The Reactions of Benzyne with Allenes

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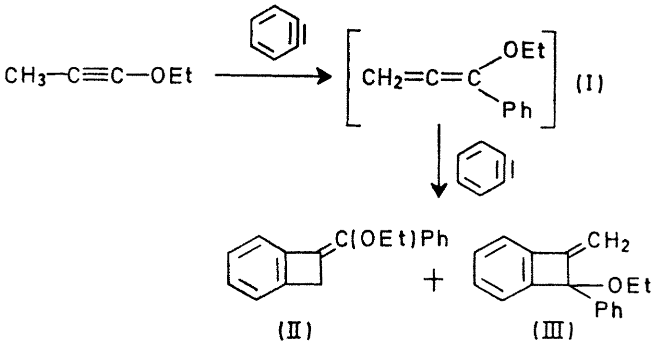
Summary The reactions of benzyne with allenes may proceed by 2 + 2 cycloaddition, or by ene-like reactions with formation of a 1,3-diene or an acetylene.

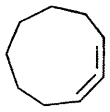
WE have previously noted[1] that the formation of the benzocyclobutene derivatives (II) and (III) in the reaction of benzyne with ethoxypropyne appears to result from a 2+2 cycloaddition of benzyne with the transient allene (I). The intermediate (I) was not isolated. We now report studies on the reactions of benzyne with a variety of allenes which show that such cycloaddition reactions do take place as one of the possible reaction paths. As is outlined below, other products are formed by competitive ene-type reactions in which addition of benzyne to the allene is followed by hydrogen abstraction with the formation of 1,3-dienes or acetylenes. The results are summarized in the Table.



The reactions were carried out by allowing benzenediazonium 2-carboxylate[2] to decompose in the presence of a 10% molar excess of allene in methylene chloride under reflux. Products were identified in the case of known materials by comparison with authentic compounds,

Reaction	Allene	Cycloadduct	1,3-Diene	Acetylene
1.	$(Me)_2C{=}C{=}CH_2$	—	$CH_2{=}C(Ph{-}C(Me){=}CH_2$[a,5] (34%)	—
2.	$MeCH{=}C{=}CHMe$	—	$MeCH{=}CH{-}C(Ph){=}CH_2$[a,6] (18%)	$PhCH(Me){-}C{\equiv}CMe$ (30%)
3.	$CH_2{=}C{=}CH_2$	—	—	$PhCH_2{-}C{\equiv}CH$[a,7] (16%)
4.	(IV)	(V) (5%)	(VI)[a,8] (31%)	—
5.	$Bu^tCH{=}C{=}CHOMe$[9]	(VII) (25%)	—	$Bu^tC{\equiv}C{-}CH(Ph)OMe$[a] (26%)
6.	$CH_2{=}C{=}CHCl$[b,10] (x) (y)	(VIII) (12%)	—	$HC{\equiv}C{-}CH(Ph)Cl$[a] (1%)
7.	$CH_2{=}C{=}CHOEt$[11]	(IX) (17%)	—	$HC{\equiv}C{-}CH(Ph)OEt$[a] (26%)
8.	$CH_2{=}C{=}CHCN$	—	—	$PhCH_2{-}C{\equiv}C{-}CN$ (15%)

[a] Identified by comparison with authentic materials synthesized through independent routes.
[b] The cycloadduct involving addition to double bond (y) was also isolated in less than 1% yield.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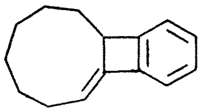
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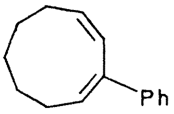
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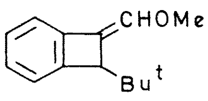
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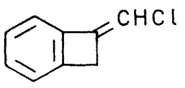
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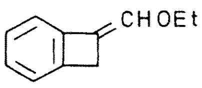
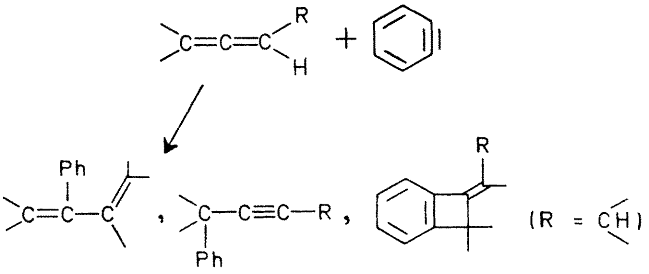

(IX)

independently synthesized. Other substances were characterized by n.m.r., i.r., u.v., and mass spectra. Satisfactory elemental analyses were obtained for all new products. 1-Ethoxymethylenebenzocyclobutene (IX) is unstable and was characterized as its dihydro-derivative, 1-ethoxymethylbenzocyclobutene. Compound (IX) could also be converted into benzocyclobutenone by ozonolysis.

Our results indicate that the reactions of benzyne with alkyl-substituted allenes normally afford 1,3-dienes through addition–hydrogen-abstraction (ene) reactions (see Scheme). Acetylene formation by addition of benzyne to a terminal carbon atom and abstraction of a vinylic hydrogen is also observed (reactions 2,3,5,6,7,8 in the Table). The failure to obtain an acetylenic product from the reaction of benzyne with the unsymmetrically disubstituted allene (reaction 1) may be due to steric effects whereby the geminal methyl groups inhibit approach of the benzyne molecule to the disubstituted carbon atom. The absence of acetylenic material in the reaction with cyclonona-1,2-diene (reaction 4) is consistent with the observation that a triple bond incorporated into a nine-membered ring is more highly strained than the corresponding allenic system from which it may be derived.[3]

In the systems studied above, 2+2 cycloaddition appears to be less favoured compared to the hydrogen abstraction reactions unless the allene is strained[4] as is 1,2-cyclononadiene (reaction 4). However, cycloaddition does compete favourably with acetylene formation in cases where the allenes are substituted with electron-rich groups[12] (reactions 5 and 7). No cycloadduct was observed in the reactions of benzyne with allene or cyanoallene (reactions 3 and 8). In the latter case, it is interesting to note that substitution of the electron-withdrawing cyano-group reverses the mode of acetylene formation relative to that found with the allenyl ethers and chloride. This suggests that the electrophilic benzyne undergoes initial reaction with the more electron-rich double bond of the allenic system.



SCHEME

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[1] H. H. Wasserman and J. M. Fernandez, *J. Amer. Chem. Soc.*, 1968, **90**, 5322.

[2] The benzenediazonium 2-carboxylate was prepared by a modification of the procedure of Stiles (personal communication from M. Stiles). This variant avoids the use of Ag_2O in the work-up; *cf.* L. Friedman, *J. Amer. Chem. Soc.*, 1967, **89**, 3071.

[3] R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, 1967, p. 318.

[4] Two strained olefinic hydrocarbons which undergo 2 + 2 cycloaddition with benzyne are norbornene (H. E. Simmons, *J. Amer. Chem. Soc.*, 1961, **83**, 1657) and *trans*-cyclo-octene (P. G. Gassman and H. P. Benecke, *Tetrahedron Letters*, 1969, 1089.)

[5] K. Alder, J. Haydn, K. Hemibach, and K. Neufang, *Annalen*, 1954, **586**, 110.

[6] E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 1956, 3333.

[7] J. E. Mulvaney, T. L. Folk, and D. J. Newton, *J. Org. Chem.*, 1967, **32**, 1674.

[8] 2-Phenylcyclonona-1,3-diene was prepared by the addition of phenyl-lithium to cyclonon-2-en-1-one (M. Santelli, M. Bertrand, and M. Ronco, *Bull. Soc. chim. France*, 1964, 3273).

[9] J. H. Van Boom, P. P. Montijn, L. Brandsma, and J. F. Arens, *Rec. Trav. chim.*, 1965, **84**, 37.

[10] T. L. Jacobs and W. F. Brill, *J. Amer. Chem. Soc.*, 1953, **75**, 1314.

[11] J. H. Van Boom, P. P. Montijn, L. Brandsma, and J. F. Arens, *Rec. Trav. chim.*, 1968, **87**, 916.

[12] H. H. Wasserman and A. J. Solodar, *J. Amer. Chem. Soc.*, 1965, **87** 4002. See also A. J. Solodar, Ph.D. Thesis, Yale University, New Haven, Connecticut, 1967.