

double salt. A mixed melting point determination with *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid showed no change in melting point.

Other experiments were carried out varying the amount of zinc chloride, but in no case was racemization observed.

Conclusions

Certain derivatives of triarylcarbinols containing an asymmetric carbon atom have been prepared. Phenylbiphenyl- α -naphthylmethylthioglycolic acid has been resolved into a pure levo form, $[\alpha]_D^{20} - 13.63^\circ$, and a mixed dextro isomer $[\alpha]_D^{20} + 10.13^\circ$. Experiments with this substance show that it forms halochromic compounds. Concentrated sulfuric acid, perchloric acid and mercuric chloride unite with it to form deep violet halochromic compounds which on pouring into ice water yield the carbinol in its optically inactive form. Titanium tetrachloride produces a deep violet halochromic salt which on decomposition with water yields the racemic phenylbiphenyl- α -naphthylmethylthioglycolic acid. However, the double salts with ferric chloride and zinc chloride on hydrolysis give *l*-phenylbiphenyl- α -naphthylmethylthioglycolic acid with no racemization.

A discussion of these facts is given with special reference to the quinonoid theory and carbonium ion theory of formulation for the explanation of color.

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SOME CHLORINE DERIVATIVES OF BENZYLPHENOLS. I. DICHLORO DERIVATIVES OF ORTHO AND PARA BENZYLPHENOLS

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This paper is the first of a series dealing with the chlorination and the chlorine derivatives of the benzylated phenols. Only a comparatively few of these compounds have been reported.

A chlorobenzyl phenol¹ was made by treating benzylphenol with sulfuric chloride. The investigator reported that the chlorine probably entered the ring in the ortho position, giving the formula $C_6H_5CH_2C_6H_3ClOH$, but gave no proof of structure. Beilstein reports its formula as $C_6H_5-CHClC_6H_4OH$ with the chlorine on the CH_2 group. Richter's Lexicon shows the substitution in the meta position.

Sentinis prepared a benzyl chlorophenyl ether² by passing chlorine into an alcoholic solution of the ether to which some mercuric oxide had been added as a catalyst. This was later shown by Baw³ to be benzyl *p*-chlorophenyl ether.

¹ Peratoner and Vitaei, *Gazz. chim. ital.*, **28**, 197 (1898).

² Sentinis, *Ann.*, **161**, 345 (1872).

³ Baw, *Quart. J. Indian Chem. Soc.*, **3**, 101 (1926).

Benzyl 2,4-dichlorophenyl ether⁴ and benzyl 2,4,6-trichlorophenyl ether were prepared by treating the respective chlorophenol in alcohol with benzyl chloride and sodium ethoxide. The bromine derivatives were prepared in the same manner.

Benzyl pentachlorophenyl ether,⁵ $C_6H_5CH_2OC_6Cl_5$, was made by warming the silver salt of pentachlorophenol with benzyl iodide.

Baw³ prepared benzyl 2-chlorophenyl and benzyl 2,4-dichlorophenyl ethers by treating the appropriate phenols with benzyl chloride and aniline.

The work on which we wish to report here was limited to those derivatives containing two chlorine atoms. The dichloro compounds of both the ortho and para benzylphenol were prepared.

The latter, 3,5-dichloro-4-hydroxydiphenylmethane, was first made by the aluminum chloride condensation of benzyl alcohol and 2,6-dichlorophenol. The structure of this compound was proved by preparing the same compound by direct chlorination of *p*-benzylphenol in chloroform using the quantitative amounts of chlorine. Needle shaped crystals were obtained. The aluminum chloride condensation, in this case, proved to be of considerable interest as we were able to isolate from the oil obtained from the condensation 2,6-dichlorophenyl benzyl ether. This is the first time that an ether has been isolated from an aluminum chloride condensation and opens a considerable field for speculation as to the mechanism of the reaction. In order to identify this ether it was later prepared by treating 2,6-dichlorophenol and benzyl chloride with metallic sodium in methyl alcohol. The boiling point at 15 mm. was 194–195°, very near that of the phenol.

The preparation of 3,5-dichloro-2-hydroxydiphenylmethane was effected in two ways: first, by the Claisen reaction in which 2,4-dichlorophenol and benzyl chloride were treated with sodium in toluene and, second, by direct chlorination of *o*-benzylphenol in chloroform with the calculated amount of chlorine. The same compound was obtained in each case.

The ether, 2,4-dichlorophenyl benzyl ether,^{3,4} was isolated from the Claisen reaction mixture by extraction with petroleum ether. This same compound was later prepared by the action of sodium on 2,4-dichlorophenol and benzyl chloride in methyl alcohol.

An attempt to substitute more than two chlorines into the ortho and para benzylphenols proved unsuccessful. Both benzyl phenols were treated with three molecular equivalents of chlorine and then with a large excess, but no compounds containing more than two atoms of chlorine were obtained. Apparently chlorine does not easily substitute in the benzyl group.

The benzoic, benzene sulfonic and toluene sulfonic esters of each of the

⁴ Auwers, *Ann.*, **357**, 85–94 (1907).

⁵ Biltz and Giese, *Ber.*, **37**, 4020 (1904).

dichlorobenzyl phenols were prepared. These all proved to be crystalline substances and served to further characterize the phenols.

Experimental

Benzyl Alcohol, 2,6-Dichlorophenol and Aluminum Chloride.—Fifty grams of benzyl alcohol and 225 g. of 2,6-dichlorophenol were suspended in 250 cc. of petroleum ether. The suspension was mechanically stirred while 30 g. of aluminum chloride was added at intervals over one hour. The phenol is only slightly soluble in the ether. Stirring was continued for thirty minutes after the aluminum chloride had been added and the mixture allowed to stand overnight. At no time during the reaction did the temperature exceed 32°. The suspension was decomposed with ice and hydrochloric acid and the petroleum ether withdrawn. The water mixture was extracted with ethyl ether. (Drying with potassium carbonate was attempted in the first condensation, but later omitted as distillation of the dried mixture gave a large amount of charred material.) The solvents were distilled, the residues combined and then fractionated.

The first fractions consisted of unchanged benzyl alcohol and 2,6-dichlorophenol. Twenty-three grams of a yellow oil was obtained between 195 and 205° at 15 mm. The material from six similar condensations was combined and purified by further distillation. The boiling point at 15 mm. after three distillations was 194–196°.

A determination of the chlorine content of the oil by the Parr bomb method showed a percentage of chlorine in two samples of 27.7 and 28.1. Since the theoretical amount of chlorine in 3,5-dichloro-4-hydroxydiphenylmethane is 28%, it was at first thought that the oil was that compound. Subsequent results showed that this was not entirely true.

The benzoyl derivative prepared by the pyridine method melted at 98.5–99°.

Chlorination of *p*-Benzylphenol.—Ten grams of *p*-benzylphenol suspended in chloroform was treated with two equivalents of chlorine.⁶ The solvent was distilled and a yellow oil obtained which was fractionated. All but a small amount came over between 190 and 205° at 15 mm. This solidified on standing and was recrystallized from petroleum ether; m. p. 58–58.5°.

Anal. Subs., 0.1840, 0.1889: cc. of 0.1 *N* AgNO₃, 14.38, 14.95. Calcd. for C₉H₁₀OC₂Cl₂: Cl, 28.0. Found: Cl, 27.8, 28.1.

Crystals of this compound seeded in the oil prepared by the aluminum chloride condensation dissolved. The benzoyl derivative in this case gave a melting point of 98.5–99°, which was identical with that prepared from the oil.

The oil from the aluminum chloride condensation was then treated with a water solution of potassium hydroxide. An oil remained undissolved. This was withdrawn and the solution acidified with hydrochloric acid. A crystalline compound was obtained which when purified proved to be identical with the compound obtained by direct chlorination of *p*-benzylphenol.

Benzyl 2,6-Dichlorophenyl Ether.—Six and one-half grams of metallic sodium was allowed to react with 100 cc. of methyl alcohol. The solution was cooled and 45 g. of 2,6-dichlorophenol added. This mixture was heated on the oil-bath at 150° for thirty minutes, cooled and 35 g. of benzyl chloride added. The entire mixture was allowed to stand overnight and then heated on the oil-bath for five hours. After cooling, the oil was extracted with petroleum ether, the ether removed and the residue distilled.

A very small amount of benzyl chloride came over at 90 to 190° at 15 mm. Practically all of the remaining oil distilled between 190 and 196°. Refractionation produced a yellow oil with a boiling point of 194–196° at 15 mm. This oil solidified after standing

⁶ Houben, "Methods of Organic Chemistry," Vol. 2, p. 799.

in the ice box for three months. A crystal of the ether so prepared was seeded in the oily residue obtained from the aluminum chloride condensation. The oil solidified immediately. The melting point of both compounds was identical, 39.5–40°.

Anal. Subs., 0.2418, 0.1930: cc. of 0.1 *N* AgNO₃, 19.05, 15.1. Calcd. for C₁₃H₁₀OCl₂: Cl, 28.0. Found: Cl, 27.9, 27.7.

3,5-Dichloro-2-hydroxydiphenylmethane.—Sodium (11.5 g.) was suspended in 130 cc. of toluene and 81.5 g. of 2,4-dichlorophenol added. The mixture was heated on the oil-bath at 150° for thirty minutes, during which time the white sodium salt was produced. The mixture was cooled and 63.3 g. of benzyl chloride added. After standing overnight it was heated for five hours on the oil-bath (160°), cooled and treated with 250 cc. of methyl alcoholic potassium hydroxide. The solution was extracted with petroleum ether. The remaining alcoholic solution was then neutralized with hydrochloric acid and the phenol extracted with ethyl ether. After removing the ether, the residue was fractionated. The fraction between 140 and 210° at 15 mm. solidified in the receiver and yielded, after recrystallization from petroleum ether, 30 g. of pure dichlorobenzyl phenol, m. p. 77.0–77.5°.

Anal. Subs., 0.2000, 0.1895: cc. of 0.1 *N* AgNO₃, 15.6, 14.82. Calcd. for C₁₃H₁₀OCl₂: Cl, 28.0. Found: Cl, 27.6, 27.7.

The same compound was prepared by direct chlorination of *o*-benzylphenol. The chlorination was carried out as before using calculated amounts of potassium permanganate to produce the chlorine. The dark colored oil was fractionated and the fraction between 190–200° at 15 mm. was purified by recrystallization from high test gasoline.

Benzyl 2,4-Dichlorophenyl Ether.—This compound was prepared by treating sodium 2,4-dichlorophenylate in methyl alcohol with the equivalent amount of benzyl chloride. The crystals obtained were purified from petroleum ether. The petroleum ether extract from the previous preparation of 3,5-dichloro-2-hydroxydiphenylmethane was also purified in a similar manner. The compounds⁴ were prisms with identical melting points (59.0–59.5°).

Attempt to Produce the Trichlorobenzylphenols.—Both the para and ortho benzylphenols were subjected to the calculated amount of chlorine for the substitution of three chlorines and later to an excess of the gas. The compounds in each case were fractionated and purified by recrystallization. Upon analysis each sample showed but two chlorine atoms and gave melting points which proved them to be the dichlorobenzylphenols previously prepared.

Esters

The benzoyl, benzene sulfonyl and the toluene sulfonyl derivatives of both dichlorobenzylphenols were prepared by the pyridine method.

Esters of 3,5-Dichloro-4-hydroxydiphenylmethane

Benzoic Ester.—Prisms from petroleum ether, m. p. 98–99°.

Anal. Subs., 0.1174, 0.1844: cc. of 0.1 *N* AgNO₃, 6.4, 11.25. Calcd. for C₂₀H₁₄O₂-Cl₂: Cl, 19.9. Found: Cl, 19.4, 19.7.

Benzene Sulfonic Ester.—Prisms from ethyl ether, m. p. 93–94°.

Anal. Subs., 0.2630, 0.2100: cc. of 0.1 *N* AgNO₃, 13.15, 10.55. Calcd. for C₂₀H₁₄-SO₃Cl₂: Cl, 18.05. Found: Cl, 17.75, 17.85.

***p*-Toluene Sulfonic Ester.**—Prisms from ethyl ether, in which it is only slightly soluble, m. p. 120–121°.

Anal. Subs., 0.1743, 0.2054: cc. of 0.1 *N* AgNO₃, 8.35, 10.05. Calcd. for C₂₁H₁₆-SO₃Cl₂: Cl, 17.42. Found: Cl, 17.15, 17.40.

Esters of 3,5-Dichloro-2-hydroxydiphenylmethane

Benzoic Ester.—Needles from 70% alcohol, m. p. 66–67°.

Anal. Subs., 0.1162, 0.1785: cc. of 0.1 *N* AgNO₃, 6.45, 9.75. Calcd. for C₂₀H₁₄O₂Cl₂: Cl, 19.9. Found: Cl, 19.65, 19.50.

Benzene Sulfonic Ester.—Elongated prisms from ethyl ether, m. p. 110–110.5°.

Anal. Subs., 0.2562, 0.2360: cc. of 0.1 *N* AgNO₃, 12.95, 11.85. Calcd. for C₂₀H₁₄SO₃Cl₂: Cl, 18.05. Found: Cl, 17.90, 17.85.

p-Toluene Sulfonic Ester.—Prismatic plates from ethyl ether, m. p. 124.5–125°.

Anal. Subs., 0.2239, 0.1822: cc. of 0.1 *N* AgNO₃, 10.95, 8.80. Calcd. for C₂₁H₁₆SO₃Cl₂: Cl, 17.42. Found: Cl, 17.35, 17.20.

Summary

1. The dichloro derivatives of both ortho and para benzylphenol and their ethers were prepared by direct chlorination and by condensation of the chlorinated phenols with benzyl alcohol.

2. The aluminum chloride condensation of 2,6-dichlorophenol and benzyl alcohol gave the ether as well as the benzylated phenol.

3. No evidence was obtained of the substitution by direct chlorination of more than two chlorines in either para or ortho benzylphenol.

4. The benzoyl, benzene sulfonyl and toluene sulfonyl derivatives of each dichlorobenzylphenol were prepared.

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

TOXICAROL. II. SOME ACETYL DERIVATIVES OF TOXICAROL

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Evidence has been presented to show that toxicarol is an hydroxy-dimethoxy compound, C₂₃H₂₂O₇.¹ The presence in the molecule of at least one hydroxyl group was demonstrated by the formation of a monobenzoyl derivative, but as the nature of four of the seven oxygen atoms was unknown, the existence of other hydroxyl groups was not excluded.

It has now been shown that a diacetyl derivative of toxicarol may be obtained, but because of the reactions which it and toxicarol undergo, it cannot be stated definitely that a second hydroxyl group exists in toxicarol *per se*. In fact, evidence is more in accord with the idea that the second acetyl group is introduced as a result of some reaction brought about by the reagents involved in the acetylation process.

An attempt to elucidate this point is in progress, but since the information upon the subject now available is interesting and will eventually contribute to the solution of the structure of the molecule, it is presented herewith.

¹ Clark, *THIS JOURNAL*, 52, 2461 (1930).