0.2521, 0.4098, 0.5616; Δt, 0.1175°, 0.1861°, 0.2485°. Calcd.: 212. Found: 215, 221, 232.

The authors desire to express their gratitude to Professor Gomberg at the University of Michigan for permitting some of the experiments and analyses to be carried out in his Laboratory.

Summary

1. The action of sodium upon boiling chlorobenzene leads to the formation of benzene, biphenyl, *o*-diphenylbenzene, *p*-diphenylbenzene (minute amount), triphenylene, *o,o'*-diphenylbiphenyl, together with unidentified resinous and tarry hydrocarbons.

2. The reaction is conveniently interpreted by assuming the intermediate formation of free phenyl and *o*-phenylene radicals.

3. The action of sodium upon *n*-heptyl bromide leads to the formation of heptane, heptylene, tetradecane, a heneicosane of undetermined structure, and hydrocarbons of higher molecular weight. This type of reaction appears to be general for the bromides of primary alcohols.

4. The action of sodium upon chlorobenzene in the presence of an excess of toluene leads to the formation of nearly 50% of benzene; biphenyl is not produced, diphenylmethane, *p*-methylbiphenyl being formed in its stead. The reaction takes an analogous course in the presence of an excess of dimethylaniline, the condensation products containing nitrogen.

5. The constitution of *o*-diphenylbenzene and *o,o'*-diphenylbiphenyl has been confirmed by synthesis.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WEST VIRGINIA UNIVERSITY]

SOME CYCLOHEXYL-PHENOLS AND PHENOL ETHERS

BY J. F. BARTLETT[1] WITH C. E. GARLAND

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Considering the many recent developments in the preparation of alkyl and aryl phenols[2] and the studies made of their germicidal properties, it was decided to prepare some of the cyclohexyl derivatives in order that they might be compared with those already known.

Previous to this time, cyclohexyl-phenol[3] is the only derivative of this particular type recorded in the literature. Wuyts prepared this compound

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[1] This communication is an abstract of a thesis submitted by J. F. Bartlett, in partial fulfilment of the requirements for the degree of Master of Arts in Chemistry, at West Virginia University.

[2] The chief contributions have been made by the following investigators. (a) Johnson and Hodge, THIS JOURNAL, **35**, 1014 (1913). (b) Johnson and Lane, *ibid.*, **43**, 348 (1921). Leonard, *J. Am. Med. Assoc.*, **83**, 2005 (1924). (c) Dohme, Cox and Miller, THIS JOURNAL, **48**, 1688 (1926). (d) Klarmann, *ibid.*, **48**, 791, 2358 (1926).

[3] Wuyts, *Bull. soc. chim. Belg.*, **26**, 304 (1912).

by condensing cyclohexanol with a large excess of phenol in the presence of toluene-4-sulfonic acid. The melting point recorded is 128°.

Applying the method Klarmann[2d] used in similar reactions, cyclohexyl chloride was condensed with resorcinol, anisole and phenetole in the presence of anhydrous aluminum chloride. For the preparation of cyclohexyl-phenol, Klarmann's modification of the method employed by Liebmann[4] was used. Cyclohexyl chloride was condensed with phenol in the presence of anhydrous aluminum chloride. It was also prepared from cyclohexyl-anisole by hydrolysis with constant-boiling hydrobromic acid. In each case the compound was the same as that prepared by Wuyts, as indicated by the melting point.

The phenol coefficients[5] of cyclohexyl-resorcinol and cyclohexyl-phenol were determined. The solubility of cyclohexyl-resorcinol in distilled water is 51 mg. per 100 cc. at 25°. Using this solution, a phenol coefficient of 23-27 was found. Apparently the cyclic structure of the side chain reduces the phenol coefficient, as compared with that of *n*-hexyl-resorcinol (46–56), to near that of the *iso*hexyl-resorcinol recorded by Dohme, Cox and Miller, which is given as 27. The solubility of cyclohexyl-phenol in distilled water is 6 mg. per 100 cc. at 25°. At this concentration no germicidal properties were indicated.

Work in the field of cyclohexyl-phenols and derivatives is being continued.

Experimental Part

Cyclohexyl-resorcinol. $C_6H_3(C_6H_{11}).(OH)_2(1,2,4)$.—Cyclohexyl chloride was prepared by treating cyclohexanol with concd. hydrochloric acid, and refluxing slowly while dry hydrogen chloride was passed through the mixture, in order to increase the yield. This was continued for a period of about three hours. The upper layer of cyclohexyl chloride was separated, washed first with dil. sodium carbonate solution and then with water. After drying with calcium chloride it was subjected to fractional distillation and a yield of 65% was obtained; b. p., 141–143° at atmospheric pressure.

For the condensation of cyclohexyl chloride with resorcinol a two-liter flask was fitted with a reflux condenser, dropping funnel and a mercury-seal stirrer. Ninety g. of resorcinol dissolved in 450 cc. of freshly distilled nitrobenzene, together with 18 g. of aluminum chloride (anhydrous) was placed in the flask. Seventy-seven g. of cyclohexyl chloride was slowly added while the reaction mixture was rapidly stirred and slowly heated to 70° on the water-bath. After about four hours, when the hydrogen chloride was practically all liberated, the contents of the flask were poured onto ice and allowed to cool. A quantity of ether equal in volume to the dark oily liquid was added and this solution extracted with 10% sodium hydroxide until it produced no further coloration. The alkaline solution was made acid with hydrochloric acid and steam distilled to remove traces of nitrobenzene. On cooling, white, crystalline plates of cyclohexyl-resorcinol separated, together with a quantity of tarry material which settled to the bottom of the flask. On standing for several days, the dried crystals turned slightly

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[4] Liebmann, *Ber.*, **14**, 1842 (1881).

[5] Phenol coefficients were determined according to the method of the Hygienic Laboratory, by Dr. R. S. Spray of the West Virginia University School of Medicine. For his coöperation the thanks of the authors are due.

brown and a solution of the substance in water, on long standing, developed a fluorescence. In alcohol and ether the substance is readily soluble, and the sodium salt is soluble in water; m. p., 124–125°; yield, about 5%.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.95; H, 8.39. Found: C, 74.75, 74.43; H, 8.28, 8.87.

Cyclohexyl-anisole. $C_6H_4(C_6H_{11}).OCH_3(1,4)$.—Forty-two g. of anisole was condensed with 30 g. of cyclohexyl chloride in the presence of 6 g. of anhydrous aluminum chloride. The procedure was the same as with cyclohexyl-resorcinol except that an additional solvent was not used. The oily liquid from the reaction was dried and subjected to distillation at 16 mm. pressure. The distillation commenced at 134° and continued to 200°. The distillate was then subjected to fractional distillation at 16 mm. and analyzed. This, together with the conversion to the free phenol, indicated that the larger fraction which came over between 146 and 148° was the cyclohexyl-anisole. This material solidified when placed in an ice-bath but remained liquid at room temperature. A very small amount of higher-boiling fraction was obtained which has not yet been identified; yield of 146–148° fraction, 15–20%; d_0^0, 1.0209; d_0^{25}, 1.0004; n_D^{25}, 1.5305; molecular refraction: calcd. 58.07, found: 58.71. The molecular weight was determined by the cryoscopic method, using benzene as a solvent.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 82.33, 82.22; H, 9.70, 9.55.

Mol. wt. Calcd. for $C_{13}H_{18}O$: 190.14. Found: 184.8.

Cyclohexyl-phenetole. $C_6H_4(C_6H_{11}).OC_2H_5(1,4)$.—Thirty-four g. of phenetole was condensed with 30 g. of cyclohexyl chloride in the presence of 6 g. of anhydrous aluminum chloride, the general procedure in this case being the same as that described above. The condensation product on distillation gave one principal fraction 155–157° (16 mm.). After standing for several days it mostly solidified to very small prismatic needles; yield, 12%; n_D^{25}, 1.5262.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.86. Found: C, 82.41, 82.17; H, 10.10, 9.80.

Cyclohexyl-phenol. $C_6H_4(C_6H_{11}).OH(1,4)$.—*Method I.* This phenol was obtained from cyclohexyl-anisole by hydrolysis with constant-boiling hydrobromic acid mixed with glacial acetic acid. It was purified by recrystallization of the sodium salt from water solution. The sodium salt on decomposition with acid gave a white, crystalline solid; m. p., 128°; yield, 14%.

Method 2. Cyclohexyl-phenol was also prepared by condensing cyclohexyl chloride with phenol in the presence of fused zinc chloride. Ninety g. of phenol was condensed with 118 g. of cyclohexyl chloride in the presence of 118 g. of fused zinc chloride. The reaction mixture was heated in a water-bath until the evolution of hydrogen chloride could no longer be observed. It was then poured onto ice and from the oily liquid the sodium salt of the phenol was obtained by alkaline extraction. The phenol was further purified as under the first method; yield, 20%; m. p., 128°.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.79; H, 9.16. Found: C, 81.67; H, 9.11.

The benzoyl ester of the cyclohexyl-phenol was prepared by the Schotten-Baumann reaction. Recrystallization from alcohol gave a white, crystalline solid; m. p., 114–114.5°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.38; H, 7.19. Found: C, 81.04, 80.96; H, 7.20, 7.21.

Summary

1. Four new compounds have been prepared; cyclohexyl-resorcinol, cyclohexyl-anisole, cyclohexyl-phenetole and the benzoyl ester of cyclo-

hexyl-phenol. The properties of these compounds have been determined. Cyclohexyl-phenol, which has been prepared previously, was obtained by two new methods.

2. Cyclohexyl-phenol was not found to have any germicidal properties in water solution because of its limited solubility. Cyclohexyl-resorcinol gave a phenol coefficient of 24–27.

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

SELECTIVE REDUCTION OF FURFURACROLEIN BY MEANS OF PLATINUM-OXIDE PLATINUM BLACK AND HYDROGEN. XVI[1]

BY R. H. BRAY[2] WITH ROGER ADAMS

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In a previous paper it was shown that aldehydes[3] could not be reduced to alcohols with hydrogen and platinum-oxide platinum black unless some promoter such as a ferrous salt was present. As these promoters for the reduction of aldehydes are poisons toward the reduction of olefins, the study of the reduction of α,β unsaturated aldehydes,[4] in particular cinnamic aldehyde and citral, resulted in the discovery that by using a ferrous salt, together with a small amount of zinc salt, it was possible to reduce quantitatively the aldehyde group to a primary alcohol without affecting the olefin linkages. Cinnamyl alcohol and geraniol, respectively, were produced.

Furfural[5] was like other aldehydes and the catalytic reduction with platinum-oxide platinum black and hydrogen would not take place unless ferrous salt or some such promoter was present. The primary product was furyl carbinol formed upon the absorption of one molecular equivalent of hydrogen. If the reduction was allowed to go until no more absorption of hydrogen took place, ordinarily slightly over four molecular equivalents of hydrogen were absorbed, and there resulted a mixture of tetrahydrofuryl carbinol, pentane-diol-1,2, pentane-diol-1,5, and a small amount of *n*-amyl alcohol, the latter three substances being produced by scission of the ring.

In the present investigation the work on selective reduction has been

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[1] (a) For previous papers in this field, see Adams, Cohen and Rees, THIS JOURNAL, **49**, 1093 (1927) (footnote 1) for references to the first thirteen articles; (b) also Hiers and Adams, *ibid.*, **49**, 1099 (1927).

[2] This communication is an abstract of a portion of a thesis submitted by R. H. Bray in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

[3] (a) Carothers and Adams, *ibid.*, **45**, 1071 (1923); (b) **46**, 1675 (1924).

[4] (a) Tuley and Adams, *ibid.*, **47**, 3061 (1925); (b) Adams and Garvey, **48**, 477 (1926).

[5] Kaufman and Adams, THIS JOURNAL, **45**, 3029 (1923).