indene chlorohydrin and phosphorus pentachloride and (c,d) both chlorohydrins and thionyl chloride show practically identical physical properties and upon hydrolysis all give the *trans*-chlorohydrin as the chief product.

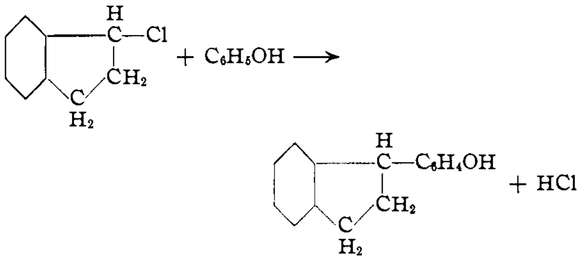
EVANSTON, ILLINOIS RECEIVED APRIL 7, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Indene Chloride with Phenols

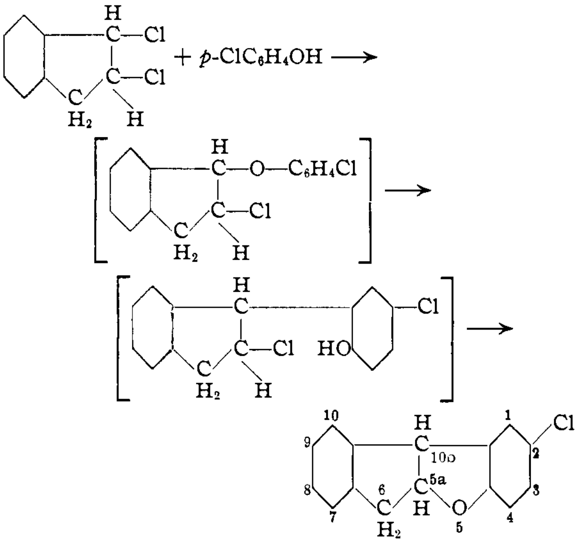
BY C. M. SUTER AND GARSON A. LUTZ

It was observed by Claisen[1] that benzyl chloride reacts readily with the sodium salt of a phenol in a non-polar solvent to give the *o*-benzylphenol rather than the ether. More recently[2] it has been shown that benzyl chloride reacts with excess phenol at temperatures above 125° to yield a mixture of *o*- and *p*-benzylphenol together with some dibenzylated product. This procedure had been mentioned previously by Courtot[3] and also in the patent literature[4] but without experimental details. Courtot[3] likewise reported that 1-chloroindane reacts with phenol in ether or benzene solution even at 15°, para substitution occurring. There are several patents describing the condensation of indene with phenols by means of acids;[5] presumably here also an intermediate indane derivative is involved.



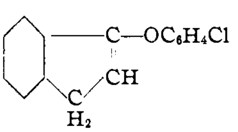
In the present investigation it has been found that indene chloride reacts readily with phenol, *m*- and *p*-cresol, and *p*-chlorophenol when the halide is added to an excess of the phenol at 145° or above with evolution of *two molecules* of hydrogen chloride. Fractional distillation of the resulting mixture after removal of the excess phenol gives in each case at least three compounds: a saturated ether containing one indane and one phenolic residue, an unsaturated phenol, and a high-boiling substance containing two phenolic groups. In the case of phenol this last material greatly predominates while for the cresols and *p*-chlorophenol the ether is obtained in considerable amount.

Taking into account the reactivity of the chlorine atom adjacent to the aromatic ring in the indene chloride the reaction with *p*-chlorophenol may be assumed to proceed as shown in the equations.

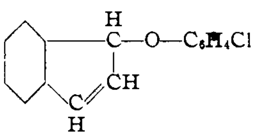


I

The evidence available concerning the nature of the ether (I) is in accord with the proposed structure. That the ether linkage is more stable than would be expected for an indenyl *p*-chlorophenyl ether (II or III) is shown by its inertness toward hydrogen iodide at high temperatures. The reaction with bromine occurs with evolution of



II



III

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(1) Claisen, *Ann.*, **442**, 237 (1925).

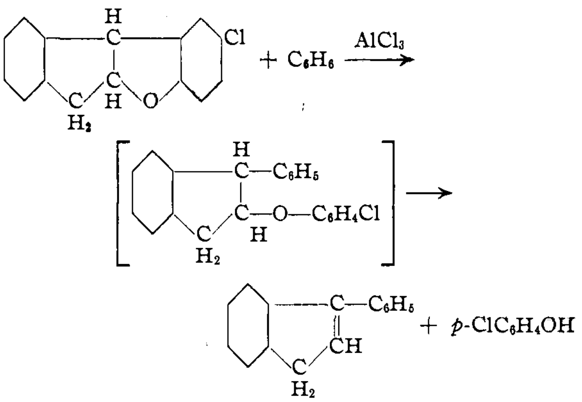
(2) McMaster and Bruner, *Ind. Eng. Chem.*, **28**, 505 (1936).

(3) Courtot, *Compt. rend.*, **187**, 661 (1928).

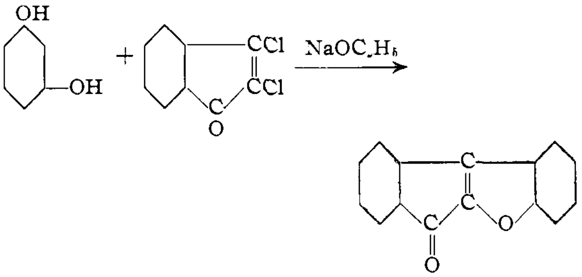
(4) Kalle and Company, German Patent 346,384; *Frdl.*, **14**, 1200 (1926).

(5) I. G. Farbenind, A.-G., French Patent 636,606, *C. A.*, **23**, 607 (1929); French Patent 39,642, *ibid.*, **26**, 4827 (1932); British Patent 297,075, *ibid.*, **23**, 2539 (1929); Müller and Kirchner, German Patent 499,587, *ibid.*, **24**, 4524 (1930); Rosenthal and Kropp, U. S. Patent 1,754,052, *ibid.*, **24**, 2549 (1930).

hydrogen bromide and potassium permanganate in acetone is not reduced. The reaction with aluminum chloride and benzene is of particular interest. There is formed a high yield of *p*-chlorophenol together with 3-phenylindene. In view of the interchangeability of aryl groups in the diaryl compounds studied by Fuson and co-workers[6] a plausible interpretation of the cleavage becomes possible.



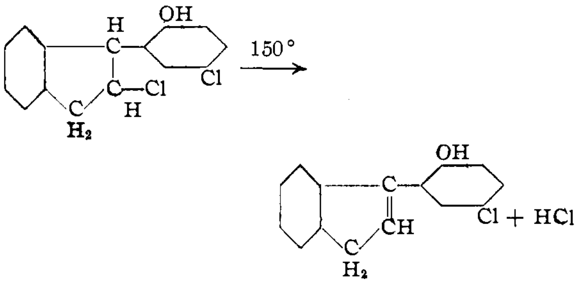
The alternative explanation involving the primary splitting of the ether linkage by the aluminum chloride seems less satisfactory because of the inertness of the compound to hydrogen iodide. The ethers obtained by the action of indene chloride upon phenol and the cresols likewise undergo cleavage with benzene and aluminum chloride giving in each case the corresponding phenol and 3-phenylindene. Assuming the structures assigned these ethers are correct they are derivatives of a ring system hitherto uninvestigated unless the compound obtained by Liebermann[7] through condensing 2,3-dichloroindone with resorcinol has the structure IV.



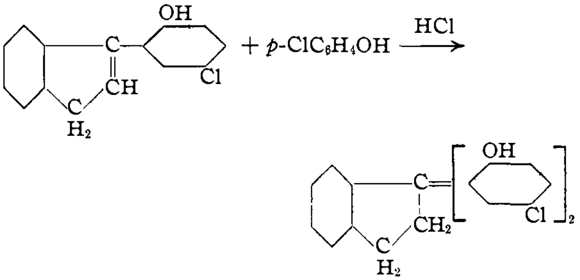
IV

The systematic name[8] for structure I is 2-chloro-5a,10b-dihydro-6-benz[*b*]indeno-[1,2-*d*]-furan and the numbering system is indicated in the formula. From a consideration of the mechanism of the condensation it is obvious that the ether from *m*-cresol may be either the 1- or 3-methyl derivative with the latter the more probable.

The second intermediate postulated to explain the formation of I may lose hydrogen chloride in another manner giving rise to the indenylphenol V. In the presence of excess *p*-chlorophenol and hydrogen chloride the majority of this condenses to the diphenol VI. Apparently there is little or no diindenyl-*p*-chlorophenol produced.



V



VI

The indenyl-*p*-chlorophenol V was isolated as the crystalline benzoate. In the reaction of indene chloride with phenol there is formed in small amount a high-melting (225°) phenolic compound to whose structure there are at present few clues. This substance is formed in small yield whether or not phenol is present in excess. Analysis indicated the presence of one indene and two phenol residues.

While the diphenolic product obtained from a para substituted phenol probably consists of a single compound of which VI is typical this is not the case for the high-boiling product obtained from phenol itself. Here the primary substitution may be expected to occur either ortho or para to hydroxyl, condensation of the resulting indenylphenols with another molecule of phenol producing three diphenols. None of these has been isolated in a pure state. Methylation and distillation of the mixture of diethers gave a product boiling over a range of about 10°, confirming

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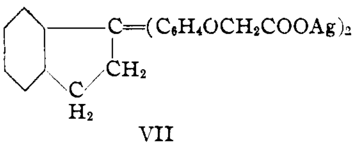
[6] Fuson, Kozacik and Eaton, THIS JOURNAL, **55**, 3800 (1933).

[7] Liebermann, *Ber.*, **32**, 923 (1899).

[8] Patterson, THIS JOURNAL, **47**, 543 (1925). We wish to thank Dr. Patterson for his advice in naming these compounds.

the idea that a mixture was present. The product obtained by reaction with chloroacetic acid in alkaline solution did not crystallize but gave an amorphous silver salt that analyzed correctly for VII.



VII

Since in one experiment a small amount of 2-chloroindene was isolated as a by-product, it seemed possible that this might be an intermediate in the reaction. It was found that 2-chloroindene does not react with phenol at temperatures considerably above 150° but if hydrogen chloride is passed into the reaction mixture the usual condensation products result.

Experimental

Reaction of Indene Chloride with *p*-Chlorophenol.—In a three-necked flask equipped with a mercury-sealed stirrer, thermometer, dropping funnel and a reflux condenser to which was attached a hydrogen chloride exit tube was placed 336 g. (2.6 moles) of *p*-chlorophenol. This was heated to 170° and 48.5 g. (0.26 mole) of indene chloride[9] added dropwise over a two-hour period. The temperature was dropped to 150–160° after evolution of the hydrogen chloride began and heating was continued until no more gas was evolved. The viscous, fluorescent mixture was transferred to a modified Claisen flask and the excess *p*-chlorophenol distilled off at 25 mm. The residue was distilled from a 250-cc. Claisen flask bearing a six-inch (15-cm.) column insulated with magnesia and attached to a wide side tube to facilitate removal of the viscous distillate. There was obtained 17.3 g. (A) distilling at 185–195° (4 mm.), 5 g. (B) b. p. 195–255° (4 mm.), and 34 g. (C) b. p. 255–265° (4 mm.).

The residue (10–15 g.) was a translucent alkali soluble glass apparently the same as fraction C. Fraction A which was mostly alkali insoluble was recrystallized from a methanol–ethyl acetate mixture and melted[10] at 114–115°.

Anal. Calcd. for $C_{15}H_{11}OCl$: Cl, 14.6. Found: Cl, 14.7.

Redistillation of fraction B gave an oily phenol, b. p. 180–190° (4 mm.), which upon treatment with pyridine and benzoyl chloride gave a crystalline benzoate, m. p. 139–140°, after crystallizing from ethyl propionate.

Anal. Calcd. for $C_{22}H_{15}O_2Cl$: Cl, 10.2. Found: Cl, 10.3.

About 15 g. of fraction C was redistilled and the portion boiling at 257–262° (4 mm.) collected. This was a light yellow viscous oil at 150° which set to a brittle glass at room temperature. It was not obtained crystalline. It dissolved readily in dilute alkali.

Anal. Calcd. for $C_{21}H_{16}O_2Cl_2$: Cl, 19.1. Found: Cl, 19.05.

Reaction of Indene Chloride with *m*- and *p*-Cresol.—These reactions were carried out in the same manner as the one with *p*-chlorophenol. From 63 g. of indene chloride and 364 g. of *m*-cresol were obtained 17 g. of the ether, b. p. 170–175° (4 mm.), m. p. (from methanol) 131.5–132.5°; 3 g. of a phenolic product, b. p. 175–185° (4 mm.), which was not obtained pure, and 40 g. of the diphenol, b. p. 250–255° (4 mm.).

Anal.[11] (of ether). Calcd. for $C_{16}H_{14}O$: C, 86.4; H, 6.35. Found: C, 86.3; H, 6.6.

The ether reacted readily with bromine in carbon tetrachloride with evolution of hydrogen bromide to give a product melting at 234.5–235° (corr.) after crystallizing from ethyl propionate.

Anal. Calcd. for $C_{16}H_{12}OBr_2$: Br, 42.1. Found: Br, 42.1.

The glassy diphenol also was analyzed.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.6; H, 6.7. Found: C, 83.2; H, 6.8.

The yields of the three compounds obtained from indene chloride and *p*-cresol were the same as for the meta isomer. The ether, b. p. 189–195° (5 mm.), melted at 85–86° when crystallized from methanol.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.4; H, 6.35. Found: C, 86.2; H, 6.5.

The diphenol distilled at 250–255° (4 mm.) and set to a brittle glass at room temperature. Attempts to crystallize it were unsuccessful.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.6; H, 6.7. Found: C, 83.2; H, 6.7.

Reaction of Indene Chloride with Phenol.—From 74.4 g. of indene chloride and 375 g. of phenol at 150–160° were obtained 6 g., b. p. 165–175° (4 mm.), 3 g. b. p. 175–200° (4 mm.) and 74 g., b. p. 250–255° (4 mm.). The first fraction after two crystallizations from methanol melted at 78.5–79°. It was insoluble in alkali.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.5; H, 5.8. Found: C, 86.5; H, 5.9.

The addition of excess bromine to 0.5 g. of the ether in 50 cc. of carbon tetrachloride gave a dibromo compound which after two crystallizations from petroleum ether melted at 195–196° with decomposition.

Anal. Calcd. for $C_{15}H_{10}OBr_2$: Br, 43.7. Found: Br, 44.0.

The second fraction contained a small amount of a phenolic compound which was slightly soluble in hot dilute sodium hydroxide but nearly insoluble in the cold. After crystallizing from benzene it melted at 224–225°. It reacted readily with bromine in carbon tetrachloride and with permanganate in acetone. The methyl ether (m. p. 208–210°) reacted with bromine but did not react with permanganate. This phenol also results from refluxing a solution of equimolecular amounts of indene chloride and phenol in bromobenzene for three hours and cooling. The yield is about 8% of the weight of indene chloride used.

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(9) Suter and Lutz, THIS JOURNAL, **60**, 1360 (1938).

(10) All melting points are corrected.

(11) The carbon and hydrogen analyses were made by Mr. Stanley Cristol working under an N. Y. A. grant.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.16; H, 6.09.

The third fraction was an amber-colored glass which did not crystallize. Reaction with excess chloroacetic acid in aqueous alkali gave an oily acid which was converted into its insoluble silver salt by adding silver nitrate to an aqueous solution of the ammonium salt.

Anal. Calcd. for $C_{25}H_{20}O_6Ag_2$: Ag, 34.0. Found: Ag, 34.3.

Analysis of the diphenol itself confirmed the formula indicated by the silver salt.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.3; H, 6.1.

The methyl ether, prepared by alkylation with methyl sulfate in alkali, b. p. 200–210° (3 mm.), reacted with benzene and aluminum chloride upon refluxing. The products were anisole and an oil, b. p. 157–165° (4 mm.), probably an impure 3-phenylindene.

Reaction of 2-Methyl-5*a*,10*b*-dihydro-6-benz[*b*]indeno[1,2,*d*]-furan with Benzene and Aluminum Chloride.—To 125 cc. of dry benzene was added 7 g. of the ether obtained from *p*-cresol and indene chloride. The solution was cooled, 20 g. of aluminum chloride was added and the mixture was refluxed for three hours. After hydrolysis with cold dilute acid extraction of the benzene layer gave a good yield of *p*-cresol, identified as the benzoate, m. p. 69–70°. Fractionation of the alkali insoluble portion gave 2.1 g. of 3-phenylindene,[12] b. p. 148–150° (3 mm.), n^{24}_{D} 1.6313, d^{27}_{4} 1.083. Using less than one equivalent of aluminum chloride instead of an excess gave substantially the same results.

In the case of the ether obtained from indene chloride and *p*-chlorophenol an 80–85% yield of *p*-chlorophenol was isolated when either benzene or toluene was used with the aluminum chloride. Phenol and *m*-cresol together with the phenylindene were obtained by treatment of the corresponding ethers with benzene and aluminum chloride.

After refluxing the ether from *p*-chlorophenol with hydriodic acid for thirty hours, or heating with the same reagent in a sealed tube at 225° for four hours most of the starting material was recovered unchanged.

Summary

1. Indene chloride reacts rapidly with phenol and its simple derivatives with loss of two molecules of hydrogen chloride.

2. One of the compounds formed in each case is an ether which is probably a derivative of a benzindenofuran. The major part of the reaction product is, however, phenolic in character.

3. A reaction mechanism is suggested that explains the formation of most of the compounds isolated.

EVANSTON, ILLINOIS RECEIVED APRIL 7, 1938

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[12] Von Braun, *Ber.*, **62B**, 1059 (1929).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of 5-Chloro-10-methyl-1,2-benzanthracene and Related Compounds

BY MELVIN S. NEWMAN

The synthesis of 7-chloro-10-methyl-1,2-benzanthracene and the corresponding 7-cyano, 7-carboxy, and carbomethoxy derivatives has recently been described.[1] These compounds were prepared in order that a study might be made of the effect of certain functional groups on the carcinogenic activity of 10-methyl-1,2-benzanthracene. It seemed advisable to prepare similar series of compounds in which the functional groups were attached at other positions of the nucleus in order to determine to what extent the positions occupied by the various functional groups affect the carcinogenicity of the resulting compounds. In this report the preparation of 5-chloro- and 5-cyano-10-methyl-1,2-benzanthracene and of the amide of 5-carboxy-10-methyl-1,2-benzanthracene is described.[2]

The method of synthesis was similar to that employed in the case of the isomeric 7-substituted compounds.[1] The Grignard reagent from 1-bromo-2-chlorobenzene (92% yield) was condensed with 1,2-naphthalic anhydride to produce a mixture of keto acids from which only the desired 2-*o*-chlorobenzoyl-1-naphthoic acid was isolated in a pure condition. The structure of this acid was proved by decarboxylation to *o*-chlorophenyl 2-naphthyl ketone. As this ketone proved difficult to crystallize, the comparison with authentic *o*-chlorophenyl 2-naphthyl ketone was effected through the crystalline 2,4-dinitrophenylhydrazone. The rest of the synthesis offered no particular difficulties and the entire scheme is indicated in the chart.

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[1] Newman and Orchin, THIS JOURNAL, **60**, 586 (1938).

[2] It was originally intended to complete the series by the synthesis of the corresponding 5-carboxy and 5-carbomethoxy derivatives, but the unexpected difficulty encountered in the hydrolysis of the nitrile, resulting in the formation of the amide, blocked efforts in this direction. Further experiments on hydrolysis of the amide were not made owing to the small amounts of amide available and it did not seem advisable at this time to repeat the entire synthesis in order to complete this part of the program.