

# Preparation, Refractive Indices, and Boiling Points of Certain Organic Liquids

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THE SYNTHESIS of the compounds described in the present report was undertaken as a part of a program designed to investigate the properties of pure organic liquids of interest as potential lubricants. Certain fundamental relationships among molecular weight, molecular structure, and viscosity characteristics were investigated. The present report includes only data of particular interest to organic chemists—e.g., the fact that a particular substance has been prepared, and its boiling range and refractive index. A complete report is available (7).

The major portion of the synthetic work resolves itself into the preparation of alcohols, alkyl halides, mercaptans, and ethers. In all, some 90 new compounds were prepared, for the most part according to standard literature procedures. Thus, the work is most effectively summarized in a series of tables giving the molecular formulas, percentage composition (calculated and found), refractive index, boiling point (or range), and yield of product (prior to ultimate purification). Typical procedures for the more important general classes are given, as are a number of more original preparative procedures. Where the alcohols, mercaptans, etc., are known substances (literature survey through 1951), their preparations and properties are omitted. Throughout the work, many of the intermediates—e.g., alcohols—though new, were not analyzed, microanalysis of the final products being taken as satisfactory confirmation of their identity. The analytical data for the compounds are summarized in Tables I through VI.

## EXPERIMENTAL

Melting and boiling points are uncorrected. Microanalyses were by MicroTech Laboratories, Skokie, Ill. Temperatures are centigrade unless otherwise stated.

**Ether-Alcohols.** 5-(2'-ETHYLHEXYLOXY)-2-HEXANOL. To 18.4 grams (0.8 mole) of finely dispersed sodium in 500 ml. of dry xylene was added 120 grams (1.0 mole) of 2,5-hexanediol. Next there was added dropwise with stirring and refluxing 135 grams (0.70 mole) of 2-ethylhexyl bromide in 100 ml. of xylene. Refluxing and stirring were continued for 12 hours and the mixture was cooled, washed thoroughly with water, dilute acid, and water, and then dried. The xylene was removed at the water pump and the residue was distilled in vacuo to give 108 grams (66%, b.p., 125°/2 mm.,  $n_D^{24} = 1.4399$ ).

**Thioether-Alcohol.** 2-(2'-ETHYLHEXYLTHIO)-ETHANOL AND CHLORIDE. A solution of 189 grams (1.3 moles) of 2-ethylhexylmercaptan in 400 ml. of 20% sodium hydroxide was cooled in an ice bath and treated dropwise and with stirring with 66 grams (1.5 moles) of ethylene oxide. The oily layer which appeared at once was diluted with 125 ml. of benzene, separated, and washed with several portions of 10% alkali and then with water until the aqueous extracts were neutral. After drying over sodium sulfate, the benzene was removed at the water pump and the residue was distilled in vacuo [b.p., 94–105°/3 mm., 191 grams (77%)]. Careful fractionation afforded 145 grams (59%) of pure product [b.p., 99° C./1 mm.,  $n_D^{25} = 1.4762$ ]. The alcohol was dissolved in 110 grams of dry chloroform and treated dropwise, to maintain gentle refluxing, with 95 grams of thionyl chloride. The mixture was allowed to stand 48 hours at room temperature and the solvent and excess thionyl chloride were removed by distillation at atmospheric pressure. The chloride distilled at 66–70°/3 mm.  $n_D^{25} = 1.4780-2$ , yield 145 grams (91%).

**Mercaptans.** 3-CYCLOPENTYLPROPANETHIOL. A mixture of 60.5 grams (0.317 mole) of 3-cyclopentylpropyl bromide, 32 grams (0.42 mole) of thiourea, and 25 ml. of water was refluxed, with stirring, for 18 hours. There was then added 26 grams (0.65 mole) of sodium hydroxide in 230 ml. of water, and refluxing was continued for 2 hours. The mixture next was cooled and separated and the aqueous phase was acidified with 6*N* hydrochloric acid and thrice extracted with ether, the extracts being added to the mercaptan layer. The resulting solution was washed with 5% sodium bicarbonate and water and was dried over magnesium sulfate. Evaporation of the ether left the mercaptan, which was distilled [b.p., 109–13°/45 mm., 28 grams (83%)].

**Selenols.** Goheen and Vaughan (3) discussed selenols.

**Esters.** The Fischer esterification was used. Where sulfuric acid was employed as a catalyst with a secondary alcohol—e.g., 2,5-hexanediol—low yields were encountered due to extensive dehydration. More satisfactory was the use of 5 ml. of concentrated hydrochloric acid per 0.25 mole of glycol in 5 ml. of xylene—e.g., compound 3. The thioester (63) was made by the common reaction of acid chloride (adipyl) with excess mercaptan.

**Hydrocarbons.** 5,14-DIETHYLOCTADECANE (20). The bis-Grignard reagent was prepared as rapidly as possible at ice-bath temperature from 244 grams (1.0 mole) of 1,6-dibromohexane, 54 grams (2.2 moles) of magnesium, and 400 ml. of dry ether (50 ml. at outset, 350 more added with halide). The mixture was refluxed for 1 hour after complete addition and then 217 grams (1.7 moles) of 2-ethylhexanal in 300 ml. of ether was added with good stirring and ice-bath cooling. Refluxing was continued overnight and then the mixture was treated with saturated ammonium chloride solution and separated. The aqueous layer was extracted once with ether, which was added to the organic layer, which was then evaporated to half its volume, dried over sodium sulfate, and distilled (after filtration and removal of the ether at the water pump) [b.p., 175°/1 mm., 228 grams (79%)]. Redistillation give a pale yellow oil, 5,14-diethyl-6,13-octadecanediol (b.p., 155°/0.002 mm.,  $n_D^{25} = 1.4670$ ).

A solution of 212 grams (0.62 mole) of 5,14-diethyl-6,13-octadecanediol in 100 ml. of dry xylene was treated dropwise at room temperature with 135 grams of phosphorus tribromide and the resulting mixture was allowed to stand overnight and then heated at 100° C. for 1.5 hours. After cooling, it was washed with water and dilute sodium carbonate solution, diluted with ether, and dried over magnesium sulfate.

After removal of the solvents, the crude 5,14-diethyl-6,13-dibromo-octadecane was mixed with 600 ml. of absolute ethanol and added to a refluxing solution of 135 grams (2.4 moles) of potassium hydroxide in 100 ml. of absolute ethanol. Refluxing was continued for 1.5 hours, after which as much alcohol as possible was removed. The residual oil was taken up in xylene and dried over magnesium sulfate. The solvent was removed at the water pump and distillation in vacuo afforded a colorless product, 153 grams (80%) (b.p., 164°/2-3 mm.), with an infrared spectrum identical with the diene produced by a phosphorus pentoxide dehydration of the glycol.

Analysis. Calcd. for  $C_{22}H_{42}$ : C, 86.19; H, 13.81. Found: C, 85.84; H, 13.54.

The diene mixture, 109 grams (0.36 mole), was hydrogenated in 200 ml. of 95% ethanol over a 5% palladium-

charcoal catalyst at 200° C./2000 p.s.i. The crude product was washed with concentrated sulfuric acid until the acid layer remained colorless, after which it was washed with sodium chloride solution containing sodium carbonate. It was dried over magnesium sulfate (b.p., 180°/1 mm.,  $n_D^{24} = 1.4486$ ).

**5,16-DIETHYL-8,13-EICOSANEDIONE (5).** This diketone was prepared in 48% yield by the standard coupling reaction between di-2-ethylhexyl cadmium and adipyl chloride in benzene. The ketone boils at 214–17°/1 mm.,  $n_D^{24} = 1.4610$ –1.4614. The bis-semicarbazone melts at 165–6° (95% ethanol).

**5,6-DIETHYLEICOSANE (10).** A mixture of 600 grams of mossy zinc, 30 grams of mercuric chloride, 30 ml. of concentrated hydrochloric acid, and 600 ml. of water was stirred for 10 minutes. The aqueous solution was decanted and the residue was thrice washed with 400-ml. portions of water, thrice with 150-ml. portions of 95% ethanol, and thrice with 400-ml. portions of absolute ethanol. To the amalgamated zinc was then added 36.0 grams of 5,16-diethyl-8,13-eicosanedione in 1 liter of absolute ethanol. Dry hydrogen chloride was passed through the alcohol at a rapid rate until an oil formed on the surface. The gas flow was then stopped and the mixture was refluxed for 10 hours (until the oil redissolved). More hydrogen chloride was passed in until more oil appeared, and then refluxing was repeated until solution occurred. These operations were continued until little or no oil appeared on addition of hydrogen chloride. The reaction mixture was then refluxed for 48 hours. After removal of the alcohol a nearly colorless oil remained. After washing with concentrated sulfuric acid until the acid layer remained colorless, the oil was taken up in benzene for azeotropic drying. Distillation afforded 10 grams (30%) of product (b.p., 208–12°/10 mm.,  $n_D^{24} = 1.4610$ ).

**Glycol Bisethers.** **1,6-BISCYCLOBUTYLMETHOXYHEXANE (76).** A slurry of 6.2 grams (0.27 mole) of sodium in 100 ml. of dry xylene was prepared in a 500-ml. 3-necked flask, equipped with a reflux condenser, dropping funnel, and efficient stirrer, by rapidly stirring the sodium while

refluxing the xylene. To the slurry was added 25 grams (0.29 mole) of cyclobutyl carbinol in 100 ml. of dry xylene. Stirring and refluxing were continued until all the sodium had reacted.

To the resulting stirred, refluxing suspension was added dropwise 34 grams (0.15 mole) of 1,6-dibromohexane in 100 ml. of dry xylene. Refluxing and stirring were continued for 12 hours. The mixture was then cooled, and 80 ml. of water was added. After separation, the xylene layer was washed with 5% hydrochloric acid, 5% bicarbonate, and water and then dried over anhydrous sodium sulfate. The xylene was removed at the water pump, and the residue was distilled through a Claisen head to give the crude bisether [b.p., 126–7°/0.45 mm., 25 grams (71%)]. Subsequent purification was by distillation through an efficient column (b.p., 112–15°/0.3 mm.,  $n_D^{25} = 1.4560$ ).

A related procedure was used for the preparation of a 1,3-trimethylene glycol ether (44) and for 2,5-hexanediol ethers, including the unsymmetrical ether (18). These substances were prepared stepwise from the halides and the monosodium salt of the glycol in xylene. Conditions approximated those just described for bisether formation. (See also the preparation of ether-alcohols above.) The preparation of compound 18 involved coupling of the sodium salt of 2-(2'-ethylhexyloxy)-5-hexanol with 2-cyclohexylethyl bromide.

**Bisthiol and Bisselenol Ethers.** A suspension of sodium sand was prepared by refluxing 60 ml. of xylene with 5.5 grams (0.24 mole) of sodium, stirring vigorously, and then cooling. The xylene was siphoned off and replaced with 60 ml. of benzene, and 0.25 mole of mercaptan in 40 ml. of benzene was added dropwise. After the vigorous reaction subsided, the mixture was stirred and heated for an hour, during which time a gelatinous precipitate appeared.

To this mixture was added dropwise a solution of 0.12 mole of 1,6-dibromohexane (or other primary dihalide) in 30 ml. of benzene, and the mixture was heated and stirred for about 7 hours. After cooling, 80 ml. of water was added and the benzene layer was separated, washed with water, 5% hydrochloric acid, 5% bicarbonate, and more

Table I. Alcohols, Glycols, Mercaptans, and Selenols

Compound	Formula	Analysis				$n_D^{25a}$	Boiling Point, ° C./Mm.	Yield, %
		Calcd.		Found				
		C	H	C	H			
<b>Alcohols</b>								
10-Pentyl-10-eicosanol	C <sub>25</sub> H <sub>52</sub> O			Not analyzed (2)			183–7/ 0.2	66
10-Hexyl-10-eicosanol	C <sub>26</sub> H <sub>54</sub> O			Not analyzed (2)			188–94/ 0.2	75
10-Heptyl-10-eicosanol	C <sub>27</sub> H <sub>56</sub> O			Not analyzed (2)			197–202/ 0.35	92
10-Octyl-10-eicosanol	C <sub>28</sub> H <sub>58</sub> O			Not analyzed (2)			202–6/ 0.25	92.5
10-Nonyl-10-eicosanol	C <sub>29</sub> H <sub>60</sub> O			Not analyzed (2)			206–9/ 0.2	91
10-Nonylhen-11-eicosanol	C <sub>30</sub> H <sub>62</sub> O			Not analyzed (2)			213–17/ 0.25	77
5-(2'-Ethylhexyl)-2-hexanol	C <sub>14</sub> H <sub>30</sub> O <sub>2</sub>	72.98	13.13	72.86	13.23	1.4399 <sup>24</sup>	125/ 2	66
2-Hexyloxy-5-methylpentanol	C <sub>12</sub> H <sub>26</sub> O <sub>2</sub>			Not analyzed		1.4365	80/ 0.5	
6-(2'-Ethylhexyloxy)-1-hexanol	C <sub>14</sub> H <sub>30</sub> O <sub>2</sub>	72.98	13.13	72.66	13.14	1.4458 <sup>23</sup>	134/ 2	31
3-Decyloxypropanol	C <sub>13</sub> H <sub>28</sub> O <sub>2</sub>			Not analyzed		1.4371	80/ 1	53
2-(2'-Ethylhexylmercapto)-ethanol	C <sub>10</sub> H <sub>22</sub> OS	63.12	11.65	62.47	11.47	1.4762	99–100/ 1	58
2-(2'-Ethylhexylmercapto)-ethyl chloride	C <sub>10</sub> H <sub>21</sub> ClS	57.53	10.13	57.20	10.24	1.4782	67–70/ 1	96
5-(2'-Cyclohexylethoxy)-2-hexanol	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	73.63	12.36	73.74	12.27	1.4620 <sup>24</sup>	136/ 2	84
<b>Glycols</b>								
3-Hexyl-1,6-hexanediol	C <sub>12</sub> H <sub>26</sub> O <sub>2</sub>			Not analyzed (4)			137–40/ 0.4	80
3-“Octyl”-1,6-hexanediol	C <sub>14</sub> H <sub>30</sub> O <sub>2</sub>			Not analyzed (4)			154–7/ 0.25	88
3-Hexyl-1,6-dibromohexane	C <sub>12</sub> H <sub>44</sub> Br <sub>2</sub>			Not analyzed			114–17/ 0.1	61
3-“Octyl”-1,6-dibromohexane	C <sub>14</sub> H <sub>28</sub> Br <sub>2</sub>			Not analyzed			124–6/ 0.1	39
<b>Mercaptan</b>								
3-Cyclopentylpropyl	C <sub>8</sub> H <sub>16</sub> S			Not analyzed			109–13/45	83
<b>Selenols</b>								
2-Ethylhexyl	C <sub>8</sub> H <sub>18</sub> Se			Not analyzed (3)			68.5–70/ 8	64.5
Cyclopentylmethyl	C <sub>6</sub> H <sub>12</sub> Se			Not analyzed (3)			61–2/13	60

<sup>a</sup>Superscripts are temperatures other than 25° C. at which refractive index was measured.

water, and then dried over anhydrous sodium sulfate. The benzene was removed at the water pump, and the residual oil was distilled in vacuo using an efficient column. Yields in general were above 60%.

This procedure is applicable to selenoethers as well. The washed benzene solution should be washed further with 10% copper sulfate solution to remove residual selenols and hydrogen selenide. This may equally well be made part of also the routine for thioether preparation. The selenoethers proved to be somewhat thermally unstable and accordingly difficult to purify (3).

**Disulfides.** Standard procedures were used for disulfide formation: iodine oxidation of the corresponding mercaptan or coupling of the corresponding alkyl halide with sodium disulfide ( $\text{Na}_2\text{S}_2$ ) in ethanol. A modification of the former method used for compound 56 has been published (6).

**Mercaptals.** The aldehyde and mercaptan were mixed in a

1 to 2 molar ratio, and treated with dry hydrogen chloride, whereupon the reaction mixture warmed to 70° to 80°. Spontaneous cooling signified completion of the reaction. The products were washed with water and sodium carbonate and dried over sodium sulfate.

**Silicon Compounds.** The standard Grignard coupling with the appropriate chloro or dichlorosilane was carried out. The chief feature of interest was the use of the bis-Grignard reagent from 1,6-dibromohexane in the preparation of 51 and 58.

**Methyl Cyclopentanecarboxylate** was prepared by a modification of a published method (1).

2-Chlorocyclohexane was prepared in 72% yield from cyclohexane (503 grams, 5.1 moles) and chlorine gas (362 grams, 5.1 moles) at 50° in 1500 ml. of water, which was saturated with sodium chloride at the end of the reaction and then was extracted with ether, the extracts being added

Table II. Hydrocarbons, Ketones, and Esters

Ref. No. of Cpd.	Compound	Formula	Analysis				$n_D^{25}$	Boiling Point, C./Mm.	Yield, %
			Calcd.		Found				
			C	H	C	H			
Saturated hydrocarbons									
20	5,14-Diethyloctadecane	$\text{C}_{22}\text{H}_{46}$	85.07	14.93	85.23	14.80	1.4486 <sup>24</sup>	140-50/0.5-1.0	
10	5,16-Diethyleicosane	$\text{C}_{24}\text{H}_{50}$	85.12	14.88	84.93	14.32	1.4610 <sup>24</sup>	208-12/10	30
67	10-Pentyleicosane	$\text{C}_{25}\text{H}_{52}$					1.4467 (2)	161/ 0.15	88.5
68	10-Hexyleicosane	$\text{C}_{26}\text{H}_{54}$					1.4481 (2)	166/ 0.15	65
69	10-Heptyleicosane	$\text{C}_{27}\text{H}_{56}$					1.4487 (2)	173/ 0.15	92
70	10-Octyleicosane	$\text{C}_{28}\text{H}_{58}$					1.4496 (2)	180/ 0.15	92.5
71	10-Nonyleicosane	$\text{C}_{29}\text{H}_{60}$					1.4503 (2)	183/ 0.10	91
72	11-Nonylheneicosane	$\text{C}_{30}\text{H}_{62}$					1.4510 (2)	193/ 0.15	77
Unsaturated hydrocarbons									
73	10-"Pentyleicosene"	$\text{C}_{25}\text{H}_{50}$	85.63	14.37	85.38	14.47	1.4542 (2)	147/ 0.05	88.5
74	11-"Nonylheneicosene"	$\text{C}_{30}\text{H}_{60}$	85.63	14.37	85.42	14.41	1.4571 (2)	183/ 0.04	77
	5,14-Diethyl-5,13-octadecadiene	$\text{C}_{22}\text{H}_{42}$	86.19	13.81	85.84	13.54	1.4600	125-7/ 0.08	80
Esters									
11	Bis-2-ethylhexyl adipate	$\text{C}_{22}\text{H}_{42}\text{O}_4$			Known compound				
63	Bis-2-ethylhexylthiol adipate	$\text{C}_{22}\text{H}_{42}\text{O}_2\text{S}_2$	65.63	10.52	65.15	10.66	1.4905	185-90/ 0.05	66
23	Bis-3,5,5-trimethylhexyl adipate	$\text{C}_{24}\text{H}_{46}\text{O}_4$			Known compound				
3	2,5-Hexaneglycol-bis-2-ethylhexanoate	$\text{C}_{22}\text{H}_{42}\text{O}_4$	71.30	11.42	71.13	11.42	1.4381-2 <sup>22</sup>	140-3/ 0.05	37

Table III. Symmetrical Hexamethylene Glycol Bisethers

Ref. No. of Cpd.	Group	Formula	Analysis				$n_D^{25}$	Boiling Point, ° C./Mm.	Yield, %
			Calcd.		Found				
			C	H	C	H			
Acyclic									
2	n-Octyl	$\text{C}_{22}\text{H}_{46}\text{O}_2$	77.12	13.63	77.21	13.30	1.4410 <sup>22</sup>	148-50/0.02	72
19	2-Octyl	$\text{C}_{22}\text{H}_{46}\text{O}_2$	77.12	13.63	76.77	13.53	1.4380	120-4/0.008	34
27	2-Methylheptyl	$\text{C}_{22}\text{H}_{46}\text{O}_2$	77.12	13.63	77.17	13.33	1.4400	180/2-3	46
50	4-Methylheptyl	$\text{C}_{22}\text{H}_{46}\text{O}_2$	77.12	13.63	77.16	13.66	1.4425	109-12/0.01	
33	6-Methylheptyl	$\text{C}_{22}\text{H}_{46}\text{O}_2$	77.12	13.63	76.89	13.58	1.4402	165/0.02	
4	2-Ethylhexyl	$\text{C}_{22}\text{H}_{46}\text{O}_2$	77.12	13.63	76.60	13.32	1.4412 <sup>23</sup>	130-3/0.02	92
41	3-Nonyl	$\text{C}_{24}\text{H}_{50}\text{O}_2$	77.77	13.60	77.64	13.67	1.4421	132-4/0.03	58
49	2-Ethylheptyl	$\text{C}_{24}\text{H}_{50}\text{O}_2$	77.77	13.60	77.84	13.60	1.4432	153-5/0.5	90
40	3-Ethylheptyl	$\text{C}_{24}\text{H}_{50}\text{O}_2$	77.77	13.60	78.26	13.86	1.4460	130-6/0.03	
24	2-Butyloctyl	$\text{C}_{31}\text{H}_{62}\text{O}_2$	79.22	13.74	79.35	13.77	1.4481 <sup>28</sup>	182-4/0.05	
Cyclic									
76	Cyclobutylmethyl	$\text{C}_{16}\text{H}_{30}\text{O}_2$	75.53	11.89	75.13	11.83	1.4560	114/0.3	71
55	Cyclopentylmethyl	$\text{C}_{18}\text{H}_{34}\text{O}_2$	76.53	12.13	77.07	12.19	1.4615 <sup>26</sup>	124/0.5	82
7	Cyclohexyl	$\text{C}_{18}\text{H}_{34}\text{O}_2$	76.54	12.13	77.27	11.97	1.4691	124-7/0.02	
29	1-Cyclohexylethyl	$\text{C}_{22}\text{H}_{42}\text{O}_2$	78.04	12.50	78.19	12.57	1.4690	145-8/0.05	61
46	2-Cyclohexylethyl	$\text{C}_{22}\text{H}_{42}\text{O}_2$	78.04	12.50	78.46	12.63	1.4690	124-6/0.02	81
47	4-Isopropylcyclohexyl	$\text{C}_{24}\text{H}_{46}\text{O}_2$	78.62	12.65	78.92	12.66	1.4699	139-42/0.03	
Heterocyclic									
54	Tetrahydrofurfuryl	$\text{C}_{16}\text{H}_{30}\text{O}_4$	67.09	10.56	66.92	10.49	1.4611 <sup>26</sup>	148-9/0.5	34

Table IV. Symmetrical Bisethers of Thio- and Selenoglycols

Ref. No. of Cpd.	Glycol and Ether Group	Formula	Analysis				$n_D^{25}$	Boiling Point, ° C./Mm.	Yield, %
			Calcd.		Found				
			C	H	C	H			
Hexamethylene bithio									
60	2-Octyl	C <sub>22</sub> H <sub>46</sub> S <sub>2</sub>	70.54	12.38	70.92	12.49	1.4822	146-50/0.02	80
9	2-Ethylhexyl	C <sub>22</sub> H <sub>46</sub> S <sub>2</sub>	70.54	12.38	70.33	12.12	1.4838	175/0.15	75
52	3,5,5-Trimethylhexyl	C <sub>24</sub> H <sub>50</sub> S <sub>2</sub>	71.59	12.52	72.12	12.81	1.4830-40	140/0.005	85
65	Cyclopentyl	C <sub>16</sub> H <sub>30</sub> S <sub>2</sub>	67.09	10.56	66.58	10.23	1.5216 <sup>24</sup>	155/0.15	72
81	Cyclopentylmethyl	C <sub>18</sub> H <sub>34</sub> S <sub>2</sub>	68.75	10.90	68.47	10.86	1.5170	154-6/0.02	73
78	3-Cyclopentylpropyl	C <sub>22</sub> H <sub>42</sub> S <sub>2</sub>	71.30	11.42	70.94	11.28	1.5076 <sup>27</sup>	195/0.1	71
53	2-Cyclohexylethyl	C <sub>22</sub> H <sub>42</sub> S <sub>2</sub>	71.30	11.42	71.39	11.80	1.5142	165/0.03	60
Hexamethylene biseleno									
77	2-Ethylhexyl	C <sub>22</sub> H <sub>46</sub> Se <sub>2</sub>	56.39	9.90	56.42	10.00	1.5030	183/0.1	76
83	Cyclopentylmethyl	C <sub>18</sub> H <sub>34</sub> Se <sub>2</sub>	52.94	8.39	52.20	8.33	1.5401-49	175-80/0.1	41
3-Octylhexamethylene bithio									
84	Cyclopentylmethyl	C <sub>26</sub> H <sub>50</sub> S <sub>2</sub>	73.19	11.81	75.33	11.91	1.5117	207-9/0.2	22
Tetramethylene bithio									
66	2-(2'-Ethylhexylthio)-ethyl	C <sub>26</sub> H <sub>54</sub> S <sub>4</sub>	61.74	10.80	61.80	10.91	1.5161-87	210-15/0.1	70

Table V. Ethers of Miscellaneous Glycols

Ref. No. of Cpd.	Glycol and Ether Group	Formula	Analysis				$n_D^{25}$	Boiling Pt., ° C./Mm.	Yield, %
			Calcd.		Found				
			C	H	C	H			
Trimethylene glycol									
44	Bisdecyl	C <sub>23</sub> H <sub>48</sub> O <sub>2</sub>	77.46	13.57	77.35	12.77	1.4405	131-3/0.04	70
Tetramethylene glycol									
13	Bisnonyl	C <sub>22</sub> H <sub>46</sub> O <sub>2</sub>	77.12	13.53	77.21	13.54	1.4417-8	147-9/0.03	74
16	Bis-3,5,5-trimethylhexyl	C <sub>22</sub> H <sub>46</sub> O <sub>2</sub>	77.12	13.53	77.37	13.65	1.4409-10 <sup>27</sup>	117/0.03	65
26	Bis-4-(2'-ethylhexyloxy)-2-hexyl	C <sub>32</sub> H <sub>66</sub> O <sub>4</sub>	74.65	12.42	74.55	12.90	1.4445	171-4/0.001	64
25	Bis-4-(2'-cyclohexylethoxy)-2-hexyl	C <sub>27</sub> H <sub>62</sub> O <sub>4</sub>	75.24	12.23	75.50	12.43	1.4647-55	175-7/0.001	45
79	Bis-2'-ethylhexylthio-2-ethyl	C <sub>24</sub> H <sub>50</sub> O <sub>2</sub> S <sub>2</sub>	66.32	11.60	65.68	11.57	1.4810-20	185-90/0.05	52
Pentamethylene glycol									
15	Bisnonyl	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	77.46	13.57	77.64	13.55	1.4437-9	139-41/0.02	48
Decamethylene glycol									
14	Bis-2-hexyl	C <sub>22</sub> H <sub>46</sub> O <sub>2</sub>	77.90	13.08	77.31	13.20	1.4420 <sup>24</sup>	127-9/0.02	63
8	Bis-2-ethylhexyl	C <sub>26</sub> H <sub>54</sub> O <sub>2</sub>	78.32	13.65	77.98	13.62	1.4461-3 <sup>22</sup>	165-7/0.04	76
3-Hexylhexamethylene glycol									
80	Biscyclopentylmethyl	C <sub>24</sub> H <sub>46</sub> O <sub>2</sub>	78.62	12.65	79.17	12.91	1.4654 <sup>24</sup>	154-6/0.06	75
1,4-Cyclohexane glycol									
82	Bis-2-ethylhexyl	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	77.58	13.02	77.87	13.08		140-2/0.1	45
Hydroquinone									
6	Bis-2-ethylhexyl	C <sub>22</sub> H <sub>38</sub> O <sub>2</sub>	78.98	11.45	78.88	12.28	1.4855	144-8/0.02	48
Catechol									
12	Bis-2-ethylhexyl	C <sub>22</sub> H <sub>38</sub> O <sub>2</sub>	78.98	11.45	78.22	11.05	1.4850	137-9/0.02	20
2,5-Hexane glycol									
39	Bisnonyl	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	75.46	13.37	75.01	13.18	1.4316	105	66
1	Bis-2-ethylhexyl	C <sub>22</sub> H <sub>46</sub> O <sub>2</sub>	77.12	13.53	77.23	13.40	1.4388 <sup>22</sup>	117-18/0.02	39
17	Bis-2-cyclohexylethyl	C <sub>22</sub> H <sub>42</sub> O <sub>2</sub>	78.04	12.50	78.08	12.58	1.4680 <sup>24</sup>	141/0.03	82
18	2-Cyclohexylethyl-2'-ethylhexyl	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	77.58	13.02	77.92	12.90	1.4530 <sup>24</sup>	161-3/0.8	81

Table VI. Disulfides, Mercaptals, and Silicon Compounds

Ref. No. of Cpd.	Compound	Formula	Analysis				$n_D^{25}$	Boiling Point, ° C./Mm.	Yield, %
			Calcd.		Found				
			C	H	C	H			
Disulfides									
59	Biscyclopentyl disulfide	C <sub>10</sub> H <sub>18</sub> S <sub>2</sub>	59.38	8.97	58.90	9.08	1.5467	85-8/1-2	47
56	Bis-2-octyl disulfide	C <sub>16</sub> H <sub>34</sub> S <sub>2</sub>	66.16	11.80	66.06	11.90	1.4820	115/0.1	82
Mercaptals									
45	1,1-Bisocetylthio-2-ethylhexane	C <sub>24</sub> H <sub>50</sub> S <sub>2</sub>	71.59	12.52	71.48	12.09	1.4818	148-50/0.005	74
Silicon compounds									
51	1,6-Bistrimethylsilylhexane	C <sub>12</sub> H <sub>30</sub> Si <sub>2</sub>	62.55	13.13	62.88	13.17	1.4318	220-5/745	30
58	1,6-Bisbutyldimethylsilylhexane	C <sub>18</sub> H <sub>42</sub> Si <sub>2</sub>	68.73	13.46	68.24	13.36	1.4480	135-8/1-2	29
64	Didecyldimethylsilane	C <sub>22</sub> H <sub>48</sub> Si	77.57	14.19	77.58	14.32	1.4423	158-60/0.3	

to the original organic phase and dried over magnesium sulfate.

Next, 2-chlorocyclohexane (484 grams, 3.65 moles) was dissolved in ether and added dropwise to a stirred suspension of sodium methoxide (213 grams, 3.94 moles) in dry ether (1200 ml.). After complete addition, the mixture was stirred with refluxing for 2 hours and then cooled. Water was added to dissolve the salts and the two layers were separated. The aqueous layer was extracted twice with 100-ml. portions of ether, the combined extracts being washed with 5% hydrochloric acid, 5% bicarbonate, and saturated sodium chloride solution and then dried over magnesium sulfate. Distillation afforded 284 to 302 grams (61 to 65%) of ester, 75–77°/48 mm. (5).

**3-Hexyl-1,6-hexanediol and 3-"Octyl"-1,6-hexanediol (4).** 3-HEXYL-1,6-HEXANEDIOL.  $\beta$ -Hexyladipic acid (4) was reduced with lithium aluminumhydride in ether according to standard procedure to give an 80% yield of glycol (b.p., 137–40°/0.4 mm.). Phosphorus tribromide in the usual manner afforded the 1,6-dibromide in 61% yield (b.p., 114–7°/0.1 mm.).

3-"OCTYL"-1,6-HEXANEDIOL. The standard lithium aluminumhydride reduction of  $\beta$ -"octyl" adipic acid (4) in ether afforded an 88% yield of glycol (b.p., 154–7°/0.25 mm.). Conversion in the usual manner by means of phosphorus tribromide afforded a 39% yield (b.p., 124–6°/0.1 mm.).

In connection with this phase of the work, the problem of corrosion of copper by sulfur compounds was encountered. Inasmuch as there are reports in the literature that certain selenides are effective antioxidants, and the impurities arising in the course of selenide preparation are more

readily removed than their sulfur analogs, it was thought that the frequently observed extensive corrosion of copper and attendant decomposition of organic sulfides might be attributable to dissolved traces of hydrogen sulfide or mercaptans. Accordingly, a sample of 1,6-bis(2'-ethylhexylthio)hexane was prepared in the usual manner and carefully distilled through a Claisen head. Neither copper nor a mixture of copper and iron was attacked during heating for 15 to 24 hours at 150° in a nitrogen atmosphere. A thorough washing of the sulfides in diethyl ether with 10% aqueous copper sulfate, followed by filtration, also was an effective way of preliminary purification. It was especially useful in purification of selenides.

#### LITERATURE CITED

- (1) Faworski, A., Boshowski, V., *J. Russ. Phys. Chem. Soc.* **50**, 582 (1917).
- (2) Goheen, D.W., Vaughan, W.R., *J. Org. Chem.* **20**, 1016 (1955).
- (3) *Ibid.*, p. 1019.
- (4) *Ibid.*, **23**, 891 (1958).
- (5) Goheen, D.W., Vaughan, W.R., *Org. Syntheses* **39**, 37 (1959).
- (6) McAllan, D.T., Cullum, T.V., Dean, R.A., Fidler, F.A., *J. Am. Chem. Soc.* **73**, 3627 (1951).
- (7) McCready, D.W., Vaughan, W.R., Brown, B.B., Goheen, D.W., Dick, M.F., Turner, A., WADC Tech. Rept. **54-45** (June 1953).

RECEIVED for review October 1, 1959. Accepted September 8, 1960. Work done under contract W 33-038-ac-21457 between Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, and University of Michigan. Released for publication by Harold Rosenberg, Senior Project Engineer, Organic Materials Branch, WADC.

## Structural Guides to the Development of High Dielectric Constant Esters for Capacitors

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THE NEED FOR dielectric liquids that may be used over a much wider range in temperature than heretofore has been recognized for some time and certain military requirements have been established for such materials to be used from –65° to 200° C. (44). In addition, low-loss liquids of higher dielectric constant than those now used would permit the design of smaller and lighter equipment components. Present commercially available dielectric liquids do not have dielectric constants much higher than 5.

If a dielectric liquid is to be used in a wide temperature range, it must be stable toward oxidation and resistant to thermal breakdown at high temperatures. Volatility must be low in order to prevent loss of the capacitor impregnant under high-temperature conditions. At low temperatures, the liquid must not crystallize or become extremely viscous, as this results in a reduction in dielectric constant, accompanied by an increase in dielectric losses. To maintain the long life of liquid-impregnated capacitors, it is essential that the liquid be stable toward hydrolysis and incapable of reaction with the capacitor metal electrodes under conditions of high temperature and electrical stress. It is also desirable that dielectric liquids be flame-resistant and have high flash points.

A number of partially fluorinated esters, synthesized for use as high-temperature lubricants and hydraulic fluids, were found to have unusual chemical, physical, and electrical properties that made them promising as capacitor impregnants (10, 28).

One of the partially fluorinated esters was tested as a capacitor impregnant (5) and found to give substantial improvement over existing commercial dielectric liquids. This led to an investigation of the factors involved in the formulation of dielectric liquids having high dielectric constants. The survey included a study of composition, molecular structure, and dipole moment of a large number of compounds and resulted in the development of methods for estimating the dielectric constant of new, unsynthesized compounds. This report outlines such methods and their use in planning syntheses of a number of partially fluorinated esters with dielectric constants above eight.

#### ELECTRICAL PROPERTIES OF LIQUIDS

Characteristics of a dielectric liquid which are of major importance include dielectric constant (sometimes referred to as specific inductive capacity), electrical loss, and electri-