LX.—*The Partial Esterification of Polyhydric Alcohols. Part XI. The Five Methyl Ethers of Glycerol and Related Compounds.*

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THE α- and β-mono-, αβ- and αγ-di-, and αβγ-tri-methyl ethers of glycerol have been separated by fractional distillation of the product from the reaction of sodium glyceroxide and methyl sulphate in glycerol. It is believed that this is the first occasion on which an indubitable αβ-dimethyl ether of glycerol has been obtained.

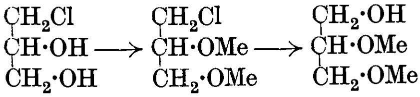
If the one secondary and both primary hydroxylic radicals in the glycerol molecule were methylated with equal facility, two parts of the α-monomethyl ether should be produced together with one of the β-isomeride, but, on further methylation, these proportions should be reversed, with the production of only one part of the αγ-isomeride and two of the αβ.

$$\begin{tikzcd}
 & \text{2 Mols. } \alpha\text{-monomethyl ether} \arrow[r] \arrow[dr] & \text{1 Mol. } \alpha\gamma\text{-dimethyl ether} \\
\text{3 Mols. glycerol} \arrow[ur] \arrow[dr] & & \text{1 Mol. } \alpha\beta\text{-} \quad \text{,,} \quad \text{,,} \\
 & \text{1 Mol. } \beta\text{-monomethyl ether} \arrow[r] & \text{1 Mol. } \alpha\beta\text{-} \quad \text{,,} \quad \text{,,}
\end{tikzcd}$$

Yields actually obtained show that the ratio of α- to β-isomeride was roughly 85 : 15 instead of 2 : 1 after the production of monomethyl ethers, and roughly 60 : 40 instead of 1 : 2 after that of the dimethyl ethers, thus indicating that the α-hydroxyls were methylated at about three times the speed of the β-hydroxyls in each case.

Glycerol β-monomethyl ether, separately methylated, yielded the αβ-*dimethyl* ether *only*, the structures of all these compounds thus being proved without recourse to conversions from and into derivatives of allyl alcohol (compare Irvine, Macdonald, and Soutar, J., 1915, **107**, 337).

Additional evidence on the identification of the dimethyl ethers has resulted from the independent synthesis of the previously unknown αβ-ether by a method mentioned in Part IX (J., 1929, 2232; *Ann. Reports*, 1929, **26**, 79), consisting in the methylation of α-monochlorohydrin and subsequent hydrolysis :



$$\begin{array}{l} CH_2Cl \\ CH\cdot OH \\ CH_2\cdot OH \end{array} \longrightarrow \begin{array}{l} CH_2Cl \\ CH\cdot OMe \\ CH_2\cdot OMe \end{array} \longrightarrow \begin{array}{l} CH_2\cdot OH \\ CH\cdot OMe \\ CH_2\cdot OMe \end{array}$$

Migratory changes of the kind frequently observed in syntheses involving chlorohydrins (see Part VII; J., 1929, 129) have here been avoided, for, in addition to the reasons recorded in Part IX for believing that hydrolyses of this particular type are immune from such complications, the product is isomeric, and not identical, with the glycerol dimethyl ether described in Part VIII (*ibid.*, p. 1151), although the *p*-nitrobenzoates of both ethers melt at the same temperature. It is also identical with the dimethyl ether obtained by the methylation of the β-monomethyl ether mentioned above. This new ether, therefore, must have the αβ-structure, and the "αγ"-dimethyl ether of Zunino (*Atti R. Accad. Lincei*, 1897, **6**, 348), called the "αβ"-dimethyl ether by Gilchrist and Purves (J., 1925, **127**, 2735), must have the αγ-structure.

The five standards of reference proposed by Irvine, Macdonald, and Soutar, and recently again urged as very desirable by Hibbert, Whelen, and Carter (*J. Amer. Chem. Soc.*, 1929, **51**, 302), are thus rendered available for the first time.

	Boiling point.	$d_{4^\circ}^{25^\circ}$.	$n_D^{25^\circ}$.	M. p. of *p*-nitro benzoate.	
Glycerol α-monomethyl ether	136°/40 mm. 220/760 mm.	1·111	1·442	108°	
Glycerol β-monomethyl ether	148/40 mm. 232/760 mm.	1·124	1·446	155	
Glycerol αβ-dimethyl ether ...	100/40 mm. 180/760 mm.	1·016	1·421	44	fuse when mixed at 26°
Glycerol αγ-dimethyl ether ...	88/40 mm. 169/760 mm.	1·004	1·417	43	
Glycerol trimethyl ether	148/760 mm.	0·937	1·401	—	

A conclusive diagnosis of the structure of any specimen of a methyl ether of glycerol can now easily be made; in the case of an unidentified dimethyl ether, for example, it is merely necessary to test whether its *p*-nitrobenzoate depresses the melting point of the readily obtainable dimethoxy-*p*-nitrobenzoyloxypropane previously described (Part VIII), and now proved to have the αγ-dimethoxy-constitution.

The fully methylated chlorohydrins have incidentally been isolated; their properties afford only slight evidence of the differences between the isomeric ethers of glycerol.

	B.p.	$d_{4^\circ}^{25^\circ}$.	$n_D^{25^\circ}$.
Monomethyl ether of αβ-dichlorohydrin	158°	1·19	1·44
Monomethyl ether of αγ-dichlorohydrin	160	1·21	1·45
Dimethyl ether of α-monochlorohydrin	156	1·08	1·43
Dimethyl ether of β-monochlorohydrin	154	1·06	1·42

Each has been hydrolysed to produce the particular ether expected, without migration of radicals (compare Part IX, *loc. cit.*; Hibbert and Whelen, *J. Amer. Chem. Soc.*, 1929, **51**, 1943).

The fully methylated ethers of the acetins have also been isolated and each has been successfully hydrolysed.

	B.p.	$d_{4^\circ}^{25^\circ}$.	$n_D^{25^\circ}$.
Monomethyl ether of $\alpha\beta$-diacetin	139—140°/40 mm. 228/760 mm.	1·097	1·422
Monomethyl ether of $\alpha\gamma$-diacetin	144—145/40 mm. 232/760 mm.	1·100	1·424
Dimethyl ether of α-monoacetin	108—109/40 mm. 195/760 mm.	1·027	1·414
Dimethyl ether of β-monoacetin	105—106/40 mm. 191/760 mm.	1·025	1·413

There would seem to be no doubt that the formation of an $\alpha\gamma$-diether from $\alpha\beta$-dibromohydrin (Part VII) is due to the intermediate production of a glycidic ring. It is in accordance with this view that the ethyl and *iso*propyl ethers of glycide have now been found to occur as separable materials during the reactions of $\alpha\gamma$-dichlorohydrin with the appropriate sodium alkyloxides.

The yields of glycerol dialkyl ethers in these reactions decrease with increasing molecular weight, and are higher from primary than from the corresponding secondary alcohols. There is evidence that these differences are largely due to the production of derivatives of diglycerol as by-products, at speeds which become relatively important under conditions which are adverse to the simple etherifications.

EXPERIMENTAL.

Glycerol β-*Monomethyl Ether*, $CH_2(OH)\cdot CH(OMe)\cdot CH_2\cdot OH$.—Contrary to the opinion originally held as a result of the experiments described in Parts I and III (J., 1921, **119**, 1035; 1925, **127**, 2759), it is clear from the simultaneous work of Gilchrist and Purves (*ibid.*, p. 2735) that the secondary alcoholic radical of glycerol is capable of etherification when monosodium glyceroxide is employed (compare Parts IX and X). Advantage has therefore now been taken of this possibility to isolate glycerol β-monomethyl ether as a by-product during the preparation of the α-monomethyl ether.

460 G. of 47% sodium hydroxide solution were added to 1,500 g. of glycerol, and water was removed at 40 mm. pressure by immersion in an oil-bath which was raised gradually to 150°; 338 g. of methyl sulphate were added during 1 hour at 120°, which temperature was maintained for a further hour, the product then being distilled up to 140°/2 mm. Repeated fractionations of this distillate (A) through a long column yielded two main fractions, the α-monomethyl ether (about 85% of the total monomethyl ethers produced), b. p. 135·5—136°/40 mm., 220°/760 mm. (Darke and Lewis, *J. Soc. Chem. Ind.*, 1928, **47**, 1073, give b. p. 196°), $d_{4^\circ}^{20^\circ}$ 1·114, $d_{4^\circ}^{25^\circ}$ 1·111, $n_D^{25^\circ}$ 1·442, and the β-monomethyl ether (about 15%), b. p. 147—148°/40 mm., 232°/760 mm., $d_{4^\circ}^{25^\circ}$ 1·124, $n_D^{25^\circ}$ 1·4456 (Found: OH, 31·8. Calc. for $C_4H_{10}O_3$: OH, 32·1%). The β-structure of the

latter is shown by the production of only one dimethyl ether on further methylation, as described below.

In this difficult separation, the main bulk was fractionated ten times from a large flask up to 140°, the residues being transferred at this point to a smaller apparatus, and distilled as represented by (*a*), (*b*), (*c*), etc., in which percentage weights distilled per degree are recorded; a maximum occurred near 148°/40 mm. in fractionation IV, and the quantity collected at this temperature steadily increased during the remaining distillations. Fractions below 135° and above 149°, and also those obtained below 140° in the smaller distillations, are not indicated in the following table.

Separation of Glycerol α- and β-Monomethyl Ethers.

Percentages distilled per degree.

Fractionation	III	IV			V			VI		
Temp. range at 40 mm.										
135—135·5°	—	—			—			—		
135—136	—	12·51			11·52			6·52		
135·5—136	—	—			—			—		
136—136·5	—	—			—			—		
136—137	17·59	19·38			24·50			34·50		
136·5—13	—	—			—			—		
137—138	26·19	20·65			20·54			15·17		
138—139	11·07	—			—			—		
138—140	—	4·32			5·89			2·88		
139—141	2·46	—			—			—		
		(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)
140—142	—	1·45	—	—	—	1·29	0·92	1·73	1·03	0·88
140—143	0·50	—	0·95	0·49	—	—	—	—	—	—
141—143	—	—	—	—	1·34	—	—	—	—	—
142—144	—	1·37	—	—	—	1·18	0·82	1·11	0·63	0·60
143—145	—	—	0·95	0·97	—	—	—	—	—	—
144—146	0·50	—	—	—	0·98	0·97	0·91	0·99	0·97	0·74
146—147	—	0·64	—	—	—	1·14	0·77	0·95	0·65	1·14
146—148	0·50	—	1·38	1·96	1·38	—	—	—	—	—
147—148	—	0·83	—	—	—	1·75	2·21	2·22	2·96	3·35
148—148·5	—	—	1·38	1·96	1·34	—	—	—	—	—
148—149	—	1·05	—	—	—	—	—	—	—	—

Percentages distilled per degree.

Fractionation	VII					VIII			IX	X				
Temp. range at 40 mm.														
135—135·5°	—					10·72			14·18	3·04				
135—136	5·94					—			—	—				
135·5—136	—					25·92			32·56	65·72 } *				
136—136·5	—					27·98			38·22	24·20 }				
136—137	34·29					—			—	—				
136·5—137	—					26·18			13·20	14·36				
137—138	14·70					8·66			6·17	1·25				
138—139	—					—			—	—				
138—140	3·00					3·44			1·24	0·65				
139—141	—					—			—	—				
	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*a*)	(*b*)	(*c*)		(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
140—142	1·92	1·26	0·90	1·66	0·45	0·73	—	0·50	—	0·83	0·73	0·82	0·59	0·59
140—143	—	—	—	—	—	—	—	—	—	—	—	—	—	—
141—143	—	—	—	—	—	—	—	—	—	—	—	—	—	—
142—144	0·86	0·39	0·81	1·05	0·65	0·85	0·72	0·58	—	0·74	0·57	0·45	0·39	0·40
143—146	—	—	—	—	—	—	—	—	—	—	—	—	—	—
144—146	0·96	1·05	0·73	1·39	0·42	0·51	0·56	0·53	—	0·55	0·54	0·58	0·52	0·44
146—147	1·41	0·87	0·65	1·04	0·74	0·40	0·66	0·37	—	1·10	0·62	0·89	0·58	0·54
146—148	—	—	—	—	—	—	—	—	—	—	—	—	—	—
147—148	3·35	3·37	4·53	4·49	5·34	5·35	6·05	6·61	—	6·66	7·10	7·50	7·65	7·85†
148—148·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—
148—149	—	—	—	—	—	—	—	—	—	—	—	—	—	—

* α-Methyl ether. † β-Methyl ether.

Both methyl radicals of the methyl sulphate were effective in the methylation, the yields of glycerol monomethyl and dimethyl ethers being 86% and 9% respectively.

The *p*-nitrobenzoates of this β-ether and of a specimen prepared from *αγ*-benzylideneglycerol β-methyl ether (Hibbert, Hill, Whelen, and Carter, *J. Amer. Chem. Soc.*, 1928, **50**, 2235; 1929, **51**, 302) melted, separately or mixed, at 154—155°.

Glycerol αβ-Dimethyl Ether, $CH_2(OMe)\cdot CH(OMe)\cdot CH_2\cdot OH$.—(i) This compound was isolated from the mixture of isomerides resulting from a further methylation of the crude monomethyl ethers (A) mentioned above (p. 447), the procedure differing from that already described in that distillation was carried up to 110°/10 mm. instead of 140°/2 mm. Repeated fractionations yielded glycerol *αγ*-dimethyl ether (about 60% of the total dimethyl ethers produced), b. p. 88—89°/40 mm., and the αβ-*dimethyl* ether (about 40%), b. p. 99—100°/40 mm., 180°/760 mm., $d^{25^\circ}_{4^\circ}$ 1·016, $d^{15^\circ}_{4^\circ}$ 1·028, $n^{25^\circ}_{\mathrm{D}}$ 1·421, $n^{15^\circ}_{\mathrm{D}}$ 1·4249 (Found for the latter: C, 49·8; H, 10·3; OH, 14·2. $C_5H_{12}O_3$ requires C, 50·0; H, 10·0; OH, 14·2%).

The course of their separation is shown in the following table: a minimum is noticeable in fractionation V, and continues to fractionation X, where it occurs at 92—94°/40 mm., the maxima being exhibited at 89—90°/40 mm. and 99—100°/40 mm.

Separation of Glycerol αβ- and αγ-Dimethyl Ethers.

	Percentage weight distilled per degree.								
Fractionation	II	III	IV	V	VI	VII	VIII	IX	X
Temp. range at 40 mm.									
88—89°	—	—	—	—	—	—	—	—	6·00*
89—90	—	—	—	—	—	—	—	5·79	6·79*
89—91	2·29	1·96	2·24	3·20	3·77	4·40	6·65	—	—
90—91	—	—	—	—	—	—	—	6·26	4·81
91—92	—	—	—	—	—	—	—	4·49	2·96
91—93	4·10	3·89	5·57	5·65	5·09	5·76	2·77	—	—
92—94	—	—	—	—	—	—	—	2·24	2·20
93—95	5·98	7·32	5·82	5·27	3·87	3·07	3·44	—	—
94—96	—	—	—	—	—	—	—	2·12	2·63
95—97	4·79	5·52	5·40	4·43	4·45	3·55	2·79	—	—
96—98	—	—	—	—	—	—	—	4·19	3·13
97—99	4·20	2·93	4·53	4·85	5·56	4·91	5·45	—	—
98—99	—	—	—	—	—	—	—	4·87	4·51
99—100	—	—	—	—	—	—	—	8·22	10·20†
99—101	—	1·73	2·09	3·17	3·45	4·11	4·48	—	—

* Glycerol *αγ*-dimethyl ether. † Glycerol *αβ*-dimethyl ether.

p-Nitrobenzoylation of the *αγ*-fraction yielded crystals melting, alone or mixed with *αγ*-di-*p*-nitrobenzoyloxy-β-methoxypropane (Part VIII), at 43°.

(ii) 46 G. of sodium were gradually dissolved in 424 g. of pure glycerol β-monomethyl ether at 120° with vigorous stirring; 126 g.

of methyl sulphate were added during 1 hour at the same temperature, which was maintained for a further hour. The product was distilled to dryness at 2 mm. from a bath at 150°, and the distillate fractionated as before. It consisted of a mixture of glycerol trimethyl ether with the αβ-dimethyl ether, none of the lower-boiling αγ-dimethyl isomeride being present. This result constitutes an independent proof of the structures of all four partly methylated glycerols, as explained in the theoretical portion.

(iii) α-Chloro-βγ-dimethoxypropane (see p. 452) was hydrolysed by boiling with *N*-sodium hydroxide for 15 hours; titration then indicated that more than half of the chlorine had reacted. The product was extracted with chloroform and converted into the *p*-nitrobenzoate; this melted at 41°, alone or mixed with γ-*p*-nitrobenzoyloxy-αβ-dimethoxypropane (see p. 454), but at about 24° in admixture with the αγ-dimethoxy-isomeride (see *Ann. Reports*, 1929, **26**, 79).

It would seem possible (compare Carter, *Ber.*, 1930, **63**, 1684) that Gilchrist and Purves (*loc. cit.*) may have obtained a specimen of this true αβ-dimethyl ether on hydrolysing their glycerol glucoside, but, if they did, they were clearly mistaken in stating that it had the properties of what they then believed to be the αβ-dimethyl ether and is now shown to be the αγ-isomeride.

Glycerol αγ-Dimethyl Ether, $CH_2(OMe)\cdot CH(OH)\cdot CH_2\cdot OMe$.—A comparative direct hydrolysis of a sample of β-chloro-αγ-dimethoxypropane (p. 452) yielded a small quantity of this ether, the constitution of which was proved by its conversion into β-*p*-nitrobenzoyloxy-αγ-dimethoxypropane (see Part VIII), identified by a mixed melting-point determination.

In confirmation of the opinion expressed in Part VIII that various processes for the production of glycerol dimethyl ethers produce this isomeride preferentially, the following properties of specimens obtained by repeating these processes are recorded :

Samples.	B. p./ 40 mm.	B. p./ 60 mm.	B. p./ 760 mm.	$d_{4^\circ}^{25^\circ}$.	$d_{4^\circ}^{15^\circ}$.	$n_D^{25^\circ}$.	$n_D^{15^\circ}$.
I.........		95—99°	167—168°	1·012		1·4183*	
II.........			167—169	1·007		1·4182*	
III.........			168—170		1·015		1·421*
IV.........			168—169	1·005		1·4183†	
V.........		97—98		1·004	1·015	1·4175†	
VI.........			168—170		1·015		1·421†
VII.........			168—170		1·016		1·422‡
VIII.........	88—89°		168—169	1·004	1·015	1·4172	1·4213§

* Prepared from epichlorohydrin (Zunino, *Atti R. Accad. Lincei*, 1897, **6**, 348).

† Prepared from αγ-dichlorohydrin (Gilchrist and Purves, J., 1925, **127**, 2735).

‡ Prepared from αβ-dibromohydrin (Gilchrist and Purves, *loc. cit.*).

§ Prepared by fractionation of the product obtained from monosodium glyceroxide, as described in this paper.

The values of $d_{4^\circ}^{15^\circ}$ and $n_D^{15^\circ}$ agree with those, 1·016 and 1·4219 respectively, obtained by Gilchrist and Purves for the supposed isomeride, but differ considerably from the values given by what is now believed to be the true αβ-dimethyl ether.

Glycerol Trimethyl Ether.—Glycerol dimethyl ether was further methylated by means of metallic sodium and methyl sulphate to yield the trimethyl ether, b. p. 146—148°/760 mm., $d_{4^\circ}^{25^\circ}$ 0·937, $d_{4^\circ}^{15^\circ}$ 0·946, $n_D^{25^\circ}$ 1·4013, $n_D^{15^\circ}$ 1·4055 (Found: C, 53·3; H, 10·4; OH, 0·18. Calc. for $C_6H_{14}O_3$: C, 53·7; H, 10·5; OH, 0·0%). The properties of the latter differed slightly from those recorded by Gilchrist and Purves (*loc. cit.*), who give $d_{4^\circ}^{15^\circ}$ 0·9401 and $n_D^{15^\circ}$ 1·4069, and the ether was miscible with water in all proportions, contrary to the statement of Darke and Lewis (*J. Soc. Chem. Ind.*, 1928, **47**, 1091).

α-Monochlorohydrin, $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$.—Rider and Hill (*J. Amer. Chem. Soc.*, 1930, **52**, 1521, 1525) prepared monochlorohydrin from allyl alcohol and hypochlorous acid, and demonstrated the presence of the α- and β-isomerides in the product by fractionation of the solid phenylurethanes. They appear to have overlooked the similar proof in Part V of this series (J., 1926, 3150) by means of the di-*p*-nitrobenzoates of the α- and β-monochlorohydrins, which differ in melting point by 15°.

p-Nitrobenzoylation has similarly been utilised in the examination of a specimen of monochlorohydrin (15 g.) prepared by the passage of hydrogen chloride through glycerol containing a small quantity of acetic acid at 120° (compare Hill and Fischer, *J. Amer. Chem. Soc.*, 1922, **44**, 2582); 14 g. of pure α-monochlorohydrin di-*p*-nitrobenzoate, m. p. 108°, and 17 g. of the mixed α- and β-monochlorohydrin di-*p*-nitrobenzoates, m. p. 98—104°, were obtained. Mixed melting-point determinations with the *p*-nitrobenzoates described in Part V established identity (108° and 98—104° respectively).

This specimen (A), therefore, must have contained the β-isomeride; its density differed from that (B) recorded by Smith (*Z. physikal. Chem.*, 1918, **92**, 717) for a preparation made from epichlorohydrin and water—a method which may have avoided any introduction of chlorine into the β-position (compare Fourneau and Marquès, *Bull. Soc. chim.*, 1926, **39**, 699). His process was therefore repeated (C), except that refluxation was substituted for treatment under pressure, a variation which would seem desirable since the monochlorohydrin decomposed slightly at 140—142°, with the formation of hydrogen chloride, chlorinated diglycerol, dichlorohydrin, and water. This decomposition was not observed during distillation at 98—99°/1 mm. (Found: Cl, 32·1. Calc. for $C_3H_7O_2Cl$: Cl, 32·1%).

The slight difference between specimens prepared by the two methods may be explained by the presence (which was proved) of monochlorohydrin acetate in (A).

In order to obtain a specimen of monochlorohydrin by the direct esterification of glycerol without the possibility of formation of an acetate, the process of Nivière (*Compt. rend.*, 1913, **156**, 1628) was repeated (D) (Found: Cl, 32·0%).

	$d_{4^\circ}^{25^\circ}$.	$d_{4^\circ}^{20^\circ}$.	$n_D^{20^\circ}$.	$n_D^{25^\circ}$.	
A	1·309	1·313	1·4773	1·4758	(contains the acetate)
B	—	1·3215	—	—	
C	1·317	1·322	1·4794	1·4778	free from the acetate
D	1·317	1·321	1·4800	1·4782	

Rider and Hill (*loc. cit.*) record d^{25° 1·3217 and $n_D^{25^\circ}$ 1·4811, for purified α-monochlorohydrin.

Allyl methyl ether was readily obtained by the action of methyl sulphate on sodium allyloxide in excess of allyl alcohol; its properties agreed with descriptions of specimens prepared by other methods (Henry, *Ber.*, 1872, **5**, 449; Irvine, Macdonald, and Soutar, *loc. cit.*).

The density (1·192) of αβ-dichloro-γ-methoxypropane, which may conveniently be prepared by chlorinating allyl methyl ether in chloroform, was erroneously recorded in Part IX (*loc. cit.*) as 1·162.

α-*Chloro*-βγ-*dimethoxypropane*.—This was prepared by the direct methylation of α-monochlorohydrin (50 g.) with methyl iodide (350 g.) and silver oxide (300 g.). Its properties agreed satisfactorily with those recorded by Blanchard (*Bull. Soc. chim.*, 1927, **41**, 824) for a specimen prepared in another way; b. p. 156°, $d_{4^\circ}^{25^\circ}$ 1·08, $n_D^{25^\circ}$ 1·43 (Found: C, 43·0; H, 8·1; Cl, 25·8. $C_5H_{11}O_2Cl$ requires C, 43·3; H, 7·9; Cl, 25·6%). Its constitution may now be established by arguments identical with those used in Part IX to decide the positions of the chlorine atoms in αγ-dichloro-β-methoxypropane; it is also independently proved by the synthesis of glycerol αβ-dimethyl ether described above (p. 450).

β-*Chloro*-αγ-*dimethoxypropane*.—(*a*) 24 G. of the glycerol dimethyl ether described in Part VIII (*loc. cit.*) were gradually treated with 42 g. of phosphorus pentachloride, and the product was cautiously introduced into excess of water. The *chlorohydrin ether* was extracted in ether, washed with water, dilute sodium bicarbonate solution, and again with water, dried with calcium chloride, concentrated, and distilled; b. p. 155—160°, $d_{4^\circ}^{25^\circ}$ 1·05, $n_D^{25^\circ}$ 1·42 (Found: C, 43·4; H, 7·8; Cl, 25·8%). This compound differs only slightly from the isomeride described above. Both compounds are moderately easily soluble in water, differing in this respect from the dichloromethoxypropanes (Part IX), which are very sparingly soluble.

As appears to be usual in the case of chloropropanes not containing a hydroxyl group (Part X; J., 1930, 382), the chlorine atoms are firmly bound, although hydrolysis is less difficult than that of the methyl and trityl ethers of αγ-dichlorohydrin (Parts IX and VII).

(*b*) Better yields were obtained when thionyl chloride was employed instead of phosphorus pentachloride. This result is of special interest as showing that it is incorrect to assume that the secondary alcoholic radical of an αγ-disubstituted glycerol must be incapable of chlorination by the former reagent (compare Grün and Corelli, *Z. angew. Chem.*, 1912, **25**, 665, 947; Heiduschka and Schuster, *J. pr. Chem.*, 1928, **120**, 145).

180 G. of thionyl chloride were gradually added to 90 g. of glycerol αγ-dimethyl ether. After the vigorous reaction had ceased, the mixture was kept over-night, heated on a water-bath for 8 hours, poured into water, and extracted with ether; the extract was washed, and dried with calcium chloride. The crude product, b. p. 145—160°, was redistilled: b. p. 154°, $d_{4^\circ}^{25^\circ}$ 1·06, $n_D^{25^\circ}$ 1·42 (Found: C, 43·1; H, 8·0; Cl, 25·8%). The structure of this compound was proved by its conversion into glycerol αγ-dimethyl ether, identified by means of the *p*-nitrobenzoate.

βγ-Diacetoxy-α-methoxypropane.—50 G. of glycerol α-methyl ether were treated with 200 g. of acetic anhydride containing 0·5% of pyridine, and the whole was gently refluxed for 1½ hours. The product was fractionated, neutralised with cold sodium hydroxide solution, and again fractionated to yield a colourless liquid, b. p. 139—140°/40 mm., 228°/760 mm., $d_{4^\circ}^{25^\circ}$ 1·097, $n_D^{25^\circ}$ 1·422, soluble in water (Found: C, 50·3; H, 7·2. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4%). Its constitution was proved by hydrolysis, extraction of the glycerol methyl ether in chloroform, and preparation of the *p*-nitrobenzoate, m. p., alone or mixed with an authentic specimen, about 108° (see Part IX).

αγ-Diacetoxy-β-methoxypropane was prepared from pure glycerol β-methyl ether in a similar manner to that described above for the isomeride; b. p. 144—145°/40 mm., 232°/760 mm., $d_{4^\circ}^{25^\circ}$ 1·100, $n_D^{25^\circ}$ 1·424 (Found: C, 50·2; H, 7·2%). Hydrolysis, followed by *p*-nitrobenzoylation, established that no migration of the methoxy-group had occurred: the product melted at about 155°, alone or mixed with the *p*-nitrobenzoate of glycerol β-methyl ether prepared directly (see Part IX), but at 103—107° when mixed with that of the α-isomeride.

γ-Acetoxy-αβ-dimethoxypropane was obtained by acetylating glycerol αβ-dimethyl ether in a similar manner to that used for the monomethyl ether, but with half the quantity of acetic anhydride. The product was soluble in water and had b. p. 108—109°/40 mm., 195°/760 mm., $d_{4^\circ}^{25^\circ}$ 1·027, $n_D^{25^\circ}$ 1·414 (Found: C, 51·8; H, 8·3. $C_7H_{14}O_4$ requires C, 51·9; H, 8·6%). Hydrolysis, and *p*-nitrobenzoylation of the product, yielded crystals melting at 43° either alone or mixed with γ-*p*-nitrobenzoyloxy-αβ-dimethoxypropane and fusing at room temperature when mixed with the αγ-dimethoxy-isomeride.

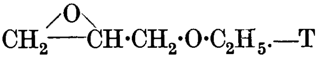
β-*Acetoxy*-αγ-*dimethoxypropane* was prepared by acetylating the glycerol dimethyl ether investigated in Part VIII. It had b. p. 105—106°/40 mm., 191°/760 mm., $d_{4^\circ}^{25^\circ}$ 1·025, $n_D^{25^\circ}$ 1·413 (Found: C, 51·6; H, 8·4%). The product of its hydrolysis yielded a *p*-nitrobenzoate which melted at 43° either alone or mixed with β-*p*-nitrobenzoyloxy-αγ-dimethoxypropane but fused at room temperature with the αβ-dimethoxy-isomeride.

γ-p-*Nitrobenzoyloxy*-αβ-*dimethoxypropane*.—5 G. of glycerol αβ-dimethyl ether were warmed with 4 g. of pyridine and 28 c.c. of a solution of *p*-nitrobenzoyl chloride in chloroform containing 27·5 g. in 100 c.c. After 48 hours, ether and water were added, and the ethereal extract was washed with water, dilute sulphuric acid, dilute sodium bicarbonate solution, and again with water, dried with calcium chloride, concentrated, and heated in a steam-oven for 1 hour. The *product* crystallised from light petroleum in tablets and melted at 44° (Found: C, 53·7; H, 5·6; N, 5·3. $C_{12}H_{15}O_6N$ requires C, 53·5; H, 5·6; N, 5·2%). Mixed with β-*p*-nitrobenzoyloxy-αγ-dimethoxypropane (Part VII; *loc. cit.*), it fused at room temperature (26°).

βγ-*Diacetoxy*-α-*ethoxypropane*.—120 G. of a sample of glycerol monoethyl ether, b. p. 114—116°/10 mm., 222°/760 mm. (compare Darke and Lewis, *loc. cit.*, who record 230°), $d_{4^\circ}^{25^\circ}$ 1·058, $n_D^{25^\circ}$ 1·440 (Found: OH, 28·3. Calc. for $C_5H_{12}O_3$: OH, 28·3%), isolated as a by-product during a preparation of glycerol diethyl ether from dichlorohydrin, and agreeing in properties with the description of Reboul (*Annalen*, Suppl., 1861, **1**, 239), were acetylated with 408 g. of acetic anhydride containing 2 g. of pyridine. The product was fractionated at 115—119°/10 mm., neutralised with 27% sodium hydroxide solution, and again fractionated at 117—119°/10 mm.; $d_{4^\circ}^{25^\circ}$ 1·062, $n_D^{25^\circ}$ 1·422 (Found: $CH_3{\cdot}CO$, 41·5. $C_9H_{16}O_5$ requires $CH_3{\cdot}CO$, 42·2%). The ethoxy-group presumably occupies the α-position.

β-*Acetoxy*-αγ-*diethoxypropane*.—Glycerol diethyl ether, prepared from sodium ethoxide and either dichlorohydrin or epichlorohydrin, had b. p. 108—109°/60 mm., 191°/760 mm., $d_{4^\circ}^{25^\circ}$ 0·952, $n_D^{23^\circ}$ 1·419 (Found: OH, 11·7. Calc. for $C_7H_{16}O_3$: OH, 11·5%). Unlike the ether described by Berthelot (*Annalen*, 1854, **92**, 303), it was completely miscible with water; it also differed from that of

Zunino (*Atti R. Accad. Lincei*, 1897, **6**, 348) in density. 500 G. were acetylated with 1000 g. of acetic anhydride containing 7·5 g. of pyridine. The product on fractionation gave an *ester*, b. p. 127—129°/60 mm., $d_{4^\circ}^{25^\circ}$ 0·980, $n_D^{25^\circ}$ 1·415 (Found: $CH_3{\cdot}CO$, 23·1. $C_9H_{18}O_4$ requires $CH_3{\cdot}CO$, 22·6%), in which the ethoxy-groups presumably occupy the αγ-positions.



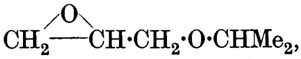
Glycidyl Ethyl Ether, $\overset{O}{CH_2\text{—}CH}{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$.—This compound is recorded by several investigators as having been prepared from α-monochlorohydrin γ-ethyl ether (Reboul, *Ann. Chim.*, 1860, **60**, 5; Henry, *Ber.*, 1872, **5**, 449; Lespieau, *Compt. rend.*, 1905, **140**, 436; Nef, *Annalen*, 1904, **335**, 191), and its structure appears to be well established by its synthesis from propargyl ethyl ether, $CH⫶C{\cdot}CH_2{\cdot}OEt$, by Peratoner (*Gazzetta*, 1894, **24**, 36), but its occurrence as an intermediate compound in the preparation of glycerol diethyl ether from dichlorohydrin and sodium ethoxide, as the probable mechanism of the reaction would require (Part X), has apparently hitherto not been detected. During fractional distillation of accumulations of lower-boiling materials produced in the reaction, a small quantity of this ether was obtained, b. p. 124—125°, $d_{4^\circ}^{25^\circ}$ 0·939, $n_D^{25^\circ}$ 1·406, $[R_L]_D$ 26·7 (calc., 26·4) (Found: C, 58·4; H, 9·3; *M*, cryoscopic in benzene, 95·8. Calc. for $C_5H_{10}O_2$: C, 58·8; H, 9·8%; *M*, 102).

Glycerol αγ-Dipropyl Ether.—129 G. of dichlorohydrin in 50 c.c. of *n*-propyl alcohol were added with mechanical stirring during 1 hour to a mixture of 85 g. of powdered sodium hydroxide in 950 c.c. of the alcohol, and the whole was refluxed for 1 hour, cooled, and neutralised with concentrated hydrochloric acid. The liquid was filtered from sodium chloride, which was washed with *n*-propyl alcohol, and the filtrate and washings were concentrated at atmospheric pressure and fractionated under diminished pressure. The dipropyl ether obtained (yield, 44%) had b. p. 135—137°/60 mm., 216–218°/760 mm., $d_{4^\circ}^{25^\circ}$ 0·927, $n_D^{25^\circ}$ 1·424, $[R_L]_D$ 48·4 (calc., 48·6), and agreed in boiling point with the ether described by Zunino (*Atti R. Accad. Lincei*, 1897, **6**, 348), who prepared it from epichlorohydrin.

*Glycerol αγ-di*iso*propyl ether*, prepared (in *iso*propyl alcohol) in the same way as its isomeride, had b. p. 123—124°/60 mm., 198—199°/760 mm., $d_{4^\circ}^{25^\circ}$ 0·914, $n_D^{25^\circ}$ 1·418, $[R_L]_D$ 48·5 (calc., 48·6) (Found: C, 61·2; H, 11·2. $C_9H_{20}O_3$ requires C, 61·4; H, 11·4%). The yield was about 17%.

A material obtained from epichlorohydrin and believed to be this compound, but boiling at 112—113° instead of 198—199°, was described by Zunino (*Atti R. Accad. Lincei*, 1900, **9**, 309. Compare

Darke and Lewis, *J. Soc. Chem. Ind.*, 1928, **47**, 1091). That the substance now obtained has the true αγ-di*iso*propyloxy-constitution is probable from analogy with the αγ-dimethyl ether already described.

Glycidyl iso*propyl ether*,  $\overset{\frown O \frown}{CH_2{-}CH}{\cdot}CH_2{\cdot}O{\cdot}CHMe_2$, was isolated in small quantity by fractionation of the crude glycerol di*iso*propyl ether mentioned above; b. p. 137—138°, $d_{4^\circ}^{25^\circ}$ 0·924, $n_D^{25^\circ}$ 1·408, $[R_L]_D$ 31·0 (calc., 31·0) (Found: C, 61·8; H, 10·1; *M*, cryoscopic in benzene, 106. $C_6H_{12}O_2$ requires C, 62·1; H, 10·3%; *M*, 116).

Glycerol α-Monobenzyl Ether.—80 G. of powdered sodium hydroxide were stirred with 1500 c.c. of benzyl alcohol at 140° for 1 hour, and cooled to 90—100°; 221 g. of monochlorohydrin were added during 1 hour and the whole was kept at 140° for a third hour, washed with water, and fractionated. The *ether* obtained had b. p. 164—166°/2 mm., $d_{4^\circ}^{25^\circ}$ 1·130, $n_D^{25^\circ}$ 1·530 (Found: C, 66·0; H, 7·5. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%).

Cross and Jacobs (*J. Soc. Chem. Ind.*, 1926, **45**, 320T) described a material under this name, b. p. 124—126°/2—3 mm., $d_{15^\circ}^{15^\circ}$ 1·196, prepared from sodium glyceroxide. Although the method is likely to cause the formation of a β-isomeride, the difference in properties could not be explained in that way: a sample of the actual product prepared by Cross and Jacobs was therefore examined and found to contain glycerol which is exceedingly difficult to separate by distillation.

Glycerol αγ-Dibenzyl Ether.—A material believed to be this compound was described by Zunino (*Atti R. Accad. Lincei*, 1900, **9**, 309) as boiling at 157—158° and having d^{15° 0·918.

70 G. of dichlorohydrin were slowly added with shaking to a solution, which had been cooled to room temperature, of 23 g. of sodium in 250 g. of benzyl alcohol (or, in later experiments, to a solution of sodium hydroxide in a large excess of benzyl alcohol at 100°). After the mixture had been kept at 140—150° for 1 hour, the product was cooled, washed with water, extracted in ether (or merely filtered when sodium hydroxide was used), concentrated, and fractionated; the *ether* obtained had b. p. 198—204°/2—3 mm., $d_{4^\circ}^{25^\circ}$ 1·100, $n_D^{25^\circ}$ 1·547 (Found: C, 74·7; H, 7·3. $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·4%). This compound probably has the structure now assigned to it, although its properties are different from those recorded in the literature.

αγ-Diphenoxy-β-acetoxypropane.—(*a*) 61 G. of glycerol diphenyl ether, prepared from dichlorohydrin and agreeing in melting point with the ether described by Boyd and Marle (P., 1908, **24**, 92; J., 1908, **93**, 838), were refluxed for 1 hour with 102 g. of acetic anhydride containing 0·8 g. of pyridine. The product was boiled with water, extracted in chloroform, washed, dried with potassium carbonate, and concentrated; white needles gradually formed, m. p. 33° after recrystallisation from alcohol (Found : $CH_3{\cdot}CO$, 15·0%). Repeated recrystallisation from alcohol did not raise the melting point (compare Rössing, *Ber.*, 1886, **19**, 65, whose specimen melted at 70—71°).

(*b*) The above preparation was repeated with double the quantity of acetic anhydride and without pyridine, 3 hours being allowed for the acetylation. Again the product melted at 33° (Found : C, 71·1 ; H, 6·1 ; $CH_3{\cdot}CO$, 15·1. Calc. for $C_{17}H_{18}O_4$: C, 71·3 ; H, 6·3 ; $CH_3{\cdot}CO$, 15·0%).

(*c*) Rössing used acetyl chloride instead of acetic anhydride. His process was therefore repeated, but the acetate obtained melted, alone or mixed with (*b*), at 32–33° (Found : $CH_3{\cdot}CO$, 15·1%).

*αγ-Di-*o*-tolyloxy-β-acetoxypropane.*—162 G. of glycerol αγ-di-*o*-tolyl ether, b. p. 196°/2—3 mm., obtained by treating αγ-dichlorohydrin with sodium *o*-tolyloxide (compare Boyd, J., 1903, **83**, 1135 ; Zunino, *Atti R. Accad. Lincei*, 1909, **18**, 254), were refluxed with 120 g. of acetic anhydride and 1·5 g. of pyridine for 2 hours. The product, concentrated at 40 mm. and fractionated, yielded a viscous, slightly yellow liquid which has not yet crystallised, b. p. 204–206°/2–3 mm., $d_{4°}^{25°}$ 1·103, $n_D^{25°}$ 1·536 (Found : C, 72·4 ; H, 7·1 ; $CH_3{\cdot}CO$, 13·7. $C_{19}H_{22}O_4$ requires C, 72·6 ; H, 7·0 ; $CH_3{\cdot}CO$, 13·7%).

No proof of the constitution of the parent di-*o*-tolyl ether appears to have been obtained, but if the syntheses of dialkyl and diaryl ethers of glycerol are sufficiently analogous, the tolyl radicals probably occupy the positions which have previously been assigned to them.

*αγ-Di-*m*-tolyloxy-β-acetoxypropane.*—Glycerol di-*m*-tolyl ether, prepared from dichlorohydrin and therefore probably having the αγ-structure, boiled at 205°/2—3 mm., its difference in boiling point from the di-*o*-isomeride mentioned above being thus in the same direction as that noted by Boyd (*loc. cit.*) and differing from that noted by Zunino (*loc. cit.*). It was acetylated in the manner just described, and the *acetate* obtained as an almost colourless, very viscous liquid, b. p. 215—217°/2—3 mm., $d_{4°}^{25°}$ 1·103, $n_D^{25°}$ 1·536 (Found : C, 72·3 ; H, 6·9 ; $CH_3{\cdot}CO$, 13·6%).

*αγ-Di-*p*-tolyloxy-β-acetoxypropane.*—Glycerol di-*p*-tolyl ether, prepared from αγ-dichlorohydrin, melted at 88°, in accordance with the description of Lindeman (*Ber.*, 1891, **24**, 2145). The *acetate* was obtained after recrystallisation from alcohol, as white needles, m. p. 49° (Found : C, 72·1 ; H, 7·2 ; $CH_3{\cdot}CO$, 13·6%).

p-*Tolyl* n-*Octoate.*—54 G. of *p*-cresol were gradually added, after the vigour of the first reaction had subsided, to a mixture of 52 g. of phosphorus pentachloride and 72 g. of *n*-octoic acid; the whole was kept at 100° for 3 hours, cooled, and washed with water, dilute sodium hydroxide solution, and again with water, ether being added to assist separation. Concentration and fractionation yielded a colourless liquid, b. p. 163—165°/10 mm., $d_{4^\circ}^{25^\circ}$ 0·957, $n_D^{25^\circ}$ 1·483, $[R_L]_D$ 69·9 (calc., 69·5) (Found: C, 77·5; H, 9·5; $C_7H_{15}\cdot CO$, 54·0. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·4; $C_7H_{15}\cdot CO$, 54·3%).

The general method of Newman, Trikojus, and Harker (*Proc. Roy. Soc., New South Wales*, 1925, **59**, 293; *Ann. Reports*, 1927, 90) for the preparation of glycerides and of esters in general by heating together an alcohol, the sodium salt of a fatty acid, and phosphorus pentachloride, presumably supposes the intermediate formation from the alcohol of a chloride which then reacts with the sodium salt of the acid. The present preparation of an ester by this method, but without the use of a sodium salt, indicates alternatively that the acid chloride produced under such conditions is capable of effecting esterification in good yield.

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