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CYCLOADDITION REACTIONS OF BENZYNE WITH CYCLIC OLEFINS

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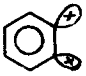
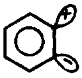
Benzyne continues to be an elusive species, and as a consequence much attention has been focused on the structure of this system.[2-3] The bulk of the experimental evidence indicates that the reactive species, hence the ground state, is a symmetric singlet diradical.[2b] This notion is supported by several theoretical studies.[3] In contrast, Tabushi and co-workers have



S



A

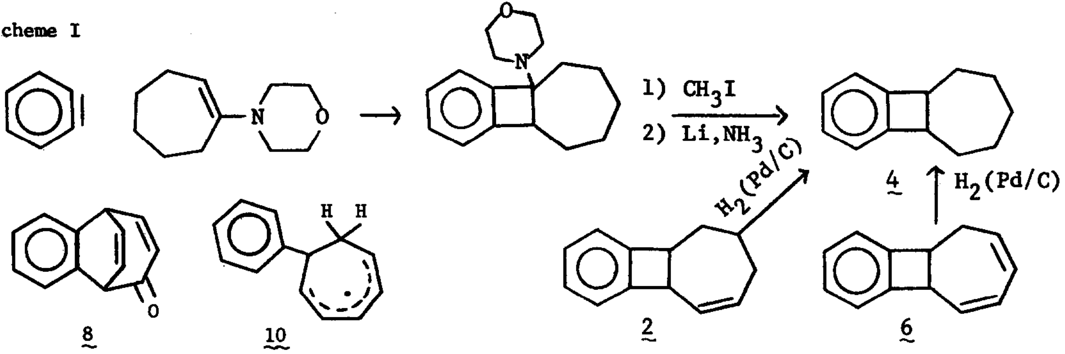
recently reported a case in which S and A appear to be equally reactive based upon their observation of a sizeable amount of 2+6 product attributed to addition of cycloheptatriene to A.[4] We have been concerned with the course of benzyne additions to cyclic polyenes under varying conditions, and we are prompted to report some of our preliminary findings which differ markedly from those of Tabushi.

Decomposition of o-benzenediazonium carboxylate[5] with 1,3-cycloheptadiene afforded two major hydrocarbon adducts in relative ratio of 70% to 28%.[6] The predominating isomer was assigned as benzobicyclo [3.2.2] nonadiene (1), formed via 2+4 cycloaddition. The pmr spectrum of 1 (Table 1) was quite similar to that observed for the related benzobicyclo [2.2.2] octadiene.[7,14] The mass spectrum showed major fragments at m/e 170, 142, 141, 128, 115, and hydrogenation over Pd/Carbon gave benzobicyclo [3.2.2] nonene (3) having pmr spectrum described in Table I and mass spectrum fragments 172, 153, 152, 146, 129, 128. The other isomer was assigned structure 2 and was derived from a 2+2 cycloaddition reaction. Pmr double irradiation experiments enabled measurement of several coupling constants (Table I): decoupling at the H_5 methylene resonances gave an AB type pattern for H_3 and H_4 (H_3 collapsed to a doubled-doublet and H_4 to a tripled-doublet), and decoupling at H_1 caused only slight sharpening of H_3 and H_4

resonances while irradiation at H_2 transformed H_3 into a doubled doublet and H_4 became a tripled-doublet. The mass spectrum of 2 showed fragments at m/e 170, 162, 161, 129, 128, 115, and hydrogenation of 2 gave 4 which was prepared by alternate synthesis shown in Scheme I.

Treatment of cycloheptatriene with benzyne derived from *o*-benzenediazonium carboxylate (or the hydrochloride salt) or from *o*-bromofluorobenzene and Mg in THF gave two major products (> 97% of the product composition) in the ratio of 1:1. These products were isolated by preparative vpc (8' carbowax column at 130°; retention times - 35 & 40 min.). The longer retention time product was identified as 7-phenyl cycloheptatriene (5) by comparison to authentic material, and it was derived from an *ene* reaction. The shorter retention time sample showed major mass spectrum fragments at m/e 168, 167, 165, 153, 152, 128, and the 100 MHz nmr spectrum displayed *unsymmetrical* multiplet patterns for both the aromatic and vinyl protons (Table 1, compound 6). From pmr decoupling experiments it was impossible to unambiguously choose between two feasible assignments - a 2+2 cycloadduct 6 or a 2+4 product 7. Chemical proof of structure as a 2+2 adduct 6 was accomplished by hydrogenation of this material over Pd/Carbon to give 4.

Scheme I



Friedman has reported that the course of benzyne cycloaddition reactions can be influenced by catalytic amounts of Ag^{+}.[8] We have observed a remarkable effect on the course of the reaction between benzyne and cycloheptatriene with added $AgClO_4$. Only a single product was observed from this reaction, and its pmr spectrum indicated it was of different constitution than 5 or 6. The mass spectral parent peak at m/e 168 of the crystalline product (mp57-57.5°) indicated a 1:1 adduct, and the i.r. confirmed the presence of an unsaturated aromatic hydrocarbon. The structure was deduced to be benzobicyclo [3.2.2] nonatriene (7) formally derived from 2+4 addition on the basis of nmr double resonance experiments (Table I). Irradiation at H_7 collapsed H_1 to a doublet, H_6 to an AB doublet, and H_5 to a quartet; irradiation at both H_1 and H_4 gave an AB pattern for H_8 & H_9 and simplified H_5 to a doublet of triplets.

Finally, decoupling at H_4 transformed H_9 into an AB type double-doublet, H_8 into a quartet, and H_5 remained as doubled-triplet. The approximate couplings measured from the spectrum (Table I) were almost identical to the corresponding values reported by Ciabattoni for benzobicyclo [3.2.2] nonatrienone (**8**).[9] Further support for this assignment was provided by hydrogenation of **7** to benzobicyclo [3.2.2] nonene (**3**).

The relative partitioning between *ene*, *2+4* and *2+2* reaction pathways for benzyne has been briefly discussed.[10] The *ene* and *2+4* reactions are considered to be concerted; whereas, the *2+2* addition is stepwise.[2b] The formation of a large amount of *2+2* product in the Ag^+ free reactions reported here represents the first such observation for addition of benzyne to a *cis*-diene chromophore.[11] These data indicate that when a diene system is sufficiently distorted from planarity as in 1,3-cycloheptadiene[12a] or cycloheptatriene[12b] stepwise *2+2* cycloaddition with benzyne becomes energetically quite favorable. In contrast, it is noteworthy that other reactive dienophiles such as maleic anhydride or acetylene dicarboxylate give exclusive *2+4* reaction with 1,3-cycloheptadiene or cycloheptatriene.[13] To account for the change in the product distribution introduced by Ag^+, we feel that a species such as **10**, derived from a benzyne-silver-olefin adduct followed by Ag^+ extrusion, may be a reactive intermediate. Experiments are in progress to provide more information on this point.[14,15]

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6. A third adduct (*ca.* 2%) was observed by vpc and presumed to be an *ene* product based upon hydrogenation of the product mixture to give phenyl cycloheptane as detected by pmr.
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11. 1,3-*cis*, *trans*-Cyclooctadiene gave only a *2+2* adduct with either benzyne or acetylenes: P. G. Gassman, H. P. Benecke, and T. J. Murphy, *Tetrahedron Lett.*, 1649 (1969).
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Geuirtz, *Tetrahedron Lett.*, 4413, 4417 (1965). Note: an *ene* type reaction for cycloheptatriene has been postulated by these authors.

14. We have also observed exclusive formation of *2+4* product in the reaction of benzyne with 1,3-cyclohexadiene in presence of added Ag^+ *vs.* the appearance of 4 products from the silver free reaction [see A. M. Braun, *J. Org. Chem.*, **35**, 1208 (1970)].
15. Benzyne and tropone undergo concurrent *2+4* and *2+6* reaction yielding **8** and benzobicyclo [4.2.0] nonatriene.[16] Such an observation in itself would not constitute grounds for proposing partial reaction *via*. *A* benzyne[4]based upon orbital symmetry arguments.[2b,17]
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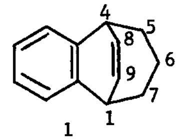
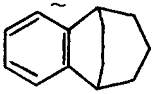
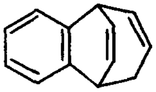
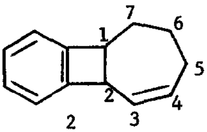
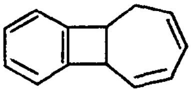
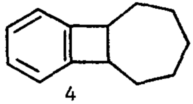
TABLE I

	Proton	Type	Coupling Constant (Hz)	Chemical Shift (ppm)[a]
 **1**	1=4	broadened[b] pentet		3.38
	8=9	quartet		6.44
	5-7	mult.		1.52
	arom	mult.		7.08-7.23
 **3**	1=4	broad singlet		2.99
	5-9	mult.		1.5-1.9
	arom	mult.		6.9-7.1
 **7**	1	mult.	1,8=6.5	3.45
	4	broad triplet	1,9=1.5	3.60
	5	c,f	4,5=8.0	6.12
	6	doubled-doublet of triplets[g]	4,6=1.0	5.02
	7	pentet[h]	4,8=1.5	2.32
	8	d,e	4,9=6.5	6.35
			5,6=11.0	
	9	d,e	6,7=3.5	6.74
	arom	mult.	8,9=8.5	7.12
 **2**	1	pentet	2,3=1.5	3.56
	2	broad singlet	2,4=3.0	4.38
	3	doublet of quartets	3,4=11.0	5.80
	4	f,i	4,5=6.0	5.50
	5	mult.		2.34
	6,7	mult.		1.4-2.2
	arom	mult.		6.9-7.2
 **6**	1,2	unsym. mult.		2.7-3.1
	3-6	unsym. mult.[j]		4.54-4.8
	7	mult.		2.7-3.1
	arom	unsym. mult.		7.2-7.8
 **4**	1.2	symm. mult.		3.50-3.76
	3-7	mult.		1.2-2.3
	arom	sym. AA'BB' mult.		7.0-7.3

(a) relative to tms at 100 MHz in CDCl$_3$; (b) irradiation at 1.52δ collapses this mult. to a quart.; (c) overlapping quart. of triplets; (d) overlapping quart of doublets, (e) 7 lines; (f) 10 lines; (g) 12 lines; (h) septet in benzene-d$_6$; (i) two sets of overlapping doublets of triplets; (j) simultaneous irradiation of $H_{1,2}$ & H_7 gave unsym. mult. of *Ca.* 9 lines for H_{3-6}.