

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF NEW HAMPSHIRE]

Formation and Rearrangement of the Diphenylmethyl Ether of *o*-Cresol

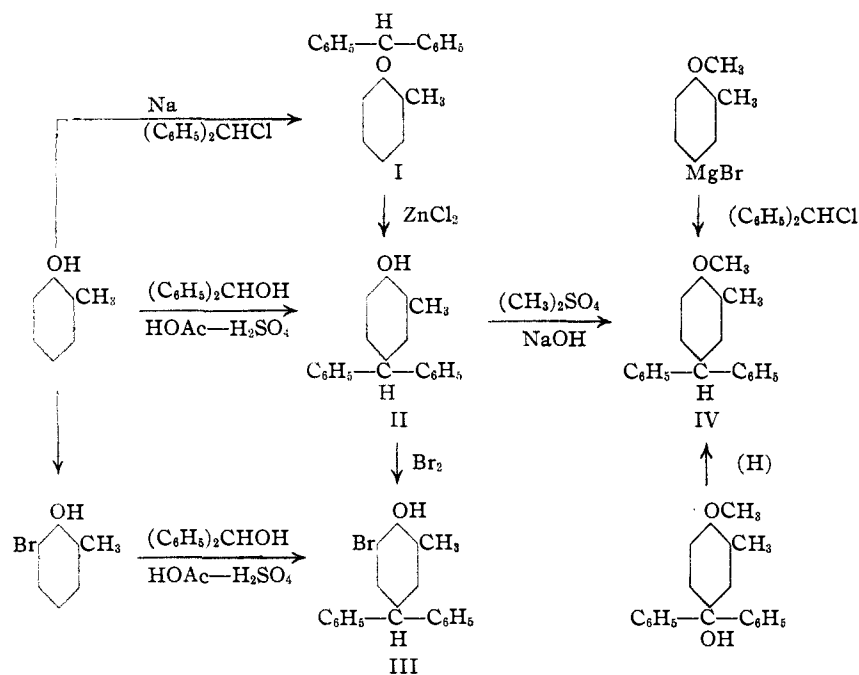
BY H. A. IDDLES, D. H. CHADWICK, J. W. CLAPP AND R. T. HART

To aid in interpreting the rearrangement of the triphenylmethyl ether of *o*-cresol, or the direct introduction of the triphenylmethyl radical into the *o*-cresol nucleus, the methyl ether of the postulated product, 3-methyl-4-hydroxyphenyltriphenylmethane was synthesized.¹ The complete agreement between rearranged and synthetic products showed that the triphenylmethyl radical had migrated to the para position of the *o*-cresol nucleus.

In similar alkylation studies, earlier investigators^{2,3,4,5} have used the less highly substituted diphenylmethyl radical and have recorded the conditions which favor the formation of the diphenylmethyl ether of phenol or lead to the introduction of one, two or three diphenylmethyl radicals into the nucleus. In one experiment, Schorigin³ treated *o*-cresol with diphenylcarbinol in acid medium and postulated the introduction of one diphenylmethyl radical ortho to the hydroxyl which seemed to be in agreement with his analytical data. Since this interpretation differed from the observed para migration of the triphenylmethyl radical¹ or the isopropyl group,⁶ and was not substantiated in any way, a further detailed study of this reaction is presented in this paper.

The direct preparation of the diphenylmethyl ether of *o*-cresol I was accomplished by treating sodium *o*-cresylate in ether solution with diphenylchloromethane. Besides the ether, some free phenolic product II was formed. This could be

prepared also by direct rearrangement of the ether with zinc chloride or through the reaction at room temperature of *o*-cresol with diphenylcarbinol in acid medium. The orientation of groups in structure II was established in the first instance by its monobromination and comparison with the diphenylmethyl derivative formed from 6-bromo-*o*-cresol and also by two direct syntheses focusing on structure IV. Thus the rearrangement of I or the direct introduction of one diphenylmethyl radical involves the para position of the *o*-cresol, as was shown in the case of the triphenylmethyl radical.

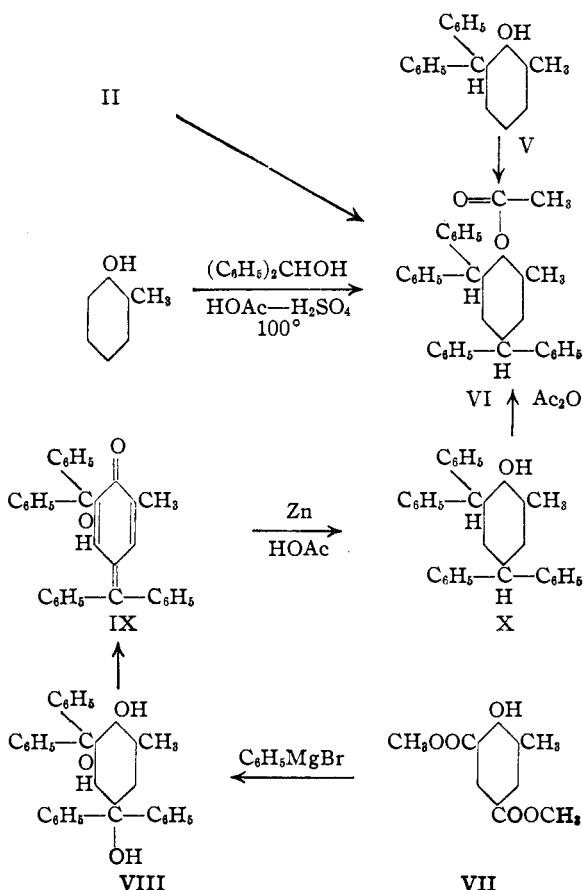


In addition it was necessary to characterize Schorigin's product, m. p. 139°, which could be prepared by heating *o*-cresol and diphenylcarbinol in an acetic-sulfuric acid medium.³ As a direct approach, Schorigin's suggested structure V was synthesized by the action of the Grignard reagent on methyl *o*-cresotinate followed by reduction of the resulting carbinol. This synthetic material was further characterized by bromination and comparison with a product formed by condensing 4-bromo-*o*-cresol with diphenylcar-

- (1) Iddles and Minckler, *THIS JOURNAL*, **62**, 2757 (1940).
- (2) Claisen, *Ann.*, **442**, 210 (1924).
- (3) Schorigin, *Ber.*, **59**, 2502 (1926); **61**, 2516 (1928).
- (4) Van Alphen, *Rec. trav. chim.*, **46**, 799 (1927).
- (5) Busch and Knoll, *Ber.*, **60**, 2243 (1927).
- (6) Niederl and Natelson, *THIS JOURNAL*, **53**, 1928 (1931).

binol. However, the synthetic material of structure V melted at 76–78°, which demonstrated its non-identity with Schorigin's material, m. p. 139°.

When it was determined that Schorigin's material could not be brominated or methylated and that structures II and V would both yield Schorigin's product when heated with diphenylcarbinol in acetic-sulfuric acid medium, then structure VI was suggested in which two diphenylmethyl groups had been introduced and the acetate formed. To establish this postulate, structure VI was synthesized by the action of phenylmagnesium bromide on the dimethyl ester of 6-hydroxyuvutinic acid VII, which passed through a di-carbinol structure VIII to form an orange-colored substance postulated to be IX. In the succeeding steps, this material was reduced by zinc and acetic acid producing a colorless phenol X and treatment with acetic anhydride gave the acetate VI of m. p. 139° which was identical with Schorigin's rearranged product.



Experimental

***o*-Tolyldiphenylmethyl Ether.**—*o*-Cresol (120 g.) in absolute ether (500 ml.) was treated with metallic sodium

(10 g.) and, after complete reaction, diphenylchloromethane (66 g.) was introduced slowly. The mixture was refluxed for sixteen hours and for three hours after evaporation of the ether. The reaction mixture was poured into water, extracted with ether and the ether layer was washed with 10% sodium hydroxide and then dried. Upon evaporating the ether, the resulting oil was taken up in ligroin (90–110°) and extracted with Claisen's solution. From the ligroin layer, 10 g. of the desired ether distilled between 175–178° at 4 mm. It was a viscous, yellowish-green oil. The Claisen's extract, upon acidification, produced a rearranged product (25 g.) which was first purified by distillation at 3 mm. pressure and 205–215°, followed by crystallization from ligroin, m. p. 99–100°.

Preparation of Rearranged Compound.—To carry out a direct rearrangement, 5 g. of the *o*-tolyldiphenylmethyl ether was heated with 3 g. of zinc chloride for five hours at 150°. The material was then dissolved in ligroin, washed with water and extracted several times with Claisen's solution. Upon acidification, 3 g. of oil was obtained which was distilled at 213–220° and 3–5 mm. and recrystallized from ligroin yielding a colorless product, m. p. 99°.

The same product was obtained when 20 g. of diphenylcarbinol⁷ and 24 g. of *o*-cresol were dissolved in 300 ml. of glacial acetic acid, and 60 g. of concd. sulfuric acid was added over a period of one hour. After standing for 7–8 days, the product was obtained by pouring the reaction mixture into water, extracting with ether, washing with 10% sodium hydroxide, water, and drying the ether extract. Upon evaporation of the ether, the residue was vacuum distilled at 180–185° and 2 mm. and twice recrystallized from ligroin yielding 15 g. of final product, m. p. 101°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}$: C, 87.5; H, 6.62. Found: C, 87.4; H, 6.62.

Bromination of 3-Methyl-4-hydroxyphenyldiphenylmethane.—Five grams of the rearranged compound, m. p. 101°, was dissolved in 200 ml. of carbon tetrachloride, and to the cooled solution 3 g. of bromine in 20 ml. of carbon tetrachloride was added. After an hour, excess bromine was removed with bisulfite solution and the product recovered. Recrystallization from alcohol gave 4 g. or a yield of 62% of light yellow product, m. p. 117–118°.

Direct Condensation of 6-Bromo-*o*-cresol and Diphenylcarbinol.—Five grams of diphenylcarbinol and 15 g. of 6-bromo-*o*-cresol⁸ were dissolved in 100 ml. of glacial acetic acid, and 20 ml. of concd. sulfuric acid was added slowly while cooling. During the addition an oil began to separate and soon solidified. After standing two days, the solid product was filtered off, washed with glacial acetic acid and recrystallized from alcohol with a yield of 7 g. or 70%, m. p. 117–117.5°. A mixed melting point with the above brominated product was 117°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{OBr}$: Br, 22.6. Found: Br, 22.4.

Methylation of Compound II.—Three grams of the rearranged compound II, suspended in 200 ml. of 2 *N* sodium hydroxide, was warmed to 40°, and 15 g. of dimethyl sulfate was added over a period of two hours. After destroying excess dimethyl sulfate, the solution was

(7) "Organic Syntheses," Collective Vol. I, 1941, p. 90.

(8) Huston and Nealey, *This Journal*, **57**, 2176 (1935).

neutralized with hydrochloric acid and the insoluble organic material separated. The product was taken up in a mixture of 1 part diethyl ether and 9 parts petroleum ether, washed with Claisen's solution and water, and finally recrystallized from alcohol with a yield of 2.11 g. or 67%, m. p. 74–76°.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.5; H, 6.98. Found: C, 87.5, 87.8; H, 7.05, 7.63.

Direct Synthesis of Compound IV. Procedure I.—A Grignard solution, prepared from 7 g. of 3-bromo-6-methoxytoluene¹ and 3 g. of magnesium turnings in 100 ml. of dry ether, was coupled by adding 7 g. of diphenylchloromethane dissolved in 100 ml. of dry ether during a period of forty minutes. After refluxing for two hours, the ethereal solution was successively washed with dilute hydrochloric acid, 10% sodium carbonate, and water and then dried. Subsequent evaporation of the ether left an oil which was recrystallized from ligroin, yielding 4.3 g. or 43%, m. p. 74–75°.

Procedure II.—Seven grams of 3-methyl-4-methoxytriphenylcarbinol¹ was dissolved in 200 ml. of glacial acetic acid and reduced by adding zinc dust⁹ and refluxing for an hour. The zinc dust was allowed to settle and the clear solution decanted into 500 ml. of water. The precipitate was dissolved in hot alcohol, treated with Norite, and yielded 5 g. or 75%, m. p. 75.5°. A mixed melting point using each of the synthetic products with the methylated rearranged product gave no depression.

Reaction of *o*-Cresol and Diphenylcarbinol at 100°.—According to Schorigin's procedure⁹ a solution of *o*-cresol (13.5 g.) and diphenylcarbinol (39 g.) in glacial acetic acid (300 ml.) was treated with concd. sulfuric acid (20 ml.) while refluxing on the steam-bath. Purification of the product from alcohol gave 8 g. of colorless material, m. p. 139–140°.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 87.1; H, 6.27. Found: C, 86.7; H, 6.42.

Preparation of Compound V.—Ten grams of 2-methyl-6-diphenylhydroxymethylphenol, prepared by the reaction of phenylmagnesium bromide on methyl-*o*-cresotinate,^{10,11} was reduced with zinc and glacial acetic acid as previously described.⁹ Recrystallization from alcohol produced colorless crystals in a yield of 6.5 g. or 70%, m. p. 76–78°.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.5; H, 6.61. Found: C, 87.1; H, 6.59.

Preparation of 2-Methyl-4-bromo-6-diphenylmethylphenol.—To characterize compound V, 2 g. was treated with 2.2 g. of bromine in carbon tetrachloride and the product recovered and crystallized from dilute alcohol, yielding 1.3 g. or 45%, m. p. 97–100°.

Further, 60 g. of 4-bromo-*o*-cresol¹² and 30 g. of diphenylcarbinol, dissolved in 400 ml. of glacial acetic acid, were heated on the steam-bath while 5 ml. of sulfuric acid was added gradually. Recovery of the condensation product in the usual way gave 17 g. of product, m. p. 100–103°. A mixed melting point of the two bromo derivatives gave no depression and either bromo derivative could be acetylated to give an acetyl derivative, m. p. 157–158°.

(9) Sachs and Thonet, *Ber.*, **37**, 3333 (1904).

(10) Guillaumin, *Bull. soc. chim.*, **7**, 374 (1910).

(11) Berlitz, *Monatsh.*, **36**, 200 (1915).

(12) Goldschmidt, Schulz and Bernard, *Ann.*, **478**, 14 (1930).

Anal. Calcd. for $C_{20}H_{17}OBr$: Br, 22.6. Found: Br, 22.4.

Preparation of the Dimethyl Ester of 6-Hydroxyvitinic Acid.—The dried potassium salt from 154 ml. of *o*-cresol was placed in the glass liner of a pressure bomb and carbon dioxide forced into the bomb under ninety pounds pressure.¹³ The bomb was heated in an electric furnace to 210°, and the pressure of carbon dioxide was increased to two hundred pounds. These conditions were maintained for fifty hours or until absorption of carbon dioxide was complete, as evidenced by no pressure drop. For purification, the solid reaction product was suspended in 700 ml. of hot water, and sodium bicarbonate added until the solution was complete, then treated with Norite, filtered and reprecipitated with dilute hydrochloric acid. After three such treatments, a yield of 105 g. or 36% of a faintly pink product was obtained, m. p. 290–295°.

The methyl ester was then prepared by refluxing 15 g. of the above acid in 200 ml. of absolute methanol and 22 ml. of concd. sulfuric acid.¹⁴ Upon cooling, the ester crystallized from the methanol in a yield of 10 g. or 60%, m. p. 129–130°.

Preparation of Compound IX.—A Grignard solution prepared from 125 g. of bromobenzene and 19.4 g. of magnesium turnings in one liter of dry ether was refluxed while adding 18 g. of compound VII dissolved in 800 ml. of ether. After refluxing for six hours, the reaction product was poured into water containing enough hydrochloric acid for complete solution. The ether layer was separated, washed with water, 10% sodium carbonate and again with water. The ether was evaporated and the residue steam distilled to remove biphenyl. On cooling, an orange solid formed and this was recrystallized from acetic acid in a yield of 27 g. or 75%, m. p. 206–208°. The color and analysis agreed with the aurin structure assigned.

Anal. Calcd. for $C_{33}H_{26}O_2$: C, 87.2; H, 5.76. Found: C, 87.3, 87.1; H, 5.80, 5.92.

Preparation of Compound X.—Ten grams of the aurin-type compound IX was dissolved in 250 ml. of hot glacial acetic acid in a three-necked flask fitted with a stirrer and reflux condenser. Zinc dust (35 g.) was added slowly and refluxing continued for eight hours. After filtering off excess of zinc dust, the reaction mixture was poured into 1000 ml. of ice water yielding a crude product of 9.6 g. No suitable solvent for recrystallization was found, but a vacuum sublimation produced an amorphous product, m. p. 50–60°, which changed to a dark gum upon standing.

Anal. Calcd. for $C_{32}H_{28}O$: C, 89.9; H, 6.41. Found: C, 89.1; H, 6.52.

Since the product could not be crystallized, it was characterized as the 3,5-dinitrobenzoate which was obtained as a colorless crystalline material from dilute acetone, m. p. 206–207°.

Anal. Calcd. for $C_{40}H_{30}O_6N_2$: N, 4.42. Found: N, 4.48.

Preparation of 2-Methyl-4,6-di-(diphenylmethyl) Phenylacetate VI.—Two grams of the phenol X was treated with 7–8 ml. of acetic anhydride and 1 ml. of concd. sulfuric acid. When the reaction mixture had cooled,

(13) Chem. Fabr. v. Heyden, German Patent 65,316, *Frdl.*, **3**, 829.

(14) Anschütz and Robitsek, *Ann.*, **346**, 358 (1906).

water was added and the gummy product recrystallized from alcohol yielding 1.3 g. (60%), m. p. 139–141°. A mixed melting point of this synthetic material with Schorigin's compound showed no depression.

Anal. Calcd. for $C_{26}H_{30}O_2$: C, 87.1; H, 6.27. Found: C, 86.8; H, 6.30.

Summary

1. The rearrangement of the diphenylmethyl ether of *o*-cresol or the direct introduction of the

diphenylmethyl group under mild conditions involves the para position of the *o*-cresol.

2. 2-Methyl-4,6-di-(diphenylmethyl) phenylacetate has been synthesized and found to be identical with Schorigin's product obtained by heating diphenylcarbinol and *o*-cresol in an acetic-sulfuric acid medium.

DURHAM, NEW HAMPSHIRE

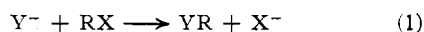
RECEIVED JUNE 27, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND HARVARD UNIVERSITY]

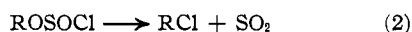
Allylic Rearrangements. XIII. Kinetics and Mechanisms of the Conversion of Crotyl and Methylvinylcarbinyl Chlorides to Acetates and Ethyl Ethers¹

BY JOHN D. ROBERTS, WM. G. YOUNG AND S. WINSTEIN²

Many investigators, notably Hughes, Ingold and collaborators,³ have demonstrated that the mechanisms of nucleophilic replacement reactions at a saturated carbon atom may be classified into three general types. One mechanism, designated as S_N2 is the familiar⁴ bimolecular, usually second-order, substitution of an electron-donor such as hydroxide ion, alkoxide ion or acetate ion for the halide or a similar group as in equation (1), the replacement resulting in a complete Walden inversion.



Another mechanism, designated as S_{Ni} , involves the internal rearrangement of an intermediate compound to give the final product with retention of configuration. An illustration of this mechanism is furnished in equation (2) by the rearrangement of the intermediate from an alcohol and thionyl chloride to produce a chloride and sulfur dioxide.



The third mechanism, designated as S_N1 , is comprised of an electrophilic attack of solvent on halogen or similar groups to yield an unfree^{3,5} carbonium ion which subsequently reacts rapidly with an electron donor to yield the final product.

(1) Most of the material of this paper was presented before the Organic Division at the St. Louis and Atlantic City meetings of the American Chemical Society, April and September, 1941.

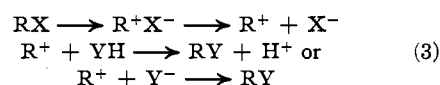
(2) National Research Fellow at Harvard University, 1939–1940.

(3) (a) Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1252 (1937); (b) Bateman, Church, Hughes, Ingold and Taher, *ibid.*, 979 (1940).

(4) (a) Olson, *J. Chem. Phys.*, 1, 418 (1933); (b) Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, 20, 161 (1933).

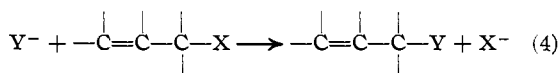
(5) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 172.

Equation (3) represents the sequence of these reactions.



A variation of the S_N1 type of reaction involves the electrophilic attack of such a reagent as silver ion on a halogen group to produce the unfree carbonium ion intermediate.^{3,6}

The application of the foregoing types of mechanisms to the replacement reactions of allylic systems⁷ has been of great value in explaining the phenomenon of the allylic rearrangement.^{7d} The recognition of the possibility of the simultaneous operation of both S_N1 and S_N2 processes, according to equations (4) and (5), has been used to correlate various results with the assumption that the



S_N2 reaction is normal and the S_N1 reaction yields a mixture, the same mixture resulting from either starting allylic isomer.

For example, the formation of similar but not identical bromide mixtures from the action of hydrogen bromide on crotyl alcohol and methylvinylcarbinol has been explained in this way.^{7a}

(6) Ref. 5, p. 138.

(7) (a) Young and Lane, *THIS JOURNAL*, 60, 847 (1938); (b) Arcus and Kenyon, *J. Chem. Soc.*, 1912 (1938); (c) Ref. 5, p. 315; (d) After the completion of this manuscript, the paper by Hughes, *Trans. Faraday Soc.*, 37, 603 (1941), appeared, which reports unpublished work in similar directions to the experiments we report in this article. The conclusions drawn by Hughes are in substantial agreement with our own.