Cycloadditions of 3,4-Diazanorcaradienes with Benzyne and 1-Diethylaminopropyne

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Summary Cycloaddition of benzyne and 1-diethylaminopropyne with 2,5-disubstituted-3,4-diazanorcaradienes (**1**) affords, after nitrogen extrusion, cycloheptatriene derivatives (**3a—c**) and (**4a**) and as such constitutes a new synthetic route to cyclohepta-1,3,5-trienes.

The reaction of 3,6-disubstituted-1,2,4,5-tetrazines with cyclopropene provides a useful route to 2,5-disubstituted-3,4-diazanorcaradienes (**1**),[1] and cycloaddition of the latter with acetylenes suggested a new synthesis of substituted cyclohepta-1,3,5-trienes. A previous report[2] that reaction of dimethyl acetylenedicarboxylate with (**1b**) gave products arising from dipolar attack at only one of the C=N bonds is irrelevant since diazanorcaradienes appear to be inverse electron demand dienes. This report establishes that (4 + 2) cycloaddition of active acetylenes to substituted 3,4-diazanorcaradienes affords a novel route to previously unreported cycloheptatriene derivatives.

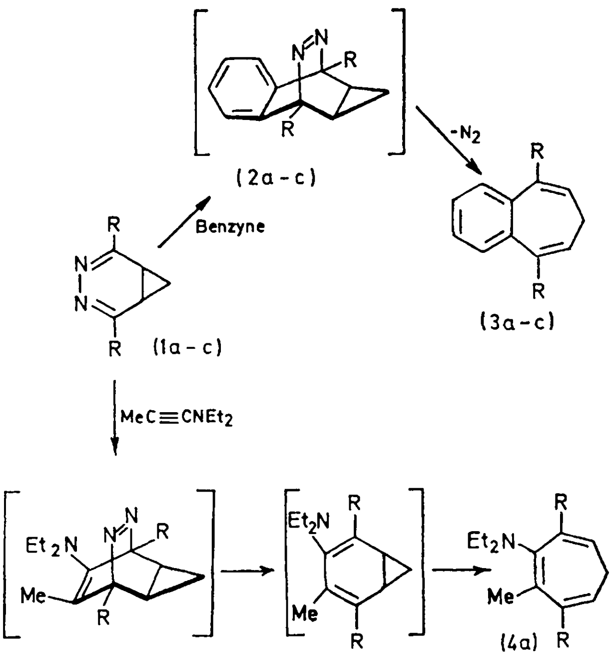
Reaction of benzyne, generated from benzenediazonium-2-carboxylate,[3] with the diazadiene (**1a**)[1b,c] in CH_2Cl_2 solution afforded the crystalline 7*H*-benzocycloheptatriene (**3a**) (38%) [δ ($CDCl_3$) 2·40 (2H, t, *J* 7·2 Hz), 3·72 (6H, s, ester-Me), 7·18 (2H, t, *J* 7·2 Hz, vinyl), 7·48 (4H, m, ArH) p.p.m.] after alumina chromatography. No other products were isolated. The initial adduct, (**2a**), was not detected and apparently extrudes nitrogen spontaneously under the reaction conditions (Scheme 1). This is the first report of spontaneous nitrogen extrusion from a Diels–Alder adduct of 3,4-diazanorcaradienes.

Similarly, reaction of benzyne with (**1b**)[1a] or (**1c**)[4] in refluxing CH_2Cl_2 gave benzocycloheptatrienes (**3b**) and (**3c**) in 11 and 40% yield respectively. Chromatography of the crude reaction mixture from (**1b**) also afforded an as yet unidentified 1:1 adduct with benzyne, m.p. 121—122° (5·2%) yield. As expected the n.m.r. spectra of (**3b**) and (**3c**) are similar to that of (**3a**); however, the olefinic triplets are now found at considerably higher field, *i.e.* δ 6·21 p.p.m. for (**3b**) and 6·30 p.p.m. for (**3c**).

Assignment of structure (**3b**) was supported by an alternative synthesis[4] from cyclopropene and the benzopyran (**5**)[5] (Scheme 2).

Entry into the non-annelated cycloheptatriene series was achieved by reaction of (**1a**) with 1-diethylaminopropyne in dry dioxan. Alumina chromatography gave (**4a**) as a yellow oil which slowly decomposed when set aside [δ ($CDCl_3$), 1·08 (6H, t, Et), 1·3—3·3 br (C-7-CH_2), 2·12 (3H, s), 2·90 (4H, q, Et), 3·66 (6H, s, shoulder in CCl_4, ester-Me), and 6·52 (2H, q, vinyl) p.p.m.].

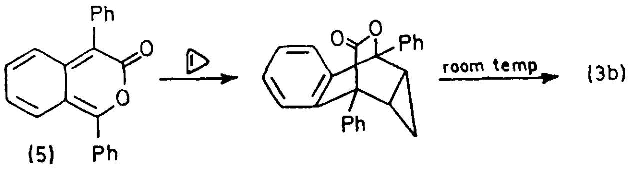
The above reaction is thought to proceed through a norcaradiene intermediate (Scheme 1) since the cyclo-



a; R = CO_2Me
b; R = Ph
c; R = p-$CF_3\cdot C_6H_4$

Scheme 1

propane ring is *exo* to the nitrogen bridge in the initial adduct.[6] A similar intermediate is presumably involved in the benzyne pathway although it is not specified in Scheme 1.



Scheme 2

Attempted reaction of 1-diethylaminopropyne with (**1b**), even under forcing conditions, yielded only starting material or decomposition products of the ynamine. This and the results from the benzyne reaction suggest that the reactivity of 3,4-diazanorcaradienes in (4 + 2) cycloadditions is strongly enhanced by electron-withdrawing substituents. Furthermore the observation that (**1a**) failed to react with either phenylacetylene or ethoxyacetylene supports the contention that highly strained,[7] electron-rich or otherwise reactive olefins and acetylenes are a necessary requisite for successful (4 + 2) cycloaddition in the diazanorcaradiene series.

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