

FORMATION OF 1-CYCLOPROPYLIDENE-2-PHENYLETHYLENE IN THE REACTION OF ETHINYLCYCLOPROPANE WITH BENZYNE

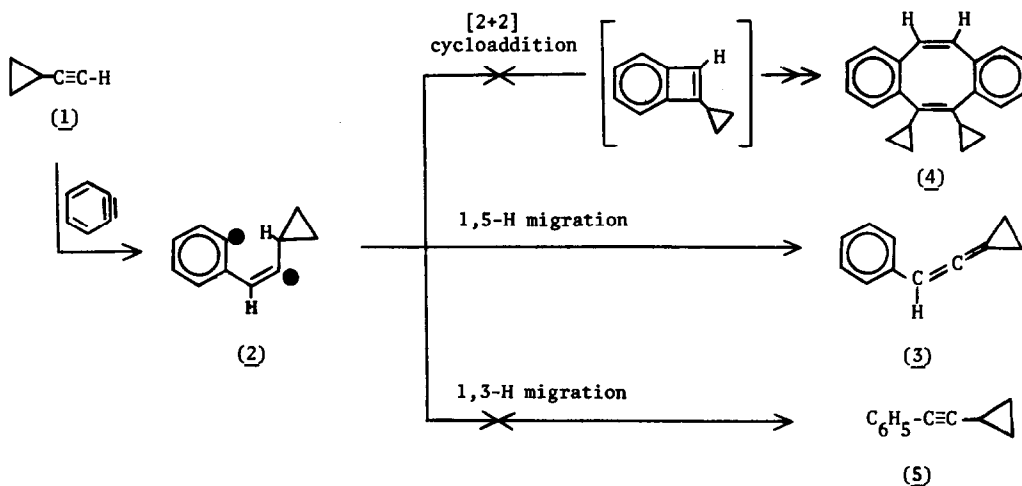
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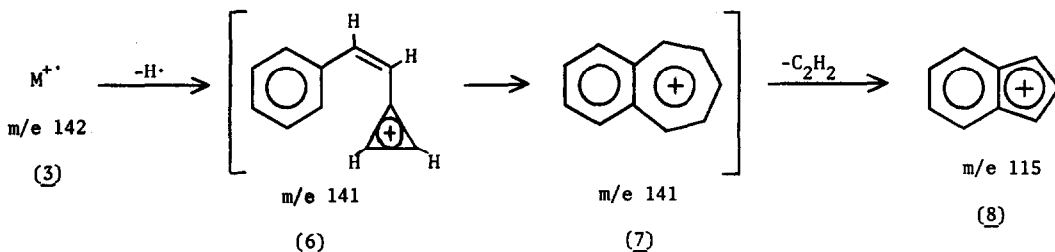
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We have lately shown that benzyne is capable of reacting with substituted vinylcyclopropanes by three main modes: (i) by "ene" reaction, when readily accessible allylic hydrogens are present; (ii) by [2+2] cycloaddition, and, if the only allylic hydrogens present are part of a cyclopropane ring (iii) by a novel "ene" reaction involving a cyclopropane-methine hydrogen.¹ This communication concerns the reaction of ethynylcyclopropane (1) with benzyne.

We found that on exposure of (1) to the action of benzyne generated by the thermolysis of benzenediazonium-2-carboxylate in ethylene dichloride a small amount of a 1:1-adduct could be isolated from the reaction mixture by preparative vapor-phase chromatography.² It was assigned the 1-cyclopropylidene-2-phenylethylene structure (3) on the basis of its spectral analysis. Its ir spectrum shows strong absorption at 1990 cm^{-1} characteristic for the allene group.³ Its uv spectrum is characterized by two well defined peaks at $263\ (\epsilon 1.6 \times 10^4)$ and $215\ \text{m}\mu\ (\epsilon 1.8 \times 10^4)$.³ The 60 Mc nmr spectrum (CCl_4) of (3) shows multiplets at $\tau\ 2.88$ (5H, phenyl group), 3.84 (1H, $J \sim 3\ \text{Hz}$, allenic proton) and 8.35 (4 H, methylenecyclopropane), in harmony with the formula. The observed splitting of the allenic resonance is probably due to long-range coupling with the small ring protons.⁴



The base peak in the mass spectrum of (3) is at m/e 142 ($M^{+\cdot}$, $C_{11}H_{10}$), and the only two other peaks with abundances $>10\%$ of the base peak are at m/e 141 ($C_{11}H_9$, 88%) and m/e 115 (8, 30%) corresponding to the stepwise loss of hydrogen and acetylene from the parent ion. The driving force for the primary mass spectral reaction (3) \rightarrow (6) probably stems from the enhanced stability of the styrylcyclopropenyl cation (6) or of the benztropylium ion (7).



The intermediacy of a vinylic biradical of structure (2) is invoked to explain the formation of the allene moiety by the favored 1,5-hydrogen migration. The less favored 1,3-hydrogen migration which could have led to formation of (5) was not observed. Neither could the formation of (4) be detected, in contrast to the behavior of arylacetylenes with benzyne.⁵

This is the first detailed account of an "ene" reaction resulting from a reaction of benzyne with 1-alkyne.^{6,7}

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REFERENCES

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3. H.D. Hartzler, *J.Amer.Chem.Soc.*, **83**, 4990 (1961).
4. See R.S. Macomber, *J.Org.Chem.*, **36**, 999 (1971), and references cited therein.
5. (a) M. Stiles, U. Burckhardt and A. Haag, *J.Org.Chem.*, **27**, 4715 (1962); (b) M. Stiles and U. Burckhardt, *J.Amer.Chem.Soc.*, **86**, 3396 (1964).
6. R.W. Hoffmann, in "Dehydrobenzene and Cycloalkynes", Academic Press, London, 1967, p. 198, cites an unpublished work of M. Stiles and A. Haag, concerning an "ene" reaction between benzyne and hexyne-1 to form 1-phenylhexa-1,2-diene in less than 4% yield.
7. See also, H.H. Wasserman and J.M. Fernandez, *J.Amer.Chem.Soc.*, **90**, 5322 (1968).