

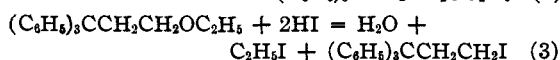
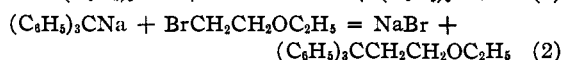
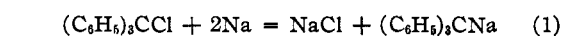
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Molecular Rearrangements Involving Spontaneous Cleavage

BY CHARLES BUSHNELL WOOSTER AND REGINALD A. MORSE

Whitmore and Stahly¹ have noted that compounds of the type $R_3C-C-CX$, where X is a group which may be removed and thus possibly give rise to the fragment R_3C-C-C^{\oplus} , are practically unknown and their synthesis is usually difficult. These authors also emphasize the importance of studying such compounds since, according to their hypothesis regarding molecular rearrangements, the fragment R_3C-C-C^{\oplus} might be expected to undergo spontaneous (or pyrolytic) cleavage with liberation of the tertiary group, R_3C^{\oplus} .

Two compounds, which appear to be of the type $R_3C-C-CX$, namely, γ,γ,γ -triphenylpropyl ether and γ,γ,γ -triphenylpropyl iodide, have been obtained in this Laboratory by the reactions expressed in the following equations



A solution of sodium in liquid ammonia completely removed the iodine from γ,γ,γ -triphenylpropyl iodide, yielding a red solution which became colorless when water was added. Triphenylmethane was isolated from the oily product on distillation and since the iodide was shown to be free from this hydrocarbon by a sensitive test with potassium amide, the triphenylmethane must have resulted from cleavage during the reaction with sodium. Parallel experiments with the iodide and the corresponding hydrocarbon have indicated that the cleavage of the iodide was not due to the direct action of sodium on the carbon-carbon bond by which the triphenylmethyl group is attached.

Mechanism of the Reaction with Sodium.—

These results are in agreement with those to be expected on the basis of Whitmore's hypothesis¹ if the positive fragment $(C_6H_5)_3CCH_2CH_2^{\oplus}$ were formed as an intermediate. The expected cleavage of this fragment into ethylene and a positive triphenylmethyl group would certainly be followed by combination of the latter with the electrons present in an ammonia solution of

sodium, yielding the triphenylmethyl negative ion which would give rise on hydrolysis to the triphenylmethane actually isolated.

Similarly, the rearrangement, analogous to those observed with neopentyl systems,² which takes place when β,β,β -triphenylethyl chloride is treated with sodium in liquid ammonia³ might be interpreted by assuming the initial formation of the positive fragment $(C_6H_5)_3CCH_2^{\oplus}$. According to Whitmore's hypothesis⁴ this fragment should rearrange to $(C_6H_5)_2C^{\oplus}CH_2C_6H_5$ and thus, after taking up electrons from the sodium solution, give rise to the negative ion $(C_6H_5)_2C-CH_2-C_6H_5$ which was actually found to be the reaction product.

However, a certain difficulty is encountered in connection with the hypothesis concerning the initial step, *i. e.*, that the halogen atoms separate as ions with completed octets leaving the positive fragments containing carbon with an "open sextet." As these halogen compounds are not spontaneously ionized in liquid ammonia, the assumed separation into ions must be attributed to the influence of the dissolved sodium or, more specifically, to the influence of the positive sodium ions or the negative ions (solvated electrons). That the sodium ions are without any effect on the halogen compounds has been demonstrated by parallel experiments in which the halogen compounds were treated with liquid ammonia solutions of sodium nitrate in place of sodium metal. On the other hand, it is extremely difficult to understand how the electrons could cause separation of the Cl^- and I^- ions from the neutral molecules without combining with the organic fragments to yield either the neutral radicals or the negative organic ions instead of the positive fragments.

These considerations suggest the possibility of alternative interpretations involving the rearrangement of either the neutral free radicals or the negative ions. On the latter basis, the reaction of sodium with β,β,β -triphenylethyl chloro-

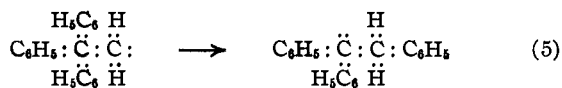
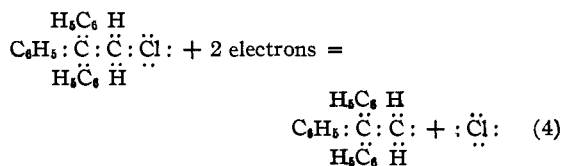
(2) Whitmore and Rothrock, *ibid.*, **54**, 3431 (1932); Edgar, Calingaert and Marker, *ibid.*, **51**, 1487 (1929); Beilstein, 4th ed., Vol. I, p. 152, Spl. Vol. I, p. 54.

(3) (a) Wooster and Mitchell, *THIS JOURNAL*, **52**, 1042 (1930); (b) Wooster and Ryan, *ibid.*, **54**, 2419 (1932).

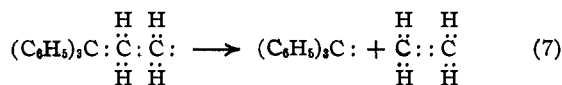
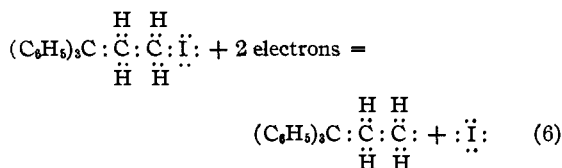
(4) Whitmore, *ibid.*, **54**, 3274 (1932).

(1) Whitmore and Stahly, *THIS JOURNAL*, **55**, 4153 (1933).

ride would be expressed by Equations 4 and 5, omitting from the equations the positive sodium ions which are not directly involved.



It is interesting to note that the rearrangement expressed in Equation 5 proceeds in the direction of the formation of that ion which would be expected to be the more stable on the basis of the benzohydril rule.^{5b} The action of sodium on the iodide might take the course indicated below.



In this instance, the unstable negative ion⁵ first formed is transformed, by a shift of a pair of electrons from an unshared to a shared position, into a neutral stable molecule of ethylene and the stable negative triphenylmethyl ion. The initial molecular rearrangement (the electron shift) thus results in a spontaneous cleavage. A similar electron shift (resulting in molecular rearrangement, but not cleavage) has been observed in the case of the alkali metal derivatives of 1,1,3-triphenylpropylene.⁶

Experimental Part

The Preparation of γ,γ,γ -Triphenylpropyl Ethyl Ether.—

To 1300 cc. of dry liquid ammonia in a two-liter three-necked flask equipped with a mechanical stirrer and an outlet for ammonia gas, 12.5 g. of sodium was added in pieces weighing approximately one gram. The mixture was stirred for about five minutes to ensure complete solu-

(5) In both instances the unstable negative ions might be expected, on the basis of the benzohydril rule, to undergo ammonolysis to the corresponding hydrocarbons if the rearrangements were not sufficiently rapid. Evidence has been obtained in previous studies [Wooster and Mitchell, *THIS JOURNAL*, **52**, 688 (1930)] that organo-alkali compounds which are susceptible to ammonolysis may, nevertheless, persist in liquid ammonia solution long enough to undergo other reactions.

(6) Schlenk and Bergmann, *Ann.*, **479**, 78-89 (1930); Ziegler and Schäfer, *ibid.*, **479**, 150-179 (1930); Wooster, *Chem. Rev.*, **4**, 55 (1932).

tion of the metal and 70 g. of triphenylchloromethane was added slowly over a period of twenty-five minutes. After stirring for five minutes longer, dry β -bromoethyl ethyl ether diluted with an equal volume of dry ether was slowly added until the red color of the solution had disappeared. This required about 35 cc. of the bromo ether. Water was then added until the flask was nearly full and the pink solid which separated was collected by filtration and washed with water. After recrystallization from ethyl alcohol, 82.5 g. of white crystals was obtained which melted at 111.5-112°.

Anal. Calcd. for $\text{C}_{21}\text{H}_{19}\text{OC}_2\text{H}_5$: C, 87.3; H, 7.6; OC_2H_5 , 14.24. Found: C, 87.4, 87.3; H, 7.9, 7.9; OC_2H_5 , 14.18.

The Preparation of γ,γ,γ -Triphenylpropyl Iodide.—Ten grams of the triphenylpropyl ethyl ether was refluxed for eleven hours with 250 cc. of constant boiling hydriodic acid while a slow stream of nitrogen gas was bubbled through the reaction mixture to facilitate the volatilization of the ethyl iodide formed. The crude product was separated by filtering the mixture through a Gooch funnel fitted with a Caswell disk so that the hydriodic acid could be recovered. The iodide was purified by dissolving it in 30 cc. of hot benzene, filtering the solution, and precipitating with 300 cc. of alcohol; 8.5 g. of white crystals, m. p. 174.5-175°, was obtained. In some experiments it was found necessary to wash the benzene solution with dilute sodium bisulfite solution to remove iodine.

Anal. Calcd. for $\text{C}_{21}\text{H}_{19}\text{I}$: C, 63.3; H, 4.8; I, 31.9. Found: C, 63.7, 63.4; H, 5.1, 5.0; I, 32.0, 31.2, 31.3.

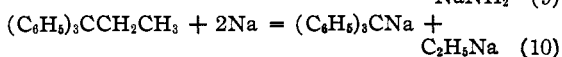
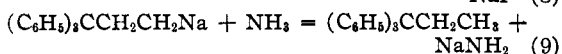
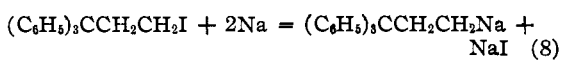
The reaction of hydriodic acid with the triphenylpropyl ethyl ether appears to proceed smoothly and normally, for the iodide has been obtained repeatedly in 67-70% yields. The fact that it is very unreactive, and particularly the isolation of triphenylmethane in the reaction about to be described, excludes migration of the phenyl groups. Although the isomeric structure $(\text{C}_6\text{H}_5)_3\text{CCHICH}_2$ is conceivable, the formula $(\text{C}_6\text{H}_5)_3\text{CCH}_2\text{CH}_2\text{I}$ may be assigned tentatively.

The Action of Sodium on γ,γ,γ -Triphenylpropyl Iodide.—The iodide was added to a solution of sodium in liquid ammonia contained in a large Dewar flask and the mixture was kept well agitated by means of a mechanical stirrer. Fresh sodium was added from time to time if necessary to keep an excess of the metal present and the stirring was continued for twenty-four hours to ensure complete reaction. At the end of this time the excess sodium was decomposed with ammonium nitrate and after the major portion of the ammonia had evaporated, water was added to the residue. The resulting mixture was then extracted with ether and the aqueous layer was acidified with nitric acid, treated with a solution of silver nitrate and the precipitated silver iodide was collected and weighed. In this way it was found that the removal of iodine from the organic compound was complete.

Evaporation of the dried ethereal extract left an oil which failed to crystallize until it was distilled under reduced pressure. The crystals which separated from the distillate were recrystallized from alcohol and shown to be identical with triphenylmethane by a mixed melting point.

The possibility that the triphenylpropyl iodide might be contaminated with triphenylmethane was excluded by adding a sample to a solution of potassium amide in liquid ammonia. Under these conditions even a trace of triphenylmethane would be revealed by an intense red coloration due to the formation of potassium triphenylmethide and it was found that the iodide did not produce the slightest perceptible change in the color of the solution.

The precursor of the triphenylmethane was doubtless sodium triphenylmethide which might conceivably have resulted from the action of sodium on the iodide in three different ways: first, through the intermediate formation and subsequent cleavage of 1,1,1-triphenylpropane; sec-



ondly, by direct cleavage of the bond between the β and γ carbon atoms in the iodide; thirdly, by a molecular rearrangement of the sodium triphenylpropide formed in accordance with Equation (8) accompanied by spontaneous cleavage as has been discussed in the introduction.

The first hypothesis has been shown definitely to be inadequate, by parallel experiments in which it was found that 1,1,1-triphenylpropane was not appreciably cleaved under the conditions which sufficed for the formation of considerable quantities of triphenylmethane from the triphenylpropyl iodide. Finely powdered portions of the two substances were stirred with solutions of two equivalents of sodium in liquid ammonia for two hours. No evidence of any cleavage of the hydrocarbon was observed⁷ and it was re-

(7) A thirty-six hour treatment of the hydrocarbon with a concentrated sodium solution is necessary to produce sufficient cleavage for the hydrolysis products to give a faint test for triphenylmethane with potassium amide.

covered unchanged when the solution was hydrolyzed. On the other hand, the iodide began to react immediately, a red coloration was observed and impure triphenylmethane was isolated from the residue, after hydrolysis, by extraction with methyl alcohol.

Although it is not possible to predict with certainty the influence of the substitution of iodine in the beta position upon the direct cleavage of the carbon-carbon bond, the third hypothesis (involving the initial formation of sodium iodide) appears to be *a priori* the more probable and certainly furnishes a more explicit interpretation of the differences in the rate of formation of sodium triphenylmethide from the triphenylpropane and the triphenylpropyl iodide.

The Behavior of γ,γ,γ -Triphenylpropyl Iodide and β,β,β -Triphenylethyl Chloride in Liquid Ammonia Solutions of Sodium Nitrate.—Solutions of 5 g. of sodium nitrate in 200 cc. of dry liquid ammonia were stirred for ten hours with 0.111 g. of the iodo compound and with 0.117 g. of the chloro compound. The greater portion of the ammonia was allowed to evaporate and water was added to the residues. After acidifying the aqueous solutions with nitric acid the absence of halogen ions was demonstrated by the addition of silver nitrate.

Summary

A solution of sodium in liquid ammonia completely removes the iodine from γ,γ,γ -triphenylpropyl iodide and triphenylmethane may be isolated after hydrolysis of the reaction products. A molecular rearrangement involving spontaneous cleavage appears to take place and the probable mechanism of this transformation is discussed.

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