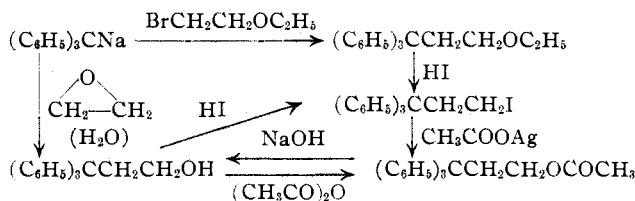


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

 **$\gamma,\gamma,\gamma$ -Triphenylpropyl Derivatives**

BY CHARLES BUSHNELL WOOSTER, H. D. SEGOOL AND T. T. ALLAN, JR.

The reaction between sodium in liquid ammonia solution and  $\gamma,\gamma,\gamma$ -triphenylpropyl iodide which results in the formation of sodium triphenylmethide was reported in a previous paper.<sup>1</sup> Because of the interesting nature of this reaction and of the observed tendency of compounds of the type  $R_3C-C-CX$  to undergo unusual reactions,<sup>2</sup> it appeared desirable to establish more thoroughly the constitution of the triphenylpropyl iodide which was used. This has now been accomplished by carrying out the reactions indicated in the flow sheet.



The iodide was prepared originally by cleavage of  $\gamma,\gamma,\gamma$ -triphenylpropyl ethyl ether the constitution of which appeared to be reasonably well established by the method of its synthesis. Furthermore, the available evidence demonstrated the presence of a triphenylmethyl group in the iodide. There remained, however, the possibility of molecular rearrangement during the action of hydriodic acid on the ether which might have led to the formation of a triphenylisopropyl iodide instead of the expected triphenyl-*n*-propyl iodide. Accordingly, the synthesis of the same iodide from triphenyl-*n*-propyl alcohol and the regeneration of this alcohol, by conversion to the acetate and hydrolysis, furnish the necessary link in the chain of evidence which shows that the iodide actually has the primary structure.

**Experimental Part****The Preparation of  $\gamma,\gamma,\gamma$ -Triphenylpropyl Alcohol.**

Sodium triphenylmethide was prepared by slowly adding 50 g. of triphenylchloromethane to a solution of 8.3 g. of sodium dissolved in about 500 cc. of liquid ammonia in a one-liter three-necked flask equipped with a mercury-sealed stirrer, a dropping funnel and an outlet for gaseous ammonia. A large excess of ethylene oxide was then added gradually in small portions. This reacted vigor-

ously with the excess sodium, but at first the deep red solution of sodium triphenylmethide showed no evidence of reaction. However, after several hours a voluminous pink precipitate had appeared in the reaction vessel, although the red color of the solution indicated the presence of some unreacted sodium triphenylmethide. These observations suggest that ethylene oxide may form an intermediate, unstable oxonium complex with the organo-alkali compound similar to those which are formed with Grignard reagents.

The addition of water to the reaction mixture discharged the red color and precipitated a yellow plastic mass which solidified on standing in contact with water after it had been washed free of most of the aqua ammonia. The product was recrystallized from commercial hexane and obtained in the form of light yellow crystals, m. p. 106.5–107.5°; yield about 30 g.

*Anal.* Calcd. for  $C_{21}H_{20}O$ : C, 87.5; H, 6.94. Found: C, 87.9, 87.7; H, 7.07, 7.05.

Attempts to oxidize this product to tritylacetic acid were unsuccessful, but its structure seems to be sufficiently well established by its thermal stability and the method of preparation. Although "abnormal" reactions with the Grignard reagent (involving isomerization to the aldehyde or ketone structures) have been reported with isobutylene oxide, styryl oxide and *sym*-dimethylethylene oxide<sup>3</sup> no such results have ever been observed with ethylene oxide itself. Furthermore, the triphenylisopropyl alcohol,  $(C_6H_5)_3CCHOHCH_3$ , which is the only likely alternative structure, would be expected to be thermally unstable since its next lower homolog  $(C_6H_5)_3CCH_2OH$ , decomposes smoothly into triphenylmethane and formaldehyde when heated slightly above its melting point (107°)<sup>4</sup> and the corresponding decompositions of triphenylacetic acid and triphenylacetaldehyde indicate the generality of such behavior. However, the reaction product was recovered unchanged after heating to 150–170° for an hour and failed to give a test for even a trace of triphenylmethane with a solution of potassium amide in liquid ammonia which instantly produces a deep red solution of potassium triphenylmethide when treated with this hydrocarbon.

**Preparation of Triphenylpropyl Iodide from the Alcohol.**

—Five grams of the alcohol was refluxed for five hours with 40 cc. of constant boiling hydriodic acid. After cooling, the product was separated and purified as previously described<sup>1</sup> and identified by a mixed melting point: yield 1.6 g.

**Preparation of Triphenylpropyl Acetate from the Alcohol.**—The alcohol seems to be quite unreactive toward many of the usual reagents; it was recovered unchanged after refluxing for one hour with acetyl chloride and thionyl chloride although a product of m. p. 134° (presumably the benzoate) was obtained by refluxing with benzoyl chloride.

(1) Wooster and Morse, *This Journal*, **56**, 1735 (1934).

(2) Whitmore and Stahly, *ibid.*, **55**, 4153 (1933).

(3) Henry, *Compt. rend.*, **145**, 21, 406 (1907); Tiffeneau and Fourneau, *ibid.*, **146**, 697 (1908).

(4) Schlenk and Ochs, *Ber.*, **49**, 610 (1916).

The determining factor seems to be the boiling point of the reagent since the acetate was obtained in satisfactory yield by the use of acetic anhydride.

Seven and three-tenths grams of the alcohol was refluxed for one hour with excess acetic anhydride, the solution poured into water and, after the hydrolysis of the anhydride was complete, the product was separated by filtration and recrystallized from alcohol: yield 6.4 g., m. p. 114–115°.

*Anal.* Calcd. for  $C_{23}H_{22}O_2$ : C, 83.6; H, 6.67. Found: C, 83.3, 83.1, 83.7; H, 6.72, 6.70, 6.75.

**Hydrolysis of the Acetate.**—Two grams of the acetate was dissolved in 50 cc. of alcohol in which 3 g. of sodium had been dissolved and 10 cc. of water was added. After refluxing for two hours the solution was poured into water, neutralized with hydrochloric acid and filtered. After crystallization from commercial hexane the product was identified as the triphenylpropyl alcohol by a mixed melting point.

**Preparation of Triphenylpropyl Acetate from the Iodide.**—An attempt to prepare the acetate by refluxing a solution of the iodo compound in glacial acetic acid with silver acetate for ten and one-half hours proved unsuccessful, possibly because the initially formed silver iodide coated over the sparingly soluble silver acetate. The reac-

tion proceeded satisfactorily, however, when an excess of silver acetate was placed in the filter thimble and the acetic acid solution of 1.88 g. of triphenylpropyl iodide was placed in the flask of a Soxhlet apparatus to prevent precipitation of the silver iodide from occurring in the presence of solid silver acetate. After the Soxhlet apparatus had been operated for about twenty hours, the solution in the flask was cooled, filtered, evaporated to small volume, diluted with water, neutralized with sodium carbonate and filtered again. The black gummy solid was crystallized from alcohol by seeding with a sample of the previously prepared acetate. After recrystallization from alcohol it was found to be halogen free and identical (by mixed melting point) with the acetate obtained from  $\gamma,\gamma,\gamma$ -triphenylpropyl alcohol and acetic anhydride.

### Summary

The product previously obtained by the action of hydriodic acid on  $\gamma,\gamma,\gamma$ -triphenylpropyl ethyl ether has been shown to be  $\gamma,\gamma,\gamma$ -triphenylpropyl iodide. Evidently no molecular rearrangement occurs during this reaction.

PROVIDENCE, R. I.

RECEIVED MAY 5, 1938

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

## Semiquinone Radicals in the Indamine and Indophenol Groups

BY G. SCHWARZENBACH<sup>1</sup> AND L. MICHAELIS

The original task of this paper was to extend the search for semiquinone radicals as intermediate steps of reversible oxidation-reduction, to the indamine and indophenol groups. The result not only was successful but in addition presented an excellent opportunity for developing the general principles concerned with the degree of stability of such radicals.

In none of the many representatives of the indophenol dyes investigated by W. M. Clark<sup>2</sup> and associates, was there any evidence for the existence of an intermediate step of reduction. On the contrary, these authors took just these dyestuffs as models to prove their assumption that in reversible bivalent oxidations the two electrons always go on and off in pairs. The experimental results can be confirmed entirely for the dyestuffs selected by these authors and for the pH range covered by their experiments. Yet it would be unjustifiable to consider this state of affairs as general. We shall demonstrate for two dyestuffs rather closely related to the group investi-

gated by these authors, that semiquinone radicals are formed in fairly large concentrations as intermediate steps. These two dyestuffs are phenol blue and Bindschedler's green, the formulas of which are given by the T-forms in the table of formulas (Fig. 7). The experimental material will be presented first, and the cause for the different behavior will be treated in the discussion.

The formulas shown in the table are electronic formulas, each stroke representing an electron pair. The totally oxidized forms T, the semiquinone forms S, and the fully reduced forms R are given in the different possible states of ionization. T, R, and S, themselves, denote the forms existing only in very alkaline solutions, where all removable protons are removed. The order represented in this scheme corresponds to the order of the ionization steps as derived from the experiments.

An open structure has been chosen for the T-forms in which the central nitrogen appears surrounded by only six electrons. The fourth electron pair can be said to be delivered by the auxochromic groups  $N(CH_3)_2$ , OH, and O. These have

(1) Under a fellowship from the Rockefeller Foundation.

(2) Hygienic Laboratory Bulletin, No. 151, United States Public Health Service, Washington, D. C., 1928.