129. *Physical Properties and Chemical Constitution. Part XII. Ethers and Acetals.*

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New measurements of the parachors and refractivities of a considerable number of aliphatic ethers and acetals have been made and the contributions of the O atom have been computed with the aid of the experimental data (or figures deduced therefrom) on the hydrocarbons (Part IX, *J.*, 1943, 133). The mean results are:

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
O (in ethers)	19·8	1·753	1·764	1·786	1·805	22·74
O (in acetals)	18·0	1·603	1·607	1·618	1·627	22·41

Similar measurements and calculations have been made on a number of phenyl alkyl ethers.

THE parachor of oxygen is given by Sugden (*J.*, 1924, **125**, 1177; "The Parachor and Valency," 1930, 38) as 20·0 but no indication of the data from which this figure was calculated is disclosed. Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 607) deduced "Athersauerstoff" O <: (*a*) by subtracting the computed refractivities of $[CH_2]_n + O^{••}$ (ketones) from the observed refractivities of esters $[CH_2]_nO^{••}O <$ (16 esters), and (*b*) by subtracting the computed refractivities of $[CH_2]_n + H_2$ from the observed refractivities of ethers $[CH_2]_nH_2O <$ (4 ethers comprising ethyl propyl ether, methylal, acetal, and paraldehyde).

Wide individual variations were found (and indeed might have been anticipated from the procedure employed), and the mean values were given as:

	R_C.	R_D.	R_F.	$R_{G'}$.
O<	1·639	1·643	1·649	1·662
O·	1·522	1·525	1·531	1·541

The figures for "Hydroxylsauerstoff" $O^{•}$, deduced by subtraction of the computed refractivities of $[CH_2]_n + O^{••}$ from the observed refractivities of the acids $[CH_2]_nO^{••}O^{•}$ (8 monocarboxylic acids), are given above for purposes of comparison.

The author computes the parachor and refractivities of the oxygen atom in aliphatic ethers by simple subtraction of his own results for the appropriate hydrocarbon (Part IX, *J.*, 1946, 133) from those of the ethers; for diethyl and di*iso*propyl ether, the values for the alkyl groups (preceding paper) have been employed, whilst for 2 : 2′-dichlorodiethyl ether the figures for $Cl·CH_2·CH_2·CH_2Cl$ (XIV, **282**) + CH_2 were subtracted. The results for aliphatic ethers are collected in Table I.

TABLE I.

O *Values for aliphatic ethers.*

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Et_2O	21·2	1·88	1·91	1·93	1·96	22·82
$Pr^n{}_2O$	19·5	1·72	1·75	1·77	1·80	22·60
$Pr^i{}_2O$ *	21·7	1·76	1·76	1·76	1·78	21·90
$Bu^n{}_2O$	19·9	1·69	1·72	1·73	1·75	22·57
$Am^n{}_2O$	20·5	1·66	1·67	1·68	1·70	22·57
$Am^i{}_2O$ †	20·1	1·71	1·72	1·74	1·76	22·43
$Am^i{}_2O$ ‡	20·6	1·85	1·88	1·90	1·91	22·34
$(C_6H_{13}{}^n)_2O$	19·9	1·77	1·77	1·80	1·82	22·47
$(C_7H_{15}{}^n)_2O$	19·3	1·71	1·71	1·74	1·75	22·53
$(C_8H_{15}{}^n)_2O$	19·8	1·83	1·83	1·86	1·90	22·48
$MeBu^nO$	19·0	1·74	1·74	1·77	1·79	23·10
$EtBu^nO$	19·6	1·79	1·80	1·83	1·84	22·69
$MeAm^nO$	19·7	1·71	1·72	1·74	1·77	23·25
$EtAm^nO$	18·5	1·76	1·76	1·78	1·80	22·79
$MeC_6H_{13}{}^nO$	18·2	1·66	1·66	1·68	1·69	23·31
$EtC_6H_{13}{}^nO$	19·3	1·77	1·78	1·81	1·83	22·80
$(Cl·CH_2·CH_2)_2O$	21·8	1·79	1·79	1·81	1·81	23·16
Mean (excluding *)	19·8	1·753	1·764	1·786	1·805	22·74
$(CH_2·CH_2·OEt)_2O$	19·6	1·76	1·77	1·79	1·80	23·12
$(MeO·CH_2·CH_2·O·CH_2·CH_2)_2O$ ...	20·5	1·73	1·74	1·75	1·77	23·50

† From Bisol fermentation *iso*amyl alcohol. ‡ From Sharples synthetic *iso*amyl alcohol.

Attention is drawn to the results for diethyleneglycol diethyl ether ("diethyl carbitol") and tetramethyleneglycol dimethyl ether ("dimethoxy tetraglycol") which, although containing three and five oxygen atoms respectively, give results in reasonable agreement with those for the simple dialkyl ethers.

The results for phenyl alkyl ethers are collected in Table II; the experimental figures for the n-alkylbenzenes (Part X, this vol., p. 607) were employed in the calculations. It will be noted that the parachor values are of the same order as those for alkyl ethers, but the refractivities are consistently higher.

TABLE II.

O *Values for phenyl alkyl ethers.*

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
PhOMe	20·0	1·77	1·78	1·85	1·90	26·23
PhOEt	19·4	1·93	1·95	2·03	[2·01]	25·32
$PhOPr^n$	18·6	1·83	1·85	1·91	1·97	24·97
$PhOPr^i$	20·8	1·98	2·00	2·08	2·14	24·76
$PhOBu^n$	19·7	1·95	1·98	2·05	2·10	24·96
$PhOAm^n$	19·5	1·88	1·91	1·96	1·99	24·85
$PhOC_6H_{13}^n$	18·8	2·05	2·09	2·17	2·20	24·64

The results for acetals, collected in Table III, were entirely unexpected. The parachor and refractivities of the oxygen atom in acetals are consistently smaller than for the oxygen atom in alkyl ethers.

TABLE III.

2O *Values for acetals.*

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$CH_2(OMe)_2$ *	39·6	3·23	3·25	3·27	3·31	44·30
$CH_2(OEt)_2$	37·1	3·24	3·25	3·28	3·31	44·98
$CH_2(OPr^n)_2$	36·4	3·20	3·20	3·23	3·24	45·03
$CH_2(OPr^i)_2$ *	38·7	3·20	3·19	3·20	3·22	44·68
$CH_2(OBu^n)_2$	36·6	3·23	3·24	3·26	3·26	45·03
$CH_2(OBu^i)_2$	36·6	3·26	3·26	3·28	3·30	44·74
$CH_2(OAm^n)_2$	35·8	3·21	3·23	3·25	3·27	45·18
$CH_2(OC_6H_{13}^n)_2$	36·9	3·12	3·14	3·16	3·18	45·18
$CH_3{\cdot}CH(OMe)_2$ *	38·3	3·11	3·13	3·15	3·18	45·71
$CH_3{\cdot}CH(OEt)_2$	36·3	3·23	3·23	3·26	3·29	44·64
$CH_3{\cdot}CH(OPr^n)_2$	35·5	3·19	3·20	3·21	3·23	44·62
$CH_3{\cdot}CH(OBu^n)_2$	34·9	3·17	3·18	3·18	3·22	44·56
$CH_3{\cdot}CH(OBu^i)_2$	34·2	3·21	3·21	3·24	3·24	44·20
Mean 2O (excluding *)	36·0	3·206	3·214	3·235	3·254	44·82
Mean O	18·0	1·603	1·607	1·618	1·627	22·41

EXPERIMENTAL.

Preparation of Symmetrical Ethers.—Diethyl ether was prepared in the usual manner from absolute ethyl alcohol and concentrated sulphuric acid, dried over anhydrous calcium chloride for 24 hours, and fractionated from sodium.

The first preparations of di-n-propyl, di-n-butyl, and di-n-amyl ethers were carried out by Popelier's method (*Bull. Soc. chim. Belg.*, 1923, **32**, 179); for the first two the excess of alcohol was removed by repeated washing with water; for the third the excess of amyl alcohol was removed by two washings with 50% (by vol.) sulphuric acid. In all cases the ether was finally refluxed and distilled from sodium to constant density and refractive index. When the physical measurements for these compounds had been completed, a new procedure was discovered for the preparation of di-n-butyl and higher ethers: this involved heating the alcohol with concentrated sulphuric acid until the theoretical volume of water was collected. The apparatus consisted of a bolt-head flask fitted with a cork carrying a thermometer (dipping almost to the bottom of the flask) and an uncalibrated Dean and Stark tube ("water separator" tube) attached to a short reflux condenser; the "water separator" tube permits of the automatic separation of the water produced in the reaction. The volume, v, of the "water separator" tube to the overflow point is first determined by adding water from a burette; the theoretical volume, v_t, of water eliminated in the formation of the ether from the alcohol is then calculated and the "water separator" tube is then charged with $(v - v_t)$ ml. of water. The apparatus is then completely assembled with the alcohol and the concentrated sulphuric acid in the bolt-head flask. The flask is then heated so that the mixture refluxes gently: the heating is stopped when the theoretical volume of water (within 10%) has been collected. In practice, it is found that the completion of the reaction usually corresponds to a definite temperature of the reaction mixture and the odour of sulphur dioxide then becomes apparent; further heating results in charring and formation of unsaturated hydrocarbons. To isolate the ether, the reaction product is distilled in steam, and the organic layer removed, dried, and fractionally distilled. The main fraction is then refluxed and distilled from sodium until the latter remains unattacked. The yield of ether may be improved by refluxing the fraction of low b. p., which contains a larger proportion of unchanged alcohol, repeatedly with sodium. For di-n-butyl ether the n-butyl alcohol may be removed more simply by washing with 50% (by weight) sulphuric acid. Some typical results are collected below. It is not advisable to raise the temperature in the *n*-octyl ether preparation above 190°, since considerable carbonisation may occur.

Ether.	Wt. of alcohol, g.	Wt. of H_2SO_4, g.	Temp. for completion of reaction.	Yield of pure ether, g.
Di-*n*-butyl	50	16	134°	15
Di-*n*-amyl	50	7	157	23
Di*iso*amyl	50	7	148	24
Di-*n*-hexyl	50	6	180	20
Di-*n*-heptyl	40	4·2	198	17
Di-*n*-octyl	27	4·9	190	13

Commercial di*iso*propyl ether was shaken successively with a concentrated solution of a ferrous salt (to remove peroxides), 0·5% potassium permanganate solution (to remove traces of aldehydes), 5% sodium hydroxide solution, and water. It was then dried ($MgSO_4$), refluxed over sodium, and distilled from fresh sodium until the latter was unattacked. 2 : 2′-Dichlorodiethyl ether (Carbon and Carbide Corporation) was similarly purified.

Preparation of Unsymmetrical Ethers.—Two difficulties arise in the preparation of higher mixed aliphatic ethers by Williamson's method : (i) the slow reaction between 1 atom of sodium and 1—2 mols. of the alcohol to give the sodium alkoxide in view of the slight solubility of the alkoxide in the alcohol, and (ii) the difficulty of removing a large proportion of alcohol from the resulting ether by refluxing with sodium. These were overcome by employing 1 atom of sodium to 8—10 mols. of the alcohol, adding 1 mol. of the alkyl bromide or iodide (*i.e.*, equivalent to the sodium used), refluxing for 1—2 hours until formation of the ether was complete, and then removing the ether formed by fractional distillation; the process could, in general, be repeated 3 times and a reasonable yield of ether was obtained. The residual alcohol may also be recovered.

Ethyl n-*butyl ether.* The apparatus consisted of a 350-ml. Claisen flask with fractionating side arm; the short neck carried a double-surface condenser in the top of which a separatory funnel was supported by means of a grooved cork : the other neck and side arm were closed by means of well-fitting corks. 148 G. of *n*-butyl alcohol (b. p. 116—117°/750 mm.) were placed in the flask, 5·75 g. of clean sodium were added, and the mixture was warmed in an air-bath until all the sodium had reacted. 39 G. of pure ethyl iodide were then added, but there was no apparent reaction in the cold; upon gentle warming, sodium iodide gradually separated and the reaction appeared complete after 90 minutes. The condenser was removed and the apparatus was arranged for distillation : the crude ether (28 g.) was collected at 94—105°. After cooling, the flask was fitted with a double-surface condenser, etc., as before, 5·75 g. of sodium were added and the flask was warmed until reaction was complete; 39 g. of ethyl iodide were then introduced, the mixture was refluxed as before and then distilled, the fraction (40 g.) boiling up to 109° (largely at 100—103°) being collected. The combined distillates were refluxed for 2 hours with excess of sodium and distilled; the distillate was distilled from fresh sodium and passed over at 101—102°. After two further distillations from sodium, the latter remained unaffected and pure ethyl *n*-butyl ether, b. p. 91·5°/757 mm., was obtained. The yield was 36 g.

Methyl n-*butyl ether.* The quantities employed were : 148 g. of *n*-butyl alcohol, 5·75 g. of sodium, and 36 g. of pure methyl iodide; this yielded 27 g. of the crude ether, b. p. 65—85°. Repetition with a further 5·75 g. of sodium and 36 g. of methyl iodide afforded 28 g. of crude ether, b. p. 65—91°. The pure methyl *n*-butyl ether, b. p. 70·5°/766 mm. (31 g.), was obtained after repeated distillation from sodium.

Methyl n-*amyl ether.* 176 G. of *n*-amyl alcohol, b. p. 136·5—137·5°/766 mm. (Kodak), 5·75 g. of sodium (the reaction was allowed to proceed overnight), and 39 g. of ethyl iodide gave 25 g. of the crude ether, b. p. 95—110°; another reaction with the same quantities of sodium and methyl iodide afforded 35 g. of the crude ether, b. p. 100—108°. The yield of pure methyl *n*-amyl ether, b. p. 99°/763 mm., was 43 g.

Ethyl n-*amyl ether.* 5·75 G. of sodium were allowed to react overnight with 220 g. of *n*-amyl alcohol, 39 g. of ethyl iodide added, the mixture was refluxed for 3 hours, and the crude ether, b. p. 110—125° (35 g.), separated by distillation. Treatment of the residual alcohol with 5·75 g. of sodium, followed by 39 g. of ethyl iodide, afforded a further 41 g. of the crude ether, b. p. 120—129°. Repeated distillation over sodium gave 27 g. of pure ethyl *n*-amyl ether, b. p. 117·5—118·5°/768 mm.

Methyl n-*hexyl ether.* 192 G. of *n*-hexyl alcohol, b. p. 156—157°/765 mm., 5·41 g. of sodium and 33·5 g. of methyl iodide yielded, as for ethyl *n*-butyl ether, 27 g. of the crude ether, b. p. 130—140°. Addition of 5·41 g. of sodium to the residue, followed, after 12 hours, by 33·5 g. of methyl iodide gave a further 35 g. of the crude ether, b. p. 130—140°. Three distillations from excess of sodium afforded 42 g. of pure methyl *n*-hexyl ether, b. p. 126°/770 mm.

Ethyl n-*hexyl ether.* 204 G. of *n*-hexyl alcohol, 5·75 g. of sodium, and 39 g. of ethyl iodide gave 27 g. of the crude ether, b. p. 143—150°. The residue was treated with 5·75 g. of sodium, allowed to react overnight, 39 g. of ethyl iodide were added, and the mixture refluxed for 2 hours : this gave 35 g. of the crude ether, b. p. up to 150°. Repeated distillation over excess of sodium afforded 33 g. of pure ethyl *n*-hexyl ether, b. p. 142—143°/773 mm.

Diethyleneglycol diethyl ether (" *diethyl carbitol* "). The Carbon and Carbide Corporation product was first distilled from sodium, and the fraction, b. p. 185—187·5°/775 mm., collected. Redistillation from sodium gave the pure compound, b. p. 187—187·5°/775 mm.

Tetraethyleneglycol dimethyl ether (" *dimethoxy tetraglycol* "). The Carbon and Carbide Corporation product was treated with excess of sodium; when the vigorous reaction had subsided, the product was distilled and the fraction, b. p. 240—265°, collected. This was thrice distilled from sodium; there was considerable fuming at the end of the distillation, presumably owing to the vaporisation of the sodium. Finally, the alcohol-free product was distilled in the absence of sodium, and the liquid, b. p. 269—270°/767 mm., collected for the physical measurements.

Preparation of Phenyl Alkyl Ethers.—*Anisole.* 46·5 G. of pure phenol were added to a solution of 20 g. of A.R. sodium hydroxide contained in a 500-ml. three-necked flask equipped with a dropping-funnel, mechanical stirrer, and reflux condenser. The mixture was vigorously stirred; heat was evolved. 63 G. of methyl sulphate were slowly added during 1 hour, and the reaction mixture was refluxed, with stirring, for 14 hours. The cold mixture was diluted with water, and the anisole layer was separated and washed with water (addition of salt facilitated the complete removal of the water), twice with dilute sulphuric acid, and finally with water until the washings were neutral to litmus, and dried ($CaCl_2$). Distillation gave 42 g. of anisole, b. p. 150—153°. Upon redistillation, the anisole boiled constantly at 151°/736 mm. and a middle fraction was used for the physical measurements. This procedure is more convenient for the preparation of small quantities of anisole than that given in *Org. Synth.*, Coll. Vol. I, 1941, 58.

Phenetole. The procedure used was similar to that for phenyl *n*-propyl ether: the quantities employed were 11·5 g. of sodium in 250 ml. of absolute ethyl alcohol, 47 g. of A.R. phenol dissolved in 50 ml. of absolute ethyl alcohol, and 78 g. of colourless ethyl iodide. The yield of phenetole, b. p. 169°/766 mm., was 37 g.

Phenyl n-*propyl ether.* Into a 1-l. round-bottomed flask, fitted with a double-surface reflux condenser, were placed 11·5 g. of sodium and 250 ml. of absolute ethyl alcohol. When all the sodium had reacted, 47 g. of A.R. phenol dissolved in 50 ml. of absolute ethyl alcohol were added, followed by 107·5 g. of pure colourless *n*-propyl iodide. The mixture was refluxed for 4 hours, but no solid separated. Most of the alcohol was then distilled off on a water-bath: upon addition of excess of water to the distillate, 23 g. of the crude iodide were recovered. The residue in the flask was treated with water, and the upper layer was separated and washed successively with 10% sodium hydroxide solution (twice), water, dilute sulphuric acid (twice), and water (twice), and then dried ($MgSO_4$). Distillation gave 50 g. of phenyl *n*-propyl ether, b. p. 187°/751 mm.

Phenyl iso*propyl ether.* The quantities employed were 11·5 g. of sodium, 300 ml. of absolute ethyl alcohol, 47 g. of A.R. phenol, and 107·5 g. of pure *iso*propyl bromide: the mixture was refluxed for 5 hours. The yield of phenyl *iso*propyl ether, b. p. 174°/758 mm., was 27 g. About 6 g. of ether but no iodide were recovered from the alcohol distillate upon dilution with water.

Phenyl n-*butyl ether.* The quantities employed were 11·5 g. of sodium in 200 ml. of absolute ethyl alcohol, a solution of 47 g. of pure phenol in 50 ml. of absolute ethyl alcohol, and 133 g. of pure, colourless *n*-butyl iodide. The mixture was refluxed for 7 hours, and the alcohol distilled off until fuming commenced. Treatment of the residue with water, etc., gave 60 g. of phenyl *n*-butyl ether, b. p. 207·5°/755 mm.

Phenyl n-*amyl ether.* An excess of halide was not used in this preparation because the iodide and ether appear to form a mixture which passes over with the alcohol. The quantities employed were 11·5 g. of sodium in 250 ml. of absolute ethyl alcohol, a solution of 47 g. of A.R. phenol in 50 ml. of absolute alcohol, and 75·5 g. of *n*-amyl bromide. The mixture was refluxed for 8 hours and the excess of alcohol was distilled off from a water-bath. The residue was diluted with water, the crude phenyl *n*-amyl ether extracted with ether, washed with 10% sodium hydroxide solution, water, dilute sulphuric acid and water, dried ($MgSO_4$), and distilled: the yield of crude ether, b. p. 220—226° (mainly 225°), was 60 g. This was refluxed with 10 g. of sodium for 1 hour and considerable darkening occurred; the ether was distilled off and then fractionated from a little fresh sodium. The yield was 45 g.; b. p. 226·5°/751 mm. The large loss upon treatment with sodium is noteworthy; some reaction appears to take place. This was the only phenyl alkyl ether purified in this manner.

Phenyl n-*hexyl ether.* The quantities employed were 11·5 g. of sodium in 250 ml. of absolute alcohol, 47 g. of pure phenol in 50 ml. of absolute alcohol, and 82 g. of *n*-hexyl bromide. The mixture was refluxed for 6 hours and yielded, after working up as usual and two distillations, 60 g.of phenyl *n*-hexyl ether, b. p. 245·5°/761 mm.

Phenyl allyl ether. This was prepared by refluxing a mixture of 47 g. of A.R. phenol, 60·5 g. of allyl bromide (b. p. 70—71°/750 mm.), 70 g. of A.R. potassium carbonate, and 75 g. of A.R. acetone for 10 hours on a water-bath (compare Claisen, *Annalen*, 1918, **418**, 78), and pouring the product into excess of water. The upper layer was separated, dissolved in ether, washed twice with dilute sodium hydroxide solution and twice with water, and then dried ($MgSO_4$). After removal of the solvent, the liquid was distilled, and yielded 50 g. of crude phenyl allyl ether, b. p. 185—194° (largely 189—191°). Redistillation gave the pure ether, b. p. 190·5°/765 mm.

141. *Diethyl ether.* B. p. 34·0°/774 mm.; M 74·12; n_C 1·35079, n_D 1·35272, n_F 1·35701, $n_{G'}$ 1·35990; R_C 22·40, R_D 22·51, R_F 22·76, $R_{G'}$ 22·92; $Mn_D^{20°}$ 100·26. Densities determined: $d_{4°}^{20°}$ 0·7135, $d_{4°}^{23·6°}$ 0·7094. Apparatus *A*.

(These headings apply to corresponding columns in all the following tables.)

t.	H.	$d_{4°}^{t°}$.	γ.	P.	t.	H.	$d_{4°}^{t°}$.	γ.	P.
18·4°	12·88	0·7153	17·25	211·5	29·4°	12·35	0·7028	16·25	212·3
23·6	12·63	0·7094	16·78	212·0				Mean	211·9

142. *Di*-n-*propyl ether.* B. p. 90—90·5°/768 mm.; M 102·17; n_C 1·37862, n_D 1·38086, n_F 1·38553, $n_{G'}$ 1·38889; R_C 31·51, R_D 31·68, R_F 32·02, $R_{G'}$ 32·27; $Mn_D^{20°}$ 141·09. Densities determined: $d_{4°}^{20°}$ 0·7487, $d_{4°}^{40·8°}$ 0·7288, $d_{4°}^{61·1°}$ 0·7088. Apparatus *D*.

21·7°	11·02	0·7470	20·33	290·4	59·8°	9·32	0·7101	16·34	290·3
42·4	10·13	0·7262	18·17	290·5				Mean	290·4

143. *Diisopropyl ether.* B. p. 68°/753 mm.; M 102·17; n_C 1·36637, n_D 1·36823, n_F 1·37262, $n_{G'}$ 1·37572; R_C 31·57, R_D 31·71, R_F 32·05, $R_{G'}$ 32·29; $Mn_D^{20°}$ 139·79. Densities determined: $d_{4°}^{20°}$ 0·7257, $d_{4°}^{40·7°}$ 0·7029, $d_{4°}^{58·1°}$ 0·6824. Apparatus *B*.

t.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.	t.	N.	$d_{4^\circ}^{t^\circ}$.	γ.	P.
14·1°	10·71	0·7323	18·39	288·9	40·7°	9·51	0·7029	15·67	289·2
24·4	10·26	0·7208	17·34	289·3	56·7	8·68	0·6840	13·92	289·5
								Mean	289·2

144. *Di*-n-*butyl ether*. B. p. 141°/765 mm.; M 130·22; n_C 1·39685, n_D 1·39896, n_F 1·40387, $n_{G'}$ 1·40741; R_C 40·69, R_D 40·89, R_F 41·33, $R_{G'}$ 41·65; $Mn_D^{20^\circ}$ 182·18. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7704, $d_{4^\circ}^{40\cdot8^\circ}$ 0·7512, $d_{4^\circ}^{60\cdot2^\circ}$ 0·7342, $d_{4^\circ}^{85\cdot7^\circ}$ 0·7117. Apparatus *B*.

12·5°	12·82	0·7771	23·65	369·5	61·8°	10·85	0·7328	18·88	370·4
40·9	11·76	0·7511	20·97	370·9	85·7	9·98	0·7117	16·86	370·8
								Mean	370·4

145. *Di*-n-*amyl ether*. B. p. 184°/739 mm.; M 158·28; n_C 1·40983, n_D 1·41192, n_F 1·41703, $n_{G'}$ 1·42064; R_C 49·94, R_D 50·17, R_F 50·71, $R_{G'}$ 51·10; $Mn_D^{20^\circ}$ 223·48. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7849, $d_{4^\circ}^{40\cdot6^\circ}$ 0·7676, $d_{4^\circ}^{61\cdot7^\circ}$ 0·7506, $d_{4^\circ}^{86\cdot4^\circ}$ 0·7310. Apparatus *A*.

12·0°	17·26	0·7915	25·58	449·7	63·8°	14·74	0·7489	20·67	450·6
20·4	16·91	0·7846	24·84	450·7	87·5	13·66	0·7301	18·67	450·7
40·7	15·85	0·7675	22·78	450·4				Mean	450·4

146A. *Di*iso*amyl ether* (from Bisol fermentation *iso*amyl alcohol). B. p. 172°/762 mm.; M 158·28; n_C 1·40575, n_D 1·40785, n_F 1·41291, $n_{G'}$ 1·41656; R_C 50·05, R_D 50·28, R_F 50·82, $R_{G'}$ 51·22; $Mn_D^{20^\circ}$ 222·84. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7765, $d_{4^\circ}^{61\cdot2^\circ}$ 0·7433, $d_{4^\circ}^{86\cdot5^\circ}$ 0·7221, $d_{4^\circ}^{121\cdot8^\circ}$ 0·6941. Apparatus *A*.

15·1°	16·05	0·7805	23·46	446·3	87·3°	12·71	0·7215	17·23	446·7
24·4	15·66	0·7729	22·66	446·8	119·5	11·20	0·6960	14·60	444·5
61·0	13·95	0·7435	19·42	446·9				Mean	446·2

146B. *Di*iso*amyl ether* (from Sharples synthetic *iso*amyl alcohol). B. p. 171°/758 mm.; M 158·28; n_C 1·40642, n_D 1·40850, n_F 1·41355, $n_{G'}$ 1·41716; R_C 50·04, R_D 50·27, R_F 50·82, $R_{G'}$ 51·21; $Mn_D^{20^\circ}$ 222·94. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7777, $d_{4^\circ}^{41\cdot8^\circ}$ 0·7605, $d_{4^\circ}^{63\cdot3^\circ}$ 0·7438, $d_{4^\circ}^{87\cdot0^\circ}$ 0·7237. Apparatus *A*.

21·7°	15·72	0·7763	22·85	445·8	60·3°	13·86	0·7462	19·37	445·0
28·0	15·45	0·7713	22·31	446·0	86·2	12·70	0·7243	17·22	445·2
40·1	14·95	0·7619	21·33	446·4				Mean	445·7

147. *Di*-n-*hexyl ether*. B. p. 223°/763 mm.; M 186·33; n_C 1·41829, n_D 1·42041, n_F 1·42560, $n_{G'}$ 1·42943; R_C 59·22, R_D 59·48, R_F 60·12, $R_{G'}$ 60·59; $Mn_D^{20^\circ}$ 264·66. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7934, $d_{4^\circ}^{40\cdot2^\circ}$ 0·7782, $d_{4^\circ}^{61\cdot6^\circ}$ 0·7628, $d_{4^\circ}^{86\cdot9^\circ}$ 0·7435. Apparatus *A*.

21·4°	17·26	0·7924	25·61	529·0	62·3	15·59	0·7623	22·25	530·9
25·3	17·19	0·7894	25·41	529·9	86·0	14·41	0·7442	20·08	530·0
41·7	16·39	0·7771	23·85	529·9				Mean	529·9

148. *Di*-n-*heptyl ether*. B. p. 258·5°/769; M 214·38; n_C 1·42531, n_D 1·42747, n_F 1·43281, $n_{G'}$ 1·43669; R_C 68·50, R_D 68·81, R_F 69·55, $R_{G'}$ 70·09; $Mn_D^{20^\circ}$ 306·03. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8008, $d_{4^\circ}^{40\cdot6^\circ}$ 0·7869, $d_{4^\circ}^{60\cdot7^\circ}$ 0·7728, $d_{4^\circ}^{86\cdot9^\circ}$ 0·7537. Apparatus *D*.

16·2°	13·79	0·8034	27·36	610·3	43·4°	12·91	0·7850	25·03	610·7
19·2	13·65	0·8014	27·02	609·9	62·1	12·26	0·7718	23·37	610·7
29·9	13·33	0·7940	26·14	610·5	86·0	11·49	0·7531	21·37	612·1
								Mean	610·7

149. *Di*-n-*octyl ether*. B. p. 288°/778 mm.; M 242·43; n_C 1·43049, n_D 1·43269, n_F 1·43803, $n_{G'}$ 1·44199; R_C 77·75, R_D 78·10, R_F 78·93, $R_{G'}$ 79·56; $Mn_D^{20^\circ}$ 347·34. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8063, $d_{4^\circ}^{41\cdot5^\circ}$ 0·7920, $d_{4^\circ}^{62\cdot3^\circ}$ 0·7781, $d_{4^\circ}^{86\cdot6^\circ}$ 0·7612. Apparatus *A*.

25·4°	18·13	0·8027	27·25	690·0	61·4°	16·63	0·7787	24·25	691·7
41·3	17·50	0·7922	26·02	691·2	85·6	15·63	0·7617	22·29	691·6
								Mean	691·1

150. *Methyl* n-*butyl ether*. B. p. 70·5°/766 mm.; M 88·15; n_C 1·37179, n_D 1·37364, n_F 1·37819, $n_{G'}$ 1·38138; R_C 26·90, R_D 27·02, R_F 27·32, $R_{G'}$ 27·52; $Mn_D^{20^\circ}$ 121·08. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7443, $d_{4^\circ}^{41\cdot4^\circ}$ 0·7237. Apparatus *A*.

17·0°	14·52	0·7472	20·32	250·7	26·5°	14·12	0·7381	19·52	251·3
18·3	14·46	0·7459	20·20	250·7	40·9	13·12	0·7242	17·79	250·4
								Mean	250·8

151. *Ethyl* n-*butyl ether*. B. p. 91·5°/757 mm.; M 102·17; n_C 1·37983, n_D 1·38175, n_F 1·38645, $n_{G'}$ 1·38965; R_C 31·58, R_D 31·73, R_F 32·08, $R_{G'}$ 32·31; $Mn_D^{20^\circ}$ 141·18. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7490, $d_{4^\circ}^{40\cdot9^\circ}$ 0·7298, $d_{4^\circ}^{58\cdot0^\circ}$ 0·7132. Apparatus *A*.

16·0°	14·93	0·7527	21·04	290·7	42·3°	13·42	0·7285	18·31	290·4
18·3	14·85	0·7506	20·87	290·9	59·3	12·40	0·7120	16·53	289·8
								Mean	290·5

152. *Methyl* n-*amyl ether*. B. p. 99°/763 mm.; *M* 102·17; n_C 1·38534, n_D 1·38729, n_F 1·39213, $n_{G'}$ 1·39543; R_C 31·50, R_D 31·65, R_F 31·99, $R_{G'}$ 32·24; $Mn_D^{20°}$ 141·74. Densities determined : $d_{4°}^{20°}$ 0·7606, $d_{4°}^{41·4°}$ 0·7406, $d_{4°}^{60·1°}$ 0·7229. Apparatus *D*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
18·0°	11·74	0·7625	22·11	290·5	42·0°	10·74	0·7400	19·63	290·8
24·0	11·50	0·7568	21·49	290·7	60·1	9·93	0·7229	17·73	290·4
								Mean	290·6

153. *Ethyl* n-*amyl ether*. B. p. 117·5—118·5°/768 mm.; *M* 116·20; n_C 1·39071, n_D 1·39270, n_F 1·39753, $n_{G'}$ 1·40097; R_C 36·20, R_D 36·36, R_F 36·75, $R_{G'}$ 37·04; $Mn_D^{20°}$ 161·83. Densities determined : $d_{4°}^{20°}$ 0·7622, $d_{4°}^{41·4°}$ 0·7428, $d_{4°}^{60·5°}$ 0·7260, $d_{4°}^{85·5°}$ 0·7019. Apparatus *A*.

16·5°	15·72	0·7654	22·53	330·8	41·7°	14·38	0·7425	20·45	330·9
19·1	15·48	0·7630	22·12	330·3	61·9	13·26	0·7247	17·99	330·6
26·5	15·18	0·7563	21·50	330·8	86·8	11·81	0·7007	15·50	329·7
								Mean	330·5

154. *Methyl* n-*hexyl ether*. B. p. 126°/770 mm.; *M* 116·20; n_C 1·39520, n_D 1·39719, n_F 1·40207, $n_{G'}$ 1·40551; R_C 36·10, R_D 36·26, R_F 36·65, $R_{G'}$ 36·93; $Mn_D^{20°}$ 162·35. Densities determined : $d_{4°}^{20°}$ 0·7721, $d_{4°}^{41·6°}$ 0·7532, $d_{4°}^{61·7°}$ 0·7356, $d_{4°}^{86·7°}$ 0·7129. Apparatus *A*.

14·3°	16·34	0·7771	23·78	330·2	41·5°	14·89	0·7533	21·00	330·2
17·0	16·17	0·7747	32·46	330·1	61·6	13·82	0·7357	19·04	330·0
24·3	15·91	0·7683	22·89	330·8	85·9	12·51	0·7136	16·72	329·7
26·5	15·77	0·7664	22·63	330·7				Mean	330·2

155. *Ethyl* n-*hexyl ether*. B. p. 142—143°/773 mm.; *M* 130·22; n_C 1·39881, n_D 1·40082, n_F 1·40576, $n_{G'}$ 1·40936; R_C 40·77, R_D 40·95, R_F 41·41, $R_{G'}$ 41·73; $Mn_D^{20°}$ 182·41. Densities determined : $d_{4°}^{20°}$ 0·7722, $d_{4°}^{41·2°}$ 0·7541, $d_{4°}^{61·1°}$ 0·7373, $d_{4°}^{87·0°}$ 0·7138. Apparatus *D*.

14·5°	12·39	0·7770	22·08	370·1	61·4°	10·50	0·7370	19·11	369·4
42·1	11·29	0·7533	21·00	370·6	87·7	9·46	0·7132	16·66	369·0
								Mean	369·8

156. 2 : 2′-*Dichlorodiethyl ether*. B. p. 178°/744 mm.; *M* 143·02; n_C 1·45475, n_D 1·45717, n_F 1·46305, $n_{G'}$ 1·46744; R_C 31·80, R_D 31·94, R_F 32·30, $R_{G'}$ 32·55; $Mn_D^{20°}$ 207·45. Densities determined : $d_{4°}^{20°}$ 1·2199, $d_{4°}^{41·8°}$ 1·1953, $d_{4°}^{61·0°}$ 1·1731, $d_{4°}^{86·7°}$ 1·1436. Apparatus *D*.

14·9°	12·75	1·2257	38·59	290·8	42·3°	11·87	1·1947	35·02	291·2
19·3	12·57	1·2207	37·89	290·7	61·9	11·26	1·1721	32·59	291·6
26·1	12·43	1·2127	37·23	291·3	86·6	10·46	1·1437	29·54	291·6
								Mean	291·2

157. *Diethyleneglycol diethyl ether* ("*diethyl carbitol*"). B. p. 187—187·5°/775 mm.; *M* 162·22; n_C 1·40940, n_D 1·41147, n_F 1·41648, $n_{G'}$ 1·42007; R_C 44·29, R_D 44·49, R_F 44·97, $R_{G'}$ 45·31; $Mn_D^{20°}$ 228·97. Densities determined : $d_{4°}^{20°}$ 0·9063, $d_{4°}^{42·0°}$ 0·8863, $d_{4°}^{60·1°}$ 0·8690, $d_{4°}^{87·1°}$ 0·8435. Apparatus *A*.

15·9°	16·21	0·9101	27·62	408·6	42·1°	15·09	0·8862	25·10	409·5
22·1	15·94	0·9043	26·99	408·9	63·2	14·10	0·8661	22·87	409·6
26·1	15·82	0·9006	26·68	409·1	87·9	11·99	0·8427	18·92	410·8
								Mean	409·4

158. *Tetraethyleneglycol dimethyl ether* ("*dimethoxy tetraglycol*"). B. p. 266—267°/767 mm. (uncorr.); *M* 222·28; n_C 1·43032, n_D 1·43249, n_F 1·43782, $n_{G'}$ 1·44171; R_C 56·96, R_D 57·21, R_F 57·82, $R_{G'}$ 58·27; $Mn_D^{20°}$ 318·42. Densities determined : $d_{4°}^{20°}$ 1·0087, $d_{4°}^{41·4°}$ 0·9912, $d_{4°}^{60·2°}$ 0·9749, $d_{4°}^{85·7°}$ 0·9514. Apparatus *D*.

20·5°	13·58	1·0083	33·84	531·6	60·7°	12·38	0·9745	29·79	532·9
41·9	12·96	0·9908	31·71	532·4	86·3	11·56	0·9509	27·15	533·6
								Mean	532·6

159. *Anisole*. B. p. 151°/736 mm.; *M*108·13; n_C 1·51298, n_D 1·51779, n_F 1·53043, $n_{G'}$ 1·54061; R_C 32·63, R_D 32·88, R_F 33·55, $R_{G'}$ 34·09; $Mn_D^{20°}$ 164·12. Densities determined : $d_{4°}^{20°}$ 0·9961, $d_{4°}^{60·4°}$ 0·9585 $d_{4°}^{86·7°}$ 0·9339, $d_{4°}^{120·9°}$ 0·9010. Apparatus *A*.

13·4°	19·46	1·0022	36·52	265·2	87·1°	15·71	0·9335	27·46	265·2
23·7	19·03	0·9927	35·37	265·6	120·3	14·09	0·9016	23·79	265·3
61·5	17·08	0·9575	30·57	265·5				Mean	265·4

160. *Phenetole*. B. p. 169°/766 mm.; *M* 122·16; n_C 1·50283, n_D 1·50736, n_F 1·51905, $n_{G'}$ 1·52877; R_C 37·42, R_D 37·70, R_F 38·44, $R_{G'}$ 39·04; $Mn_D^{20°}$ 184·14. Densities determined : $d_{4°}^{20°}$ 0·9648, $d_{4°}^{4·00°}$ 0·9472, $d_{4°}^{59·6°}$ 0·9295, $d_{4°}^{86·9°}$ 0·9040. Apparatus *C*.

18·9°	14·49	0·9658	33·15	304·1	61·2°	12·83	0·9290	28·30	303·3
22·0	14·37	0·9630	32·85	303·7	86·8	11·98	0·9041	25·71	304·3
40·2	13·59	0·9470	30·55	303·3				Mean	303·7

161. *Phenyl* n-*propyl ether*. B. p. 187°/751 mm.; M 136·19; n_C 1·49705, n_D 1·51034, n_F 1·51228, $n_{G'}$ 1·52127; R_C 41·98, R_D 42·28, R_F 43·07, $R_{G'}$ 43·70; $Mn_D^{20°}$ 204·26. Densities determined: $d_{4°}^{20°}$ 0·9494, $d_{4°}^{41·2°}$ 0·9312, $d_{4°}^{60·6°}$ 0·9141, $d_{4°}^{86·2°}$ 0·8914. Apparatus *A*.

t.	H.	$d_{4°}^{t°}$.	γ.	P.	t.	H.	$d_{4°}^{t°}$.	γ.	P.
19·5°	18·11	0·9498	32·21	341·6	61·5°	16·23	0·9133	27·76	342·3
25·8	17·85	0·9453	31·60	341·6	86·7	15·06	0·8910	25·13	342·2
41·5	17·13	0·9309	29·86	342·0				Mean	341·9

162. *Phenyl* iso*propyl ether*. B. p. 174°/758 mm.; M 136·19; n_C 1·49328, n_D 1·49753, n_F 1·50837, $n_{G'}$ 1·51732; R_C 42·09, R_D 42·39, R_F 43·18, $R_{G'}$ 43·81; $Mn_D^{20°}$ 203·95. Densities determined: $d_{4°}^{20°}$ 0·9408, $d_{4°}^{41·0°}$ 0·9221, $d_{4°}^{60·1°}$ 0·9037, $d_{4°}^{85·2°}$ 0·8805. Apparatus *A*.

18·9°	17·53	0·9418	30·91	341·0	61·0°	15·62	0·9029	26·41	341·9
25·2	17·33	0·9360	30·37	341·6	86·0	14·52	0·8798	23·92	342·3
40·7	16·55	0·9224	28·58	341·4				Mean	341·6

163. *Phenyl* n-*butyl ether*. B. p. 207·5°/755 mm.; M 150·21; n_C 1·49297, n_D 1·49708, n_F 1·50747, $n_{G'}$ 1·51603; R_C 46·73, R_D 47·06, R_F 47·90, $R_{G'}$ 48·57; $Mn_D^{20°}$ 224·88. Densities determined: $d_{4°}^{20°}$ 0·9341, $d_{4°}^{41·5°}$ 0·9169, $d_{4°}^{61·5°}$ 0·9002, $d_{4°}^{85·8°}$ 0·8793. Apparatus *A*.

18·7°	18·09	0·9352	31·68	381·1	60·9°	16·28	0·9007	27·46	381·7
25·4	17·72	0·9297	30·85	380·8	86·4	15·24	0·8788	25·08	382·5
40·4	17·13	0·9179	29·44	381·2				Mean	381·7

164. *Phenyl* n-*amyl ether*. B. p. 226·5°/751 mm.; M 164·24; n_C 1·49074, n_D 1·49469, n_F 1·50466, $n_{G'}$ 1·51239; R_C 51·28, R_D 51·64, R_F 52·52, $R_{G'}$ 53·20; $Mn_D^{20°}$ 245·49. Densities determined: $d_{4°}^{20°}$ 0·9270, $d_{4°}^{39·9°}$ 0·9111, $d_{4°}^{60·0°}$ 0·8948, $d_{4°}^{84·3°}$ 0·8756. Apparatus *E*.

14·7°	14·58	0·9312	32·23	420·2	60·3°	13·15	0·8946	27·93	422·0
41·3	13·77	0·9100	29·75	421·5	87·7	12·25	0·8729	25·39	422·3
								Mean	421·5

165. *Phenyl* n-*hexyl ether*. B. p. 244·5°/761 mm.; M 178·26; n_C 1·48825, n_D 1·49203, n_F 1·50166, $n_{G'}$ 1·50938; R_C 56·00, R_D 56·38, R_F 57·32, $R_{G'}$ 58·06; $Mn_D^{20°}$ 265·99. Densities determined: $d_{4°}^{20°}$ 0·9174, $d_{4°}^{40·5°}$ 0·9024, $d_{4°}^{60·9°}$ 0·8872, $d_{4°}^{86·7°}$ 0·8670. Apparatus *D*.

17·3°	13·82	0·9193	31·38	459·0	61·5°	12·60	0·8868	27·59	460·8
24·5	13·68	0·9141	30·88	459·8	86·9	11·85	0·8669	25·37	461·5
41·3	13·22	0·9018	29·44	460·5				Mean	460·3

166. *Phenyl allyl ether*. B. p. 190·5°/765 mm.; M 134·17; n_C 151746, n_D 1·52232, n_F 1·53480, $n_{G'}$ 1·54475; R_C 41·41, R_D 41·73, R_F 42·68, $R_{G'}$ 43·23; $Mn_D^{20°}$ 204·25. Densities determined: $d_{4°}^{20°}$ 0·9811, $d_{4°}^{42·4°}$ 0·9609, $d_{4°}^{62·0°}$ 0·9439, $d_{4°}^{86·5°}$ 0·9212. Apparatus *D*.

18·0°	14·00	0·9829	33·98	329·6	41·5°	13·28	0·9617	31·54	330·6
25·4	13·87	0·9762	33·44	330·5	86·9	11·69	0·9208	26·58	330·9
								Mean	330·4

Ethers derived from Formaldehyde and Acetaldehyde.—Methylal. The commercial product was repeatedly refluxed and distilled from sodium until the latter was unaffected; b. p. 41·5°/754 mm.

Ethylal. The commercial product was shaken with a mixture of "20-volume" hydrogen peroxide and 2% sodium carbonate solution at 40—45° (compare Adams, *J. Amer. Chem. Soc.*, 1925, **47**, 1366), then twice with water, dried (K_2CO_3), and refluxed with and finally distilled from sodium; b. p. 86·5—87°/749 mm.

n-*Propylal.* The commercial product was purified as under ethylal; b. p. 136·5°/751 mm.

n-*Butylal.* The following modification of Trillatt and Cambier's method (*Bull. Soc. chim.*, 1894, **11**, 754) was employed. A mixture of 15 g. of pure paraformaldehyde, 74 g. of pure *n*-butyl alcohol, and 2 g. of A.R. anhydrous ferric chloride was refluxed for 10 hours. The lower layer (3—4 ml.) was discarded and the iron in solution in the residue was removed as ferric hydroxide by shaking with 50 ml. of 10% sodium carbonate solution; the product was shaken with a mixture of 40 ml. of "20-volume" hydrogen peroxide and 5 ml. of 10% sodium carbonate solution at 45° (to remove any residual aldehyde), washed with water, and dried (K_2CO_3). Distillation from excess of sodium yielded 62 g. of crude *n*-butylal, b. p. 170—185°. Repeated refluxing with and distillation from sodium gave the pure ether of b. p. 180·5°/760 mm.

iso*Butylal.* A mixture of 15 g. of paraformaldehyde, 74 g. of pure *iso*butyl alcohol, and 2 g. of anhydrous ferric chloride yielded, as for *n*-butylal, 57 g. of crude *iso*butylal, b. p. 155—170°. Repeated distillation over sodium gave the pure compound, b. p. 163·5—164°/766 mm.

n-*Amylal.* A mixture of 15 g. of paraformaldehyde, 88 g. of *n*-amyl alcohol (b. p. 137°/733 mm.), and 2 g. of A.R. anhydrous ferric chloride gave, as before, 55 g. of crude *n*-amylal, b. p. 210—220°. Repeated distillation from sodium afforded the pure compound, b. p. 218·5—219°/761 mm.

n-*Hexylal.* A mixture of 15 g. of paraformaldehyde, 102 g. of *n*-hexyl alcohol (b. p. 156—157°/752 mm.), and 2 g. of anhydrous ferric chloride gave 75 g. of crude *n*-hexylal, b. p. 253—260°. Two distillations from sodium yielded the pure compound, b. p. 255—255·5°/770 mm.

iso*Propylal.* A mixture of 15 g. of paraformaldehyde, 60 g. of pure *iso*propyl alcohol and 2 g. of A.R. anhydrous ferric chloride furnished 28 g. of crude *iso*propylal, b. p. 119—123°. The pure compound, b. p. 120·5—121°/765 mm., was obtained after two distillations from sodium.

Dimethyl acetal, $CH_3\cdot CH(OCH_3)_2$. The pure commercial product was treated with alkaline hydrogen peroxide solution at 40—45° (owing to the solubility of the compound in water, it was necessary to saturate the solution with salt), dried (K_2CO_3), and distilled from sodium; b. p. 64°/762 mm.

Diethyl acetal. The commercial product was purified as for dimethyl acetal; b. p. 102·5°/755 mm.

Di-n-propyl acetal. A mixture of 44 g. of paraldehyde, 150 g. of pure *n*-propyl alcohol, and 4 g. of *p*-toluenesulphonic acid was refluxed for 8 hours. The excess of acid was removed by washing with a solution containing 2·5 g. of anhydrous sodium carbonate; shaking with a mixture of 50 ml. of " 20-volume " hydrogen peroxide and 10 ml. of 10% sodium carbonate solution at 40—45° removed any residual aldehyde. The product was dried (K_2CO_3) and fractionally distilled: 89 g. of unchanged alcohol were recovered at 88—101° and the yield of crude acetal, b. p. 142—148°, was 52 g. Two distillations from sodium gave the pure compound, b. p. 147—147·5°/760 mm.

Di-n-butyl acetal. A mixture of 44 g. of paraldehyde, 187·5 g. of pure *n*-butyl alcohol, and 5 g. of *p*-toluenesulphonic acid yielded, as detailed for di-*n*-propyl acetal, 67 g. of unreacted, but impure, *n*-butyl alcohol, b. p. 110—120°, and 115 g. of crude di-*n*-butyl acetal, b. p. 181—188°. Two distillations from sodium afforded the pure acetal, b. p. 187·5°/774 mm.

Diisobutyl acetal. The reaction between 33 g. of paraldehyde, 127 g. of pure *iso*butyl alcohol, and 3 g. of *p*-toluenesulphonic acid yielded, as detailed for di-*n*-propyl acetal, 41 g. of impure unreacted *iso*butyl alcohol, b. p. 105—115°, and 70 g. of crude di*iso*butyl acetal, b. p. 167—170°. The pure acetal, b. p. 169·5—170°/757 mm., was obtained after one distillation from sodium.

167. *Methylal.* B. p. 41·5°/754 mm.; M 60·09; n_C 1·35134, n_D 1·35298, n_F 1·35704, $n_{G'}$ 1·35986; R_C 19·12, R_D 19·20, R_F 19·40, $R_{G'}$ 19·54; $Mn_D^{20°}$ 102·95. Densities determined: $d_{4°}^{20.0°}$ 0·8593, $d_{4°}^{14.0°}$ 0·8669. Apparatus *A*.

t.	H.	$d_{4°}^{t°}$.	γ.	P.	t.	H.	$d_{4°}^{t°}$.	γ.	P.
14·5°	13·52	0·8661	21·93	190·4	24·2°	12·91	0·8541	20·65	190·3
18·5	13·23	0·8612	21·33	190·3				Mean	190·3

168. *Ethylal.* B. p. 86·5—87°/749 mm.; M 104·15; n_C 1·37072, n_D 1·37262, n_F 1·37691, $n_{G'}$ 1·37996; R_C 28·40, R_D 28·53, R_F 28·83, $R_{G'}$ 29·04; $Mn_D^{20°}$ 142·96. Densities determined: $d_{4°}^{20°}$ 0·8308, $d_{4°}^{40.2°}$ 0·8094, $d_{4°}^{59.3°}$ 0·7893. Apparatus *A*.

18·5°	13·74	0·8323	21·41	269·2	40·7°	12·53	0·8089	18·98	269·0
21·1	13·55	0·8297	21·05	268·9	59·7	11·49	0·7889	15·97	268·5
								Mean	268·9

169. n-*Propylal.* B. p. 136·5°/751 mm.; M 132·20, n_C 1·39068, n_D 1·39261, n_F 1·39728, $n_{G'}$ 1·40056; R_C 37·64, R_D 37·80, R_F 38·20, $R_{G'}$ 38·48; $Mn_D^{20°}$ 184·07. Densities determined: $d_{4°}^{20°}$ 0·8338, $d_{4°}^{40.9°}$ 0·8139, $d_{4°}^{58.8°}$ 0·7974, $d_{4°}^{85.1°}$ 0·7716. Apparatus *D*.

16·6°	11·44	0·8360	23·62	348·6	60·0°	9·88	0·7963	19·43	348·5
21·3	11·27	0·8326	23·17	348·3	85·1	8·94	0·7716	17·11	348·0
40·7	10·55	0·8141	21·21	348·4				Mean	348·4

170. n-*Butylal.* B. p. 180·5°/760 mm.; M 160·25; n_C 1·40374, n_D 1·40573, n_F 1·41062, $n_{G'}$ 1·41410; R_C 46·89, R_D 47·09, R_F 47·59, $R_{G'}$ 47·95; $Mn_D^{20°}$ 225·27. Densities determined: $d_{4°}^{20°}$ 0·8354, $d_{4°}^{40.5°}$ 0·8191, $d_{4°}^{60.9°}$ 0·8023, $d_{4°}^{85.9°}$ 0·7813. Apparatus *A*.

17·4°	15·77	0·8375	24·74	426·7	40·7	14·82	0·8187	22·72	427·3
22·7	15·62	0·8332	24·37	427·3	61·5	13·93	0·8018	20·87	427·4
25·5	15·54	0·8309	24·18	427·7	86·4	12·83	0·7809	18·76	427·1
								Mean	427·3

171. iso*Butylal.* B. p. 163·5—164°/766 mm.; M 160·25; n_C 1·39833, n_D 1·40029, n_F 1·40515, $n_{G'}$ 1·40868; R_C 46·95, R_D 47·15, R_F 47·66, $R_{G'}$ 48·02; $Mn_D^{20°}$ 224·40. Densities determined: $d_{4°}^{20°}$ 0·8244, $d_{4°}^{41.1°}$ 0·8063, $d_{4°}^{61.5°}$ 0·7886, $d_{4°}^{87.0°}$ 0·7654. Apparatus *A*.

21·0°	14·64	0·8235	22·57	424·2	61·3°	12·85	0·7888	18·98	424·0
40·9	13·77	0·8065	20·80	424·3	87·0	11·74	0·7654	16·83	424·0
								Mean	424·1

172. n-*Amylal.* B. p. 218·5—219°/761 mm.; M 188·30; n_C 1·41419, n_D 1·41626, n_F 1·42127, n_G 1·42489; R_C 56·13, R_D 56·38, R_F 56·97, $R_{G'}$ 57·40; $Mn_D^{20°}$ 266·69. Densities determined: $d_{4°}^{20°}$ 0·8387, $d_{4°}^{41.0°}$ 0·8221, $d_{4°}^{60.9°}$ 0·8066, $d_{4°}^{85.9°}$ 0·7868. Apparatus *D*.

16·3°	12·68	0·8416	26·35	506·9	41·4°	11·85	0·8219	24·00	507·1
19·8	12·51	0·8389	25·92	506·5	60·8	11·14	0·8067	22·19	506·6
23·3	12·41	0·8361	25·62	506·6	87·2	10·38	0·7858	19·68	504·8
								Mean	506·4

173. n-*Hexylal.* B. p. 255—255·5°/770 mm.; M 216·35; n_C 1·42130, n_D 1·42341, n_F 1·42856, $n_{G'}$ 1·43216; R_C 65·26, R_D 65·55, R_F 66·25, $R_{G'}$ 66·74; $Mn_D^{20°}$ 307·95. Densities determined: $d_{4°}^{20°}$ 0·8412, $d_{4°}^{40.7°}$ 0·8255, $d_{4°}^{62.0°}$ 0·8098, $d_{4°}^{86.1°}$ 0·7912. Apparatus *D*.

17·4°	13·11	0·8432	27·30	586·5	61·9°	11·72	0·8099	23·44	587·8
21·0	12·98	0·8404	26·90	586·5	87·0	10·95	0·7905	21·38	588·5
41·3	12·37	0·8250	25·20	587·6				Mean	587·4

174. iso*Propylal.* B. p. 120·5—121°/765 mm.; M 132·20; n_C 1·38227, n_D 1·38413, n_F 1·38870, $n_{G'}$ 1·39194; R_C 37·64, R_D 37·79, R_F 38·19, $R_{G'}$ 38·47; $Mn_D^{20°}$ 182·98. Densities determined: $d_{4°}^{20°}$ 0·8181, $d_{4°}^{43·2°}$ 0·7965, $d_{4°}^{61·7°}$ 0·7786, $d_{4°}^{86·6°}$ 0·7536. Apparatus D.

t.	H.	$d_{4°}^{t°}$.	γ.	P.	t.	H.	$d_{4°}^{t°}$.	γ.	P.
20·3°	10·39	0·8178	20·98	346·0	59·9°	9·07	0·7794	17·46	346·7
22·1	10·32	0·8160	20·80	346·0	86·3	8·13	0·7539	15·14	346·5
41·4	9·64	0·7982	19·00	345·8				Mean	346·2

175. *Dimethyl acetal,* $CH_3·CH(OCH_3)_2$. B. p. 64°/762 mm.; M 90·12; n_C 1·36472, n_D 1·36646, n_F 1·37066, $n_{G'}$ 1·37359; R_C 23·63, R_D 23·73, R_F 23·98, $R_{G'}$ 24·14; $Mn_D^{20°}$ 123·15. Densities determined: $d_{4°}^{20°}$ 0·8516, $d_{4°}^{41·0°}$ 0·8279, $d_{4°}^{60·4°}$ 0·8063. Apparatus D.

15·3°	10·45	0·8569	22·11	228·1	41·3°	9·33	0·8276	19·07	228·0
20·0	10·27	0·8516	21·60	228·1	60·1	8·51	0·8066	16·95	227·5
26·1	10·02	0·8447	20·90	228·1				Mean	228·0

176. *Diethyl acetal.* B. p. 102·5°/755 mm.; M 118·17; n_C 1·37871, n_D 1·38054, n_F 1·38502, n_G 1·38821; R_C 33·02, R_D 33·16, R_F 33·51, $R_{G'}$ 33·76; $Mn_D^{20°}$ 163·13. Densities determined: $d_{4°}^{20°}$ 0·8264, $d_{4°}^{41·6°}$ 0·8042, $d_{4°}^{60·5°}$ 0·7843, $d_{4°}^{86·3°}$ 0·7566. Apparatus D.

15·0°	10·72	0·8316	22·02	307·8	41·5°	9·59	0·8043	19·05	306·9
18·0	10·55	0·8285	21·59	307·5	60·9	8·82	0·7839	17·07	306·9
21·8	10·44	0·8245	21·26	307·7	86·3	7·86	0·7566	14·69	306·7
								Mean	307·3

177. *Di-*n*-propyl acetal.* B. p. 147—147·5°/760 mm.; M 146·22; n_C 1·39476, n_D 1·39670, n_F 1·40142, $n_{G'}$ 1·40470; R_C 42·19, R_D 42·37, R_F 42·81, $R_{G'}$ 43·13; $Mn_D^{20°}$ 204·23. Densities determined: $d_{4°}^{20°}$ 0·8304, $d_{4°}^{41·3°}$ 0·8096, $d_{4°}^{60·8°}$ 0·7914, $d_{4°}^{86·3°}$ 0·7665. Apparatus A.

12·4°	15·22	0·8378	23·88	385·8	41·5°	13·78	0·8094	20·88	386·2
17·3	15·00	0·8330	23·40	386·1	60·3	12·85	0·7919	19·05	385·8
20·2	14·85	0·8302	23·09	386·1	88·3	11·57	0·7646	16·56	385·8
								Mean	386·0

178. *Di-*n*-butyl acetal.* B. p. 187·5°/774 mm.; M 174·28; n_C 1·40650, n_D 1·40850, n_F 1·41333, $n_{G'}$ 1·41698; R_C 51·45, R_D 51·68, R_F 52·21, $R_{G'}$ 52·62; $Mn_D^{20°}$ 245·47. Densities determined: $d_{4°}^{20°}$ 0·8329, $d_{4°}^{41·8°}$ 0·8147, $d_{4°}^{61·1°}$ 0·7989, $d_{4°}^{85·4°}$ 0·7779. Apparatus A.

15·2°	15·81	0·8372	24·78	464·5	41·3°	14·72	0·8151	22·47	465·4
91·3	15·67	0·8338	24·47	464·9	62·1	13·69	0·7981	20·46	464·4
22·0	15·58	0·8315	24·26	465·2	86·1	12·63	0·7773	18·38	464·3
								Mean	464·8

179. *Di*iso*butyl acetal.* B. p. 169·5—170°/757 mm.; M 174·28; n_C 1·40060, n_D 1·40258, n_F 1·40745, $n_{G'}$ 1·41085,; R_C 51·52, R_D 51·75, R_F 52·31, $R_{G'}$ 52·69; $Mn_D^{20°}$ 244·45. Densities determined: $d_{4°}^{20°}$ 0·8211, $d_{4°}^{44·4°}$ 0·7997, $d_{4°}^{61·6°}$ 0·7847, $d_{4°}^{85·9°}$ 0·7626. Apparatus A.

16·3°	14·74	0·8244	22·75	461·7	61·0°	12·77	0·7852	18·78	462·0
22·3	14·48	0·8191	22·21	461·9	85·8	11·60	0·7627	16·57	461·0
41·3	13·62	0·8024	20·46	462·0				Mean	461·7

The author's thanks are due to Dr. G. H. Jeffery, F.R.I.C., for assistance in the development of the procedure for the preparation of the higher symmetrical aliphatic ethers as well as for their actual preparation, and to Dr. D. M. Cowan for the preparation of the phenyl alkyl ethers (except phenyl *n*-amyl ether).

Woolwich Polytechnic, London, S.E.18. [*Received, May* 28*th*, 1947.]