

The authors desire to express their indebtedness to the Carnegie Trust for a Research Scholarship and a Research Fellowship awarded to one of them.

Summary

1. 2,3,6-Trimethyl- γ -methylglucoside has been prepared and its constitution determined by conversion into 2,3,5,6-tetramethyl- γ -glucose. The glucoside therefore conforms to the γ -type.

2. When hydrolyzed, the liberated 2,3,6-trimethyl- γ -glucose transforms into the stable crystalline variety which is the only form isolated.

3. The oxidation of 2,3,6-trimethylglucose by bromine may lead to either the corresponding γ - or δ -lactones according to variations in the concentration of hydrogen bromide present.

4. The presence of halogen hydride is a determining factor in converting 2,3,6-trimethylglucose into the γ -form.

5. The combined results show that the formation of 2,3,6-trimethylglucose in the constitutional studies of carbohydrates by the methylation method is ambiguous as are also the results of oxidation methods in certain cases.

ST. ANDREWS, SCOTLAND

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

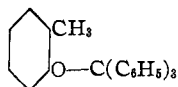
THE REARRANGEMENT OF TRIPHENYLMETHYL ORTHO-TOLYL ETHER

BY GEORGE S. PARSONS AND C. W. PORTER

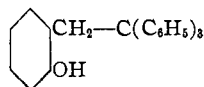
RECEIVED SEPTEMBER 17, 1931

PUBLISHED JANUARY 7, 1932

In 1926 Schorigin¹ prepared the triphenylmethyl ether of *o*-cresol and a year later Van Alphen² made the corresponding derivative of phenol. These ethers rearrange when heated with hydrochloric acid or with zinc chloride. In the case of phenyl triphenylmethyl ether the triphenylmethyl group migrates from the oxygen atom to the *p*-position in the ring, as would be expected, but the change in the case of *o*-tolyl triphenylmethyl ether was reported by Schorigin and by Van Alphen as a migration of the triphenylmethyl group from the oxygen atom to the ortho side chain.



o-Tolyl triphenylmethyl ether



α -2-Hydroxyphenyl- β,β -triphenylethane

The evidence in support of this mechanism comprised the isolation of triphenylcarbinol as an oxidation product and triphenylmethane as a

¹ Schorigin, *Ber.*, 59, 2506 (1926).

² Van Alphen, *Rec. trav. chim.*, 46, 287 (1927).

reduction product of the rearranged compound. This proof of the structure was considered inadequate and we undertook to obtain more definite information concerning the nature of the final product.

We tried to oxidize the rearranged product to salicylic acid, but we were unable to obtain salicylic acid in an amount sufficient to produce a color with ferric ions. Oxidation was accomplished by dichromate and by permanganate ions but no positive test for the presence of salicylic acid could be obtained. Apparently the ring to which the hydroxyl group is attached is ruptured by the oxidizing agent. By methylating the hydroxyl group before treatment with permanganate this difficulty was overcome and methoxybenzoic acid was produced. This result confirms the claim of Schorigin and of Van Alphen.

Further evidence in support of this structure was obtained by a direct synthesis of the methyl derivative of the rearranged product through the Grignard reaction. Triphenylmethylmagnesium bromide was made by Gomberg's method³ and an excess of this reagent was added to *o*-methoxybenzaldehyde. The addition product which formed immediately was reduced by the excess of the reagent so that, upon hydrolysis, α -methoxyphenyl- β,β,β -triphenylethane was obtained instead of the expected secondary alcohol. This compound melts at 172°. The compound obtained from *o*-tolyl triphenylmethyl ether by rearrangement and subsequent methylation has the same melting point and the melting point is not changed when the two products are mixed.

Experimental Part

1. **Preparation of *o*-Tolyl Triphenylmethyl Ether.**—The ether was made by warming on a water-bath a mixture of 50 g. of triphenylchloromethane and 25 g. of *o*-cresol in 200 cc. of dry pyridine for six hours. After cooling and diluting with water the product was extracted with a large volume of ether. The ether extract was freed from pyridine by washing with 6 *N* hydrochloric acid and cresol was removed by washing with 3 *N* sodium hydroxide. The ether extract was then evaporated to dryness. The residue was taken up in petroleum ether and this solution was washed with Claisen's solution (see paragraph 2) to remove the small amount of Van Alphen's "crypto phenol" which forms during the reaction and which is not removed by the treatment with aqueous sodium hydroxide. The petroleum ether extract was finally washed with water and dried and the major part of the solvent was evaporated. The precipitated product was purified by recrystallization from alcohol or from petroleum ether (m. p. 112.5°).

2. **Rearrangement of the Ether.**—Tolyl triphenylmethyl ether was converted into α -2-hydroxyphenyl- β,β,β -triphenylethane by heating the compound with half its weight of dry zinc chloride for one hour at 180°. The product was isolated by the method described by Van Alphen² (m. p. 182°). The same product may be obtained in better yield from triphenylchloromethane and *o*-cresol directly by modifying the procedure described in paragraph 1. The necessary changes are (a) a higher temperature—the solution is boiled under a reflux condenser for six or eight hours, (b) a higher concentration of the reagents—only half as much pyridine being used. The product is

³ Gomberg, THIS JOURNAL, 52, 2455 (1930).

isolated by diluting the reaction mixture with water and extracting with ether. The ether extract is washed successively with water, dilute hydrochloric acid and dilute sodium hydroxide. It is then evaporated and the residue is taken up in Claisen's solution (50 cc. of methyl alcohol mixed with 50 cc. of 50% aqueous potassium hydroxide). The solution is filtered, then acidified, and the precipitated product is recrystallized from a mixture of ethyl alcohol and water.

3. **Preparation of the Methyl Derivative of the Rearranged Product.**—The phenol (10 g.), obtained as described in paragraph 2, was mixed with methyl iodide (50 g.) and silver oxide (25 g.) in a 300-cc. flask. Visible action began spontaneously and continued for about an hour. The mixture was then heated on a water-bath for three hours. The product was extracted with ether and recrystallized from hot alcohol (m. p. 172°).

4. **Oxidation of the Methyl Derivative.**—The methyl derivative (3 g.) in 50 cc. of glacial acetic acid was added to a solution of 3 g. of potassium permanganate in 25 cc. of water. The mixture was warmed on a water-bath for one hour, then filtered, and the filtrate was extracted with ether. The ether was washed with water until free from acetic acid and then shaken with a dilute solution of sodium hydroxide. The aqueous extract was acidified with hydrochloric acid and methoxybenzoic acid precipitated (m. p. 98°).

5. **Synthesis of α -2-Hydroxyphenyl- β,β,β -triphenylethane.**—*o*-Methoxybenzaldehyde was made from salicylaldehyde by treatment with methyl iodide and silver oxide. The product (b. p. 242°) was dissolved in ether and treated with triphenylmethylmagnesium bromide. The addition product was hydrolyzed with warm dilute hydrochloric acid and the hydrolysis product was purified by crystallizing it from hot alcohol. This compound melted at 172° and when mixed with the methyl derivative of the rearranged product referred to in paragraph 3, the melting point was unchanged. The Grignard reagent apparently reduced the normal addition product.

Anal. Calcd. for α -2-methoxyphenyl- β,β,β -triphenylethane: C, 88.97; H, 6.64. Found: Product obtained by rearrangement and methylation: C, 88.4; H, 6.31. Product obtained through Grignard reaction: C, 88.8; H, 6.29.

Summary

o-Tolyl triphenylmethyl ether, when heated with zinc chloride, rearranges to α -2-hydroxyphenyl- β,β,β -triphenylethane. The structure of the final product has been established by direct synthesis and by the identification of oxidation products of its methyl ether.

The structure of the rearranged product corresponds to that postulated by Van Alphen and by Schorigin.

BERKELEY, CALIFORNIA