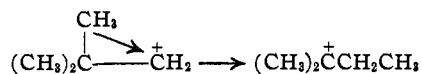


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Reactions of Certain Neopentyl Systems with Electrophilic Reagents¹

BY PHILIP SKELL AND CHARLES R. HAUSER

Whitmore and co-workers have shown that neopentyl systems react with electrophilic reagents to yield largely rearranged products. Thus, neopentyl alcohol with hydrogen bromide gives mainly *t*-amyl bromide,² while neopentyl iodide with silver nitrate or mercuric chloride yields largely *t*-amyl alcohol.³ These reactions have been considered to involve the removal of X (hydroxyl or halogen) with its complete octet of electrons, leaving a carbon atom with only a sextet of electrons.⁴ This carbon atom is stabilized by acquiring an electron pair from the adjacent carbon atom, the shifting electron pair carrying with it the attached methyl group.



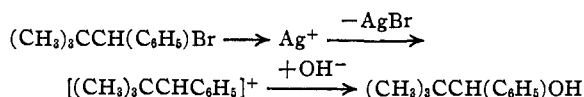
The tertiary carbonium ion thus formed acquires the bromide or hydroxyl ion from the medium, yielding the *t*-amyl bromide or alcohol.

A corollary to this theory (applied to various carbon skeletons) might be that the ease of rearrangement is dependent upon the relative electron-attraction of the α -carbon atom in the positive fragment and upon the ease of migration of the electron pair with its attached group. On this basis one might expect that the tendency to rearrangement in the neopentyl system would be decreased if the hydrogens on the α -carbon atom were substituted by electron donating groups, such as alkyl or phenyl groups.⁵ That the substitution of two alkyl groups on the α -carbon atom may impede rearrangement in the neopentyl system is indicated by the fact that, in contrast to α -methylneopentyl alcohol which on dehydration gives mainly rearranged olefins,⁶ α, α' -methyl-ethylneopentyl and α, α' -dimethylneoheptyl alcohols on dehydration yield mainly unrearranged olefins.⁷ We have demonstrated that even one

α -phenyl substituent stabilizes the neopentyl system.

In contrast to the reactions of unsubstituted neopentyl systems, α -phenylneopentyl alcohol reacts with hydrogen bromide to yield largely the corresponding bromide, and this bromide reacts with silver nitrate to regenerate mainly the original alcohol. Other workers have shown that α, α -diphenylneopentyl systems can similarly be made to undergo "metathetical" reactions with electrophilic reagents to yield largely unrearranged products,⁸ although rearrangement products have also been obtained under certain conditions.⁹ Thus, α, α -diphenylneopentyl alcohol with thionyl chloride gives the corresponding chloride which with silver acetate yields the corresponding acetate; the latter on hydrolysis regenerates an alcohol which may be converted to the original chloride.⁸

The first step in these reactions probably involves the formation of a coordination complex between the alcohol or halide and the electrophilic reagent (ROH_2^+ or $\text{RBr} \rightarrow \text{Ag}^+$). This facilitates the removal of X with its complete octet of electrons. With neopentyl systems having at least one phenyl or two alkyl groups (in which the unrearranged product is formed) the complex decomposes probably yielding the carbonium ion as intermediate¹⁰ which then acquires an anion (halide or hydroxyl) from the medium. The reaction of α -phenylneopentyl bromide with silver ion, for example, may be represented as



With neopentyl alcohol or halide, however, the

hydration (possibly involving the simultaneous elimination of the elements of water from adjacent atoms) it would appear that the tendency to rearrangements is less with these alcohols, since the α -methylneopentyl alcohol which also has the required structure for dehydration without rearrangement, nevertheless mainly rearranges. Moreover, Bartlett and Knox (THIS JOURNAL, 61, 3191 (1939)) have shown that, in contrast to the reaction of neopentyl alcohol with hydrogen bromide, α, α' -diethylneopentyl alcohol reacts with anhydrous hydrogen chloride apparently without rearrangement.

(1) This paper is taken from a portion of a Ph.D. thesis by Philip Skell.

(2) Whitmore and Rothrock, THIS JOURNAL, 54, 3431 (1932).

(3) Whitmore, Wittle and Popkin, *ibid.*, 61, 1586 (1939).

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

(5) That alkyl and phenyl function as electron donating groups when present on the α -carbon atom of alkyl halides is demonstrated by the increased tendency to ionization of the halides; see, especially, Hughes, Ingold, Masterman and McNulty, *J. Chem. Soc.*, 899 (1940).

(6) Whitmore and Meunier, THIS JOURNAL, 55, 3721 (1933).

(7) Whitmore and Laughlin, *ibid.*, 54, 4011 (1932). While the rearrangements may be precluded to some extent because of the de-

(8) Ramart-Lucas, *Compt. rend.*, 154, 1088 (1912); *Ann. chim. phys.*, [8] 30, 368 (1913).

(9) Marvel and Bateman, THIS JOURNAL, 49, 2914 (1927).

(10) In this connection see especially Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 139-140; "Annual Reports," *J. Chem. Soc.*, 236-247 (1940).

solved in concentrated sulfuric acid at room temperature. A momentary flash of bright yellow was produced and on pouring the solution into water a high yield of pure tetraphenylethylene was obtained.

Summary

1. In contrast to unsubstituted neopentyl systems, α -phenylneopentyl systems react with electrophilic reagents to yield largely unrearranged products. α -Phenylneopentyl alcohol with hydrogen bromide yields largely the corre-

sponding bromide, and the latter with silver nitrate regenerates mainly the original alcohol.

2. Asymmetrical tetraphenylethyl alcohol with hydrogen bromide or concentrated sulfuric acid at room temperature yields tetraphenylethylene.

3. The effect of substituents on the tendency to rearrangement of neopentyl systems is discussed.

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Acetylenic Ethers. III.¹ Halogen Derivatives of Phenoxyacetylene

BY THOMAS L. JACOBS AND WENDELL J. WHITCHER²

At the outset of our study of acetylenic ethers it seemed possible that these compounds would exhibit many of the peculiarities of halogenated acetylenes since in both classes the carbon-carbon triple bond is directly attached to an atom bearing unshared pairs of electrons. Actually very few close similarities have been observed. The only one worthy of mention is the great tendency toward polymerization exhibited in both series by those members which have an acetylenic hydrogen ($\text{HC}\equiv\text{COR}$ and $\text{HC}\equiv\text{CX}$); compounds in which this hydrogen is replaced by an alkyl group are relatively stable. Dihalogenated acetylenes, $\text{XC}\equiv\text{CX}$, are likewise characterized by ready polymerization. The preparation of halogenated phenoxyacetylenes, $\text{C}_6\text{H}_5\text{OC}\equiv\text{CX}$, was therefore undertaken in order to compare these two series more closely and to examine further the reactions of acetylenic ethers. Since phenoxyacetylene was the most readily available of these ethers it was used throughout this investigation.

Three general methods have been used for the preparation of halogenated acetylenes: the action of halogens or certain halogenating agents on metallic derivatives of acetylenes, the reaction between hypohalite ion and acetylenes, and the treatment of dihaloethylenes with alkaline reagents.

(1) For the second paper of this series see Jacobs, Cramer and Hanson, *THIS JOURNAL*, **64**, 223 (1942).

(2) The greater part of this paper is taken from a thesis presented by Wendell J. Whitcher to the Faculty of Arts and Sciences of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Mr. Whitcher's present address is E. I. du Pont de Nemours and Co., Wilmington, Delaware.

Iodoacetylenes have been prepared in excellent yield by the action of iodine on acetylenic Grignard reagents; at 0° neither diacetylene formation nor iodine addition occurred.³ Sodium, copper and silver acetylides have also been used and the iodination of the first of these in liquid ammonia is a good synthetic method.⁴ Diiodoacetylene has been prepared in excellent yield by passing acetylene into potassium hydroxide solution while iodine in potassium iodide solution was being added.⁵ This reaction has not been applied to the synthesis of substituted iodoacetylenes.

All of these methods were tried unsuccessfully in an attempt to prepare iodophenoxyacetylene. The reaction of phenoxyethynylmagnesium bromide with the theoretical amount of iodine at 0° failed to give this compound. Phenoxytriiodoethylene was obtained in fair yield and was the only product isolated. Sodium phenoxyacetylide was similarly treated with iodine and only a small amount of phenoxytriiodoethylene resulted. The main product polymerized when distillation was attempted at 4 mm. pressure, but at much lower pressures a clear distillate was obtained. This was a mixture containing phenoxyacetylene and unstable iodo compounds. Treatment with iodine gave only phenoxyacetylene diiodide and no phenoxytriiodoethylene. The distillate darkened rapidly and could not be purified successfully. An attempt to hydrate the undistilled product with mercuric acetate and hydrochloric acid was unsuccessful.

(3) Grignard and Perrichon, *Ann. chim.*, **5**, 5 (1926).

(4) Vaughn and Nieuwland, *THIS JOURNAL*, **55**, 2150 (1933).

(5) Blitz and Küppers, *Ber.*, **37**, 4412 (1904).