

colored and this interfered with the accuracy of the determination of the saponification value. There was at least, therefore, 0.1047 g. of arachidic acid in the residue and this is equivalent to 0.04% of the glyceride in the original oil.

TABLE IV.  
Composition of Saturated Acids.

	G.	%.	% of original oil.	% of glycerides in original oil.
Palmitic acid.....	29.23	65.97	12.12	12.73
Stearic acid.....	14.13	31.89	5.86	6.12
Arachidic acid.....	0.05	0.11	0.02	0.02
Oleic acid.....	0.90	2.03	0.17	0.18
Linolic acid.....			0.20	0.21
Total.....	44.31	100.00	18.37	19.26

### Summary.

The chemical and physical characteristics of a sample of cold pressed Hubbard squash seed oil have been determined. An exhaustive study has been made of the composition of the oil, the results of which are given in the following table:

Glycerides of	{	Palmitic acid.....	%.
		Stearic acid.....	13
		Arachidic acid, trace about.....	0.04
		Oleic acid.....	37
		Linolic acid.....	44
Unsaponifiable matter.....		1	

WASHINGTON, D. C.

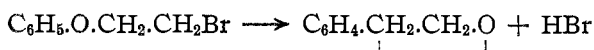
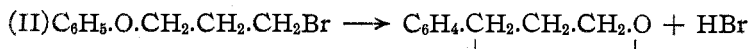
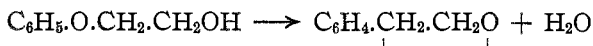
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

## SYNTHESES OF CHROMANES AND COUMARANES. II.

By R. E. RINDFUSZ, P. M. GINNINGS AND V. L. HARNACK.

Received November 4, 1919.

In a previous article<sup>1</sup> it was shown that chromane and coumarane may be easily prepared by either of two methods:



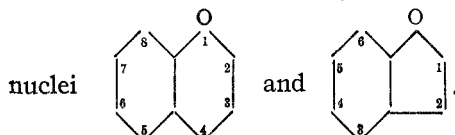
The procedure in each case is to heat the hydroxy or bromo ether with zinc chloride. The same products may also be obtained by heating free

<sup>1</sup> THIS JOURNAL, 41, 665 (1919).

phenol with ethylene or trimethylene chlorohydrin, but the yields are very low.

It was pointed out that, since phenol forms the starting point in each case, it should be possible by using substituted phenols to prepare various derivatives of the chromanes and coumaranes. The object of the present research was to make such compounds, as well as to compare and to improve the methods already given.

The system followed in naming the substituted chromanes and coumaranes is that of Stoermer,<sup>1</sup> numbering the positions on their respective



The inconsistency of starting to number from the oxygen in chromane and from the  $\alpha$ -carbon in coumarane is obvious; and since there can be no substitution on the oxygen, the second plan seems preferable. However, these two methods are already in use<sup>2</sup> and analogous systems are employed for coumarin,<sup>3</sup> for  $\gamma$ -benzo-pyrone (chromone)<sup>4</sup> and for benzo furane (coumarone).<sup>5</sup> So it seems best not to attempt a change.

During the course of this investigation it was found that phosphorus pentoxide could be used to dehydrate the hydroxy-ethyl or hydroxy-propylphenyl ether instead of the zinc chloride as in the reactions indicated above. The products in each case are the same. This reagent does not affect the halogen substituted ether as does the zinc chloride. Thus it is shown that the closing of the ring is a simple dehydration between the hydroxy group of the side chain and the hydrogen of the ring, and is not a substitution of halogen followed by elimination of halogen acid, as was suggested as a possibility in the first paper.

The yields by the phosphorus pentoxide dehydration are better than those by either method using the zinc chloride and the procedure rather more simple since there is not the tendency for carbonization. In general, the reaction is carried out as follows: The hydroxy ether to be dehydrated is dissolved in some inert solvent as toluene or ethyl methyl ketone which will allow refluxing at a fairly high temperature and still be easily fractionated from the cyclic ether which is to be prepared. Then phosphorus pentoxide is added in small quantities, allowing one molecule of the dehydrating agent for two molecules of the water to be taken up. The flask is frequently shaken, since at first there is a tendency to cake.

<sup>1</sup> *Ber.*, 36, 2872-2877 (1903).

<sup>2</sup> Richter, *Lexikon*, 1, 17-18.

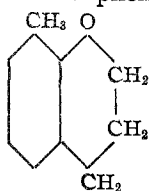
<sup>3</sup> *C. A.*, 12, 2985 (1918). (Index.)

<sup>4</sup> *C. A.*, 11, 3769 (1917). (Index.)

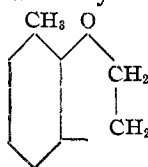
<sup>5</sup> *C. A.*, 12, 2941 (1918). (Index.)

In some cases, the order is reversed, the phosphorus pentoxide being suspended in the solvent and the hydroxyether run in. The mixture is refluxed for about an hour, and then most of the solvent is distilled off. The remaining liquid when cool is poured from the mass of phosphorus compounds at the bottom of the flask, ether is added and the solution washed with alkali and with water. After drying with calcium chloride, the ether is evaporated and the product distilled. This method was not discovered until the work was well under way and not all of the preparations previously carried out were repeated. However, each method was used in enough experiments to demonstrate clearly the superiority of this one.

The phenols used are (1) *o*-cresol which yields 8-methylchromane,

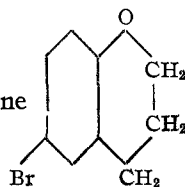


and 6-methylcoumarane,



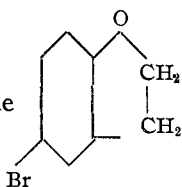
(2) *p*-Bromophenol

which gives as final products 6-bromochromane



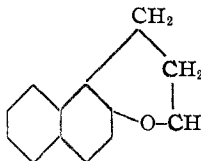
and 4-

bromocoumarane



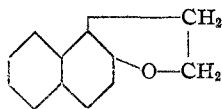
(3)  $\beta$ -naphthol which allows the pre-

paration of  $\beta$ -naphtho-dihydro-pyrane



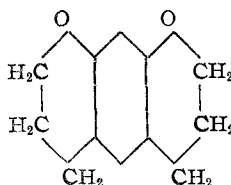
and  $\beta$ -naphtho-

dihydro-furane

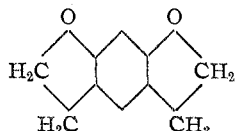


and (4) resorcinol which gives sym-

metrical benzo-tetrahydro-dipyrane,



and symmetrical

benzo-tetrahydro-difurane, . An attempt was made to

prepare the derivatives from *p*-nitrophenol.  $\gamma$ -Hydroxypropyl-*p*-nitrophenyl ether is easily prepared by refluxing the phenol with trimethylene chlorohydrin in the presence of sodium carbonate. On attempting the dehydration with either zinc chloride or phosphorus pentoxide, a violent reaction takes place and the whole goes almost instantly to tars and carbon.

Further investigations are being carried on to study the applicability of these reactions to the preparation of various cyclic compounds.

### Experimental Part.

#### Derivatives of *o*-Cresol.

$\gamma$ -Hydroxypropyl-*o*-tolyl Ether,  $C_6H_4(CH_3)(O-CH_2CH_2CH_2OH)^2$ . — Sodium was dissolved in absolute alcohol and the theoretical quantity of *o*-cresol added. Following this the mixture was treated with an equimolecular amount of trimethylene chlorohydrin and refluxed on the steam bath for about two hours. Most of the alcohol was then distilled off and the residue diluted with water. The product was extracted with ether, washed with sodium hydroxide and with water, and dried over potassium carbonate and distilled. The ether was obtained in 65% yield as a colorless oil boiling at 174–176° at 42 mm.;  $n_D^{27}$ , 1.523;  $d_{29}$ , 1.053.

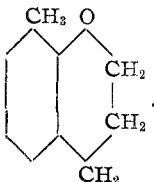
Subs., 0.2864:  $CO_2$ , 458.9 cc. (30.7°, 741.3 mm.).

Calc. for  $C_{10}H_{14}O_2$ : C, 72.3. Found: 71.9.

$\gamma$ -Bromopropyl-*o*-tolyl Ether,  $C_6H_4(CH_3)(O-CH_2CH_2CH_2Br)^2$ . — Twenty-three g. of sodium was dissolved in 200 cc. of absolute alcohol and 108 g. of *o*-cresol added. This was then refluxed for two hours with twice the molecular amount, 405 g., of trimethylene bromide. After this the mixture was treated as was the hydroxy ether above. The product which was fractionated from the excess trimethylene bromide was a clear oil with a rather fragrant odor and boiled at 154–6° at 20 mm. Yield, 25%;  $n_D^{27}$ , 1.535;  $d_{29}$ , 1.299.

Subs., 0.2816: AgBr, 0.2280.

Calc. for  $C_{10}H_{13}OBr$ : Br, 34.9. Found: 34.5.

8-Methylchromane, . (1) Preparation from  $\gamma$ -bromo-

propyl-*o*-tolyl ether. 50 g. of the ether just described was heated

under a reflux with 5 g. of anhydrous zinc chloride. Copious fumes of hydrogen bromide were given off. After about half an hour the material was allowed to cool, and was then taken up in ether, washed with alkali and with water and dried over calcium chloride. The product distilled at  $114^{\circ}$  to  $116^{\circ}$  at 20 mm., and was a colorless oil with an odor very like cresol;  $n_D^{27}$ , 1.542;  $d_{20}$ , 1.039.

Subs., 0.3716:  $\text{CO}_2$ , 623.1 cc. ( $24^{\circ}$ , 747 mm.).

Calc. for  $\text{C}_{10}\text{H}_{12}\text{O}$ : C, 81.1. Found: 81.4.

(2) Preparation from  $\gamma$ -hydroxypropyl-*o*-tolyl ether and zinc chloride.  $\gamma$ -Hydroxypropyl-*o*-tolyl ether was refluxed with  $1/10$  its weight of anhydrous zinc chloride. The temperature rose to  $235^{\circ}$  and then dropped gradually to  $180^{\circ}$  where it remained constant. The product was then fractionally distilled in 10 to 15% yield.

(3) Preparation from  $\gamma$ -hydroxypropyl-*o*-tolyl ether and phosphorus pentoxide. Forty g. of phosphorus pentoxide was suspended in 200 cc. of dry benzene and 100 g. of the hydroxy ether slowly added with shaking. After refluxing for a short time, the mixture was poured from the phosphorus compounds and distilled. The product may be washed with alkali and with water and redistilled with very little loss. An excellent grade of material practically all boiling at  $114$ – $115^{\circ}$  at 20 mm. was obtained in 76% yield.

(4) Preparation from *o*-cresol, trimethylene chlorohydrin and zinc chloride. 64 g. of trimethylene chlorohydrin, 74 g. of *o*-cresol and 5 to 10 g. of zinc chloride were heated together under a reflux condenser until the temperature became practically constant. After taking up in ether and washing with alkali, and with water, the mixture was fractionated giving 2 to 5% yields.

**$\beta$ -Hydroxyethyl-*o*-tolyl Ether**,  $\text{C}_6\text{H}_4(\text{CH}_3)(\text{OCH}_2\text{CH}_2\text{OH})^2$ .—This was prepared exactly as the  $\gamma$ -hydroxypropyl-*o*-tolyl ether described above by substituting ethylene chlorohydrin for the trimethylene compound. The clear colorless product boils at  $143$ – $145^{\circ}$  at 20 mm. Yield, 72%;  $n_D^{27}$ , 1.528;  $d_{20}$ , 1.079.

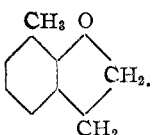
Subs., 0.4700:  $\text{CO}_2$ , 750.0 cc. ( $30.9^{\circ}$ , 739.1 mm.).

Calc. for  $\text{C}_9\text{H}_{12}\text{O}_2$ : C, 71.05. Found: 71.25.

**$\beta$ -Bromoethyl-*o*-tolyl Ether**,  $\text{C}_6\text{H}_4(\text{CH}_3)(\text{OCH}_2\text{CH}_2\text{Br})^2$ .—The directions given above for  $\gamma$ -bromopropyl-*o*-tolyl ether were followed in this preparation, ethylene bromide being substituted for trimethylene bromide. The product is a sweet-smelling, colorless liquid boiling at  $133$ – $4^{\circ}$  at 20 mm. Yield, 40%;  $n_D^{27}$ , 1.544;  $d_{20}$ , 1.360.

Subs., 0.4902: AgBr, 0.4332.

Calc. for  $\text{C}_9\text{H}_{11}\text{OBr}$ : Br, 37.2. Found: 37.4.

**6-Methylcoumarane**, .—This substance was prepared

by each of the methods given above for 8-methylchromane with very similar yields in each case. The dehydration of  $\beta$ -hydroxyethyl-*o*-tolyl ether by the use of phosphorus pentoxide gave a 50% yield. The compound is a colorless liquid boiling at 119–120° at 65 mm.;  $n_D^{27}$ , 1.527;  $d_{29}$ , 1.000.

Subs., 0.2258; CO<sub>2</sub>, 377.2 (24°, 747 mm.).

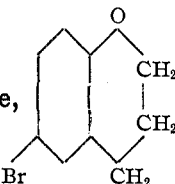
Calc. for C<sub>9</sub>H<sub>10</sub>O: C, 80.6. Found: 80.9.

#### Derivatives of *p*-Bromophenol.

**$\gamma$ -Hydroxypropyl-*p*-bromophenyl Ether**, Br.C<sub>6</sub>H<sub>4</sub>.O.CH<sub>2</sub>.CH<sub>2</sub>.CH<sub>2</sub>OH.—To obtain this substance, sodium *p*-bromophenolate was treated with trimethylene chlorohydrin in the manner given above for the corresponding *o*-tolyl ether. The product is a colorless liquid boiling at 206° at 48 mm. Yield, 75%;  $n_D^{22}$ , 1.563;  $d_{24}$ , 1.442.

Subs., 0.1930; AgBr, 0.1560.

Calc. for C<sub>9</sub>H<sub>11</sub>O<sub>2</sub>Br: Br, 34.6. Found: 34.4.

**6-Bromochromane**, .—The hydroxy ether just described

was dehydrated by heating with zinc chloride, and the product was purified by the method given. It is a water clear liquid with a pleasant odor, and is obtained in 7 to 10% yields. Phosphorus pentoxide would probably be a more satisfactory dehydrating agent than the one used. B. p. 143–144° at 18 mm.;  $n_D^{22}$ , 1.580;  $d_{25}$ , 1.465.

Subs., 0.2124; AgBr, 0.1902.

Calc. for C<sub>9</sub>H<sub>9</sub>OBr: Br, 37.6. Found: 38.0.

**$\beta$ -Bromo-ethyl-*p*-bromophenyl Ether**, Br.C<sub>6</sub>H<sub>4</sub>.O.CH<sub>2</sub>.CH<sub>2</sub>Br.—For the synthesis of this compound, the directions given for the analogous cresol derivative were followed. The yield was about 25%. It boils at 165° at 16 mm. and changes on standing to a white solid melting at 55–56°.

Subs., 0.1743; AgBr, 0.2356.

Calc. for C<sub>8</sub>H<sub>8</sub>OBr<sub>2</sub>: Br, 57.2. Found: 57.5.

**4-Bromocoumarane**.—When the ether just described was heated with  $\frac{1}{10}$  its weight of fused zinc chloride, the temperature rose to 245° and hydrogen bromide fumes were given off. The thermometer reading gradually dropped to 200°. After taking up in ether and washing with

alkali and water in the usual way, the product was obtained as a colorless liquid with a pleasant odor boiling at  $135^{\circ}$  at 20 mm.;  $n_D^{22}$ , 1.555;  $d_{20}$ , 1.436.

Subs., 0.2156: AgBr, 0.2047.

Calc. for  $C_8H_7OBr$ : Br, 40.2. Found: 40.5.

**$\beta$ -Hydroxyethyl-*p*-bromophenyl Ether**,  $Br.C_6H_4.O.CH_2.CH_2OH$ .—This ether was prepared from ethylene chlorohydrin and *p*-bromophenol following the procedure already given. The substance distilled as a water clear liquid at  $184^{\circ}$  at 20 mm. On standing it solidified and melted at  $49-50^{\circ}$ . The yield was about 40%. On treatment with phosphorus pentoxide it dehydrated to give the 4-bromocoumarane described above.

Subs., 0.3000: AgBr, 0.2552.

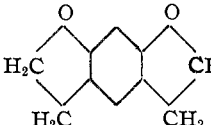
Calc. for  $C_8H_9O_2Br$ : Br, 36.8. Found: 36.5.

#### Derivatives of Resorcinol.

**Di- $\beta$ -hydroxyethyl-*m*-phenylene Ether**,  $C_6H_4(O.CH_2.CH_2OH)_2^{1,8}$ .—For the preparation of this compound, sodium was dissolved in absolute alcohol, and resorcinol and ethylene chlorohydrin added in equivalent quantities. After refluxing, the mixture was fractionally distilled without aqueous dilution since the product is soluble in water. It was obtained from  $230-234^{\circ}$  at 30 mm. as a viscous liquid which slowly solidified on standing. After washing with alcohol it was pure white and melted at  $81^{\circ}$ . It is soluble in alcohol and methylethyl ketone but insoluble in ether, benzene or ligroin. Yield, 40%.

Subs., 0.2000:  $CO_2$ , 259.7 cc. ( $24.3^{\circ}$ , 749.9 mm.).

Calc. for  $C_{10}H_{14}O_4$ : C, 60.6. Found: 60.9.

**Symmetrical Benzotetrahydro-difurane**, .—The

ether just described was dehydrated in methyl ethyl ketone solution by the action of phosphorus pentoxide according to the usual procedure. After most of the methyl ethyl ketone was distilled off water was added and the product extracted with ether. After washing and drying the cyclic ether was obtained as a disagreeably smelling, colorless liquid, boiling at  $110-113^{\circ}$  at 148 mm.;  $n_D^{22}$ , 1.448;  $d_{25}$ , 0.861.

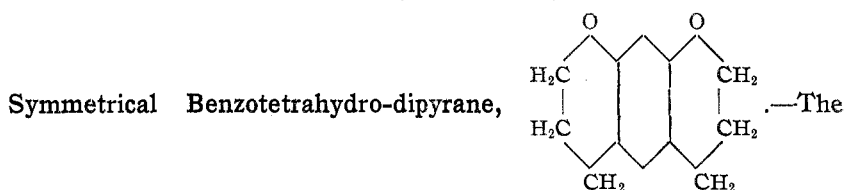
Subs., 0.2415:  $CO_2$ , 380.8 cc. ( $24.5^{\circ}$ , 734.5 mm.).

Calc. for  $C_{10}H_{10}O_2$ : C, 74.0. Found: 72.7.

**Di- $\gamma$ -hydroxypropyl-*m*-phenylene Ether**,  $C_6H_4(O.CH_2.CH_2.CH_2OH)_2^{1,8}$ .—Resorcinol was added to sodium alcoholate and then treated with trimethylene chlorohydrin, equivalent quantities of each being used. After refluxing for several hours, the sodium chloride was filtered off and the mixture fractionated. The product is a pale yellow, viscous liquid. B. p.,  $246-248^{\circ}$ , at 20 mm.;  $n_D^{34}$ , 1.529;  $d_{31}$ , 1.145.

Subs., 0.2747: CO<sub>2</sub>, 386.8 cc. (30.3°, 738.8 mm.).

Calc. for C<sub>12</sub>H<sub>18</sub>O<sub>4</sub>: C, 63.7. Found: 63.2.



ether just prepared was treated with phosphorus pentoxide in methyl ethyl ketone solution. After heating for some time, the most of the ketone was distilled off, the residue taken up in ether, washed with alkali and water, dried and distilled. B. p., 97°, at 75 mm. Yield 15%;  $n_D^{34}$ , 1.448.

Subs., 0.1012: CO<sub>2</sub>, 167.1 cc. (28.6°, 743.4 mm.).

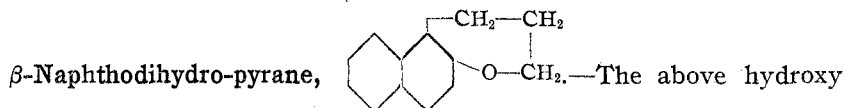
Calc. for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>: C, 75.7. Found: 75.3.

#### Derivatives of $\beta$ -Naphthol.<sup>1</sup>

$\gamma$ -Hydroxypropyl- $\beta$ -naphthyl Ether, C<sub>10</sub>H<sub>7</sub>O.CH<sub>2</sub>.CH<sub>2</sub>.CH<sub>2</sub>OH.—This was prepared in 25% yields by the usual method, and is a white solid which may be crystallized from benzene. M. p., 99–99.5°.

Subs., 0.3000: CO<sub>2</sub>, 522.3 cc. (32.3°, 742.9 mm.).

Calc. for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>: C, 77.2. Found: 77.5.



ether was dehydrated by phosphorus pentoxide in toluene in the usual way, and gave a viscous liquid which solidified on standing. After crystallization from alcohol, a white solid melting at 41–42° was obtained in 33% yield.

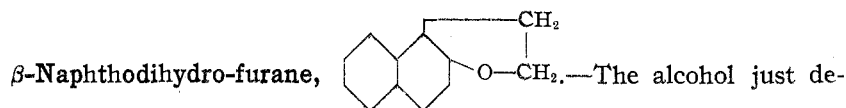
Subs., 0.3000: CO<sub>2</sub>, 570.1 cc. (32.6°, 742.5 mm.).

Calc. for C<sub>13</sub>H<sub>12</sub>O: C, 84.7. Found: 84.4.

$\beta$ -Hydroxyethyl- $\beta$ -naphthyl Ether, C<sub>10</sub>H<sub>7</sub>.O.CH<sub>2</sub>.CH<sub>2</sub>OH.—By the usual method, this compound was obtained as an impure solid which was purified with considerable difficulty. From 50% alcohol it separated as an amorphous compound, but from benzene it crystallized, and melted at 76–77°.

Subs., 0.3000: CO<sub>2</sub>, 520.5 cc. (32.8°, 742.9 mm.).

Calc. for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>: C, 76.6. Found: 76.9.



scribed was dehydrated in benzene solution according to the usual method. The final product was a viscous dark oil boiling at 185° at 10 mm. and

<sup>1</sup> Assistance in experimental work was given by L. H. Brede.



tending to decompose during distillation. The yields were low and the material not entirely pure;  $n_D^{33}$ , 1.482;  $d_{30}$ , 1.0066.

Subs., 0.2319; CO<sub>2</sub>, 451.2 cc. (32.5°, 742.5 mm.).

Calc. for C<sub>12</sub>H<sub>10</sub>O: C, 84.8. Found: 86.2.

**$\beta$ -Bromo-ethyl- $\beta$ -naphthyl Ether**, C<sub>10</sub>H<sub>7</sub>O.CH<sub>2</sub>.CH<sub>2</sub>Br.—Sodium naphthylate in absolute alcohol was treated with twice the theoretical amount of ethylene bromide. After refluxing, the alcohol and the excess ethylene bromide were distilled off and the desired product crystallized from alcohol. Melting point 91.5–92.5°. Yield 30%. Attempts to prepare  $\beta$ -naphthodihydro-furane from this by treatment with zinc chloride gave only carbonization and tars.

Subs., 0.3000; AgBr, 0.2221.

Calc. for C<sub>12</sub>H<sub>11</sub>OBr: Br, 31.87. Found: 31.51.

### Summary.

1. Cyclic ethers condensed to a benzene nucleus are easily prepared by dehydrating the appropriate hydroxy-alkyl-aryl ethers.

2. Zinc chloride or phosphorus pentoxide may be used for this, but the latter in general is the more satisfactory.

3. The following compounds were prepared:

	B. p. Degrees.	M. p. Degrees.	<i>d.</i>	<i>n.</i>
$\gamma$ -Hydroxypropyl- <i>o</i> -tolyl ether.....	174–6 (42 mm.)	..	1.053 (29°)	1.523
$\gamma$ -Bromopropyl- <i>o</i> -tolyl ether.....	154–6 (20 mm.)	..	1.299 (29°)	1.535
8-Methylchromane.....	114–6 (20 mm.)	..	1.039 (29°)	1.542
$\beta$ -Hydroxyethyl- <i>o</i> -tolyl ether.....	143–5 (20 mm.)	..	1.079 (29°)	1.528
$\beta$ -Bromo-ethyl- <i>o</i> -tolyl ether.....	133–4 (20 mm.)	..	1.360 (29°)	1.544
6-Methylcoumarane.....	119–20 (65 mm.)	..	1.000 (29°)	1.527
Hydroxypropyl- <i>p</i> -bromophenyl ether... .	206 (48 mm.)	..	1.442 (24°)	1.563
6-Bromochromane.....	143–4 (18 mm.)	..	1.465 (25°)	1.580
$\beta$ -Bromo-ethyl- <i>p</i> -bromophenyl ether....	165 (16 mm.)	56	.....	...
4-Bromocoumarane.....	135 (20 mm.)	..	1.436 (22°)	1.555
$\beta$ -Hydroxyethyl- <i>p</i> -bromophenyl ether... .	184 (20 mm.)	50	.....	...
Di- $\beta$ -hydroxyethyl- <i>m</i> -phenylene ether... .	230–4 (30 mm.)	81	.....	...
Symmetrical benzotetrahydrodifurane... .	110–3 (148 mm.)	..	0.861 (25°)	1.448
Di- $\gamma$ -hydroxypropyl- <i>m</i> -phenylene ether..	246–8 (20 mm.)	..	1.145 (31°)	1.529
$\gamma$ -Hydroxypropyl- $\beta$ -naphthyl ether.....	.....	99.5	.....	...
$\beta$ -Naphthodihydro-pyrane.....	.....	41–2	.....	...
$\beta$ -Hydroxyethyl- $\beta$ -naphthyl ether.....	185 (10 mm.)	..	1.007 (30°)	1.482
$\beta$ -Bromo-ethyl- $\beta$ -naphthyl ether.....	.....	92	.....	...
Symmetrical benzotetrahydro-dipyrane..	97 (75 mm.)	..	.....	1.448