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REACTION OF BENZYNE WITH CYCLIC OLEFINS - III. A NOVEL PHENYLATION OF CAMPHENE[1]

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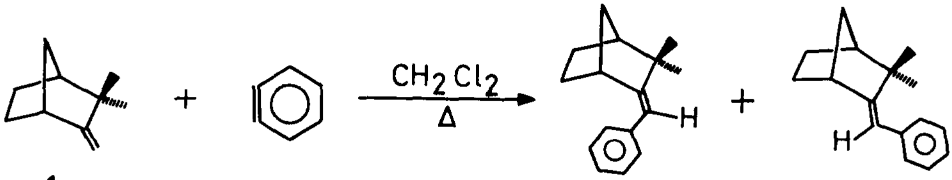
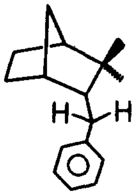
Benzyne generally reacts with olefins and dienes by any of the three principal pathways.[2] Most alkenes and 1,3-dienes react with benzyne to furnish products derived via an 'ene' reaction or 2+4 cycloaddition. Alternately, a 2+2 cycloaddition with benzyne may be favoured, particularly with olefins in which optimal geometry for a concerted 'ene' or 2+4 addition is not attainable.[3] We wish to report here a reaction between benzyne and a sterically constrained olefin, camphene 1 that provides an interesting and novel variant on the usually encountered benzyne-olefin reactions.



1 2 3

Reaction of benzenediazonium-2-carboxylate with excess of 1 in refluxing CH_2Cl_2 and elution chromatography ($AgNO_3$-silica gel column) gave a 2:1 mixture of (E)- and (Z)-ω-phenyl camphenes 2 and 3 in 15% yield. The isomers 2 and 3 could not be separated but their presence was established by spectral data. The mixture analysed for $C_{16}H_{20}$ and the PMR spectrum (100 MHz) exhibited olefinic proton singlets at δ 6.18 and 6.08 (ratio 1:2) due to the α-protons of a β,β-dimethylstyrene moiety present in 2 and 3. The signal at δ 6.18 is due to the (Z)- isomer 3 and at 6.08 due to the (E)-isomer 2. This assignment is based on the relative deshielding of olefinic proton in (Z)-isomer compared to the (E)-isomer for several ω-substituted camphene derivatives.[4] The rest of the spectrum consisted of doublets at 3.35 and 3.05 due to C_1 proton of 2 and 3, aromatic proton multiplet at 7.73 and methyl singlets between 0.92 and 1.1. The presence of the styrene chromophore in the benzyne addition product was further substantiated by its UV spectrum: λ_{max}^{MeOH} 260 nm (ϵ = 11,200). Catalytic hydrogenation of 2 & 3 over Adams catalyst resulted in the formation of a dihydro derivative 4.



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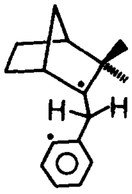

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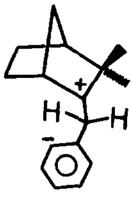

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Since both (E)- & (Z)-isomers 2 & 3 are formed in the phenylation of camphene with benzyne, they must be derived from a common intermediate in which rotation about C-C bond could occur. Either 5 or 6 might be considered as representing this intermediate and can lead via sequential 1,2- and 1,4-hydrogen or hydride shifts to products. The absence of rearrangement products in the addition of benzyne to 1, known for its marked propensity to carbonium ion type rearrangements,[6] rules out of contention the intermediate 6 and supports the view[7] that nonconcerted benzyne-olefin reactions proceed through diradical intermediates. In the reaction with 1 this intermediate is represented by 5.

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4. The olefinic proton resonances due to (E)- & (Z)-isomers in the mixture of ω-chlorocamphenes are at δ 5.5 & 5.75, in ω-bromocamphenes[5b] at 5.66 & 5.88 and in ω-nitrocamphenes[5c] at 6.7 and 6.93. Even camphene 1 exhibits this behaviour and shows up[5d] its *syn*- and *anti*- exomethylene protons at 4.65 & 4.44 respectively.
5. (a) H. G. Richey, J. E. Grant, T.J. Garback & D.L. Dull, J. Org. Chem., 30, 3909 (1965); (b) G. Mehta, Unpublished results; (c) Private communication from Dr. S. Ranganathan; (d) S. H. Grover and J. B. Stothers, J. Am. Chem. Soc., 91, 4331 (1969).
6. In fact, attempted preparation of 2 & 3 via reaction sequence that may involve polar intermeadiates led exclusively to the formation of 2-phenylbornene and other rearrangement products.
7. P. G. Gassman and H. P. Benecke, Tetrahedron Letters, 1089 (1969); I. Tabushi, K. Okazaki and R. Oda, Tetrahedron, 25, 4401 (1969).