8. *Physical Properties and Chemical Constitution. Part VII. Alkyl Sulphides, Disulphides, Sulphites, Sulphates, and Orthophosphates.*

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The refractive indices for the C, D, F, and G′ lines at 20·0°, and the surface tensions and densities over a range of temperatures, have been determined for numerous alkyl compounds, particularly sulphides and disulphides. The molecular refractivities and parachors have been evaluated. The data obtained have been employed in the calculation of preliminary values for the constants of sulphur and for the contribution of the oxygen atom in alkyl sulphites and sulphates.

The literature contains but few trustworthy experimental results from which the physical constants (refractivities, molecular refraction coefficient, and parachor) of sulphur may be deduced (compare Eisenlohr, "Spektrochemie organischer Verbindungen," 1912, pp. 64 *et seq.*; Sugden, Reed, and Wilkins, J., 1925, **127**, 1533; Baroni, *Atti R. Accad. Lincei*, 1931, **14**, 28; Bezzi, *Gazzetta*, 1935, **65**, 693). The most satisfactory method for evaluating the constants for sulphur is from dialkyl sulphides: new data for a comprehensive series of such compounds are now presented. Since trustworthy figures for carbon and hydrogen are not available (largely because of the uncertainty of the CH_2 value), the necessary calculations will be made in a future communication. For the present, attention is directed to the following results for the various isomeric sulphides.*

Isomeric Alkyl Sulphides.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$\mathrm{MeBu^{\alpha}S}$	280·1	32·92	33·10	33·53	33·94	150·93
$\mathrm{MeBu^{\beta}S}$	279·6	32·99	33·17	33·60	33·93	150·41
$\mathrm{MeBu^{\gamma}S}$	277·9	33·10	33·29	33·73	34·08	150·14
$\mathrm{EtBu^{\alpha}S}$	320·3	37·68	37·89	38·38	38·75	171·29
$\mathrm{EtBu^{\gamma}S}$	317·2	37·93	38·12	38·63	39·02	170·44
$\mathrm{Bu^{\alpha}{}_2S}$	399·3	46·82	47·06	47·64	48·10	212·54
$\mathrm{Bu^{\beta}{}_2S}$	395·4	47·04	47·29	47·90	48·32	211·65
sec.-$\mathrm{Bu_2S}$	395·0	46·90	47·14	47·74	48·19	212·19

* For significance of abbreviations in the Table, see p. 18.

The facile conversion of thiols into disulphides by means of iodine, $2RS^- + I_2 = R{\cdot}S{\cdot}S{\cdot}R$ (I.) $+ 2I^-$, would seem to support formula (I) for disulphides (compare *X*-ray studies of Egartner, Halla, and Schacherl, *Z. physikal. Chem.*, 1932, *B*, **18**, 189). By subtracting the experimental values for sulphides from those of disulphides, a direct determination of the sulphur contribution is obtained. The results are collected below. This, of course, will correspond to linkages of the type C·S·S and may not be identical with C·S·C (deducible from alkyl sulphides alone) (compare Smyth, " Dielectric Constant and Molecular Structure," 1931, p. 152).

Values for Sulphur ($R_2S_2 - R_2S$).

R.	*P*.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Methyl	50·8	7·95	8·02	8·21	8·39	54·53
Ethyl	49·6	8·05	8·14	8·30	8·45	54·13
n-Propyl	49·6	8·04	8·11	8·30	8·47	53·85
*iso*Propyl	50·1	8·02	8·06	8·28	8·42	53·98
n-Butyl	48·4	8·10	8·15	8·35	8·49	53·65
*iso*Butyl	48·0	7·90	7·98	8·14	8·33	53·49
n-Amyl	47·6	8·12	8·21	8·41	8·57	53·44
*iso*Amyl	48·3	7·97	8·04	8·23	8·41	53·53
Mean	49·1	8·019	8·089	8·278	8·441	53·78

The results for isomeric disulphides are presented in the next table.

Isomeric Alkyl Disulphides.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$Bu^{\alpha}{}_2S_2$	447·7	54·92	55·21	55·99	56·59	266·19
$Bu^{\beta}{}_2S_2$	443·4	54·94	55·27	56·04	56·65	265·14
$Bu^{\gamma}{}_2S_2$	440·9	55·54	55·87	56·68	57·31	265·73

In order to provide information as to the nature of the linkage in sulphites and sulphates, measurements have been made on alkyl sulphites and sulphates. By comparison with the corresponding sulphides ($R_2SO_3 - R_2S$ and $R_2SO_4 - R_2S$), the contribution of the oxygen atom may be calculated. The final results are in the following tables.

Contribution of the Oxygen Atom in Alkyl Sulphites, ($R_2SO_3 - R_2S$)/3.

R.	*P*.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Methyl	18·9	1·113	1·110	1·103	1·097	22·00
Ethyl	18·7	1·123	1·127	1·107	1·097	21·79
n-Propyl	18·8	1·167	1·167	1·157	1·147	21·82
*iso*Propyl	18·9	1·090	1·077	1·073	1·057	21·66
n-Butyl	18·1	1·147	1·150	1·140	1·123	20·98
*iso*Butyl	18·4	1·093	1·090	1·073	1·073	21·86
n-Amyl	18·3	1·143	1·140	1·140	1·120	21·82
*iso*Amyl	17·9	1·087	1·080	1·070	1·060	21·96
Mean	18·5	1·120	1·118	1·108	1·097	21·74

Contribution of the Oxygen Atom in Alkyl Sulphates, ($R_2SO_4 - R_2S$)/4.

Methyl	18·7	0·818	0·813	0·790	0·775	21·45
Ethyl	18·7	0·815	0·810	0·780	0·758	21·46
n-Propyl	18·3	0·800	0·793	0·768	0·745	21·57
n-Butyl	17·9	0·808	0·800	0·775	0·753	21·58
Mean	18·2	0·810	0·804	0·778	0·758	21·52

The low values for the refractivities as well as their *decrease* in the series $R_C \longrightarrow R_{G'}$ are noteworthy [compare, *e.g.*, R_D for O (carbonyl) 2·211, O (ether) 1·643, O (hydroxyl) 1·525; Eisenlohr, *op. cit.*, 1912, p. 48; *Z. physikal. Chem.*, 1911, **75**, 585] : these provide new evidence for co-ordinate links in sulphites and sulphates. The subject will be discussed in detail, particularly from the viewpoint of the refraction of election groups (von Steiger, *Ber.*, 1921, **54**, 1381; Smyth, *Phil. Mag.*, 1925, **50**, 361; *op. cit.*, p. 150; Fajans and Knorr, *Ber.*, 1926, **59**, 249), in a later communication.

Measurements upon trialkyl orthophosphates have also been made, but detailed parallel calculations cannot be given because suitable data on the constants of phosphorus are lacking. However, from the scanty refractivity data available [R_D for PEt_3 at 18·6° (Zecchini, *Gazzetta*, 1893, **23**, 97; 1894, **24**, 34); R_C, R_D, and R_F for $PPr^{\alpha}{}_3$ and $PBu^{\alpha}{}_3$ at 25° (Jones, Davies, and Dyke, *J. Physical Chem.*, 1933, **37**, 584)] analogous results are obtained (see below).

Contribution of the Oxygen Atom in Trialkyl Phosphates ($R_3PO_4 - R_3P$)/4.

R.	R_C.	R_D.	R_F.
Ethyl	—	0·370	—
n-Propyl	0·450	0·430	0·375
n-Butyl	0·493	0·435	0·433

A comparison of the properties of *s*.- and *as*.-ethyl sulphite (ethyl ethanesulphonate) is given below.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
s.-Ethyl sulphite	297·6	31·76	31·91	32·27	32·54	195·44
as.- ,, ,,	293·4	30·15	30·21	30·57	30·77	196·27

EXPERIMENTAL.

Physical Measurements.—The surface tensions and refractive indices were determined exactly as described in earlier papers (*e.g.*, Part III, J., 1938, 1325). Four Pyrex surface-tension apparatus *A*, *B*, *C*, and *D* were used, the constants of which, determined with "AnalaR" sodium-dried benzene, were 1·8725, 2·3449, 2·3740, and 2·4696 respectively. Except where another apparatus is specified, apparatus *A* was used. In the determination of the densities, the sample and *all* the apparatus (pycnometer, and the small container for filling it with the sample) were kept in the thermostat at 20° ± 0·01° for at least **3** hours before the actual measurements; the room temperature was maintained as near 20° as possible. This procedure probably gave more trustworthy values of $d_{4^\circ}^{20\cdot0^\circ}$ than those obtained in the earlier measurements.

For convenience of reference all the compounds studied in this and future communications will be numbered in Clarendon type. In the tabulated results t is the temperature, h is the observed difference in height (in mm.) in the two arms of the **U**-tube, H the corrected value, $d_{4^\circ}^{t^\circ}$ the density (calculated from the observed densities by assuming a linear variation with temperature), γ the surface tension (dynes/cm.) computed from the equation $\gamma = KHd$, P the parachor, and $Mn_D^{20^\circ}$ the molecular refraction coefficient. The parachor was calculated in the usual way, allowance for the density of the vapour (computed by Sugden's method, J., 1925, **127**, 1540) being made when the temperature of measurement was within 60° of the b. p. All the measurements of the refractive indices were carried out at 20° ± 0·02°. Where 20° is used, 20·0° is to be understood; n_C, n_D, n_F, $n_{G'}$ are to be taken as referring to $n_C^{20\cdot0^\circ}$, etc.; and R_C, etc., to $[R_L]_C$, etc. Unless otherwise stated, all b. p.'s are corrected.

Previous Work.—Parachor values, the source of which is not indicated, are taken from Sidgwick, Sugden, and Adam (*Brit. Assoc. Rep.*, 1932, 265). Reference is also made to what appears to be the most trustworthy of the earlier values of the refractive indices for comparison; an exhaustive survey of all previous work would serve no useful purpose.

Disulphides and Sulphides.—Most of the original measurements were made with samples supplied by Eastman Kodak. These were rigorously purified by chemical methods and by distillation until $d_{4^\circ}^{20^\circ}$ and $n_D^{20^\circ}$ were constant. Some of the samples were prepared by us (sulphides from alkyl bromides and anhydrous sodium sulphide in alcoholic solution, and disulphides by oxidation of a solution of the sodium thiol with iodine); excellent agreement was obtained in the physical properties of the synthetic and the purchased samples. In order to economise space the results of the measurements on the duplicate preparations will not be given.

The disulphides were first distilled, and the middle fraction was mechanically shaken with one-third of its volume of 5—10% sodium hydroxide solution, this treatment with alkali being repeated twice; the products were then washed with distilled water until neutral, dried with calcium chloride (shaking machine for ½ hour), kept overnight over fresh calcium chloride, filtered, and again dried by shaking with the same desiccant, and distilled to constant $d_{4^\circ}^{20^\circ}$ and $n_D^{20^\circ}$.

The sulphides were similarly purified except that 10—15% alkali solution was used and that for those thio-ethers which were distilled at atmospheric pressure, the final distillation was made from sodium. Where distillation under diminished pressure was necessary, the purified sulphide was first dried over calcium chloride, then refluxed over sodium at 120° for at least 6 hours, filtered, and distilled under diminished pressure to constant $d_{4^\circ}^{20^\circ}$ and $n_D^{20^\circ}$.

1. *Dimethyl disulphide* (Eastman Kodak). B. p. 109·5°/774 mm.; M 94·19; n_C 1·52167, n_D 1·52599, n_F 1·53690, $n_{G'}$ 1·54573; R_C 26·97, R_D 27·15, R_F 27·62, $R_{G'}$ 28·00; $R_{G'-C}$ 1·03, R_{F-C} 0·65; $Mn_D^{20^\circ}$ 143·73. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0647, $d_{4^\circ}^{41\cdot5^\circ}$ 1·0391, $d_{4^\circ}^{61\cdot9^\circ}$ 1·0162, $d_{4^\circ}^{86\cdot5^\circ}$ 0·9886.

t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.	t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.
14·1°	13·95	13·71	1·0715	34·87	213·6	62·3°	12·02	11·78	1·0157	28·40	214·1
41·0	12·89	12·65	1·0397	31·22	214·1					Mean	213·9

2. *Diethyl disulphide.* This was prepared by a modification of Kekulé and Linnemann's method (*Annalen*, 1862, **123**, 277). 77 G. of ethylthiol (Eastman Kodak, b. p. 35°/768 mm.) were dissolved in 350 c.c. of 15% sodium hydroxide solution (calculated quantity for the formation of SEtNa) contained in a 1-litre three-necked Pyrex flask fitted with a mechanical stirrer and a double-surface condenser. Stirring was continued until all the thiol had reacted; the flask was cooled in ice. With constant stirring, 135 g. of pure iodine were gradually added (2 hours) by momentarily removing the rubber bung from the third aperture of the flask and replacing it immediately the iodine had been added. After each addition, the iodine gradually disappeared and an oily layer formed on the surface of the liquid. The mixture was stirred for a further 2·5 hours and kept for 2·5 hours. The colourless upper layer was separated, and the aqueous layer extracted with ether; the combined liquids were washed with one-third the volume of 15% sodium hydroxide solution, then twice with water, and partly dried with calcium chloride, and the ether removed. The resultant colourless liquid was shaken three times with one-third of its volume of 5% sodium hydroxide solution, washed with water until free from alkali, and dried with calcium chloride. The yield of crude product was 53·5 g. (70%); the main bulk boiled constantly at 152°/754 mm.; a middle fraction was collected for the physical measurements. B. p. 152°/754 mm.; M 122·24; n_C 1·50329, n_D 1·50704, n_F 1·51653, $n_{G'}$ 1·52404; R_C 36·44, R_D 36·67, R_F 37·25, $R_{G'}$ 37·70; $R_{G'-C}$ 1·26, R_{F-C} 0·81; $Mn_D^{20^\circ}$ 184·21. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9920, $d_{4^\circ}^{43\cdot6^\circ}$ 0·9702, $d_{4^\circ}^{60\cdot7^\circ}$ 0·9534, $d_{4^\circ}^{90\cdot5^\circ}$ 0·9246.

17·3°	16·99	16·75	0·9946	31·19	290·5	61·4°	15·10	14·86	0·9527	26·51	291·1
41·1	16·05	15·81	0·9726	28·79	291·1	86·2	14·07	13·83	0·9288	24·05	291·5
										Mean	291·1

(Baroni, *loc. cit.*, gives $d_{4^\circ}^{20^\circ}$ 0·9926, P 287·6; Bezzi, *loc. cit.*, gives b. p. 152—154°/760 mm., $d_{4^\circ}^{20^\circ}$ 0·9927, $n_D^{20^\circ}$ 1·5070.)

3. *Di-*n*-propyl disulphide* (Eastman Kodak). B. p. 193·5°/750 mm.; M 150·29; n_C 1·49465, n_D 1·49813, n_F 1·50679, $n_{G'}$ 1·51359; R_C 45·63, R_D 45·90, R_F 46·58, $R_{G'}$ 47·11; $R_{G'-C}$ 1·48, R_{F-C} 0·95; $Mn_D^{20^\circ}$ 225·15. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9599, $d_{4^\circ}^{61\cdot2^\circ}$ 0·9237, $d_{4^\circ}^{86\cdot7^\circ}$ 0·9010.

18·8°	17·29	17·05	0·9609	30·68	368·1	87·3°	14·40	14·16	0·9004	23·87	369·0
61·8	15·43	15·19	0·9232	26·26	368·5					Mean	368·5

(Bezzi, *loc. cit.*, gives b. p. 191—192°/760 mm., $d_{4^\circ}^{20^\circ}$ 0·9525, $n_D^{20^\circ}$ 1·4981.)

4. *Di*iso*propyl disulphide.* This was prepared as for diethyl disulphide except that the iodine was dissolved in 40% aqueous potassium iodide solution, thus permitting the use of a dropping funnel. The quantities used were: 24 g. of *iso*propylthiol (Eastman Kodak, b. p. 50—51°/753 mm.), 12·6 g. of sodium hydroxide dissolved in 85 c.c. of water in a 500-c.c. three-necked flask, and 38 g. (slight defect below theoretical quantity) of iodine in 100 c.c. of 40% aqueous potassium iodide solution. The yield of the crude product was 14 g. B. p. 176°/767 mm.; M 150·29; n_C 1·48812, n_D 1·49164, n_F 1·50021, $n_{G'}$ 1·50687; R_C 45·90, R_D 46·18, R_F 46·87, $R_{G'}$ 47·40; $R_{G'-C}$ 1·50, R_{F-S} 0·86; $Mn_D^{20^\circ}$ 224·17. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9435, $d_{4^\circ}^{41\cdot7^\circ}$ 0·9247, $d_{4^\circ}^{59\cdot6^\circ}$ 0·9085, $d_{4^\circ}^{87\cdot4^\circ}$ 0·8853.

Apparatus *B*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
18·4°	13·15	12·91	0·9449	28·60	367·8	63·0°	11·59	11·35	0·9055	24·06	367·6
41·9	12·37	12·13	0·9245	26·30	368·1	86·4	10·94	10·70	0·8862	22·24	368·3
										Mean	368·0

5. *Di*-n-*butyl disulphide* (Eastman Kodak). B. p. 230·5°/755 mm., 84°/3 mm.; *M* 178·34; n_{C} 1·48950, n_{D} 1·49259, n_{F} 1·50079, $n_{\mathrm{G'}}$ 1·50712; R_{C} 54·92, R_{D} 55·21; R_{F} 55·99, $R_{\mathrm{G'}}$ 56·59; $R_{\mathrm{G'-C}}$ 1·67, $R_{\mathrm{F-C}}$ 1·07; $Mn_{\mathrm{D}}^{20^\circ}$ 266·19. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9383, $d_{4^\circ}^{60\cdot4^\circ}$ 0·9044, $d_{4^\circ}^{85\cdot9^\circ}$ 0·8840.

15·5°	17·82	17·58	0·9419	31·01	446·8	86·3°	15·00	14·76	0·8837	24·42	448·3
61·4	15·96	15·72	0·9036	26·60	448·0					Mean	447·7

(Bezzi, *loc. cit.*, gives b. p. 143—144°/83 mm., $d_{4^\circ}^{20^\circ}$ 0·9306, $n_{\mathrm{D}}^{20^\circ}$ 1·49208.)

6. *Di*iso*butyl disulphide.* This was prepared and purified as described under **2**. 43·5 G. of *iso*butylthiol (Eastman Kodak, b. p. 87·5°/764 mm.), 135 c.c. of 15% sodium hydroxide solution, and 52 g. of solid iodine yielded 37 g. of crude disulphide. B. p. 215°/767 mm. and 76·5°/5 mm.; *M* 178·34; n_{C} 1·48342, n_{D} 1·48666, n_{F} 1·49471, $n_{\mathrm{G'}}$ 1·50102; R_{C} 54·94, R_{D} 55·27, R_{F} 56·04, $R_{\mathrm{G'}}$ 56·65; $R_{\mathrm{G'-C}}$ 1·71, $R_{\mathrm{F-C}}$ 1·10; $Mn_{\mathrm{D}}^{20^\circ}$ 265·14. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9275, $d_{4^\circ}^{41\cdot4^\circ}$ 0·9090, $d_{4^\circ}^{61\cdot6^\circ}$ 0·8922, $d_{4^\circ}^{86\cdot3^\circ}$ 0·8718.

17·1°	16·49	16·25	0·9298	28·29	442·2	60·7°	14·80	14·56	0·8929	24·34	443·7
41·6	15·53	15·29	0·9088	26·02	443·2	86·2	13·87	13·63	0·8719	22·25	444·3
										Mean	443·4

7. *Di*-tert.-*butyl disulphide.* This was prepared from 30 g. of *tert.*-butylthiol (Eastman Kodak, b. p. 63—64°/753 mm., $d_{4^\circ}^{20^\circ}$ 0·7985, $n_{\mathrm{D}}^{20^\circ}$ 1·42246), 94 c.c. of 15% sodium hydroxide solution, and 36 g. of iodine dissolved in 100 c.c. of 40% aqueous potassium iodide solution. The yield of pure product was 18 g. B. p. 64°/5·5 mm. (Rheinboldt, Mott, and Motzkus, *J. pr. Chem.*, 1932, **134**, 257, give b. p. 72°/11 mm.); *M* 178·34; n_{C} 1·48664, n_{D} 1·49003, n_{F} 1·49844, $n_{\mathrm{G'}}$ 1·50501; R_{C} 55·54, R_{D} 55·87, R_{F} 56·68, $R_{\mathrm{G'}}$ 57·31; $R_{\mathrm{G'-C}}$ 1·77, $R_{\mathrm{F-C}}$ 1·12; $Mn_{\mathrm{D}}^{20^\circ}$ 265·73. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9229, $d_{4^\circ}^{43\cdot7^\circ}$ 0·9039, $d_{4^\circ}^{60\cdot4^\circ}$ 0·8906, $d_{4^\circ}^{84\cdot3^\circ}$ 0·8713.

17·5°	16·02	15·78	0·9249	27·33	440·9	64·8°	14·14	13·90	0·8871	23·09	440·7
41·5	15·09	14·85	0·9057	25·18	441·1	87·9	13·29	13·05	0·8684	21·22	440·8
										Mean	440·9

8. *Di*-n-*amyl disulphide* (Eastman Kodak). B. p. 119°/7 mm.; *M* 206·40; n_{C} 1·48549, n_{D} 1·48887, n_{F} 1·49673, $n_{\mathrm{G'}}$ 1·50280; R_{C} 64·21, R_{D} 64·59, R_{F} 65·47, $R_{\mathrm{G'}}$ 66·15; $R_{\mathrm{G'-C}}$ 1·94, $R_{\mathrm{F-C}}$ 1·26; $Mn_{\mathrm{D}}^{20^\circ}n$ 307·31. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9221, $d_{4^\circ}^{61\cdot7^\circ}$ 0·8906, $d_{4^\circ}^{87\cdot1^\circ}$ 0·8708, $d_{4^\circ}^{120\cdot7^\circ}$ 0·8444.

18·5°	17·43	17·19	0·9233	29·72	522·0	87·1°	15·16	14·92	0·8708	24·33	526·4
61·0	15·96	15·72	0·8911	26·23	524·3	120·7	13·76	13·52	0·8444	21·38	525·6
										Mean	524·6

9. *Di*iso*amyl disulphide* (Eastman Kodak). B. p. 115°/9 mm.; *M* 206·40; n_{C} 1·48320, n_{D} 1·48637, n_{F} 1·49423, $n_{\mathrm{G'}}$ 1·50035; R_{C} 64·15, R_{D} 64·51, R_{F} 65·39, $R_{\mathrm{G'}}$ 66·09; $R_{\mathrm{G'-C}}$ 1·94, $R_{\mathrm{F-C}}$ 1·24; $Mn_{\mathrm{D}}^{20^\circ}$ 306·79. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9192, $d_{4^\circ}^{61\cdot5^\circ}$ 0·8854, $d_{4^\circ}^{86\cdot6^\circ}$ 0·8655, $d_{4^\circ}^{121\cdot5^\circ}$ 0·8378.

Apparatus *C*.

13·4°	13·49	13·25	0·9245	29·08	518·5	86·8°	11·41	11·17	0·8653	22·95	522·1
61·7	12·11	11·87	0·8852	24·94	521·1	120·2	10·48	10·24	0·8388	20·39	522·9
										Mean	521·2

10. *Methyl sulphide* (Eastman Kodak). B. p. 37·8°/765 mm.; *M* 62·13; n_{C} 1·43272, n_{D} 1·43570, n_{F} 1·44310, $n_{\mathrm{G'}}$ 1·44831; R_{C} 19·02, R_{D} 19·13, R_{F} 19·41, $R_{\mathrm{G'}}$ 19·61; $R_{\mathrm{G'-C}}$ 0·59, $R_{\mathrm{F-C}}$ 0·39; $Mn_{\mathrm{D}}^{20^\circ}$ 89·20. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8486, $d_{4^\circ}^{25\cdot0^\circ}$ 0·8456.

A	12·9°	15·87	15·63	0·8529	24·96	163·0	*C*	14·5°	12·60	12·36	0·8519	25·00	163·3
B	17·3	12·60	12·36	0·8502	24·64	163·0						Mean	163·1

11. *Methyl ethyl sulphide* (Eastman Kodak). B. p. 66°/747 mm.; *M* 76·15; n_{C} 1·43744, n_{D} 1·44033, n_{F} 1·44697, $n_{\mathrm{G'}}$ 1·45306; R_{C} 23·62, R_{D} 23·75, R_{F} 24·06, $R_{\mathrm{G'}}$ 24·35; $R_{\mathrm{G'-C}}$ 0·73, $R_{\mathrm{F-C}}$ 0·44; $Mn_{\mathrm{D}}^{21^\circ}$ 109·68. Densities determined: $d_{4^\circ}^{9\cdot7^\circ}$ 0·8557, $d_{4^\circ}^{20^\circ}$ 0·8455, $d_{4^\circ}^{40\cdot7^\circ}$ 0·8203.

A	6·5°	16·84	16·60	0·8603	26·74	201·4	*B*	7·6°	13·41	13·17	0·8580	26·50	201·5
A	16·5	16·35	16·11	0·8494	25·62	201·8	*B*	22·3	12·85	12·61	0·8430	24·93	202·0
A	40·9	14·82	14·58	0·8201	22·39	202·3	*B*	41·3	11·79	11·55	0·8196	22·20	202·0
												Mean	201·9

12. *Ethyl sulphide.* This was prepared by distilling an aqueous solution of sodium ethyl sulphate with excess of sodium sulphide until the temperature of the reaction mixture was 120°. The sulphide layer in the aqueous distillate was removed, shaken several times with 20% sodium hydroxide solution, then kept over sodium hydroxide pellets for 24 hours, washed with water until neutral, dried with calcium chloride, and distilled over sodium. B. p. 92°/761 mm.; *M* 90·18; n_{C} 1·43987, n_{D} 1·44235, n_{F} 1·44979, $n_{\mathrm{G'}}$ 1·45523; R_{C} 28·39, R_{D} 28·53, R_{F} 28·95, $R_{\mathrm{G'}}$ 29·25; $R_{\mathrm{G'-C}}$ 0·86, $R_{\mathrm{F-C}}$ 0·56; $Mn_{\mathrm{D}}^{20^\circ}$ 130·08. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8369, $d_{4^\circ}^{41\cdot4^\circ}$ 0·8155, $d_{4^\circ}^{60\cdot5^\circ}$ 0·7961.

13·5°	16·61	16·37	0·8434	25·85	241·1	61·5°	14·04	13·80	0·7950	20·54	241·9
41·3	15·14	14·90	0·8156	22·75	241·5					Mean	241·5

(Baroni, *loc. cit.*, gives $d_{4^\circ}^{20^\circ}$ 0·8367, γ_{20° 22·19, *P* 239·1; Bezzi, *loc. cit.*, gives b. p. 93—94°/760 mm., $d_{4^\circ}^{20^\circ}$ 0·8278, $n_{\mathrm{D}}^{20^\circ}$ 1·44303.)

13. n-*Propyl sulphide* (Eastman Kodak). B. p. 142°/762 mm.; M 118·23; n_{C} 1·44622, n_{D} 1·44896, n_{F} 1·45567 $n_{\mathrm{G'}}$ 1·46077; R_{C} 37·59, R_{D} 37·79, R_{F} 38·28, $R_{\mathrm{G'}}$ 38·64; $R_{\mathrm{G'-C}}$ 1·05, $R_{\mathrm{F-C}}$ 0·69; $Mn_{\mathrm{D}}^{20^\circ}$ 171·30. Densities determined $d_{4^\circ}^{20^\circ}$ 0·8391, $d_{4^\circ}^{61\cdot9^\circ}$ 0·8013, $d_{4^\circ}^{85\cdot8^\circ}$ 0·7804.

t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.	t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.
16·4°	17·19	16·95	0·8423	26·72	319·1	86·7°	13·60	13·36	0·7791	19·49	318·8
61·9	14·77	14·53	0·8013	21·80	318·8					Mean	318·9

(Mann and Purdie, J., 1935, 1549, give b. p. 139°, d^{24° 0·84315; Bezzi, *loc. cit.*, gives b. p. 140—143°/760 mm., $d_{4^\circ}^{20^\circ}$ 0·8302, $n_{\mathrm{D}}^{20^\circ}$ 1·44904.)

14. iso*Propyl sulphide.* This was prepared by adding 181 g. of *iso*propyl bromide, b. p. 59—59·5°/765 mm., slowly to a boiling mixture of 224 g. of finely-powdered anhydrous sodium sulphide and excess of rectified spirit, the whole refluxed for 7 hours, and the alcohol distilled off (compare Winssinger, *Bull. Soc. chim.*, 1887, **48**, 109; Mann and Purdie, *loc. cit.*). The distillate was diluted with excess of water, and the crude sulphide (70 g.) purified in the usual manner with 10% sodium hydroxide solution, etc. B. p. 119°/761 mm.; M 118·23; n_{C} 1·43628, n_{D} 1·43950, n_{F} 1·44574, $n_{\mathrm{G'}}$ 1·45093; R_{C} 37·88, R_{D} 38·12, R_{F} 38·59, $R_{\mathrm{G'}}$ 38·98; $R_{\mathrm{G'-C}}$ 1·10, $R_{\mathrm{F-C}}$ 0·71; $Mn_{\mathrm{D}}^{20^\circ}$ 170·19. Densities determined: d^{20° 0·8166, $d_{4^\circ}^{41\cdot4^\circ}$ 0·7960, $d_{4^\circ}^{61\cdot2^\circ}$ 0·7775, $d_{4^\circ}^{87\cdot4^\circ}$ 0·7534.

Apparatus *B*.

9·5°	12·78	12·54	0·8266	24·31	317·6	60·6°	10·76	10·52	0·7781	19·19	318·2
42·3	11·42	11·18	0·7951	20·84	317·7	86·2	9·75	9·51	0·7545	16·83	318·1
										Mean	317·9

(Mann and Purdie, *loc. cit.*, give b. p. 120°.)

15. n-*Butyl sulphide* (Eastman Kodak). B. p. 187°/765 mm.; M 146·28; n_{C} 1·45031, n_{D} 1·45297, n_{F} 1·45954, $n_{\mathrm{G'}}$ 1·46458; R_{C} 46·82, R_{D} 47·06, R_{F} 47·64, $R_{\mathrm{G'}}$ 48·10; $R_{\mathrm{G'-C}}$ 1·28, $R_{\mathrm{F-C}}$ 0·82; $Mn_{\mathrm{D}}^{20^\circ}$ 212·54. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8402, $d_{4}^{61\cdot2^\circ}$ 0·8040, $d_{4^\circ}^{86\cdot1^\circ}$ 0·7843.

Apparatus *B*.

18·3°	14·12	13·88	0·8417	27·40	397·6	87·8°	11·65	11·41	0·7828	20·94	400·0
61·7	12·66	12·42	0·8036	23·40	400·4					Mean	399·3

(Mann and Purdie, *loc. cit.*, give b. p. 185—185·5°, d^{24° 0·8352, γ_{24° 26·45, P 395·5; Bezzi, *loc. cit.*, gives b. p. 182—184°/760 mm., $d_{4^\circ}^{20^\circ}$ 0·8334, n_{D}^{20} 1·45405.)

16. iso*Butyl sulphide* (Eastman Kodak). B. p. 169°/772 mm.; M 146·28; n_{C} 1·44420, n_{D} 1·44686, n_{F} 1·45353, $n_{\mathrm{G'}}$ 1·45823; R_{C} 47·04, R_{D} 47·29, R_{F} 47·90, $R_{\mathrm{G'}}$ 48·32; $R_{\mathrm{G'-C}}$ 1·28, $R_{\mathrm{F-C}}$ 0·86; $Mn_{\mathrm{D}}^{20^\circ}$ 211·65. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8263, $d_{4^\circ}^{41\cdot2^\circ}$ 0·8106, $d_{4^\circ}^{62\cdot7^\circ}$ 0·7918, $d_{4^\circ}^{87\cdot5^\circ}$ 0·7712.

14·7°	16·60	16·36	0·8306	25·44	395·5	62·3°	14·38	14·14	0·7922	20·98	395·2
41·1	15·39	15·15	0·8107	23·00	395·1	88·2	13·32	13·08	0·7706	18·87	395·7
										Mean	395·4

(Mann and Purdie, *loc. cit.*, give b. p. 174°, d^{24° 0·8301, γ_{24° 24·90, P 392·8.)

17. sec.-*Butyl sulphide.* This was prepared from 68·5 g. of *sec.*-butyl bromide, b. p. 90·5—92°/756 mm., 58·5 g. of finely-powdered anhydrous sodium sulphide, and 200 c.c. of boiling rectified spirit as detailed under **14**. The yield of crude thio-ether was 26 g. B. p. 164·5°/739 mm.; M 146·28; n_{C} 1·44793, n_{D} 1·45062, n_{F} 1·45715, $n_{\mathrm{G'}}$ 1·46220; R_{C} 46·90, R_{D} 47·14, R_{F} 47·74, $R_{\mathrm{G'}}$ 48·19; $R_{\mathrm{G'-C}}$ 1·29, $R_{\mathrm{F-C}}$ 0·84; $Mn_{\mathrm{D}}^{20^\circ}$ 212·19. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8348, $d_{4^\circ}^{41\cdot3^\circ}$ 0·8163, $d_{4^\circ}^{61\cdot3^\circ}$ 0·7996, $d_{4^\circ}^{85\cdot0^\circ}$ 0·7800.

Apparatus *C*.

12·0°	13·53	13·29	0·8416	26·55	394·6	62·0°	11·76	11·52	0·7990	21·85	395·7
25·2	13·12	12·88	0·8304	25·39	395·4	85·6	10·76	10·52	0·7795	19·47	394·2
40·8	12·46	12·22	0·8167	23·69	395·2					Mean	395·0

tert.-*Butyl sulphide.* All attempts to prepare this compound from *tert.*-butyl bromide, b. p. 72·5—73·5°/765 mm., and anhydrous sodium sulphide in alcoholic solution were unsuccessful.

18. n-*Amyl sulphide* (Eastman Kodak). B. p. 84·5°/4 mm.; M 174·34; n_{C} 1·45352, n_{D} 1·45617, n_{F} 1·46262, $n_{\mathrm{G'}}$ 1·46750; R_{C} 56·09, R_{D} 56·38, R_{F} 57·06, $R_{\mathrm{G'}}$ 57·58; $R_{\mathrm{G'-C}}$ 1·49, $R_{\mathrm{F-C}}$ 0·97; $Mn_{\mathrm{D}}^{20^\circ}$ 253·87. Densities determined: $d_{4}^{20^\circ}$ 0·8409, $d_{4^\circ}^{62\cdot7^\circ}$ 0·8091, $d_{4^\circ}^{85\cdot7^\circ}$ 0·7904.

17·3°	18·01	17·77	0·8429	28·05	476·0	86·9°	15·11	14·97	0·7895	21·98	478·1
62·2	16·10	15·86	0·8095	24·04	476·9					Mean	477·0

(Mann and Purdie, *loc. cit.*, give b. p. 108—109°/15 mm., d^{24° 0·8408, γ_{24° 27·60, P 474·8.)

19. iso*Amyl sulphide* (Eastman Kodak). B. p. 85·5°/5 mm.; M 174·34; n_{C} 1·45002, n_{D} 1·45267, n_{F} 1·45912, $n_{\mathrm{G'}}$ 1·46403; R_{C} 56·18, R_{D} 56·47, R_{F} 57·16, $R_{\mathrm{G'}}$ 57·68; $R_{\mathrm{G'-C}}$ 1·50, $R_{\mathrm{F-C}}$ 0·98; $Mn_{\mathrm{D}}^{20^\circ}$ 253·26. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8340, $d_{4^\circ}^{60\cdot0^\circ}$ 0·8031, $d_{4^\circ}^{86\cdot5^\circ}$ 0·7830, $d_{4^\circ}^{120\cdot3^\circ}$ 0·7567.

Apparatus *B*.

15·2°	13·71	13·47	0·8377	26·46	472·0	87·4°	11·37	11·13	0·7823	20·42	473·7
62·0	12·14	11·90	0·8016	22·37	473·0	121·8	10·20	9·96	0·7555	17·64	473·0
										Mean	472·9

20. n-*Hexyl sulphide.* This was prepared from 69 g. of *n*-hexyl bromide, b. p. 154·5—156°/759 mm. [from *n*-hexyl alcohol, b. p. 156—157°/765 mm. (Carbide and Carbon Chemicals Corporation) by hydrogen bromide–sulphuric acid method], 49 g. of anhydrous sodium sulphide, and 88 c.c. of rectified spirit, and refluxing for 20 hours on the steam-bath (compare **14**). The yield of crude product was 38 g. B. p. 113·5°/4 mm.; M 202·39; n_{C} 1·45596, n_{D} 1·45856, n_{F} 1·46492, $n_{\mathrm{G'}}$ 1·46965; R_{C} 65·41, R_{D} 65·73, R_{F} 66·51, $R_{\mathrm{G'}}$ 67·10; $R_{\mathrm{G'-C}}$ 1·69, $R_{\mathrm{F-C}}$ 1·10; $Mn_{\mathrm{D}}^{20^\circ}$ 295·21. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8411, $d_{4^\circ}^{41\cdot0^\circ}$ 0·8264, $d_{4^\circ}^{58\cdot4^\circ}$ 0·8140, $d_{4^\circ}^{85\cdot7^\circ}$ 0·7941.

Apparatus *D*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
25·3°	13·78	13·54	0·8373	28·00	556·0	62·3°	12·64	12·40	0·8113	24·84	556·9
28·9	13·65	13·41	0·8348	27·65	555·9	88·7	11·82	11·58	0·7921	22·65	557·4
41·9	13·25	13·01	0·8258	26·53	556·2					Mean	556·5

(Mann and Purdie, *loc. cit.*, give b. p. 136—138°/20 mm., d^{24° 0·8447, γ_{24° 27·83, *P* 549·2.)

21. n-*Heptyl sulphide*. This was prepared from 60 g. of *n*-heptyl bromide, b. p. 178—179°/762 mm. (from *n*-heptyl alcohol, b. p. 175·5—176·5°/771 mm.; "Organic Syntheses," 1926, **6**, 52, by hydrogen bromide–sulphuric acid method), 39 g. of anhydrous sodium sulphide, 70 c.c. of rectified spirit, and refluxing on the steam-bath for 20 hours. The yield of the crude dry product was 35·5 g. B. p. 141·5°/4·5 mm.; *M* 230·44; n_C 1·45799, n_D 1·46055, n_F 1·46687, $n_{G'}$ 1·47137; R_C 74·72, R_D 75·09, R_F 75·96, $R_{G'}$ 76·59; $R_{G'-C}$ 1·87, R_{F-C} 1·24; $Mn_D^{20^\circ}$ 336·58. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8416, $d_{4^\circ}^{41\cdot5^\circ}$ 0·8277, $d_{4^\circ}^{60\cdot6^\circ}$ 0·8147, $d_{4^\circ}^{86\cdot7^\circ}$ 0·7968.

20·2°	18·82	18·58	0·8414	29·27	637·0	60·7°	17·30	17·06	0·8146	26·02	638·8
41·4	18·05	17·81	0·8278	27·61	638·1	87·7	16·21	15·97	0·7961	23·81	639·4
										Mean	638·4

(Mann and Purdie, *loc. cit.*, give b. p. 164°/20 mm., d^{24° 0·8402, γ_{24° 28·61, *P* 633·6.)

22. n-*Octyl sulphide*. This was prepared from 64 g. of *n*-octyl bromide, b.p. 200—200·5°/764 mm. (from *n*-octyl alcohol, b. p. 193—194°/763·5 mm., Deutsche Hydrierwerke Akt., by the same method as **21**), 39 g. of anhydrous sodium sulphide, 70 c.c. of rectified spirit, and refluxing for 20 hours on the steam-bath. The yield of the crude dry product was 39·5 g. B. p. 161·5°/4 mm.; *M* 258·49; n_C 1·45958, n_D 1·46215, n_F 1·46848, $n_{G'}$ 1·47310; R_C 83·75, R_D 84·16, R_F 85·14, $R_{G'}$ 85·86; $R_{G'-C}$ 2·11, R_{F-C} 1·39; $Mn_D^{20^\circ}$ 377·96. Densities determined: $d_{4^\circ}^{25\cdot0^\circ}$ whence $d_{4^\circ}^{20^\circ}$ 0·8447 (extrap.), $d_{4^\circ}^{41\cdot0^\circ}$ 0·8295, $d_{4^\circ}^{60\cdot0^\circ}$ 0·8164, $d_{4^\circ}^{87\cdot4^\circ}$ 0·7977.

Apparatus *D*.

21·7	14·78	14·54	0·8434	30·28	719·0	61·1°	13·27	13·03	0·8156	26·25	717·3
25·9	14·65	14·41	0·8405	29·91	719·2	87·4	12·50	12·26	0·7977	24·15	718·4
41·3	13·82	13·58	0·8293	27·81	716·0					Mean	718·0

(Mann and Purdie, *loc. cit.*, give b. p. 184—185°/20 mm., d^{24° 0·8409, γ^{24° 29·10, *P* 713·5.)

23. *Methyl* n-*butyl sulphide*. 23·5 G. of *n*-butylthiol, b. p. 98—98·5°/766 mm. (Eastman Kodak, redistilled), were dropped slowly into 205 c.c. of 10% aqueous sodium hydroxide solution with vigorous stirring which was continued until the liquid was homogeneous. 32·2 G. of methyl sulphate were added during 1 hour. The liquid soon became cloudy and heat was evolved. Stirring was continued for 2 hours at room temperature, and the mixture set aside for 6 hours. The upper layer of sulphide was then removed, washed 4 times with one-quarter of its volume of 10% sodium hydroxide solution, then with water until neutral, and dried with calcium chloride. The yield of the crude dry product was 22·5 g. It was distilled from sodium in a fractionating Claisen flask and a middle fraction collected. B. p. 122·5°/761 mm.; *M* 104·21, n_C 1·44498, n_D 1·44776, n_F 1·45452, $n_{G'}$ 1·45974; R_C 32·92, R_D 33·10, R_F 33·53, $R_{G'}$ 33·94; $R_{G'-C}$ 1·02; R_{F-C} 0·61; $Mn_D^{20^\circ}$ 150·93. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8427, $d_{4^\circ}^{40\cdot7^\circ}$ 0·8239, $d_{4^\circ}^{60\cdot6^\circ}$ 0·8055, $d_{4^\circ}^{87\cdot1^\circ}$ 0·7809.

21·0°	16·83	16·59	0·8418	26·15	280·1	61·6°	14·74	14·50	0·8046	21·85	280·1
42·1	15·77	15·53	0·8226	23·92	280·3	91·3	13·19	12·95	0·7770	18·84	280·0
										Mean	280·1

24. *Methyl* iso*butyl sulphide*. This was prepared from 24·3 g. of *iso*butylthiol (Eastman Kodak, b. p. 87·5°/764 mm.), 210 c.c. of 10% sodium hydroxide solution, and 33·2 g. of methyl sulphate as under **23**. The yield of crude product was 24 g. B. p. 112·5°/760 mm.; *M* 104·21; n_C 1·44062, n_D 1·44333; n_F 1·45004, $n_{G'}$ 1·45515; R_C 32·99, R_D 33·17, R_F 33·60, $R_{G'}$ 33·93; $R_{G'-C}$ 0·94, R_{F-C} 0·61; $Mn_D^{20^\circ}$ 150·41. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8335, $d_{4^\circ}^{42\cdot4^\circ}$ 0·8145, $d_{4^\circ}^{61\cdot2^\circ}$ 0·7971, $d_{4^\circ}^{84\cdot2^\circ}$ 0·7757.

20·7°	16·22	15·98	0·8329	24·92	279·6	63·3°	14·17	13·93	0·7953	20·74	279·6
43·4	15·20	14·96	0·8136	22·79	279·9	88·1	12·80	12·56	0·7723	18·16	279·1
										Mean	279·6

25. *Methyl* tert.-*butyl sulphide*. This was prepared from 23 g. of *tert*.-butylthiol (Eastman Kodak, redistilled), b. p. 63—64°/753 mm., 200 c.c. of 10% sodium hydroxide solution, and 31·5 g. of methyl sulphate as under **23**. The yield of crude product was 19·5 g. B. p. 99°/766 mm. (Rheinboldt, Mott, and Motzkus, *loc. cit.*, give b. p. 101—102°); *M* 104·21; n_C 1·43743, n_D 1·44023, n_F 1·44703, $n_{G'}$ 1·45229; R_C 33·10, R_D 33·29, R_F 33·73, $R_{G'}$ 34·08; $R_{G'-C}$ 0·98; R_{F-C} 0·63; $Mn_D^{20^\circ}$ 150·14. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8257, $d_{4^\circ}^{40\cdot9^\circ}$ 0·8060, $d_{4^\circ}^{64\cdot5^\circ}$ 0·7836.

19·0°	15·48	15·24	0·8266	23·59	277·9	62·8°	13·20	12·96	0·7852	19·05	278·0
41·4	14·34	14·10	0·8055	21·27	277·9					Mean	277·9

26. *Ethyl* n-*butyl sulphide* (Eastman Kodak). B. p. 142·5°/758 mm.; *M* 118·23; n_C 1·44604, n_D 1·44876, n_F 1·45549, $n_{G'}$ 1·46069; R_C 37·68, R_D 37·89, R_F 38·38, $R_{G'}$ 38·75; $R_{G'-C}$ 1·09, R_{F-C} 0·70; $Mn_D^{20^\circ}$ 171·29. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8367, $d_{4^\circ}^{41\cdot4^\circ}$ 0·8200, $d_{4^\circ}^{60\cdot3^\circ}$ 0·8034.

Apparatus *D*.

18·9°	13·10	12·86	0·8377	26·60	320·5	41·1°	12·23	11·99	0·8202	24·29	320·0
23·5	12·93	12·69	0·8339	26·13	320·5	60·9	11·52	11·28	0·8029	22·37	320·2
										Mean	320·3

27. *Ethyl* tert.-*butyl sulphide*. This was prepared from 17·7 g. of *tert*.-butylthiol, 200 c.c. of 10% sodium hydroxide solution, and 30·3 g. of ethyl sulphate as under **23**. The yield of crude product was 15 g. B. p. 119·5°/761 mm. (Rheinboldt, Mott, and Motzkus, *loc. cit.*, give b. p. 56—57°/109 mm.); *M* 118·23; n_C 1·43890, n_D 1·44164, n_F 1·44844, $n_{G'}$ 1·45356; R_C 37·93, R_D 38·12, R_F 38·63, $R_{G'}$ 39·02; $R_{G'-C}$ 1·09, R_{F-C} 0·70; $Mn_D^{20^\circ}$ 170·44. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8200, $d_{4^\circ}^{41\cdot3^\circ}$ 0·8021, $d_{4^\circ}^{60\cdot9^\circ}$ 0·7848, $d_{4^\circ}^{86\cdot7^\circ}$ 0·7615.

21·5°	15·48	15·24	0·8187	23·36	317·5	59·6°	13·66	13·42	0·7859	19·75	317·1
43·0	14·52	14·28	0·8006	21·41	317·7	87·5	12·23	11·99	0·7608	17·08	316·6
										Mean	317·2

28. *Phenyl sulphide.* This was prepared from redistilled sulphur monochloride, b. p. 133—134°/750 mm., and sodium-dried " AnalaR " benzene by the Friedel–Crafts reaction (" Organic Syntheses," 1934, **14**, 36); a perfectly colourless and constant-boiling product was obtained. B. p. 145°/8 mm.; *M* 186·26; n_{C} 1·62575, n_{D} 1·63343, n_{F} 1·65375, $n_{G'}$ 1·67158; R_{C} 59·19, R_{D} 59·77, R_{F} 61·29, $R_{G'}$ 62·60; $R_{G'-C}$ 3·41, R_{F-C} 2·10; $Mn_{D}^{20^\circ}$ 304·24. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1136, $d_{4^\circ}^{60\cdot1^\circ}$ 1·0823, $d_{4^\circ}^{84\cdot8^\circ}$ 1·0628, $d_{4^\circ}^{120\cdot8^\circ}$ 1·0352.

Apparatus *B*.

t.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
16·4°	16·49	16·25	1·1164	42·54	426·1	86·4°	14·64	14·40	1·0616	35·85	429·3
61·9	15·27	15·03	1·0809	38·10	428·1	121·6	13·44	13·20	1·0346	32·02	428·3
										Mean	428·0

29. *Phenyl selenide.* This was obtained as a reddish-yellow liquid as described in " Organic Syntheses," 1938, **18**, 27. B. p. 141°/4 mm.; *M* 233·16; n_{D} 1·65002*; R_{D} 62·93; $Mn_{D}^{20^\circ}$ 384·71. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·3515, $d_{4^\circ}^{58\cdot5^\circ}$ 1·3174, $d_{4^\circ}^{88\cdot7^\circ}$ 1·2902, $d_{4^\circ}^{120\cdot7^\circ}$ 1·2628.

Apparatus *B*.

23·5°	13·86	13·62	1·3484	43·07	443·0	88·5°	12·35	12·11	1·2904	36·64	444·6
61·0	13·17	12·93	1·3152	39·88	445·5	121·3	11·50	11·26	1·2623	33·33	443·8
										Mean	444·2

Alkyl Sulphites.—The general method of preparation consisted in placing redistilled thionyl chloride (0·5 mol.) in a 100-c.c. Claisen flask, cooling it in ice, and adding the pure alcohol (0·75 mol.) from a tap-funnel during about 1 hour. Hydrogen chloride was rapidly evolved, and it was necessary to shake the flask vigorously and frequently in order to ensure complete interaction. The mixture was refluxed for 45—75 mins. in order to complete the reaction, and then distilled. *n*-Butyl, *n*-amyl, and *iso*amyl sulphites were distilled under diminished pressure.† The crude sulphite was thoroughly dried with anhydrous sodium sulphate, redistilled, and a middle fraction collected for the physical measurements. The latter were made on the same day as the final distillation, for the sulphites slowly decompose on keeping. The yields were excellent.

The alcohols employed were: A.R. absolute methyl and ethyl alcohol (Burrough), *n*-propyl alcohol, b. p. 96—97°/760 mm. (Bisol), *iso*propyl alcohol, b. p. 82—83°/751 mm. (Bisol), *n*-butyl alcohol, b. p. 116—117°/762 mm. (Bisol), *iso*butyl alcohol, b. p. 106·5—107·5°/766 mm. (Bisol), *n*-amyl alcohol, b. p. 136·5—137·5°/765 mm. (Sharples), and *iso*amyl alcohol, b. p. 129—130°/765 mm. (Sharples, synthetic). All the alcohols were dried over A.R. potassium carbonate before fractionation.

30. *Methyl sulphite.* B. p. 126°/760 mm.; *M* 110·13; n_{C} 1·40712, n_{D} 1·40929, n_{F} 1·41464, $n_{G'}$ 1·41847; R_{C} 22·36, R_{D} 22·46, R_{F} 22·72, $R_{G'}$ 22·90; $R_{G'-C}$ 0·54, R_{F-C} 0·36; $Mn_{D}^{20^\circ}$ 155·21. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·2129, $d_{4^\circ}^{61\cdot9^\circ}$ 1·1587, $d_{4^\circ}^{87\cdot3^\circ}$ 1·1256.

Apparatus *C*.

17·8°	12·10	11·86	1·2158	34·23	219·1	87·6°	9·77	9·53	1·1252	25·46	219·1
61·9	10·71	10·47	1·1587	28·80	220·0					Mean	219·7

31. *Ethyl sulphite.* B. p. 157°/763 mm.; *M* 138·18; n_{C} 1·41223, n_{D} 1·41441, n_{F} 1·41974, $n_{G'}$ 1·42367; R_{C} 31·76, R_{D} 31·91, R_{F} 32·27, $R_{G'}$ 32·54; $R_{G'-C}$ 0·78, R_{F-C} 0·51; $Mn_{D}^{20^\circ}$ 195·44. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0829, $d_{4^\circ}^{41\cdot1^\circ}$ 1·0604, $d_{4^\circ}^{61\cdot0^\circ}$ 1·0396, $d_{4^\circ}^{85\cdot3^\circ}$ 1·0125.

Apparatus *D*.

22·9°	11·21	10·97	1·0798	29·25	297·6	61·0°	10·05	9·81	1·0396	25·19	297·8
29·0	11·03	10·79	1·0733	28·60	297·7	85·9	9·25	9·01	1·0119	22·52	297·5
43·1	10·56	10·32	1·0583	26·97	297·6					Mean	297·6

32. n-*Propyl sulphite.* B. p. 191°/764 mm. (uncorr.); *M* 166·23; n_{C} 1·42200, n_{D} 1·42426, n_{F} 1·42969, $n_{G'}$ 1·43358; R_{C} 41·09, R_{D} 41·29, R_{F} 41·75, $R_{G'}$ 42·08; $R_{G'-C}$ 0·99, R_{F-C} 0·66; $Mn_{D}^{20^\circ}$ 236·76. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0280, $d_{4^\circ}^{61\cdot7^\circ}$ 0·9880, $d_{4^\circ}^{85\cdot5^\circ}$ 0·9642, $d_{4^\circ}^{121\cdot3^\circ}$ 0·9269.

18·9°	15·22	14·98	1·0291	28·87	374·4	86·2°	12·72	12·48	0·9635	22·52	375·8
61·9	13·60	13·36	0·9878	24·71	375·2	121·3	11·39	11·15	0·9269	19·35	376·2
										Mean	375·4

33. iso*Propyl sulphite.* B. p. 169·5°/764 (uncorr.); *M* 166·23; n_{C} 1·41255, n_{D} 1·41476, n_{F} 1·42009, $n_{G'}$ 1·42399; R_{C} 41·15, R_{D} 41·35, R_{F} 41·81, $R_{G'}$ 42·15; $R_{G'-C}$ 1·00, R_{F-C} 0·66; $Mn_{D}^{20^\circ}$ 235·18. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0064, $d_{4^\circ}^{62\cdot3^\circ}$ 0·9644, $d_{4^\circ}^{86\cdot9^\circ}$ 0·9387, $d_{4^\circ}^{120\cdot8^\circ}$ 0·9015.

18·6°	14·21	13·97	1·0078	26·36	373·8	87·4°	11·63	11·39	0·9383	20·01	374·7
61·5	12·57	12·33	0·9652	22·28	374·2	120·8	10·42	10·18	0·9015	17·18	375·4
										Mean	374·5

34. n-*Butyl sulphite.* B. p. 90·5°/5 mm.; *M* 194·28; n_{C} 1·42864, n_{D} 1·43098, n_{F} 1·43638, $n_{G'}$ 1·44036; R_{C} 50·26, R_{D} 50·51, R_{F} 51·06, $R_{G'}$ 51·47; $R_{G'-C}$ 1·21, R_{F-C} 0·80; $Mn_{D}^{20^\circ}$ 275·47. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9957, $d_{4^\circ}^{41\cdot1^\circ}$ 0·9775, $d_{4^\circ}^{60\cdot8^\circ}$ 0·9603, $d_{4^\circ}^{85\cdot6^\circ}$ 0·9381.

Apparatus *D*.

19·0°	11·99	11·75	0·9966	28·92	452·1	42·2°	11·32	11·08	0·9765	26·72	452·5
22·4	11·89	11·65	0·9940	28·60	452·0	62·4	10·78	10·54	0·9589	24·96	452·9
30·5	11·71	11·47	0·9866	27·95	451·7	86·0	10·14	9·90	0·9378	22·93	453·8
										Mean	452·5

35. iso*Butyl sulphite.* B. p. 209°/741 mm.; *M* 194·28; n_{C} 1·42451, n_{D} 1·42676, n_{F} 1·43223, $n_{G'}$ 1·43631; R_{C} 50·32, R_{D} 50·56, R_{F} 51·12, $R_{G'}$ 51·54; $R_{G'-C}$ 1·22, R_{F-C} 0·80; $Mn_{D}^{20^\circ}$ 277·20. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9862, $d_{4^\circ}^{61\cdot7^\circ}$ 0·9484, $d_{4^\circ}^{87\cdot5^\circ}$ 0·9225, $d_{4^\circ}^{121\cdot7^\circ}$ 0·8897.

* C line almost coincident with D; F and G′ lines not visible.

† Compare " Organic Syntheses," 1939, **19**, 29, for *n*-butyl sulphite; these details were published after the authors' work was completed in 1937—38.

t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.	t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.
15·2°	15·11	14·87	0·9905	27·58	449·5	87·9°	12·43	12·19	0·9221	21·05	451·3
62·0	13·39	13·15	0·9481	23·35	450·4	122·4	11·17	10·93	0·8891	18·20	451·3
										Mean	450·6

36. n-*Amyl sulphite.* B. p. 111·5°/5 mm.; M 222·34; n_C 1·43393, n_D 1·43620, n_F 1·44178, n_G 1·44584; R_C 59·52, R_D 59·80, R_F 60·48, $R_{G'}$ 60·94; $R_{G'-C}$ 1·42, R_{F-C} 0·96; $Mn_D^{20^\circ}$ 319·33. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9726, $d_{4^\circ}^{61\cdot5^\circ}$ 0·9385, $d_{4^\circ}^{88\cdot0^\circ}$ 0·9160, $d_{4^\circ}^{120\cdot3^\circ}$ 0·8878.

16·0°	16·26	16·02	0·9758	29·27	530·0	87·5°	13·72	13·48	0·9164	23·10	531·9
61·7	14·75	14·51	0·9383	25·49	532·5	122·3	12·55	12·31	0·8862	20·43	533·4
										Mean	532·0

37. iso*Amyl sulphite.* B. p. 98·5°/4 mm.; M 222·34; n_C 1·43318, n_D 1·43550, n_F 1·44104, n_G ·1·44521; R_C 59·44, R_D 59·71, R_F 60·37, $R_{G'}$ 60·86; $R_{G'-C}$ 1·42, R_{F-C} 0·93; $Mn_D^{20^\circ}$ 319·15. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9726, $d_{4^\circ}^{40\cdot9^\circ}$ 0·9552, $d_{4^\circ}^{61\cdot5^\circ}$ 0·9381, d $0_{4^\circ}^{85\cdot2^\circ}$·9181.

15·5°	15·71	15·47	0·9763	28·28	525·2	62·7°	13·97	13·73	0·9371	24·09	525·6
41·4	14·79	14·55	0·9548	26·01	525·9	87·0	13·14	12·90	0·9166	22·14	526·2
										Mean	525·7

38. *Ethyl ethanesulphonate* (as.-*ethyl sulphite*). Pure silver sulphite (from Johnson and Matthey's silver nitrate, pure recrystallised) was refluxed with colourless ethyl iodide in dry ethereal solution (Biltz and Biltz, " Laboratory Methods of Inorganic Chemistry," 1928, 211; Kurbatow, *Annalen*, 1874, **173**, 7); the resultant ester (poor yield) was purified by repeated fractionation. B. p. 210°/760 mm.; M 138·18; n_C 1·41842, n_D 1·42036, n_F 1·42496, $n_{G'}$ 1·42819; R_C 30·15, R_D 30·21, R_F 30·57, $R_{G'}$ 30·77; $R_{G'-C}$ 0·62, R_{F-C} 0·42; $Mn_D^{20^\circ}$ 196·27. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1560, $d_{4^\circ}^{42\cdot0^\circ}$ 1·1356, $d_{4^\circ}^{62\cdot5^\circ}$ 1·1150, $d_{4^\circ}^{87\cdot0^\circ}$ 1·0906.

19·3°	16·84	16·60	1·1567	35·96	292·5	62·0°	15·43	15·19	1·1155	31·73	294·0
30·1	16·53	16·29	1·1463	34·97	293·0	86·2	14·52	14·28	1·0914	29·18	294·3
41·9	16·14	15·90	1·1357	33·81	293·4					Mean	293·4

(Sugden *et al.* give P 295·8.)

Alkyl Sulphates.—Commercial methyl sulphate (B.D.H., 100 g.) was kept over " AnalaR " potassium carbonate for 36 hours and then twice distilled. Ethyl sulphate (B.D.H.), *n*-propyl and *n*-butyl sulphates (Eastman Kodak) were purified as follows. 50 G. were shaken for 10 mins. with 15 c.c. of saturated sodium carbonate solution, the ester layer separated, shaken mechanically for 30 mins. with calcium chloride, filtered, and kept over a large quantity of calcium chloride for 24 hours with occasional shaking. The ester was again filtered into a large excess of " AnalaR " potassium carbonate, kept for 24 hours, and distilled (compare Barkenbus and Owen, *J. Amer. Chem. Soc.*, 1934, **56**, 1024).

39. *Methyl sulphate.* B. p. 187·5°/763 mm.; M 126·13; n_C 1·38574, n_D 1·38740, n_F 1·39123, $n_{G'}$ 1·39389; R_C 22·29, R_D 22·38, R_F 22·57, $R_{G'}$ 22·71; $R_{G'-C}$ 0·42, R_{F-C} 0·28; $M_D^{20^\circ}$ n175·00. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·3283, $d_{4^\circ}^{43\cdot9^\circ}$ 1·3003, $d_{4^\circ}^{61\cdot8^\circ}$ 1·2777, $d_{4^\circ}^{86\cdot8^\circ}$ 1·2478.

15·1°	16·05	15·81	1·3342	39·50	237·0	61·4°	14·44	14·20	1·2782	33·99	238·3
40·6	15·23	14·99	1·3043	36·61	237·3	86·5	13·61	13·37	1·2482	31·25	238·9
										Mean	237·9

(Sugden, Reed, and Wilkins, J., 1925, **127**, 1539, give b. p. 187·5°/769 mm., P 238·9; the value for $d_{4^\circ}^{20^\circ}$ extrapolated from their results is 1·3322.)

40. *Ethyl sulphate.* B. p. 75°/5 mm.; M 154·18; n_C 1·39861, n_D 1·40037, n_F 1·40457, $n_{G'}$ 1·40756; R_C 31·65, R_D 31·77, R_F 32·07, $R_{G'}$ 32·28; $R_{G'-C}$ 0·63, R_{F-C} 0·42; $Mn_D^{20^\circ}$ 215·81. Densities determined: $d_{4}^{23^\circ}$ 1·1774, $d_{4^\circ}^{61\cdot7^\circ}$ 1·1350, $d_{4^\circ}^{86\cdot4^\circ}$ 1·1095, $d_{4^\circ}^{120\cdot9^\circ}$ 1·0719.

Apparatus *C*.

14·9°	12·36	12·12	1·1825	34·02	314·9	86·4°	10·48	10·24	1·1095	26·97	316·7
61·9	11·18	10·94	1·1348	29·47	316·6	120·7	9·56	9·32	1·0721	23·72	317·4
										Mean	316·4

[Sugden, Reed, and Wilkins, *loc. cit.*, give b. p. 110°/30 mm., P 313·8, $d_{4^\circ}^{20^\circ}$ (extrap.) 1·188; Buehler, Gardner, and Clemens, *J. Org. Chem.*, 1927, **2**, 170, give b. p. 77·8—78·0°/6 mm., P 318·4.]

41. n-*Propyl sulphate.* B. p. 94°/5 mm.; M 182·23; n_C 1·41144, n_D 1·41336, n_F 1·41788, $n_{G'}$ 1·42104; R_C 40·79, R_D 40·96, R_F 41·35, $R_{G'}$ 41·62; $R_{G'-C}$ 0·83, R_{F-C} 0·56; $Mn_D^{20^\circ}$ 257·56. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1102, $d_{4^\circ}^{63\cdot2^\circ}$ 1·0683, $d_{4^\circ}^{87\cdot7^\circ}$ 1·0452, $d_{4^\circ}^{119\cdot9^\circ}$ 1·0135.

13·3°	15·89	15·65	1·1167	32·73	390·3	87·0°	13·41	13·17	1·0459	25·79	392·6
61·7	14·26	14·02	1·0695	28·08	392·2	120·1	12·32	12·08	1·0133	22·92	393·4
										Mean	392·2

42. n-*Butyl sulphate.* B. p. 109·5°/4 mm.; M 210·28; n_C 1·41929, n_D 1·42126, n_F 1·42597, $n_{G'}$ 1·42936; R_C 50·05, R_D 50·26, R_F 50·74, $R_{G'}$ 51·11; $R_{G'-C}$ 1·06, R_{F-C} 0·69; $Mn_D^{20^\circ}$ 298·87. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0616, $d_{4^\circ}^{60\cdot9^\circ}$ 1·0227, $d_{4^\circ}^{85\cdot9^\circ}$ 1·0039, $d_{4^\circ}^{119\cdot5^\circ}$ 0·9727.

13·6°	16·14	15·90	1·0673	31·77	467·9	85·5°	13·80	13·56	1·0043	25·50	470·5
62·3	14·49	14·25	1·0214	27·25	470·4	120·6	12·54	12·30	0·9717	22·38	470·7
										Mean	469·9

Trialkyl Orthophosphates.—These were prepared by the action of redistilled phosphorus oxychloride upon the sodium alkoxides as described by Evans, Davies, and Jones (J., 1930, 1310), and were purified by at least two distillations under diminished pressure. The b. p.'s of the alcohols employed are those given under *Alkyl Sulphites.* The agreement of the authors' measurements of the densities and refractive indices with those of Evans, Davies, and Jones (*loc. cit.*) is moderate.

43. *Trimethyl orthophosphate.* B. p. 62°/5 mm.; *M* 140·08; n_{C} 1·39452, n_{D} 1·39630, n_{F} 1·40049, $n_{\mathrm{G'}}$ 1·40154; R_{C} 27·67, R_{D} 27·74, R_{F} 27·99, $R_{\mathrm{G'}}$ 28·06; $R_{\mathrm{G'-C}}$ 0·39, $R_{\mathrm{F-C}}$ 0·32; $Mn_{\mathrm{D}}^{20°}$ 195·59. Densities determined: $d_{4°}^{20°}$ 1·2144, $d_{4°}^{60·9°}$ 1·1722, $d_{4°}^{86·7°}$ 1·1436, $d_{4°}^{119·9°}$ 1·1062.

t.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*h*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
17·5°	16·86	16·62	1·2152	37·76	285·9	86·9°	14·17	13·93	1·1432	29·82	286·3
60·9	15·22	14·98	1·1722	32·88	286·2	120·7	12·83	12·59	1·1053	26·06	286·3

Mean 286·2

[Evans, Davies, and Jones, *loc. cit.*, give b. p. 73°/10 mm., $d_{4°}^{25°}$ 1·2052, $d_{4°}^{25°}$ 1·2104 (extrap.), $n_{\mathrm{C}}^{25°}$ 1·3934, $n_{\mathrm{D}}^{25°}$ 1·3950, $n_{\mathrm{F}}^{25°}$ 1·3990; R_{C} 27·769, R_{D} 27·869, R_{F} 28·119.]

44. *Triethyl orthophosphate.* B. p. 75·5°/5 mm.; *M* 182·16; n_{C} 1·40343, n_{D} 1·40533, n_{F} 1·40983, $n_{\mathrm{G'}}$ 1·41308; R_{C} 41·60, R_{D} 41·77, R_{F} 42·18, $R_{\mathrm{G'}}$ 42·48; $R_{\mathrm{G'-C}}$ 0·88; $R_{\mathrm{F-C}}$ 0·58; $Mn_{\mathrm{D}}^{20°}$ 255·19. Densities determined: $d_{4°}^{20°}$ 1·0695, $d_{4°}^{60·9°}$ 1·0301, $d_{4°}^{86·7°}$ 1·0021, $d_{4°}^{120·1°}$ 0·9708.

Apparatus *B*.

18·3°	12·27	12·03	1·0712	30·22	398·7	87·4°	10·26	10·02	1·0014	23·53	400·6
61·7	11·01	10·77	1·0293	25·99	399·6	121·1	9·35	9·11	0·9698	20·72	400·7

Mean 399·9

[Sugden, Reed, and Wilkins, *loc. cit.*, give b. p. 108°/25 mm., $d_{4°}^{20°}$ 1·0737 (extrap.), *P* 399·1; Evans, Davies, and Jones, *loc. cit.*, give b. p. 90°/10 mm., $d_{4°}^{25°}$ 1·0637, $d_{4°}^{20°}$ 1·0685 (extrap.), $n_{\mathrm{C}}^{25°}$ 1·4021, $n_{\mathrm{D}}^{25°}$ 1·4039, $n_{\mathrm{F}}^{25°}$ 1·4082; R_{C} 41·706, R_{D} 41·870, R_{F} 42·263.]

45. *Tri-*n*-propyl orthophosphate.* B. p. 107·5°/5 mm.; *M* 224·24; n_{C} 1·4148, n_{D} 1·41646, n_{F} 1·42120, $n_{\mathrm{G'}}$ 1·42467; R_{C} 55·42, R_{D} 55·66, R_{F} 56·21, $R_{\mathrm{G'}}$ 56·62; $R_{\mathrm{G'-C}}$ 1·20, $R_{\mathrm{F-C}}$ 0·79; $Mn_{\mathrm{D}}^{20°}$ 317·63. Densities determined: $d_{4°}^{20°}$ 1·0121, $d_{4°}^{62·1°}$ 0·9743, $d_{4°}^{87·1°}$ 0·9518, $d_{4°}^{120·7°}$ 0·9209.

16·9°	15·78	15·54	1·0149	29·46	516·0	87·6°	13·17	12·93	0·9513	23·04	516·4
63·0	13·98	13·74	0·9735	25·05	515·3	121·8	11·88	11·64	0·9199	20·05	515·8

Mean 515·9

[Evans, Davies, and Jones, *loc. cit.*, give b. p. 121°/10 mm., $d_{4°}^{25°}$ 1·0023, $d_{4°}^{20°}$ 1·0071 (extrap.), $n_{\mathrm{C}}^{25°}$ 1·4118, $n_{\mathrm{D}}^{25°}$ 1·4136, $n_{\mathrm{F}}^{25°}$ 1·4182; R_{C} 55·635, R_{D} 55·849, R_{F} 56·394.]

46. *Tri*iso*propyl orthophosphate.* B. p. 83·5°/5 mm.; *M* 224·24; n_{C} 1·40376, n_{D} 1·40573, n_{F} 1·41034, $n_{\mathrm{G'}}$ 1·41366; R_{C} 55·56, R_{D} 55·79, R_{F} 56·34, $R_{\mathrm{G'}}$ 56·76; $R_{\mathrm{G'-C}}$ 1·20, $R_{\mathrm{F-C}}$ 0·88; $Mn_{\mathrm{D}}^{20°}$ 315·21. Densities determined: $d_{4°}^{20°}$ 0·9867, $d_{4°}^{62·5°}$ 0·9472, $d_{4°}^{87·5°}$ 0·9237, $d_{4°}^{119·9°}$ 0·8931.

15·3°	14·08	13·84	0·9909	25·68	509·4	87·1°	11·50	11·26	0·9241	19·48	509·8
61·7	12·36	12·12	0·9478	21·51	509·5	120·4	10·45	10·21	0·8926	17·06	510·6

Mean 509·9

47. *Tri-*n*-butyl orthophosphate.* B. p. 138·5°/6 mm.; *M* 266·32, n_{C} 1·42295, n_{D} 1·42496, n_{F} 1·42988, $n_{\mathrm{G'}}$ 1·43343; R_{C} 69·44, R_{D} 69·57, R_{F} 70·43, $R_{\mathrm{G'}}$ 70·93; $R_{\mathrm{G'-C}}$ 1·49, $R_{\mathrm{F-C}}$ 0·99; $Mn_{\mathrm{D}}^{20°}$ 379·50. Densities determined: $d_{4°}^{20°}$ 0·9766, $d_{4°}^{62·3°}$ 0·9431, $d_{4°}^{87·1°}$ 0·9226, $d_{4°}^{120·5°}$ 0·8941.

16·6°	15·59	15·35	0·9794	28·15	626·3	87·3°	13·20	12·96	0·9224	22·38	628·0
62·1	14·39	14·15	0·9433	24·99	631·3	121·6	12·24	12·00	0·8932	20·07	631·1

Mean 629·2

[Evans, Davies, and Jones, *loc. cit.*, give b. p. 150°/10 mm., $d_{4°}^{25°}$ 0·9727, $d_{4°}^{20°}$ 0·9774 (extrap.), $n_{\mathrm{C}}^{25°}$ 1·4203, $n_{\mathrm{D}}^{25°}$ 1·4224, $n_{\mathrm{F}}^{25°}$ 1·4274; R_{C} 69·312, R_{D} 69·616, R_{F} 70·336. They state that it is "slightly yellowish, the colour indicating incipient decomposition." Our specimen was perfectly colourless, and its properties did *not* change on distillation under diminished pressure.]

48. *Tri*iso*butyl orthophosphate.* B. p. 117°/5·5 mm.; *M* 266·32; n_{C} 1·41729, n_{D} 1·41931, n_{F} 1·42416, $n_{\mathrm{G'}}$ 1·42775; R_{C} 69·22, R_{D} 69·51, R_{F} 70·22, $R_{\mathrm{G'}}$ 70·68; $R_{\mathrm{G'-C}}$ 1·52, $R_{\mathrm{F-C}}$ 1·00; $Mn_{\mathrm{D}}^{20°}$ 377·99. Densities determined: $d_{4°}^{20°}$ 0·9681, $d_{4°}^{61·2°}$ 0·9324, $d_{4°}^{85·1°}$ 0·9128, $d_{4°}^{120·3°}$ 0·8818.

15·3°	14·93	14·69	0·9721	26·74	623·0	87·3°	12·60	12·36	0·9109	21·08	626·5
61·2	13·48	13·24	0·9329	23·13	626·0	120·6	11·36	11·12	0·8815	18·35	625·3

Mean 625·2

[Evans, Davies, and Jones, *loc. cit.*, give b. p. 138°/10 mm., $d_{4°}^{25°}$ 0·9617, $d_{4°}^{20°}$ 0·9665 (extrap.), $n_{\mathrm{C}}^{25°}$ 1·4152, $n_{\mathrm{D}}^{25°}$ 1·4173, $n_{\mathrm{F}}^{25°}$; R_{C} 69·358, R_{D} 69·666, R_{F} 70·383.]

49. *Tri-*n*-amyl orthophosphate.* B. p. 167°/5 mm. (through an all-glass apparatus; rubber bungs are slightly attacked); *M* 308·39; n_{C} 1·42975, n_{D} 1·43188, n_{F} 1·43701, $n_{\mathrm{G'}}$ 1·44085; R_{C} 82·88, R_{D} 83·24, R_{F} 84·09, $R_{\mathrm{G'}}$ 84·74; $R_{\mathrm{G'-C}}$ 1·86, $R_{\mathrm{F-C}}$ 1·21; $Mn_{\mathrm{D}}^{20°}$ 441·58. Densities determined: $d_{4°}^{20°}$ 0·9608, $d_{4°}^{62·4°}$ 0·9285, $d_{4°}^{87·0°}$ 0·9083, $d_{4°}^{120·6°}$ 0·8816.

The parachor results were unsatisfactory, the parachor increasing appreciably with rise of temperature. [Evans, Davies, and Jones, *loc. cit.*, give b. p. 225°/50 mm., $d_{4°}^{25°}$ 0·9497, $d_{4°}^{20°}$ 0·9542 (extrap.), $n_{\mathrm{C}}^{25°}$ 1·4262, $n_{\mathrm{D}}^{25°}$ 1·4283, $n_{\mathrm{F}}^{25°}$ 1·4332; R_{C} 83·209, R_{D} 83·567, R_{F} 84·401.]

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