

TABLE III

DETERMINATION OF WATER IN THE ETHER EXTRACT

Initial volume of ether, 50.0 ml.			
Fe ^{III} present (millimoles)	Total H ₂ O recov., ml.	Corrected H ₂ O, ml.	Ratio: H ₂ O/Fe
37.8	4.97	3.11	4.56
39.8	5.4	3.41	4.76
40.3	5.4	3.40	4.68
39.8	5.1	3.11	4.34
38.6	5.13	3.06	4.40
40.7	5.23	3.32	4.53
40.6	5.21	3.22	4.40

Mean 4.52

molecule of iron. The average ratio is 4.52; this value and the formula assigned to the iron compound in the ethyl ether phase by Kato and Isii⁸ suggests the possibility that at least two iron atoms are associated in the molecule existing in the ether phase; however, because of the large corrections applied in obtaining the water volumes, and because a water determination was made with only one concentration of acid and of iron, too great significance should not be placed on the ratio values.

No attempt was made to determine the extent to which the ether may be associated with the iron compound. That there may be such association is indicated by the fact that the compounds FeCl₃·(C₂H₅)₂O² and FeCl₃·HCl·2(C₂H₅)₂O⁸ have been prepared, and by the results of Kato and Isii. Although the first of the compounds mentioned is stated to be immediately decomposed by water, this does not preclude the possibility of the existence in an ether solution of

(8) Houben and Fischer, *J. prakt. Chem.*, **123**, 89 (1929).

a mixed compound containing both water and ether molecules. Because of the uncertainty regarding the association of ether molecules, an exact formulation of the compound or its structure cannot be made. It seems probable that the four chlorides are bonded tetrahedrally to the iron and that the waters are held by hydrogen bonds to the chlorides. As previously stated, Schwarz and Meyer could not prepare anhydrous HFeCl₄, which indicates that these hydrogen bonds are needed to stabilize the tetrahedral complex.

Acknowledgment: The authors are greatly indebted to Mr. John Gates and Mr. R. C. Jones for carrying out an extensive series of preliminary experiments. These experiments were of value in showing the dependence of the distribution ratio on the acid concentration and in establishing the ratio of acid and of chloride to iron in the ether solution.

Summary

The distribution of ferric iron between hydrochloric acid solutions and β,β'-dichloroethyl ether has been studied for various concentrations of acid and iron. Dichloroethyl ether can be used for the quantitative extraction of ferric iron from solutions greater than 7 formal in hydrochloric acid.

Chemical analyses of the ether solution have shown that one molecule of hydrochloric acid and from four to five molecules of water are present for each molecule of iron present in the ether layer. Neglecting polymerization and the possible presence of ether in the molecule, the empirical formula can be written as HFeCl₄·4-5H₂O.

PASADENA, CALIFORNIA

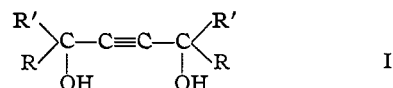
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[CONTRIBUTION FROM RÖHM AND HAAS COMPANY, INC.]

Cycli-Alkylation of Aromatic Compounds by the Friedel and Crafts Reaction

BY HERMAN ALEXANDER BRUSON AND JOHN W. KROEGER

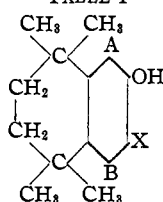
The method recently described by Kazarian¹ for preparing acetylenic alcohols by the interaction of calcium carbide, potassium hydroxide and a ketone, has made more readily available, many acetylenic tertiary glycols heretofore obtainable only with considerable difficulty and expense. These acetylenic tertiary glycols have the general formula (I)



(1) Kazarian, *J. Gen. Chem. (U. S. S. R.)*, **4**, 1347 (1934), *C. A.* **29**, 3978 (1935); Russian Patent 41,516 (1935), *C. A.* **30**, 8241 (1936); *J. Gen. Chem. (U. S. S. R.)*, **7**, 956 (1937), *C. A.* **31**, 5320 (1937).

Upon catalytic hydrogenation with Raney nickel at 60-85° and 100 lb. pressure/square inch (7 atm.), the acetylenic bond of these glycols can be completely saturated with hydrogen, thus making available in quantity 1,4-ditertiary glycols (II) having unique interest for further synthetic work.

TABLE I



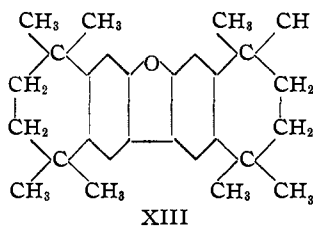
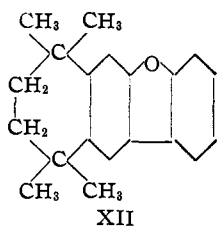
Phenol used	X	Values of		Formula	M. p., °C.	Analyses, %				
		A	B			Calculated	Found			
						C	H	C	H	
Phenol	H	H	H	C ₁₄ H ₂₀ O	145	82.29	9.87	81.92	9.34	
<i>o</i> -Cresol	CH ₃	H	H	C ₁₅ H ₂₂ O	125.5-126	82.50	10.16	82.18	9.88	
<i>m</i> -Cresol	H	H	CH ₃	C ₁₅ H ₂₂ O	134-135	82.50	10.16	82.51	9.84	
2,6-Dimethylphenol	CH ₃	CH ₃	H	C ₁₆ H ₂₄ O	164.5	82.69	10.42	81.72	9.58 ^a	
Pyrocatechol	OH	H	H	C ₁₄ H ₂₀ O ₂	182-183	76.38	9.15	76.84	9.11	
<i>o</i> -Phenylphenol	C ₆ H ₅	H	H	C ₂₀ H ₂₄ O	98	85.66	8.63	85.46	8.17	
<i>o</i> -Cyclohexylphenol	C ₆ H ₁₁	H	H	C ₂₀ H ₃₀ O	109-110	83.8	10.58	83.07	10.60	
<i>o</i> -Chlorophenol	Cl	H	H	C ₁₄ H ₁₉ OCl	103.5-104	Cl, 14.86		Cl, 15.1		
<i>m</i> -HO-C ₆ H ₄ -O-CH ₂ CH ₂ -O-CH ₂ CH ₂ Cl (1)	H	H	C ₄ H ₉ O ₂ Cl	C ₁₃ H ₂₇ O ₃ Cl	107-108	66.2	8.34	66.15	8.06	
						Cl, 10.85		Cl, 10.65		
<i>m</i> -HO-C ₆ H ₄ -O-CH ₂ CH ₂ -O-CH ₂ CH ₂ Cl (2)	H	H	C ₄ H ₉ O ₂ Cl	C ₁₃ H ₂₇ O ₃ Cl	71-75	66.2	8.34	65.67	8.12	
						Cl, 10.85		Cl, 10.65		

^a This compound rapidly oxidizes in the air, which accounts for the low analysis.

compound obtained by condensing (IV) with phenetole.

Most aromatic ethers, such as phenetole, guaiacol, ethyl *p*-cresyl ether, diphenyl ether, phenoxyacetic acid, and *m*-hydroxyphenoxyethoxy ethyl chloride, HOC₆H₄OCH₂CH₂OCH₂CH₂Cl, condense in the presence of aluminum chloride with compound (IV), so as to introduce one additional cycle in a manner analogous to that of phenol. The ether-phenol last mentioned gave two isomers, one, m. p. 107-108°, and the other, m. p. 71-75°.

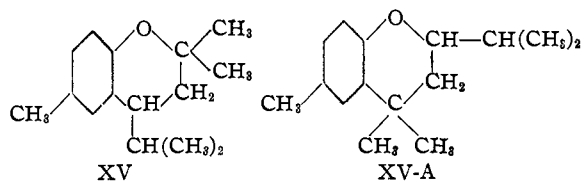
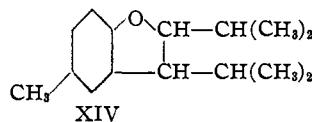
Diphenylene oxide, however, gave both a mono-cycli-alkylated and a di-cycli-alkylated compound, represented, respectively, by the probable formulas (XII) and (XIII).



The following phenols were each condensed with (IV) in the presence of anhydrous aluminum chloride to produce the corresponding analogs of (VII), the properties of which are given in Table I.

p-Cresol, however, reacted with 2,5-dichloro-2,5-dimethylhexane and aluminum chloride to give a mixture of two isomeric ether-like compounds having the empirical formula C₁₅H₂₂O, one of which is a liquid of faint minty odor, b. p. 107-108° (1 mm.), the other a crystalline compound, m. p. 100-101°. These compounds are believed

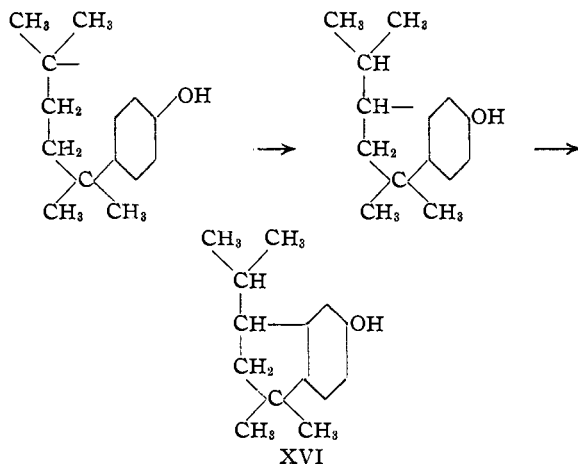
to be coumaranes or chromanes which may be tentatively represented as (XIV), (XV) or (XV-A). A small quantity of a di-cycli-alkylated derivative, m. p. 193-195°, also was isolated.



Reactions with Sulfuric Acid or Boron Trifluoride.—In all of the above condensations, aluminum chloride was used as the condensing agent. When the aluminum chloride was replaced by sulfuric acid or boron trifluoride, phenol condensed with compounds (III), (V) or (VI) to give not the tetramethyltetrahydronaphthol (VII) but a phenolic compound isomeric therewith melting at 97-98°. This substance gave a crystalline oxyacetic acid derivative, m. p. 112-113°. It did not give a crystalline derivative with formaldehyde, nor did it yield any identifiable acid upon oxidation with permanganate. It is believed to be a hydroxy-indane³ derivative (XVI) formed by rearrangement of the cycli-alkylating group, rather than an *alpha* isomer of compound (VII).

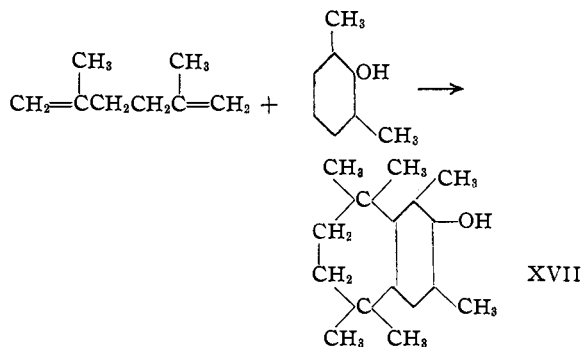
The formation of such a compound would result from the internal stabilization of an intermediate such as that shown below.

(3) Niederl, Niederl and Reznick, *THIS JOURNAL*, **58**, 657 (1936).



The net result of this stabilization is a shifting of a hydrogen atom from a secondary to a tertiary carbon atom⁴ followed by ring closure on the depleted carbon atom.

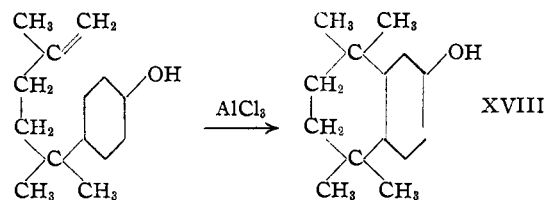
The possibility that compound (XVI) might be an *alpha* isomer of (VII) appears to be unlikely, since if the entering cycli-alkylene group did not rearrange, then a compound such as 2,6-dimethylphenol should condense to give only one compound (XVII), regardless of which catalyst was used.



However, 2,6-dimethylphenol behaves like phenol and gives two isomers, one with aluminum chloride (m. p. 165°) and the other with sulfuric acid (liquid, b. p. 156° (6 mm.)) as catalyst. Since two isomers are obtained, isomerism must occur in the entering group, unless the methyl groups of the phenol nucleus itself are assumed to wander. This appears unlikely under the conditions used.

That the second isomer in the case of phenol and of 2,6-dimethylphenol is not an open-chain para-substituted phenol, but a bicyclic structure, is shown by the fact that these compounds are unchanged by heating with aluminum chloride. If they had an open chain structure, aluminum

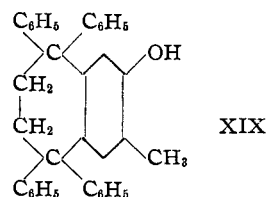
chloride should cause cyclization to the higher melting isomer, as follows



It has already been pointed out that in the alkylation of aromatic compounds with olefins, sulfuric acid shows a greater tendency to bring about rearrangements than does aluminum chloride.⁵ The hydroxy-indane compound (XVI) was not obtained when aluminum chloride was employed as the condensing agent under a wide variety of conditions.

When boron trifluoride was used as a catalyst at 90° for condensing *p*-cresol and (V), the liquid isomer (XIV) previously mentioned, together with a crystalline di-cycli-alkylated product (XVIII) melting at 193–195°, was obtained. At 0°, however, the rearranging tendencies of boron trifluoride are greatly reduced, phenol, for example, reacting with (V) to give the tetramethyltetrahydronaphthol (VII), together with the hydroxyindane (XVI) and the benzochromane (VIII).

Reactions with Other Cycli-alkylating Compounds.—It was of interest to investigate the action of phenols in the presence of aluminum chloride upon 1,1,4,4-tetraphenylbutane-1,4-diol (made from benzophenone, calcium carbide and potassium hydroxide, followed by catalytic hydrogenation), since this compound might undergo internal ring closure before appreciable cycli-alkylation occurred. The reaction with phenol, or *o*-chlorophenol, led mainly to dehydration of the glycol with formation of 1,1,4,4-tetraphenyl-1,3-butadiene. With *o*-cresol, however, the reaction yielded, in addition to 1,1,4,4-tetraphenyl-1,3-butadiene, a definite compound, m. p. 330–332°, the analysis of which corresponds to the probable structure (XIX).



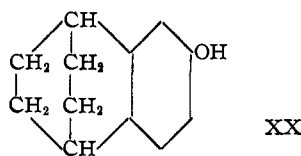
(4) Whitmore, *THIS JOURNAL*, **54**, 3274 (1932).

(5) Ipatieff, Pines and Schmerling, Printed Abstracts of 96th Meeting, Am. Chem. Soc., Sept. 5–9, 1938, Organic Division, p. 9.

TABLE II

Reacting thiophenol	Catalyst used	R	Alkylating agent	M. p., °C.	Formula of product	Analyses, %					
						C	Calculated H	S	Found C	Found H	S
Thiophenol	AlCl ₃	..	IV	79-80	C ₂₀ H ₂₆ S ₂	72.7	7.94	19.4	72.80	7.96	19.35
<i>o</i> -Thiocresol	AlCl ₃	CH ₃	IV	75-76	C ₂₂ H ₃₀ S ₂	73.8	8.45	17.9	73.88	8.29	17.83
<i>o</i> -Thiocresol	BF ₃	CH ₃	V	75-76	C ₂₂ H ₃₀ S ₂	73.8	8.45	17.9
<i>m</i> -Thiocresol	AlCl ₃	CH ₃	IV	105-106	C ₂₂ H ₃₀ S ₂	73.8	8.45	17.9	73.86	8.30	17.90
<i>m</i> -Thiocresol	AlCl ₃	CH ₃	V	105-106	C ₂₂ H ₃₀ S ₂	73.8	8.45	17.9
<i>p</i> -Thiocresol	AlCl ₃	CH ₃	IV	128-129	C ₂₂ H ₃₀ S ₂	73.8	8.45	17.9	73.80	8.48	17.85

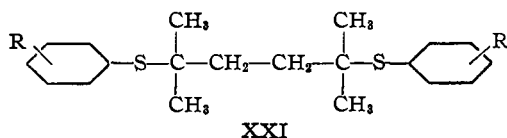
An attempt was made to obtain a compound with an internal bridge such as shown in formula (XX) by condensing phenol in the presence of anhydrous aluminum chloride with 1,4-dichlorocyclohexane.



A phenolic crystalline substance was obtained which melted at 124-127° and contained 0.35% chlorine. It appears probable that this is the desired compound (XX) in impure condition.

Finally, it should be pointed out that secondary aliphatic 1,4-glycols condense with phenol in the presence of 77% sulfuric acid to cycli-alkylate the aromatic nucleus. For example, 2,5-dihydroxyhexane and phenol gave a liquid phenolic product which appears to be a hydroxyindane derivative. 1,4-Dihydroxybutane, however, did not condense with phenol in the presence of 77% sulfuric acid to give tetrahydronaphthol.

Condensation with Thiophenols.—In contrast to phenol and its homologs, the thiophenols condense with compounds (IV) or (V) to form dithio ethers, instead of undergoing cycli-alkylation. The same dithio ethers are obtained, regardless of whether aluminum chloride or boron trifluoride is used as the catalyst. These dithio ethers are beautifully crystalline compounds of the general formula (XXI).



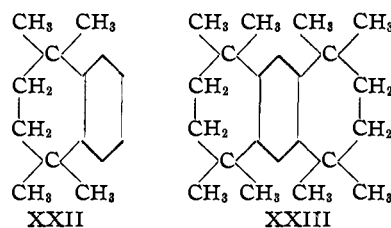
Their properties are given in Table II.

The unusual tendency for olefins and thiophenols to condense even in the absence of catalysts to form thiophenol ethers already has been pointed out by Ipatieff, Pines and Friedman,⁶

(6) Ipatieff, Pines and Friedman, *THIS JOURNAL*, **60**, 2731 (1938).

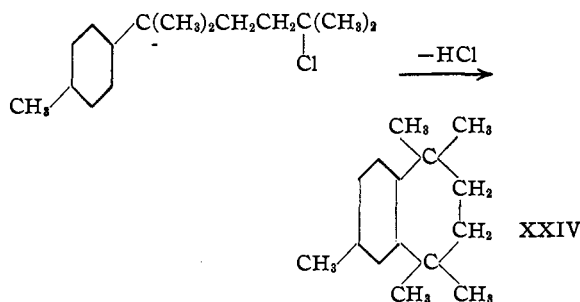
and may thus account for the non-formation of cycli-alkylation products.

Cycli-alkylation of Aromatic Hydrocarbons.—The condensation of 2,5-dichloro-2,5-dimethylhexane with benzene in the presence of anhydrous aluminum chloride yields a liquid mono- and a crystalline di-cycli-alkylation product, (XXII) and (XXIII), respectively.



It is assumed that the entering group in the case of hydrocarbons has the same configuration as in the case of phenols, since there was no difference in the method of preparation. The analytical data checked the formulas given.

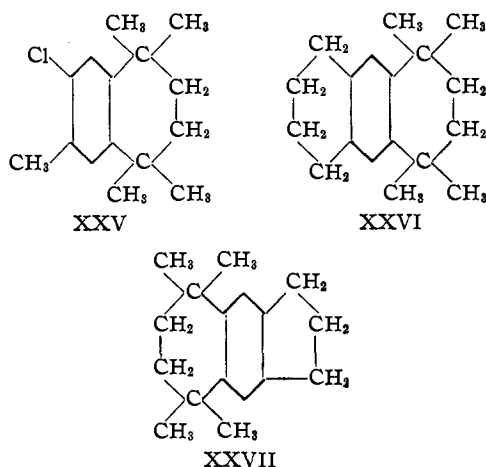
When only catalytic quantities of aluminum chloride are used, nearly quantitative yields of compound (XXIII) are obtained. Larger amounts of aluminum chloride favor the formation of the mono-cycli-alkylation product. Toluene, however, gave only a liquid mono-cycli-alkylation product. It already has been pointed out⁷ that in the cyclo-dehydration of *m*-CH₃C₆H₄CH₂CH₂C(CH₃)₂OH ring closure occurs so that the entering group takes a position as far removed as possible from the substituent already present in the ring. It is highly probable that in the case of



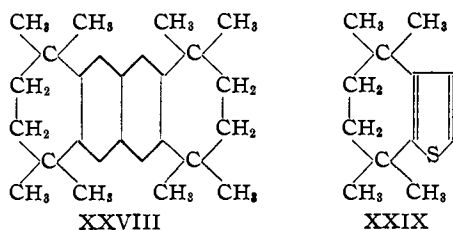
(7) Bogert, Davidson and Apfelbaum, *ibid.*, **56**, 959 (1934)

toluene the entering group is first introduced into the para position and immediately undergoes cyclo-dehydrohalogenation to give the mono-cycli-alkylation product (XXIV).

o-Chlorotoluene, tetralin and hydrindene each give crystalline mono-cycli-alkylation products with (IV) in the presence of aluminum chloride. These compounds may be represented by formulas (XXV), (XXVI) and (XXVII), respectively.



Naphthalene, however, gave only a di-cycli-alkylated derivative. The high melting point of this compound (319–320°) and the tendency for naphthalene to alkylate first in the beta position, is indicative that the compound is probably a hydronaphthacene derivative (XXVIII).



On the other hand, thiophene condenses with (IV) in the presence of stannic chloride as catalyst, to give only a mono-cycli-alkylation product (XXIX), which is believed to be a tetramethyl-tetrahydrobenzothiophene.

Although the exact formulas of these compounds have not as yet been proved, it is none the less certain that this simple method of introducing hydroaromatic rings into aromatic compounds may be of unusual interest at the present time, in connection with the synthesis of higher polynuclear structures in vitamin and hormone research.

Experimental

Preparation of Intermediates

2,5-Dimethyl-3-hexyn-2,5-diol.—Technical calcium carbide (20–35 mesh, 80%) was powdered by grinding with benzene in a ball mill. Seven hundred grams of this suspension, containing 1.75 moles of calcium carbide, was diluted with 800 g. of benzene, and 196 g. (3.50 moles) of powdered potassium hydroxide was added. The mixture was stirred vigorously, while 305 g. of acetone (5.25 moles) was added during seven hours. The temperature was held at 21–24° by external cooling and by controlling the rate of addition of the acetone.

Stirring was continued for ninety-six hours at about 20°; then the pasty mass was hydrolyzed by slow addition of 750–800 g. of 37% hydrochloric acid, which left the mixture neutral or faintly acid. The aqueous layer was discarded and the organic layer was heated to boiling and filtered. The clear yellow filtrate deposited 183 g. of 2,5-dimethyl-3-hexyn-2,5-diol on cooling. This was filtered off and washed with a little benzene; then the combined filtrate and washings were distilled to recover the remaining glycol, b. p. 115–140° (30 mm.), 60 g. The total yield of white, crystalline product was 243 g. or 98%. The material was pure enough for preparative purposes. A sample recrystallized from petroleum ether melted at 94–95° and had the following analysis: calcd. for $C_8H_{14}O_2$: C, 67.55; H, 9.93. Found: C, 67.47; H, 10.09.

(III) **2,5-Dimethylhexane-2,5-diol.**—This compound was prepared by hydrogenating 2,5-dimethyl-3-hexyn-2,5-diol dissolved in water or alcohol at 60–85° under 100 lb./square inch (7 atm.) pressure of hydrogen in the presence of Raney nickel. The product was obtained in excellent purity by simply evaporating the solvent *in vacuo*, m. p. ($-6H_2O$) 38°, m. p. (anhydrous) 88–89°; yield 95–99%.⁸

(IV) **2,5-Dichloro-2,5-dimethylhexane.**—III was dissolved in concentrated hydrochloric acid and the solution was saturated with hydrogen chloride at room temperature. During this last operation, the product crystallized as small, white leaflets. This was filtered off, washed thoroughly with water, finally with a little methanol, then air-dried or dried *in vacuo*. The yield was quantitative. The dichloride melted at 63–64° and had a strong menthol-like odor.⁹

(V) **2,5-Dimethyl-1,5-hexadiene.**—This compound was prepared by the usual Grignard technique from methyl allyl chloride and magnesium¹⁰ in a molar ratio of 2 to 1, b. p. 114.5° (763 mm.).

(VI) **2,2,5,5-Tetramethyltetrahydrofuran.**—This compound was obtained, together with a small amount of 2,5-dimethyl-2,4-hexadiene, by distilling (III) in the presence of 3% of aniline hydrobromide. It boiled at 112–114° (768 mm.).⁹

Cycli-alkylated Products

(VII) **5,5,8,8-Tetramethyl-5,6,7,8-tetrahydro-2-naphthol.** (a) (From phenol and IV).—Twenty-nine grams of phenol, 55 g. of (IV) and 3 g. of anhydrous aluminum

(8) Dupont, *Ann. chim. phys.*, (8) **30**, 485 (1913); *C. A.*, **8**, 1579 (1914).

(9) Henry, *Compt. rend.*, **143**, 497 (1906).

(10) Schales, *Ber.*, **70**, 117 (1937).

chloride were suspended and partly dissolved in 30 g. of petroleum ether (b. p. 90–100°). This mixture was stirred at room temperature for about one hour or until the first vigorous evolution of hydrogen chloride had abated. The suspension was then heated on a steam-bath for two hours, 2 g. of aluminum chloride added, and heating continued for two hours more. The product was stirred with cold, dilute hydrochloric acid, and the light gray crystalline tetrahydronaphthol derivative which separated was filtered off (42 g.). Evaporation of the organic layer gave an additional 6 g.; total yield, 48 g., 80%.

The product was recrystallized to constant melting point from petroleum ether or benzene, and separated as long, thick, colorless prisms, m. p. 145.0–145.2° (uncorr.). It gave an emerald-green color with alcoholic ferric chloride, and had a hydroxyl number of 279.9; calculated value, 275. The oxyacetic acid derivative (XI) melted at 164–165°. *Anal.* Calcd. for $C_{16}H_{22}O_3$: C, 73.23; H, 8.46. Found: C, 73.08; H, 8.48.

The ethyl ether boiled at 132° (5 mm.). *Anal.* Calcd. for $C_{16}H_{24}O$: C, 82.70; H, 10.42. Found: C, 81.91; H, 10.06.

Attempted oxidation of this ether with dilute nitric acid gave a crystalline yellow mono-nitro derivative, m. p. 106–108°. *Anal.* Calcd. for $C_{16}H_{23}O_3N$: C, 69.3; H, 8.37; N, 5.05. Found: C, 68.90; H, 7.92; N, 5.70.

(X), m. p. 232°, was prepared by condensing the substituted naphthol with aqueous formaldehyde in the presence of hydrochloric acid. *Anal.* Calcd. for $C_{20}H_{30}O$: C, 82.79; H, 9.59. Found: C, 82.91; H, 9.30.

Oxidation of (VII) with neutral potassium permanganate gave a small quantity of 1,1,4,4-tetramethyladipic acid, m. p. 190–193° (uncorr.). *Anal.* Calcd. for $C_{10}H_{18}O_4$: C, 59.36; H, 8.97. Found: C, 58.73; H, 8.05.

From the combined recrystallization liquors of several preparations of (VII), a small amount of a disubstituted derivative, the benzochromane (VIII) was isolated. This crystallized from petroleum ether in large, oblique hexahedra, m. p. 240–241°. Its hydroxyl number was zero. *Anal.* Calcd. for $C_{22}H_{34}O$: C, 84.00; H, 10.90. Found: C, 84.42; H, 10.68.

(b) (From Phenol and III).—Twenty-one grams of (III), 54 g. of phenol, and 50 g. of anhydrous aluminum chloride were suspended in 200 cc. of petroleum naphtha and stirred at 85–90° for eight hours. The mixture was hydrolyzed with cold, dilute hydrochloric acid, then the organic layer was taken up in benzene, washed with 5% sodium carbonate solution, and distilled. The fraction boiling from 150–165° (3 mm.) weighed 21 g. and crystallized on standing. Recrystallization from petroleum ether gave the pure compound, m. p. 145°.

(c) (From Phenol and VI).—Thirteen grams of phenol, 12.8 g. of (VI) and 13 g. of aluminum chloride were suspended in 30 g. of petroleum ether (b. p. 90–100°) and cooled for five minutes. The mixture was then stirred at room temperature for five hours and refluxed for two hours. The mixture was then hydrolyzed and filtered, giving 16 g. of crude product. After one recrystallization from petroleum ether, it melted at 143–145°.

(d) (From Phenol and V).—Forty grams of phenol and 4 g. of anhydrous aluminum chloride were suspended in 20 g. of 90–100° petroleum ether and cooled to 0° or below.

Forty-four grams of (V) was then added slowly with stirring, while the temperature was kept below 0°. The temperature was then allowed to rise slowly, the mixture was stirred at 25° for sixteen hours, and finally at 50° for one hour. The product was worked up as in (b). The fraction boiling from 128–150° (1 mm.) crystallized partly. On recrystallization from petroleum ether the solid melted at 145°.

Mixed melting points of products (a), (b), (c) and (d) showed no depressions.

(XI) **5,5,8,8-Tetramethyl-5,6,7,8-tetrahydro-2-naphthoxyacetic Acid.**—Four grams of (IV), 3.5 g. of phenoxyacetic acid, and 3.5 g. of anhydrous aluminum chloride were suspended in 30 g. of ethylene dichloride and stirred for one hour at room temperature. The mixture next was refluxed for five hours and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated and the solvent was evaporated by a stream of air, leaving 5.5 g. of greenish crystals. The solid was dissolved in petroleum ether and boiled with Norite for an hour. On cooling, the product separated in glistening white plates. A second crystallization from petroleum ether and two from 33% alcohol gave the pure compound, m. p. 164–165°. The melting point was not raised by the last recrystallization, and showed no depression when mixed with the oxyacetic acid derivative prepared by heating chloroacetic acid with an aqueous sodium hydroxide solution of (VII).

The properties of other substituted naphthols prepared in the manner described in (a) above are given in Table I.

***m*-Hydroxyphenoxyethoxyethyl Chloride.**—This compound was obtained as a crystalline solid, m. p. 46–47°, by condensing resorcinol in aqueous potassium carbonate solution with β,β' -dichlorodiethyl ether.¹¹

Six grams of *m*-hydroxyphenoxyethoxyethyl chloride, 5 g. of (IV) and 0.5 g. of anhydrous aluminum chloride were mixed and heated at 65° for four hours. Hydrolysis with dilute hydrochloric acid gave a dough-like mass which crystallized partly on macerating with water. The organic material was dissolved in 90–100° petroleum ether, and cooled, giving crystals which melted at 102–103°. Concentration of the mother liquor gave a second compound, m. p. 69–71°. Both these compounds were recrystallized twice more and the first was decolorized with Norite. The final melting points were 107–108° and 71–75°, respectively.

(XVI) **1,1-Dimethyl-3-isopropyl-5-hydroxyindane.**—Twenty-five grams of phenol and 54.5 g. of (III) were melted together and the melt was dropped slowly into 96 g. of 77% sulfuric acid, which was well stirred and held at 10°. The temperature was allowed to rise slowly to 35°, the mixture was stirred at room temperature for twenty-two hours, and at 85–95° for one hour, then was poured into 200 ml. of cold water. The oil was extracted with benzene, washed with water and dilute sodium carbonate solution, and distilled. The fraction boiling from 145–170° (5 mm.) (b. p. 160–165° (5 mm.)), weighing 30 g., solidified on standing. After several recrystallizations from petroleum ether, the pure compound was obtained as tiny needles, m. p. 97–98°. *Anal.* Calcd. for $C_{14}H_{20}O$: C, 82.29; H, 9.87. Found: C, 82.60; H, 9.70.

(11) Bruson, U. S. Patent 2,098,204 (1937).

This compound, like (VII), gave an emerald-green color with alcoholic ferric chloride, and formed a sparingly soluble sodium salt when dissolved in warm 10% sodium hydroxide. It did not give a crystalline methylene derivative with formaldehyde, but treatment of the sodium salt with chloroacetic acid gave an oxyacetic acid derivative, m. p. 112–113°. It was unchanged by warming with aluminum chloride in petroleum ether.

2,6-Dimethylphenol was condensed similarly with 2,5-dimethylhexane-2,5-diol in the presence of 77% sulfuric acid to give a compound of b. p. 156° (6 mm.). *Anal.* Calcd. for $C_{10}H_{24}O$: C, 82.69; H, 10.42. Found: C, 82.66; H, 10.34.

(XIX) 5,5,8,8-Tetraphenyl-3-methyl-5,6,7,8-tetrahydro-2-naphthol.—Eight grams of 1,1,4,4-tetraphenylbutane-1,4-diol, 10 g. of *o*-cresol, and 8 g. of anhydrous aluminum chloride were suspended in 100 ml. of petroleum ether (b. p. 30–60°) and refluxed for fourteen hours. After hydrolysis with 200 ml. of dilute hydrochloric acid, the product was filtered out (6 g.). Two recrystallizations from toluene gave the pure compound, m. p. 330–332°, as glistening, white needles. *Anal.* Calcd. for $C_{36}H_{50}O$: C, 90.08; H, 6.48. Found: C, 89.81; H, 5.94.

Evaporation of the mother liquors gave a small amount of 1,1,4,4-tetraphenyl-1,3-butadiene. After several recrystallizations from toluene, it was obtained as pale violet needles m. p. 195–196° (uncorr.). *Anal.* Calcd. for $C_{28}H_{22}$: C, 93.80; H, 6.19. Found: C, 93.67; H, 6.24.

(XX) 5,8-Endoethylene-5,6,7,8-tetrahydro-2-naphthol (?).—Fourteen grams of 1,4-dichlorocyclohexane (*cis* and *trans*), 8 g. of phenol, 1 g. of aluminum chloride, and 20 g. of petroleum ether were stirred for a half hour and refluxed for six hours; 9 g. of aluminum chloride was added and the mixture was stirred for four hours, then hydrolyzed with ice and hydrochloric acid. The organic layer was washed and distilled and the fraction boiling from 110–180° (3 mm.) was saved. Two recrystallizations from di-isobutylene gave white needles, m. p. 124–127°. *Anal.* Calcd. for $C_{12}H_{14}O$: C, 82.70; H, 8.10. Found: C, 81.00; H, 8.77; Cl, 0.35%.

2,5-Dimethylhexane-2,5-bis-(*p*-tolyl sulfide).—Nine g. of (IV), 6.2 g. of *p*-thiocresol, and 1.0 g. of anhydrous aluminum chloride were suspended and partly dissolved in 30 g. of petroleum ether (b. p. 90–100°), and refluxed for four hours. The product was hydrolyzed with dilute hydrochloric acid and the organic layer was cooled and evaporated to give 4 g. of the crystalline dithio ether. This was recrystallized to constant melting point from petroleum ether, giving long, white needles, m. p. 128–129°. Data on this compound and other dithio ethers prepared in the same manner are given in Table II. The compounds were insoluble in hot 5% sodium hydroxide.

(XXII) 1,1,4,4-Tetramethyl-1,2,3,4-tetrahydronaphthalene.—Thirty-six grams of (IV) was dissolved in 78 g. of benzene and stirred at 30° or lower, while 16 g. of anhydrous aluminum chloride was added in small portions. The thick suspension was then stirred at room temperature for twenty-one hours, refluxed for two hours, and poured into ice and dilute hydrochloric acid. The organic layer was washed with water and dilute sodium carbonate solution and distilled. A 61% yield (22.5 g.) of crude (XXII) was obtained, boiling from 95–125° (4 mm.). The

pure compound was a water-white oil and had the following properties: b. p. 82–84° (3 mm.); 248° (760 mm.); n_D^{27} 1.5278; d_4^{27} 0.9482; MR_D calcd., 61.06; found, 61.09.

(XXIII) 1,1,4,4,5,5,8,8-Octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene.—Thirty-six grams of (IV), 78 g. of benzene, and 1 g. of anhydrous aluminum chloride were stirred and refluxed for four hours. The product was hydrolyzed without cooling by adding warm, dilute hydrochloric acid; then the hot organic layer was separated and chilled. The substituted anthracene separated in large, white prisms which were filtered off and the filtrate was evaporated to recover the remainder (total, 26 g.). It was purified by recrystallization to constant melting point from benzene or carbon tetrachloride-methanol mixture (2:1) and melted at 220–222° (uncorr.). In the evaporation mentioned above, a small amount of oil remained, which contained 3.5 g. of the substituted naphthalene (XXII).

When treated with nitric and sulfuric acids (2:1), this compound formed a nitro derivative, m. p. 259–261°.

(XXVI) 1,1,4,4-Tetramethyl-1,2,3,4,5,6,7,8-octahydroanthracene.—Thirteen grams of tetralin, 18 g. of (IV) and 1 g. of anhydrous aluminum chloride were suspended in 30 g. of petroleum ether (b. p. 90–100°) and refluxed for five hours. The product was hydrolyzed with ice-cold, dilute hydrochloric acid, filtered, then the organic layer was taken up in benzene, washed and distilled. Two fractionations gave 7 g. of yellow sirup boiling from 150–160° (4 mm.) which crystallized on standing for four days. The solid was recrystallized four times from methanol containing a few drops of ethyl acetate, m. p. 90–91°.

(XXVII) 5,5,8,8-Tetramethyl-5,6,7,8-tetrahydro- β -naphthindane.—Fifteen grams of hydrindene, 18 g. of (IV) and 1 g. of aluminum chloride were suspended in 30 g. of petroleum ether and stirred at room temperature for two hours. The mixture was then refluxed for four hours and worked up as in the previous experiment. The fraction boiling from 110–150° (3 mm.) weighed 3 g. and crystallized in the receiver. The product was recrystallized four times from a mixture of methanol and ethyl acetate and finally separated as large square plates, m. p. 93–94°.

(XXVIII) 1,1,4,4,7,7,10,10-Octamethyl-1,2,3,4,7,8,9,10-octahydronaphthalene.—Thirty-eight grams of naphthalene, 55 g. of (IV) and 5 g. of aluminum chloride were suspended in 100 g. of petroleum ether (b. p. 90–100°) and refluxed for four hours. The product was hydrolyzed with cold, dilute hydrochloric acid and filtered. The crystalline solid was then washed with four 50-cc. portions of cold benzene to remove unchanged naphthalene, and air-dried; yield, 42 g., 80.5%. Two recrystallizations from toluene gave the pure product in the form of beautiful white needles, m. p. 319–320°.

Other hydrocarbons prepared in this way are described in Table III.

(XXIX) Thiophene and (IV).—Nine grams of (IV) and 8.4 g. of thiophene were dissolved in 30 g. of petroleum ether and 2.0 g. of anhydrous stannic chloride was slowly dropped in. The solution was stirred for one hour at room temperature, refluxed for three hours, then the product hydrolyzed, washed, filtered from a trace of black impurity, and distilled. The fraction boiling from 90–130° (6 mm.) was saved and redistilled. The pure compound had a boiling point of 94° (6 mm.). *Anal.* Calcd. for

TABLE III

Hydrocarbon used	Formula	M. p. or b. p., °C.	Analyses, %			
			Calculated C	Calculated H	Found C	Found H
Benzene (mono)	XXII C ₆ H ₆	B. 82-84 (3 mm.)	89.29	10.72	89.44	10.32
Benzene (di)	XXIII C ₁₂ H ₁₈ ^a	M. 221-222	88.5	11.5	88.50	12.02
Toluene	XXIV C ₇ H ₈	B. 95 (4 mm.)	89.1	10.95	88.85	11.07
<i>o</i> -Chlorotoluene	XXV C ₇ H ₇ Cl	M. 104-105	76.07	8.95	76.28	8.75
				Cl, 14.98		14.70
Tetralin	XXVI C ₁₀ H ₈	M. 90-91	89.2	10.82	89.25	11.18
Hydrindene	XXVII C ₁₇ H ₁₄	M. 93-94	89.4	10.61	88.71	10.70
Naphthalene (di)	XXVIII C ₁₀ H ₈ ^b	M. 319-320	89.59	10.42	90.05	10.35

^a Molecular weight (Rast): calcd., 298; found, 286. ^b Molecular weight (Rast): calcd., 348; found, 342.

C₁₂H₁₈S: C, 74.17; H, 9.34; S, 16.48. Found: C, 74.46; H, 9.70; S, 16.20.

p-Cresol and IV.—Thirty-three grams of *p*-cresol, 55 g. of (IV) and 3 g. of aluminum chloride were suspended and partly dissolved in 50 g. of petroleum ether. The mixture was then stirred for a half hour at room temperature and at 85-90° for two hours. Two grams of aluminum chloride was added and heating and stirring was continued for two hours more. The product was hydrolyzed, washed and distilled. The fraction boiling from 91-115° (2 mm.) (26.5 g.) gave the liquid isomer (A) as a water-white oil, having a pleasant, minty odor. It had the following properties: b. p. 107-108° (1 mm.); *n*_D²⁵ 1.5137; *d*₄²⁵ 0.953.

The fraction boiling from 115-140° (2 mm.) (6 g.) crystallized partly when diluted with petroleum ether and chilled. Recrystallization to constant melting point gave small prisms, m. p. 100-101° (B).

The above experiment was repeated, using (V) as a cycli-alkylating agent and boron trifluoride as a catalyst. Small amounts of the liquid isomer (A) and a disubstituted derivative (C) melting at 193-195° were obtained. The analytical data are as follows: calcd. for C₁₅H₂₀O (XIV and XV): C, 82.50; H, 10.16. Found (A): C, 83.02; H, 10.09. Found (B): C, 82.81; H, 9.92. Calcd. for the disubstituted derivative (C); C₂₃H₃₀O: C, 84.07; H, 11.05. Found: C, 84.27; H, 10.81.

Diphenylene Oxide and IV.—Nine grams of (IV), 8.5 g. of diphenylene oxide, and 1 g. of anhydrous aluminum chloride were suspended in 30 g. of petroleum ether (b. p. 30-60°) and stirred for eight and one-half hours at room temperature. The mixture was then refluxed for one hour, hydrolyzed, washed and distilled. The fraction boiling from 170-240° (4 mm.) (5.5 g.) was a thick yellow sirup (XII) and was analyzed. Calcd. for C₂₀H₂₂O: C, 86.27; H, 7.97. Found: C, 86.91; H, 8.38. From this it appeared the compound (XII) was contained in this fraction.

The residue of the above distillation was recrystallized three times from an ethyl acetate-methanol mixture as colorless crystals, m. p. 201-202°. *Anal.* (XIII) Calculated for C₂₃H₃₀O: C, 86.53; H, 9.34. Found: C, 87.00; H, 9.50.

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Summary

1. Di-tertiary 1,4-glycols condense in the presence of aluminum chloride with aromatic hydrocarbons, phenols, or phenol ethers, so as to introduce a new hydroaromatic cycle into the aromatic nucleus. The use of boron trifluoride or of 77% sulfuric acid as condensing agent in place of aluminum chloride, gives isomers of the above compounds. Phenols which are blocked in the para-position give chromanes or coumaranes.

2. Similar condensation products are obtained by using di-tertiary 1,4-dichlorides, 1,5-diolefins, and 2,2,5,5-tetraalkyltetrahydrofurans in place of the 1,4-glycols.

3. Thiophenols behave differently from phenols and give diaryl dithio ethers. Thiophene takes up a hydroaromatic cycle.

4. Certain aromatics, notably benzene, naphthalene and diphenylene oxide, readily take up two hydroaromatic cycles.

5. The term "cycli-alkylation" has been proposed for these reactions.

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