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FORMATION OF INDENES BY ADDITION OF CARBONIUM IONS TO DIPHENYLACETYLENE

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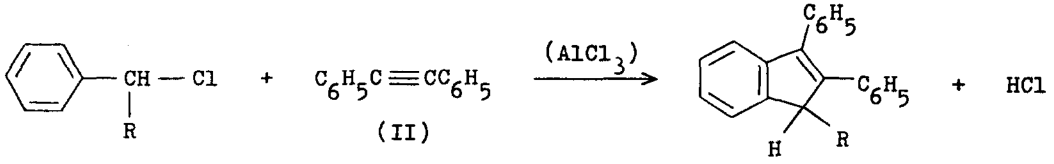
Electrophilic additions to triple bonds are receiving increasing attention, and clear evidence has been obtained that they occur <u>via</u> vinyl cations or related species.[1] Little is known, however, on the addition of carbonium ions to acetylenes,[1,2] which represents a potential useful method of formation of a new carbon-carbon bond. In this context, we wish to report that diphenylmethyl and benzyl chlorides readily react with diphenylacetylene in the presence of a Lewis acid to give 1:1 adducts and/or indene derivatives. This reaction may be regarded as a new one-step method of synthesis of substituted indenes.

Reaction of diphenylmethyl chloride (Ia) with diphenylacetylene (II) (in the ratio of 1:5) in boiling dichloromethane in the presence of a catalytic amount of $AlCl_3$ for 6 hours afforded, after chromatography on silica gel, a white crystalline hydrocarbon (61%), mp 131-132° (from ethanol), identified as 1,2,3-triphenylindene (IIIa) on the basis of its analytical and spectral data and by comparison with an authentic sample, prepared as described in the literature.[3] From the reaction mixture was also isolated a small amount of a hydrocarbon $C_{40}H_{30}$, mp 165-166° (from ethanol), which was demonstrated to arise from a subsequent attack of the diphenylmethyl cation on the indene (IIIa).

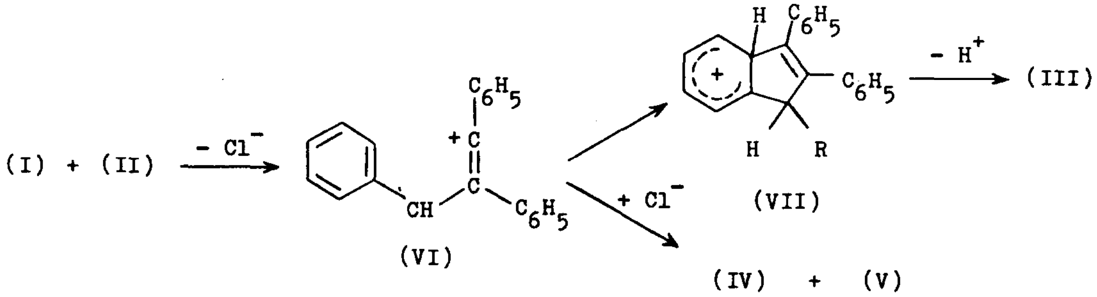


(Ia), R = C_6H_5
(Ib), R = H

(IIIa), R = C_6H_5, 61%
(IIIb), R = H, 15%

A similar reaction carried out with benzyl chloride (Ib) afforded a 15% yield of 2,3-diphenylindene (IIIb), mp 107-108° (from ethanol), identified by comparison with an authentic sample,[4] and a 50% yield of a mixture of (E)- and (Z)-1-chloro-1,2,3-triphenylpropene (IV) and (V), colorless oil, which are the products of the formal 1:1 addition of the two reagents (Ib) and (II). Also isolated was a small amount of a hydrocarbon $C_{28}H_{22}$, mp 125-126° (from ethanol), which arises from a subsequent attack of the benzyl cation on the indene (IIIb).

The reaction may be rationalized allowing the initial formation of a vinyl cation (VI), which undergoes intramolecular cyclization to give finally the indene derivative (III), or reacts with the chloride ion to give the 1:1 adducts (IV) and (V).



The former path is largely preferred in the case of the addition of diphenylmethyl chloride (Ia), the latter in the case of benzyl chloride (Ib). The competition between the two paths may be related to the relative reactivity of linear vinyl cations towards internal and external nucleophiles.[1] The formation of indenes, however, may suggest the occurrence of a γ-participation by aromatic π-systems in reactions at vinylic centers. This point, which cannot be resolved by the results so far obtained, is under active investigation in this laboratory.

REFERENCES

1. H. G. Richey and J.M. Richey in " Carbonium Ions ", Ed. G. A. Olah and P.v.R. Schleyer, Vol. 2, Wiley-Interscience, New York, 1970, p. 899; M. Hanack, Accounts Chem. Res., 3, 209 (1970); G. Modena and U. Tonellato, Adv. Phys. Org. Chem., 9, 185 (1971), and references cited therein.
2. T. Sasaki, S. Eguchi, and T. Toru, Chem. Comm., 780 (1968); K. Bott, Tetrahedron Letters, 1747 (1969); K. Bott, Chem. Comm., 1349 (1969); D. R. Kell and F. J. McQuillin, Chem. Comm., 599 (1970).
3. J. E. Hodgkins and M. P. Hughes, J. Org. Chem., 27, 4187 (1962).
4. J. J. McCullough, Canadian J. Chem., 46, 43 (1968).