to dryness in a vacuum-desiccator. The residue was extracted with alcohol and the solution passed through a column of alumina. The solution, on concentration, deposited 3-*cyano*-4-*pyrrolidone* (0·5 g.), m. p. 165—166° (Found : C, 54·7; H, 5·5. $C_5H_6ON_2$ requires C, 54·5; H, 5·4%).

The authors thank Imperial Chemical Industries Limited, Dyestuffs Division, for a gift of acrylonitrile.

TRINITY COLLEGE, DUBLIN. [*Received, October 27th,* 1951.]

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211. *Certain 2-Pyrrolidinoethyl Ketones.*

By S. W. PELLETIER and ALDEN D. JOSEY.

IN connection with the synthesis of a series of 3-aminopropyl benzoates for study as local anæsthetics, it became necessary to prepare some representative 2-pyrrolidinoethyl ketones as intermediates. Since the use of pyrrolidine in the Mannich reaction has been little studied, we investigated the reaction between pyrrolidine and several ketones known to give good yields of the corresponding piperidino-derivatives. Though the study has been interrupted, it seemed useful to record the satisfactory synthesis of two pyrrolidinoalkyl ketones by the Mannich reaction. β-Pyrrolidinopropiophenone hydrochloride was obtained in 40% yield from pyrrolidine hydrochloride, formaldehyde, and acetophenone; and 2-β-pyrrolidinopropionylthiophen hydrochloride was obtained in 74% yield from 2-acetylthiophen. Attempts to prepare solid pyrrolidino-derivatives of *cyclo*pentanone and 1- and 2-acetylnaphthalene by a similar procedure were unsuccessful.

Experimental.—M. p.s are corrected. Analyses are by E. Davis and K. Pih.

Pyrrolidine hydrochloride. Two brief references describe this compound as a very hydroscopic material which does not lend itself to analysis (Ladenburg, *Ber.*, 1887, **20**, 443; Petersen, *ibid.*, 1888, **21**, 291). Its preparation has not been described. When an ethereal solution of pyrrolidine was saturated with " anhydrous " hydrogen chloride, an oily slush resulted which gave little or no yield of product when used in the Mannich reaction. By working at low temperatures and using only the stoicheiometric amount of thoroughly dried hydrogen chloride, a crystalline product was obtained which gave good yields of product in the Mannich condensation. The following represents a superior method of preparation.

Hydrogen chloride, dried over sulphuric acid, was bubbled slowly into a solution of freshly distilled pyrrolidine (20·0 g., 0·28 mole; dried over potassium hydroxide) in absolute ether (200 ml.), cooled in solid carbon dioxide–acetone, until precipitation was just complete. The ether was decanted and the product (29·4 g., 98%) stored *in vacuo* over phosphoric oxide.

β-*Pyrrolidinopropiophenone hydrochloride.* A mixture of acetophenone (38·6 g., 0·30 mole), paraformaldehyde (10·0 g., 0·33 mole), and pyrrolidine hydrochloride (26·7 g., 0·25 mole) in absolute ethanol (50 ml.) was boiled under reflux for 3 hours, and then kept overnight in the refrigerator. 28·6 g. (41%) of a hygroscopic product were obtained, of m. p. 105°. Drying at 100° furnished material melting at 162—164°. Crystallization from ethanol–acetone (1 : 9) gave the *hydrochloride* as fine, white crystals melting at 163—164° (Found : C, 65·3; H, 7·6; N, 5·9. $C_{13}H_{17}ON,HCl$ requires C, 65·1; H, 7·6; N, 5·8%).

2-β-*Pyrrolidinopropionylthiophen hydrochloride.* Freshly distilled 2-acetylthiophen (20·0 g., 0·16 mole), paraformaldehyde (10·0 g.) and pyrrolidine hydrochloride (29·8 g.) in absolute ethanol were treated as described above, except that after one hour's heating paraformaldehyde (2·0 g.) was added to the reaction mixture. A similar addition was made after the third hour of heating. After being heated for a further 30 minutes, the mixture was kept in the refrigerator for 6 hours. The yield of *hydrochloride* melting at 95—110° was 28·8 g. (74%). Crystallization from ethanol–acetone (75% recovery) furnished white needles melting at 168·6—169·2° (Found : C, 54·3; H, 6·8; N, 5·9. $C_{11}H_{15}ON,HCl$ requires C, 53·75; H, 6·6; N, 5·7%).

NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS.

[*Received, November 2nd,* 1951.]

212. *Some New Amine Arylsulphonates.*

By L. BAUER, J. N. BAXTER, J. CYMERMAN, and W. J. SHELDON.

A NUMBER of new amine arylsulphonates and hydrochlorides, prepared in the course of other work, are described in the table below.

Reduction of 2-nitrodibenzofuran with zinc and calcium chloride, and of *p*-nitrodiphenylsulphone with stannous chloride and hydrochloric acid afforded, apart from the expected primary amines, the corresponding azoxy-compounds in 15% and 8% yield, respectively. Although formation of azoxy-compounds from nitro-compounds is generally regarded as occurring only in alkaline media, reduction of, *e.g.*, *o*-nitrobenzamide to the

Salt	M. p.	Solvent [1]	Formula	Found : N, %	Reqd. : N, %
p-*Aminoazobenzene toluene*-p-*sulphonate* [2]	187—189° *	P	$C_{19}H_{19}O_3N_3S$	11·4	11·3
p-Aminoazobenzene hydrochloride [3]	>360	E	$C_{12}H_{12}N_3Cl$	18·3	18·0
p-*Aminodiphenylammonium toluene*-p-*sulphonate*	207—208	P	$C_{19}H_{20}O_3N_2S$	7·6	7·85
p-*Aminodiphenylammonium chloride* [4] ...	240—241	M	$C_{12}H_{13}N_2Cl$	12·95	12·7
p-*Aminodiphenyl sulphide toluene*-p-*sulphonate*	183·5—184·5	P	$C_{19}H_{19}O_3NS_2$	3·65	3·75
p-*Aminodiphenyl sulphide hydrochloride*	197—198 *	M	$C_{12}H_{12}NSCl$	6·05	6·05
p-*Aminodiphenylsulphone toluene*-p-*sulphonate*	215	P	$C_{19}H_{19}O_5NS_2$	3·5	3·45
2-*Aminofluorene toluene*-p-*sulphonate* ...	271 *	P	$C_{20}H_{19}O_3NS$	4·45	4·0
p-*Phenoxyanilinium toluene*-p-*sulphonate*	180	W	$C_{19}H_{19}O_4NS$	4·1	3·9
p-cyclo*Hexylanilinium toluene*-p-*sulphonate*	273—274 *	W	$C_{19}H_{25}O_3NS$	4·3	4·0
2-*Aminodibenzofuran toluene*-p-*sulphonate*	255—256 *	W	$C_{19}H_{17}O_4NS$	3·9	3·9
p-*Aminodiphenylmethane toluene*-p-*sulphonate*	210—212	W	$C_{20}H_{21}O_3NS$	4·1	3·9
5-*Aminoacridinium toluene*-p-*sulphonate* [5]	261—262	M	$C_{20}H_{18}O_3N_2S$	7·8	7·6
2-*Aminothiazole benzenesulphonate*	135	A	$C_9H_{10}O_3N_2S_2$	10·4	10·85
2-*Aminopyrimidinium benzenesulphonate*	156	P	$C_{10}H_{11}O_3N_3S$	†	†
4 : 4′-*Diaminodiphenylsulphone dihydrochloride*	244—246 *	E	$C_{12}H_{14}O_2N_2SCl_2$	8·95	8·75

* M. p. with decomposition.
† Found : C, 47·6; H, 4·4; S, 12·7. Required : C, 47·4; H, 4·4; S, 12·65%.
[1] A = acetone; M = methanol; E = ethanol; P = *iso*propanol; W = water. [2] Red.
[3] Violet. Morgan and Micklethwait (*J.*, 1907, **95**, 1513) do not record a m. p. [4] Blue-grey. [5] Yellow.

azoxy-compound in 10—15% yield by means of zinc dust and acetic acid is recorded by Heller (*Ber.*, 1910, **43**, 1913), and a number of aromatic nitro-compounds containing electron-attracting substituents are known to give azoxy-compounds with stannous chloride and hydrochloric acid (Flürscheim, *J. pr. Chem.*, 1905, **71**, 497), and zinc dust and sulphuric acid (Reissert and Grube, *Ber.*, 1909, **42**, 3711).

Experimental.—The arylsulphonates and hydrochlorides were prepared by standard methods; they crystallised in white needles unless otherwise indicated (table).

2 : 2′-*Azoxydibenzofuran.*—Reduction of 2-nitrodibenzofuran (30 g.) in aqueous alcohol (1000 c.c.; 80%) was effected by refluxing the solution with zinc (300 g.) and calcium chloride (10 g.) for 2 hours. The hot solution was filtered into water (2000 c.c.), and the yellow precipitate dried and extracted with acetone (150 c.c.) and ether (500 c.c.), giving 2-aminodibenzofuran in 65% yield. The residue (insoluble in acetone and ether) crystallised from benzene in orange needles, m. p. 271°, of 2 : 2′-*azoxydibenzofuran* (Found: C, 75·9; H, 3·8; N, 7·5. $C_{24}H_{14}O_3N_2$ requires C, 76·2; H, 3·7; N, 7·4%) in 15% yield.

pp′-*Diphenylsulphonylazoxybenzene.*—Reduction of *p*-nitrodiphenylsulphone (13·1 g.) in alcohol (130 c.c., 95%) by stannous chloride (37 g.) and hydrochloric acid (43 c.c., 10N) for 10 hours under reflux gave, on cooling, an orange solid (0·9 g., 8%) crystallising from methanol in orange needles, m. p. 262—263°, of the *azoxy*-compound (Found: C, 60·3; H, 3·9; N, 5·95. $C_{24}H_{18}O_5N_2S_2$ requires C, 60·25; H, 3·75; N, 5·85%).

This work was carried out under the auspices of the National Health and Medical Research Council, to whom we are indebted for financial assistance.

ORGANIC CHEMISTRY DEPARTMENT, UNIVERSITY OF SYDNEY. [*Received, November 19th*, 1951.]

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213. *A Correction to "Magnetochemistry of the Heaviest Elements. Part V. Uranium Tetrafluoride–Thorium Tetrafluoride Solid Solutions."*

By J. K. DAWSON.

OWING to arithmetical error the concentrations of the uranium in the solid solutions reported earlier (*J.*, 1951, 2889) were erroneous. Consequently, the susceptibilities and magnetic moments of the uranium ion derived from the gram-susceptibilities are considerably altered as shown in the following revised tables:

TABLE II.

Concentration, %	*T*, °K	$10^6\chi_g$.	$10^6\chi_m$.	$10^6\chi_{U(IV)}$	Composition, %	*T*, °K	$10^6\chi_g$.	$10\chi_m$.	$10^6\chi_{U(IV)}$
U, 100	90	22·39	7030	7091	U, 39·7	90	10·26	3186	8178
	197	14·61	4588	4649	Th, 60·3	199	5·94	1842	4791
	300	10·67	3530	3411		300	4·24	1317	3469
	332	9·92	3117	3176		328	3·76	1168	3094
U, 94·9	90	22·27	6988	7483	U, 20·6	90	5·66	1751	8807
Th, 5·1	200	13·41	4208	4555	Th, 79·4 ...	200	2·822	872·8	4535
	301	10·01	3141	3431		303	1·837	568·2	3054
	334	9·21	2889	3164		355	1·579	488·4	2667
U, 86·2	90	20·60	6453	7606	U, 10·4	90	2·903	896·3	9171
Th, 13·8 ...	199	12·60	3947	4701	Th, 89·6 ...	199	1·437	443·6	4831
	295	9·22	2888	3471		300	0·936	289·0	3347
	328	8·47	2653	3199		330·5	0·814	251·3	2986
U, 67·6	90	16·92	5301	7908					
Th, 32·4 ...	200	10·11	3155	4761					
	298	7·38	2303	3500					
	334	6·62	2066	3149					

TABLE III.

U, %	100	94·9	86·2	67·6	39·7	20·6	10·4
Δ	102	102	78	68	56	22	25
μ	3·30	3·30	3·20	3·17	3·11	2·82	2·92

Within experimental error, both the susceptibility at room temperature and the moment extrapolated to infinite dilution agree with the values predicted for two unpaired spins with the orbital contribution to the moment completely quenched ($\chi = 3333 \times 10^{-6}$, $\mu = 2{\cdot}83$). This result is very similar to that obtained in the urania–thoria solid solutions and is taken to imply an electron configuration of $6d^2$ for the uranous ion, since $5f$ electrons would be expected to exert some orbital contribution owing to the screening effect of the $6s$ and the $6p$ electrons.

ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, NEAR DIDCOT, BERKS.

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214. *ω-Halogenomethyl-pyridines, -quinolines, and -isoquinolines. Part III.* The Reduction of ωωω-Tribromoquinaldine by Alcohol in the Presence of Sulphuric Acid.*

By A. ASTELL-BURT and D. LL. HAMMICK.

ωωω-TRIBROMOQUINALDINE can readily be reduced by conventional reagents (stannous bromide, etc.); it can also be converted smoothly into ωω-dibromoquinaldine and with rather more difficulty into ω-monobromoquinaldine by means of tetralin or other hydrocarbons, in processes which probably involve free radicals (Brown and Hammick, *J.*, 1950, 628: Brown, Grice, Hammick, and Thewlis, *J.*, 1951, 1149). Dirstine and Bergstrom (*J. Org. Chem.*, 1946, **11**, 55) reduced the tribromoquinaldine to the dibromo-compound by ethyl alcohol in the presence of excess of concentrated sulphuric acid; because of charring, they were unsuccessful with other alcohols. Sharp (*J. Pharm. Pharmacol.*, 1949, **1**, 395), apparently unaware of Dirstine and Bergstrom's work, has also effected 88% reduction to the dibromo-compound by ethyl alcohol and sulphuric acid.

In the strongly acid media used by the above workers homolytic reactions would appear to be unlikely and this view is confirmed by our experiments which show that in dilute alcoholic solutions of sulphuric acid the rate of reduction is proportional to the concentration of acid.

Experimental.—Our experience and that of other workers (see above) is that in both concentrated and dilute ethanolic solutions of sulphuric acid the reduction of ωωω-tribromoquinaldine is practically quantitative. It is not, however, possible to give more than a qualitative account of the oxidation products of the alcohol. The tribromo-compound boiled in alcohol in the absence of acid gives a small quantity of acetaldehyde (identified as its dinitrophenylhydrazone); in the presence of sulphuric acid a complex mixture of alcohol and brominated products is produced. These may result from the primary formation of acetaldehyde, which in fact reduces tribromoquinaldine very readily. About 20% of the bromine removed from the tribromo-compound can be recovered as ethyl bromide; bromoform can also be obtained by the action of alkali on the products of the oxidation of the alcohol. We have been less concerned with the fate of the bromine than with the effects of acidity on the rate of the reduction, and to this end we have followed the rate of reduction by ethyl alcohol at 100° alone and in the presence of increasing concentrations of sulphuric acid. Solutions (3 g. of tribromoquinaldine in 60 c.c. of ethyl alcohol) were sealed in glass tubes which were then heated for 1 hour in boiling water; the residual tribromoquinaldine was hydrolysed by refluxing the contents of the tubes with dilute aqueous sulphuric acid for several hours (dibromoquinaldine is untouched by such treatment). After partial neutralisation, quinaldinic acid was precipitated as the copper salt, which was washed, dried, and weighed. Control experiments showed that (i) hydrolysis of tribromoquinaldine to quinaldinic acid during the hour's heating at 100° was small (2%), and (ii) quinaldinic acid can be estimated to an accuracy of ±3% by the method adopted. The

* Part II, *J.*, 1951, 1149.

results are given in the following table, where the initial concentration of tribromoquinaldine is 0·132 mole/l.; and 60 c.c. of the solution were used in each experiment, equivalent to 0·153 mole

$[H^+]$, Mole/l.	0	0·025	0·050	0·20	0·250	0·50	1·00
X	1·334	1·315	1·290	1·200	1·148	1·036	0·832
$-\log_{10} X$	−0·1252	−0·1189	−0·1106	−0·0792	−0·0600	−0·0149	+0·0799

copper quinaldinate; X is the quantity in g. of copper quinaldinate obtained from tribromoquinaldine remaining after 1 hour. $T = 100°$.

It will be seen that even in the absence of acid, reduction is considerable. By denoting the concentration of tribromoquinaldine as [A], we can tentatively write, for a solution containing an excess of alcohol :

$$-\mathrm{d}[A]/\mathrm{d}t = k_1[A] + k_2[A][H^+]$$

Bearing in mind that any quantity of tribromoquinaldine is proportional to the weight, X, of copper quinaldinate into which it can be converted, we have, for unit time $\mathrm{d}t = 1$ hour, $-\log_{10} X = a + b[H^+]$. A satisfactory straight line can be drawn through the plot of $-\log X$ against $[H^+]$.

A few experiments have been carried out with other alcohols. As might be expected, *iso*-propyl alcohol reduces tribromoquinaldine much more rapidly than does ethyl alcohol; under the same conditions, methyl and *tert.*-butyl alcohols are practically unreactive.

DYSON PERRINS LABORATORY, UNIVERSITY OF OXFORD. [*Received, November 30th*, 1951.]

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215. *The Degradation of the Side Chain of Lanostadienol.*

By R. G. CURTIS and H. SILBERMAN.

A DESCRIPTION of work done in this laboratory on the degradation of the side chain of lanostadienol is made desirable by the appearance of a paper by Voser, Mijovic, Jeger, and Ruzicka (*Helv. Chim. Acta*, 1951, **34**, 1585) on this subject. As these authors have emphasized, one of the difficulties of this side-chain degradation has been the small yield of trisnorlanostenolic acid obtained when lanostadienol is ozonised. However, by modification of the conditions of ozonolysis it has now been found that a 30% yield of the acid can be obtained from the mixed wool-wax triterpenes; that is a 60% conversion of the lanostadienol content. It thus seemed possible to degrade the side chain without oxidation of the four-ring system in the neighbourhood of the " inactive " double bond; the method of approach thus differed from that described by Voser *et al.* One cycle of a Wieland degradation has been completed, giving the acid, $C_{26}H_{42}O_3$, lacking four of the side-chain carbon atoms of lanostadienol.

Attempts were also made to degrade the chain by bromination, and the monobromolanostadienol (I) was obtained in good yield. The bromine atom is extremely inert; that it

$$(C_{25}H_{41}O)\text{—}CH_2\cdot CBr{:}CMe_2 \quad (I)$$

is located as formulated, follows from the conversion of (I) by ozonolysis into trisnorlanostenolic acid and from the ready reduction of (I) to lanostenol.

Experimental.—Trisnorlanostenolic acid. Wool-wax triterpenes (10 g.) in chloroform (200 ml.) were ozonised (10 minutes; 6 l. of oxygen containing 5% of ozone) at 0°. Water (100 ml.) was added to the solution, and the chloroform then removed by distillation. The ozonide was decomposed by refluxing it for 12 hours with 1·0N-ethanolic sodium hydroxide (200 ml.) and hydrogen peroxide (10 ml.), the solvents were distilled under reduced pressure, and the last traces of water were removed azeotropically with benzene. The residual, dried sodium salt was washed with ether in an extractor and dissolved in aqueous ethanol, and the solution acidified with mineral acid. The crude acid was washed with a little chloroform–methanol (1 : 1) and crystallised from ethyl acetate, forming fine needles (3·2 g.), m. p. 260—261°.

Methyl trisnorlanostenolate. A solution of diazomethane in ether at 0° was added to one of the acid (5 g.) in acetone (120 ml.) and chloroform (120 ml.). After the excess of diazomethane

had been distilled into acetic acid, the solvents were removed until the methyl ester began to crystallise; it (4·6 g.) formed needles, m. p. 155°, $[\alpha]_D^{21}$ +58·4° (*c*, 3·0 in chloroform).

27 : 27-*Diphenyltrisnorlanosten*-2 : 27-*diol*.* Phenylmagnesium bromide, prepared from magnesium (4 g.), bromobenzene (17 ml.), and ether (250 ml.), was added slowly to methyl trisnorlanostenolate (4·6 g.) dissolved in anisole (250 ml.); the ether was then distilled off and the anisole solution heated at 100° for 5 hours. After the mixture had cooled to 0° and had been decomposed with ice-cold dilute sulphuric acid, the anisole layer was separated and washed with water until neutral. The anisole and diphenyl were removed by steam-distillation and the residue was filtered off and refluxed in 1·0N-ethanolic sodium hydroxide solution (400 ml.) for 4 hours. Water (400 ml.) was added and the neutral material was extracted into benzene and crystallised from methanol. The *diol* formed needles (3·7 g.), m. p. 172°, which solidified again at 174° and finally re-melted at 197—198°, $[\alpha]_D^{20}$ +52·3° (*c*, 1·5 in chloroform) (Found: C, 84·7; H, 9·5. $C_{33}H_{54}O_2$ requires C, 84·9; H, 9·5%).

27-*Hydroxy*-27 : 27-*diphenyltrisnorlanosten*-2-*yl acetate*. The 2 : 27-diol (3·7 g.), pyridine (20 ml.), and acetic anhydride (20 ml.) were heated for 2 hours on a steam-bath and finally refluxed (30 minutes). The solution was poured into cold water, and the precipitated *acetate* crystallised from acetic acid. It formed needles (3·8 g.), m. p. 220—221°, $[\alpha]_D^{20}$ +59·3° (*c*, 3·0 in chloroform) (Found: C, 82·6; H, 9·0. $C_{41}H_{56}O_3$ requires C, 82·5; H, 9·0%).

Dehydration of 27-*hydroxy*-27 : 27-*diphenyltrisnorlanosten*-2-*yl acetate*. The alcohol (5 g.), glacial acetic acid (300 ml.), and acetic anhydride (20 ml.) were refluxed for 24 hours; on cooling 27 : 27-*diphenyltrisnorlanosta*-9 : 26-*dien*-2-*yl acetate* separated. It formed glistening plates (4·8 g.), m. p. 207—208°, $[\alpha]_D^{20}$ +65° (*c*, 1·5 in chloroform) (Found: C, 84·9; H, 9·1. $C_{41}H_{54}O_2$ requires C, 85·1; H, 9·4%).

The C_{26} *acid*. The diphenylethylene compound (2 g.), m. p. 207—208°, was ozonised as described for the preparation of trisnorlanostenolic acid. The *tetrakisnorlanostenolic acid* crystallised from chloroform–methanol (2 : 1) in needles (0·2 g.); these contained methanol of crystallisation which was evolved on melting; m. p. 258—259°, $[\alpha]_D^{20}$ +36° (*c*, 1·0 in chloroform) (Found, on a sample dried in a vacuum at 140° for 8 hours: C, 77·6; H, 10·2. $C_{26}H_{42}O_3$ requires C, 77·6; H, 10·5%). The *methyl* ester had m. p. 156—157° (Found: C, 77·5; H, 10·5. $C_{27}H_{44}O_3$ requires C, 77·8; H, 10·7%).

27-*Bromolanostadienol*. A solution of bromine (2·3 ml.) in glacial acetic acid (140 ml.) was added at 0° to wool-wax triterpenes (25 g.) in ether (500 ml.). After 24 hours the excess of bromine was destroyed by the addition of sodium hydrogen sulphite solution, and the ether removed. The crystalline material was filtered off, washed with water and then with methanol, and refluxed for 4 hours in 1·0N-ethanolic alkali (700 ml.). On cooling, fine needles (18 g.), m. p. 172—175°, separated. These were washed with methanol and recrystallised first from ethanol, then from *iso*propanol, and finally several times from chloroform–methanol (1 : 1), giving the pure 27-*bromolanostadienol* (9 g.), m. p. 196—198°, $[\alpha]_D^{20}$ +51·4° (*c*, 3·0 in chloroform) (Found: C, 70·8; H, 9·6. $C_{30}H_{49}OBr$ requires C, 71·2; H, 9·8%).

Ozonolysis of 27-bromolanostadienol (1 g.) by the method used for the preparation of trisnorlanostenolic acid from wool-wax triterpenes yielded this acid (0·5 g.), m. p. 260—261°, and bromine.

Reduction of 27-bromolanostadienol (0·5 g.) in ethanol (100 ml.) at 100° with Raney nickel catalyst yielded lanostenol, which crystallised from methanol (15 ml.) and benzene (3 ml.). It formed needles (0·3 g.), m. p. 146—147°, $[\alpha]_D^{20}$ +58° (*c*, 3·0 in chloroform).

This work was carried out as part of the research programme of this Division.

Division of Industrial Chemistry,
C.S.I.R.O., Box 4431, G.P.O., Melbourne. [*Received, December 11th*, 1951.]

* The side chain is here numbered outwards from its point of attachment to the nucleus, so that the terminal carbon atoms are numbered 29 and 30. This avoids assumption of the position at which it is attached to the nucleus and also of more of the nature of the side chain than has been rigidly proved.

216. *A Linear Acetal of Ethylene Glycol.*

By J. D. Bryan.

Certain batches of commercial ethylene glycol were thought to contain traces of 1 : 1-bis-2′-hydroxyethoxyethane (II), the linear acetal of the glycol. The note describes the synthesis of this compound, no mention of which could be found in the literature.

The corresponding acetate (I) was obtained in 18% yield by the reaction of acetylene with ethylene glycol monoacetate under anhydrous conditions in the presence of mercuric

(I) $CH_3{\cdot}CH(O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_3)_2$ $CH_3{\cdot}CH(O{\cdot}CH_2{\cdot}CH_2{\cdot}OH)_2$ (II)

oxide and methanolic boron trifluoride (Neiuwland, Vogt, and Foohey, *J. Amer. Chem. Soc.*, 1930, **52**, 1018; Coffman, U.S.P. 2 387 495). Treatment of this compound with excess of methanol containing sodium methoxide as a catalyst gave the required acetal (II).

Experimental.—The microanalysis is by Drs. Weiler and Strauss, Oxford.

1 : 1-*Bis*-2′-*acetoxyethoxyethane* (I). Red mercuric oxide (1 g.) was partly dissolved in a 55—65% solution of boron trifluoride in methanol (5 g.) by gentle heat. Ethylene glycol monoacetate (160 g.) was then added and dry acetylene passed over the stirred mixture at 25—30° until the calculated quantity (20 g.) had been absorbed. The mixture was cooled to 10° and stirred for 10 minutes with anhydrous sodium carbonate (10 g.). Saturated aqueous sodium carbonate (25 ml.) was then added and the mixture extracted with ether. The residue, obtained on removal of the ether from the dried (K_2CO_3) extract, was fractionated under reduced pressure; the second fraction, b. p. 108°/0·8 mm., immiscible with water, was 1 : 1-bis-2′-acetoxyethoxyethane. The saponification value of the product indicated a purity of 98·6%.

1 : 1-*Bis*-2′-*hydroxyethoxyethane* (II). The acetate (I) (30 g.) was refluxed with absolute methanol (100 ml.) and 0·1N-sodium methoxide solution (12 ml.) for 6 hours. The residue obtained on removal of methyl acetate and methanol was distilled under reduced pressure to give 1 : 1-*bis*-2′-*hydroxyethoxyethane* (15 g.), b. p. 100°/0·5 mm., n_D^{25} 1·4467, d_4^{25} 1·1088 (Found : C, 48·3; H, 9·3. $C_6H_{14}O_4$ requires C, 48·0; H, 9·4%). The product was hygroscopic.

Hydrolysis of 1 : 1-*bis*-2′-*hydroxyethoxyethane*. The acetal (4 g.) was shaken with cold 1·0N-sulphuric acid (50 ml.) in a stoppered flask for 15 minutes. After neutralisation with sodium hydroxide solution, treatment of the solution with dimedone gave the derivative of acetaldehyde, m. p. 141°; benzoylation gave ethylene glycol dibenzoate, m. p. 73°.

British Cellophane, Ltd., Bridgwater, Somerset. [*Received, November* 10*th*, 1951.]