Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.81; H, 9.76.

A magnesium enolate solution was also obtained from an ethereal solution of the lithium enolate **19**, formed by reaction of 738 mg (3.6 mmol) of the silyl ether **11** with 4.0 mmol of MeLi in 2.7 ml of Et_2O for 60 min. The resulting solution was treated with 0.8 ml of a solution containing 1.9 mmol of $MgBr_2$ in an Et_2O–PhH mixture (1:1, v/v).

A solution of the zinc enolate of phenylacetone was obtained from a solution of the lithium enolate **19** (from 1.650 g or 8.0 mmol of the silyl ether **11** and 8.25 mmol of MeLi) in 5.0 ml of DME. To the solution was added 6.0 ml of an Et_2O solution containing 4.25 mmol of anhydrous $ZnCl_2$. A white precipitate (primarily LiCl) separated from the DME–Et_2O solution on standing. Analyses of the precipitate and the supernatant liquid gave the following results: precipitate, 1.2 mmol of Cl^-, 1.4 mmol of Li^+, and 0.1 mmol of Zn^{2+}; solution, 4.2 mmol of Zn^{2+}, 6.8 mmol of Cl^-, and 8.0 mmol of Li^+. When a comparable solution was prepared and immediately concentrated under reduced pressure to remove the bulk of the Et_2O, no LiCl precipitated from the DME solution.

In a similar experiment the lithium enolate **19**, from 1.331 g (7.6 mmol) of the enol acetate **18** and 16.5 mmol of MeLi, in 6.0 ml of DME was treated with 11.0 ml of an Et_2O solution containing 8.05 mmol of anhydrous $ZnCl_2$. The precipitate contained 0.2 mmol of Zn^{2+}, 6.0 mmol of Cl^-, and 7.8 mmol of Li^+ and the solution contained 8.1 mmol of Zn^{2+}, 9.7 mmol of Cl^-, and 12.0 mmol of Li^+. Quenching an aliquot of the solution followed by glpc analysis indicated that 92% of the ketone **24** was in the solution.

Reaction of the Potassium Enolate of Cyclohexanone with Ethyl Chloroformate.[18]—A solution of triphenylmethylpotassium, prepared[19] from 7.82 g (0.20 g-atom) of potassium and 53.8 g (0.22 mol) of Ph_3CH in 120 ml of DME, was treated with 17.27 g (0.176 mol) of cyclohexanone. The resulting suspension of the potassium enolate was added, dropwise and with stirring, to a solution of 20.6 g (0.19 mol) of $ClCO_2Et$ in 50 ml of DME. The mixture was stirred at ambient temperature for 1 hr and then partitioned between Et_2O and H_2O. The organic phase was dried, concentrated, and distilled to separate early fractions, bp 50–78° (9 mm), containing (glpc, Carbowax 20 M on Chromosorb P) mixtures of cyclohexanone (12.6 min) and the enol carbonate **33** (41.8 min), and 11.3 g (39%) of a fraction, bp 79–81° (9 mm) [lit.[20] bp 108–110° (20 mm)], containing >96% of the enol carbonate **33**: ir (CCl_4) 1760 (enol ester C=O) and 1690 cm^{-1} (enol C=C); nmr (CCl_4) δ 5.3–5.6 (1 H m, vinyl CH), 4.22 (2 H q, J = 7.5 Hz, OCH_2), 1.5–2.5 (8 H m, aliphatic CH), and 1.33 (3 H t, J = 7.5 Hz, ethoxyl CH_3); mass spectrum M^+ at m/e 170 with abundant fragment peaks at m/e 98, 97, 83, 70, 55, and 41.

Registry No.—**6**, 37160-45-5; **9**, 37160-46-6; **10**, 37160-47-7; **12**, 37406-76-1; **13**, 37160-48-8; **15**, 21300-30-1; **17**, 35249-09-3; **19**, 37392-64-6; **21**, 37392-65-7; **22a**, 933-06-2; **23**, 37160-52-4; **25**, 37392-66-8; **27a**, 37413-04-0; **27b**, 37413-05-1; **28**, 37160-53-5; **36a**, 698-87-3; **38**, 37406-77-2.

[18] This experiment was performed in our laboratories by Dr. Jean Jacques Riehl.

[19] H. O. House and V. Kramar, *J. Org. Chem.*, **27**, 4146 (1962).

[20] A. Haller and E. Bauer, *Ann. Chim. (Paris)*, **10**, 294 (1924).

Cycloadditions of Benzyne with Cyclic Olefins. Competition between 2 + 4, Ene, and 2 + 2 Reaction Pathways[1]

PHILLIP CREWS* AND JOHN BEARD

Division of Natural Sciences, University of California at Santa Cruz, Santa Cruz, California 95060

Received August 8, 1972

The course of benzyne reaction with six- to eight-membered ring polyenes is examined and the factors which control the relative partitioning between 2 + 4, 2 + 2, or ene cycloaddition are delineated. The relative amounts of products derived from 2 + 4 or ene reaction were observed to be sensitive to conformational features of the cyclic olefins. This behavior is consistent with the known concerted character of benzyne 2 + 4 cycloadditions. Arguments are advanced supporting concerted character for the ene addition.

As a synthetic reagent *o*-benzyne occupies a position of particular utility.[2] It behaves essentially as a reactive ethylenic chromophore and the observed stereochemistry of reaction products derived from $2_s + 2_s$ or $2_s + 4_s$ cycloadditions are consistent with predictions from orbital symmetry rules.[3] Therefore it is not surprising that approximate molecular orbital calculations predict a symmetric singlet *o*-benzyne ground state.

It should be mentioned that in contrast to most reactive olefins, benzyne participates readily in the ene cycloaddition reaction.[5] The outcome of benzyne cycloadditions can be controlled by a judicious choice of coreactants. A variety of enamines react with *o*-benzyne to give primarily 2 + 2 addition products (eq 1).[6] 2-Methylvinyl acetate or cyclohexene each give only ene reactions (eq 2),[7] and cyclopentadiene reacts entirely *via* 2 + 4 cycloaddition (eq 3).[8] However, there are many examples where products from all three reaction pathways can simultaneously be observed.[2] In view of the fact that much attention has been given to the reaction of benzyne *via* 2 + 2 and 2 + 4 cycloadditions,[3,7a,9] it is surprising to find that there is a paucity of discussion in the literature on the relative partitioning of benzyne between the three primary reaction paths.[10] We have previously noted

---

[1] (a) Support from the Committee on Research at UCSC and the Frederick G. Cottrell Fund of the Research Corp. is gratefully acknowledged. (b) For a preliminary report see ref 11.

[2] (a) R. W. Hoffman, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, Chapters 2 and 3; (b) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes, and Arynes," Appleton Century Crofts, New York, N. Y., 1969, Chapters 8 and 9.

[3] M. Jones, Jr., and R. H. Levin, *J. Amer. Chem. Soc.*, **91**, 6411 (1969).

[4] R. Hoffman, A. Imamura, and W. J. Hehre, *ibid.*, **90**, 1499 (1968); J. F. Olsen, *J. Mol. Struct.*, **8**, 307 (1971); R. W. Atkin and T. A. Claxton, *Trans. Faraday Soc.*, **66**, 257 (1970); D. L. Wilhite and J. L. Whitten, *J. Amer. Chem. Soc.*, **93**, 2858 (1971).

[5] The *ene* reaction has recently been reviewed: (a) H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969); (b) E. C. Keung and H. Alper, *J. Chem. Educ.*, **49**, 97 (1972).

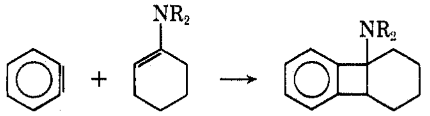
[6] D. J. Keyton, G. W. Griffin, M. E. Kuehne, and C. E. Bayha, *Tetrahedron Lett.*, 4163 (1969); M. E. Kuehne, *J. Amer. Chem. Soc.*, **84**, 837 (1962).

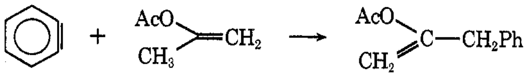
[7] (a) L. Friedman, R. J. Osiewicz, and P. W. Rabideau, *Tetrahedron Lett.*, 5735 (1968); (b) G. Ahlgren and B. Akermark, *ibid.*, 3047 (1970).

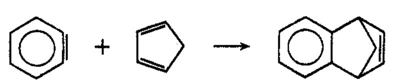
[8] G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

[9] (a) P. G. Gassman, H. P. Benecke, and T. J. Murphy, *Tetrahedron Lett.*, 1649 (1969); (b) P. G. Gassman and H. P. Benecke, *ibid.*, 1089 (1969); (c) H. H. Wasserman, A. J. Solodar, and L. S. Keller, *ibid.*, 5597 (1968).

[10] L. Friedman, J. G. Miller, and R. Osiewicz, Abstracts, 159th National meeting of the American Chemical Society, Houston, Texas, Feb. 22–27, 1970, 104-Petr; ref 2a, pp 197–199.


(1)


(2)


(3)

that the course of benzyne addition to cyclic olefins can be markedly influenced by traces of Ag^+.[11] It seemed to us that, before the mechanism of this effect could be fully understood, it would first be necessary to have a firm grasp upon the features which control the relative rates for the cycloaddition routes. We now report the results of our work on benzyne addition to cyclic olefins in which the factors controlling the relative rates of ene, 2 + 2, and 2 + 4 reactions for benzyne are identified.

Description of Coreactants.—Polyenes ranging in size from six- to eight-membered rings were chosen as coreactants for benzyne. These compounds were completely devoid of polar functionality and have known conformations over the di- or triene chromophore. The major parameters which vary over this compound series are the interplanar angle between the vinyl groups (angle θ, Figure 1) and the angle subtended between the plane of the vinyl, allylic CC–H bond and the plane of the double bond p orbitals (angle ϕ, Figure 1).

The 2 + 2 cycloaddition between benzyne and simple olefins is known to be stepwise.[3,9] It can be presumed that this reaction is initiated by attack of benzyne at the least hindered carbon from the direction of least steric hindrance. The degree of steric bulk changes very little within the set of six- to eight-membered ring olefins considered here. Thus, it seems reasonable to assume that the rate of 2 + 2 addition by benzyne will be approximately constant over the entire range of experiments described below.

The $2_s + 4_s$ cycloaddition between benzyne and 1,3-dienes is known to be concerted.[3] As a first assumption one would expect to find the net reaction for this type of cycloaddition to be sensitive to the extent of overlap in the transition state for the reacting π orbitals. Hence, the rate of 2 + 4 cycloaddition of benzyne to a diene should be chiefly dependent upon the diene interplanar angle (θ).

There does not seem to be agreement concerning the concerted or stepwise nature of the ene reaction. The reaction of an optically active olefin **6** with maleic anhydride has been shown to give optically active ene product **7**;[12] however, it has also been pointed out that it is not clear to what extent chirality is preserved during this reaction (eq 4).[5a] Others[13a] have suggested that the regiospecificity observed in the reactions of substituted olefins with benzyne is explained by a stepwise addition followed by hydrogen migration (eq 5).

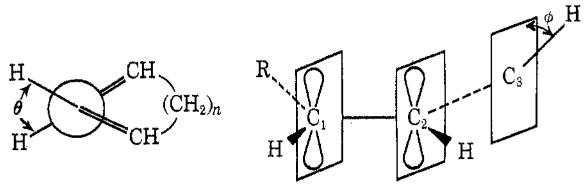
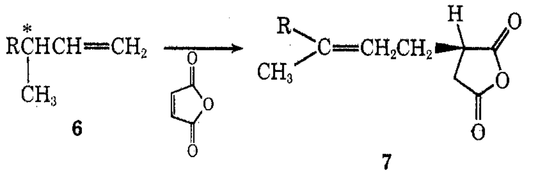
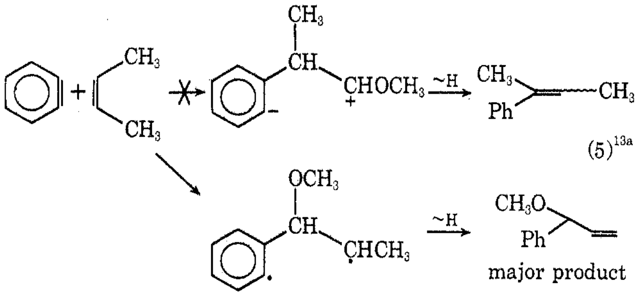


Figure 1.—Interplanar angle (θ) between 1,3 double bonds and angle ϕ between the plane of the C_2 p orbital and the plane containing C_2C_3–H.



(4)[12]

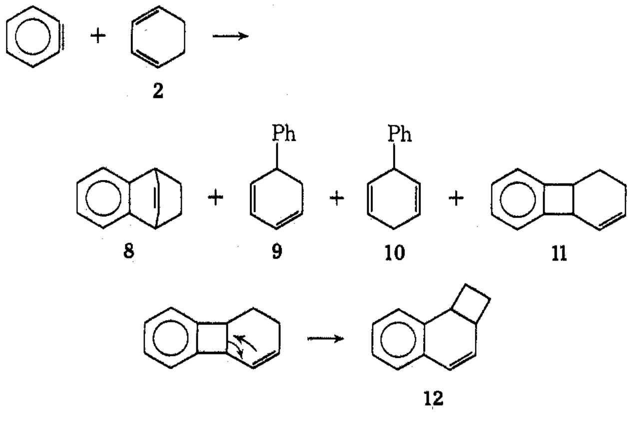


(5)[13a]

Two contrasting situations can then be expected for the ene reaction. A stepwise ene reaction, occurring most probably by an intermediate in common with the 2 + 2 cycloaddition,[13b] should result in a minimal sensitivity of the reaction rate to cyclic olefin type. On the other hand, a concerted ene reaction should have a sizable rate variation with different angles of ϕ shown in Figure 1.

Results

The reaction between benzyne and cyclohexadiene has been reported by several authors.[14-16] Recently Braun reported the characterization of four hydrocarbon products, **8**, **9**, **10**, and **12**.[16] Benzobicyclo[2.2.2]octadiene (**8**) results from 2 + 4 reaction, and the two phenylcyclohexadienes, **9** and **10**, arise from ene reaction. Hydrocarbons **8–10** were reported earlier by Simmons[14] and Huisgen and Knorr,[15] but the unusual hydrocarbon **12** was not reported in these older papers.



---

[11] P. Crews, M. Loffgren, and D. J. Bertelli, *Tetrahedron Lett.*, 4697 (1971); see also ref 17 and 31.

[12] R. K. Hill and M. Rabinovitz, *J. Amer. Chem. Soc.*, **86**, 965 (1964).

[13] (a) I. Tabushi, K. Okazaki, and R. Oda, *Tetrahedron*, **25**, 4401 (1969). (b) See, for example, M. Pomarantz, R. N. Wilke, G. W. Gruber, and U. Roy, *J. Amer. Chem. Soc.*, **94**, 2752 (1972).

[14] H. E. Simmons, *ibid.*, **83**, 1657 (1961).

[15] R. Huisgen and R. Knorr, *Tetrahedron Lett.*, 1017 (1963).

[16] A. M. Braun, *J. Org. Chem.*, **35**, 1208 (1970).

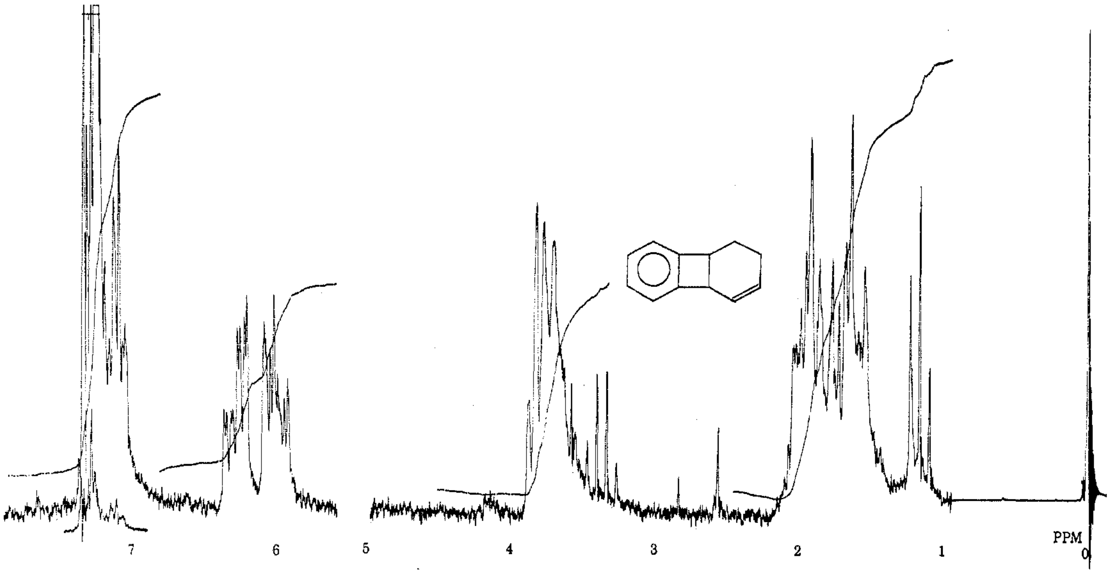
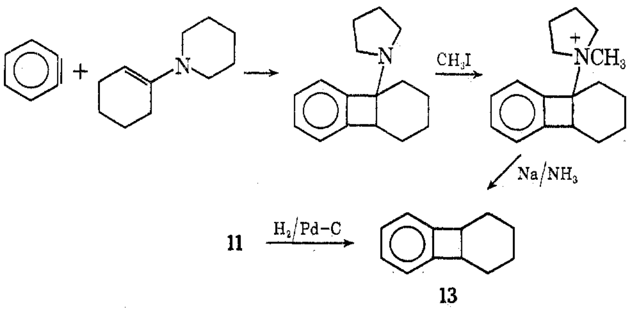


Figure 2.—Pmr spectrum of **11** at 100 MHz in $CDCl_3$ (see text for assignments); diethyl ether impurity.

SCHEME I

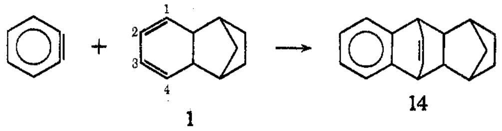


Braun suggested that **12** was formed by rearrangement of **11**, and it was isolated in 3% overall yield.

We repeated this reaction using both *o*-benzendiazonium carboxylate[17] and 1,2,3-benzothiadiazole 1,1-dioxide[18] as benzyne sources, and found by pmr analyses of vpc collected samples the three hydrocarbon products **8–10** in agreement with earlier reports. However, in contrast to Braun's assignment, the fourth hydrocarbon required assignment as **11** (4.4% net yield). The pmr spectrum (Figure 2) displayed an unsymmetrical aromatic region (δ 7.07–7.40, A = 4), a vinyl absorption of two separate multiplets (centered at δ 6.30, A = 1; 6.00, A = 1), the methine H's as two sets of overlapping multiplets (centered at δ 3.97, A = 2), and a fairly complex alaphatic region (δ 1.70–2.40, A = 4). The ir spectrum confirmed the presence of unsaturation as the only functionality. The mass spectrum showed parent ion m/e 156 ($C_{12}H_{12}$) and principal fragments m/e 155, 141, 128, and 115. Our structural assignment of the 2 + 2 product as **11** was confirmed by hydrogenation of this material over Pd/C to yield hydrocarbon **13**. This latter compound was prepared by an alternate route, as outlined in Scheme I.[19]

Tricycloundeca-3,5-diene (**1**) was prepared by a route previously published by Wege and coworkers.[21,22]

Inspection of a Drieding model of this system shows that the bicyclic bridge constrains the diene group into a planar configuration.[23] Only one hydrocarbon product was observed from decomposition of *o*-benzendiazonium carboxylate in a slight excess of **1**. This product was assigned as **14** and was characterized by its



pmr spectra (Figure 3b); the general features of the aromatic, olefinic, and bridgehead regions were closely similar to the spectra obtained from 2 + 4 addition of benzyne to 1,3-cyclohexadiene (Figure 3a). The ir spectrum confirmed that **14** was a hydrocarbon and the mass spectrum gave m/e 222 ($C_{17}H_{18}$) as a parent ion with the following major fragments: m/e 179, 165, 152, 141, and 128.

In a preliminary account of this work we described the results of decomposition of *o*-benzenediazonium carboxylate with 1,3-cycloheptadiene and 1,3,5-cycloheptatriene, respectively.[11] The reaction with cycloheptadiene yielded two major hydrocarbon products, **15** and **16**, arising from 2 + 4 and 2 + 2 addition, along with a minute amount of material presumed to be an ene product on the basis of its relative vpc retention time (eq 6). In contrast, the cycloheptatriene reaction yielded no 2 + 4 product (**17**) but gave almost equivalent amounts of 2 + 2 and ene products **18** and **19** (eq 7).

The remaining cyclic olefin examined in the study was 1,3,5-cyclooctatetriene. This compound differs relative to the other olefins examined in that there is an equilibrium between a monocyclic and a bicyclic form

---

[17] L. Friedman, *J. Amer. Chem. Soc.*, **89**, 3071 (1967).

[18] G. Wittig and R. W. Hoffmann, *Chem. Ber.*, **95**, 2718 (1962).

[19] Apparently Braun's vpc conditions promoted a vinylcyclobutane-like rearrangement of **11** to **12**. Levin has also noted a similar occurrence for 2-vinylbenzocyclobutene derivatives.[20]

[20] R. Levin, Ph.D. Thesis, Princeton University, 1970.

[21] We thank Professor W. G. Dauben for furnishing us with complete experimental details.

[22] R. McCulloch, A. R. Rye, and D. Wege, *Tetrahedron Lett.*, 5231 (1969).

[23] Analysis of the AA'BB' spectrum of the vinyl protons of **1** by computer simulation gave vicinal couplings of J_{12} = 9.69 and J_{23} = 5.47 Hz *vs.* 9.56 and 4.95 Hz computed for 1,3-cyclohexadiene (**2**) at 300 MHz; the increase in J_{23} is consistent with an increase in angle θ (Figure 1) from 0 to 17°. P. Crews, *J. Amer. Chem. Soc.*, in press.

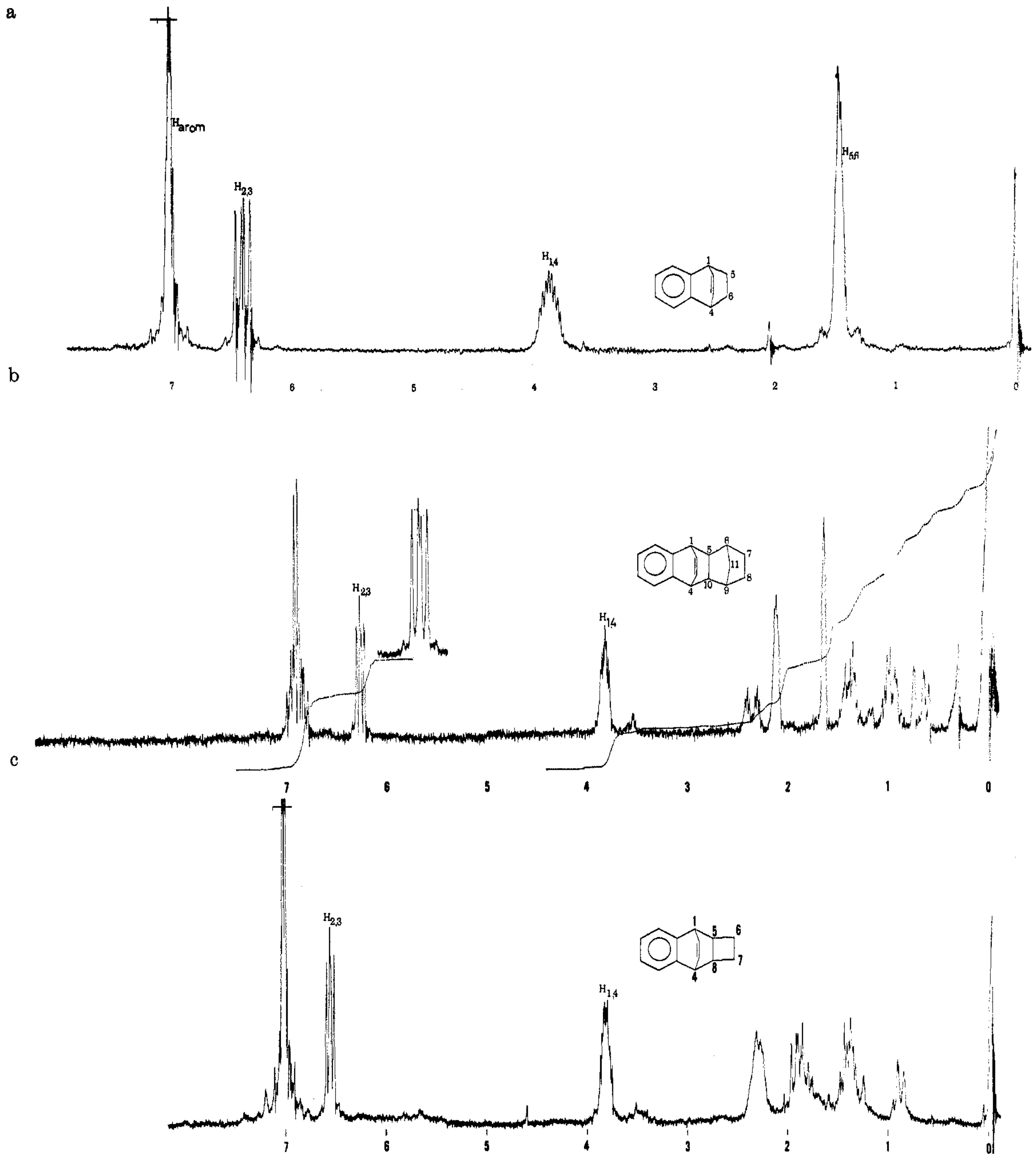


Figure 3.—60-MHz spectrum of **8** in CDCl with multiplet centers: $H_{arom} = \delta\ 7.0$ (A = 4.0); $H_{2,3}$ = 6.4 (apparent J' s = 3.2, 4.2 Hz, A = 2.0); $H_{1,4}$ = 3.86 (A = 2.0); $H_{5,6}$ = 1.47 (A = 4.0). (b) 100-MHz spectrum of **14** in $CDCl_3$ with multiplet centers: $H_{arom} = \delta\ 6.9$; $H_{2,3}$ = 6.25 (apparent J's = 3.2, 4.5 Hz); $H_{1,4}$ = 3.8; H_{11n} = 2.35 ($J_{11n-11x}$ = 10.0 Hz); $H_{6,9}$ = 2.1; $H_{5,10}$ = 1.65 ($W^{1/2}$ = 3 Hz); $H_{7,8}$ = two multiplets 1.4/1.0; H_{11x} 0.7 ($J_{11x-11n}$ = 10.0 Hz). Assignments of H_{11x}, H_{11n}, and $H_{5,10}$ are based upon similar arguments of R. McCulloch, A. R. Rye, and D. Wege [*Tetrahedron Lett.*, 5163 (1969)] and expected bottom-side attack by benzyne on **1** to give endo position for $H_{5,10}$. (c) 100-MHz spectrum of **20** in $CDCl_3$ with multiplet centers: $H_{arom} = \delta\ 7.0$ (A = 4.0); $H_{2,3}$ = 6.55 (apparent J's = 3, 4 Hz, A = 1.9); $H_{1,4}$ = 3.8 (A = 1.9); $H_{5,8}$ = 2.3 (A = 2.1); H_6 and H_7, two multiplets 1.9/1.45 (A = 4.1).

(**5a** ⇌ **5b**) each of which is present in significant amounts.[24] Reaction of this isomeric mixture with benzyne gave only one hydrocarbon product, **20** (eq 8), which results from benzyne addition to **5b**. Structural assignment of this product was made on the basis of the mass spectrum: *m/e* 182 ($C_{14}H_{14}$) the parent ion and other major fragments, 178, 167, 165, 153, 152, 141, and 129. The ir spectrum confirmed the presence of an unsaturated hydrocarbon, and the pmr spectrum (Figure 3c) was very similar to that of analogous hydrocarbon products **8** and **14**.

Discussion

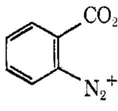
A summary of the relative product distributions obtained from the various benzyne reactions is collected in Table I. Before considering the trends in the product ratios, some discussion of the conformation of the cyclic olefins is needed.

In a previous section we mentioned that tricyclic diene **1** appears to be entirely rigid from Drieding models and can be assumed to have a planar diene chromophore.[23] Electron and X-ray diffraction work

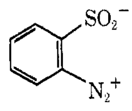
---

[24] R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *Tetrahedron Lett.*, 5215 (1968). Cycloheptatriene does not contain spectroscopically detectable amounts of the norcaradiene valence tautamer: J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3896 (1965), and ref 26.

TABLE I
SUMMARY OF PRODUCT RATIOS FROM BENZYNE ADDITION TO CYCLIC OLEFINS



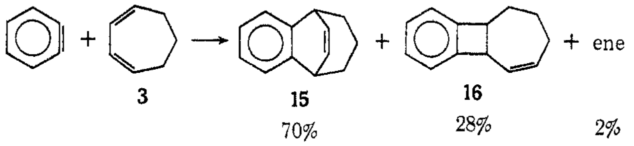
A



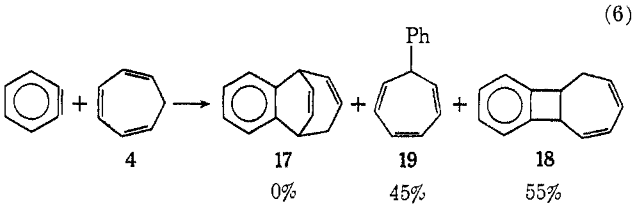
B

Benzyne precursor	Olefin	Net yield, %	% Product ratios			
			8	**9**	**10**	**11**
A[a]	**2**	36	48	18	21	13
B[b]		28	51	22	13	14
					14	
A	**1**				100	
			15		Ene	**16**
A	**3**	25	70		2	28
			17		**19**	**18**
A	**4**	46	0		45	55
					19	
A	**5a** ⇌ **5b** (90%) (10%)	35			100	

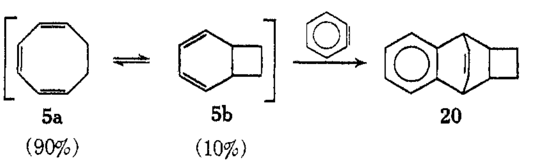
[a] Registry no.: 1608-42-0. [b] Registry no.: 37150-27-9.



(6)

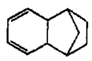
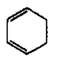
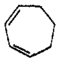
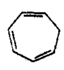
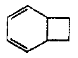


(7)



(8)

TABLE II
CONFORMATIONAL PARAMETERS FOR CYCLIC OLEFINS

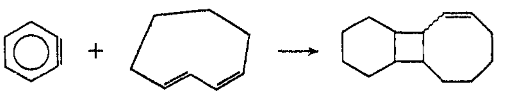
Olefin	Interplanar or dihedral angle, deg	Ref	φ,[a] deg
 **1**	0	*a*, 23	~30
 **2**	17	25	~5
 **3**	20–25	27	~37
 **4**	40	26	~33
 **5a**	~60	*b*	~42
 **5b**	0	*a*	~30

[a] Based upon inspection of Drieding models; see Figure 1 for description. [b] Based upon arguments in the text and ref 28–30.

has shown 1,3-cyclohexadiene[25] and 1,3,5-cycloheptatriene,[26] respectively, to have twist angles of 17 and 40° between the carbon–carbon double bonds. Recent pmr work from our laboratory indicates the corresponding twist angle for 1,3-cycloheptadiene as *ca.* 20–25°.[27] Although no exact structural data is available, cyclooctatriene in its monocyclic tub form (**5a**) can be assumed to have an interplanar angle of approximately 60° by virtue of its expected similarity to *cis,cis*-1,3-cyclooctadiene, which has been suggested to have an interplanar angle of ~60° from its molar Kerr constant[28] and from pmr data;[29] and cyclooctatetraene, which has been estimated[30] to have an angle of ~75° between the planes of the double bonds based upon X-ray data. The other structural parameter which varies with the cyclic olefin type is the angle φ, and this angle was estimated from examination of Drieding models (Table II).

The planar tricycloundeca-2,5-diene (**1**) can be expected to have optimal geometry for 2 + 4 cycloaddition, and it is seen that *only* this type of addition product results with benzyne, and 2 + 2 reaction is entirely excluded. When the diene chromophore is skewed by an intermediate angle, 17 or ~23°, 2 + 4 reaction no longer predominates but is reduced to ~50% of the product mixture for cyclohexadiene (2 + 2 competes to the extent of 13%) and 70% of the product mixture for 1,3-cycloheptadiene (2 + 2 as 28%). When the skew angle is large, ~40° or greater, *no* 2 + 4 products are observable; for cycloheptatriene ~55% of the products arise by way of the 2 + 2 route; and for cyclooctatriene no products are derived from the predominating tub conformer; instead, exclusive 2 + 4 reaction occurs *via* the planar bicyclic form. Assuming that the rate of 2 + 2 reaction is constant (see earlier discussion), a simple change in the diene dehedral angle (d.a.) from 0 to 40° has changed the ratio of 2 + 4/2 + 2 cycloaddition from ∞ (d.a. 0°) to 3.7 and 2.5 (d.a. 17 and ~23°) to finally 0 (d.a. >40°). It is apparent that a qualitative correlation can be drawn between the relative rate of 2 + 4 reaction and the degree of overlap between the diene p orbitals (angle θ).

The above argument can also account for the results of cycloaddition of benzyne to *cis,trans*-1,3-cyclooctadiene studied by Gassmann,[9a] in which only reaction *via* 2 + 2 addition was observed (eq 9). Molecular models show that the cis,trans diene system is badly skewed (d.a. ~60°) with no possibility of alignment in a planar cis conformation.



(9)

---

(25) H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969); S. S. Butcher, *J. Chem. Phys.*, **42**, 1830 (1965).

(26) M. Traetteberg, *J. Amer. Chem. Soc.*, **86**, 4265 (1964).

(27) P. Crews, *Chem. Commun.*, 583 (1971).

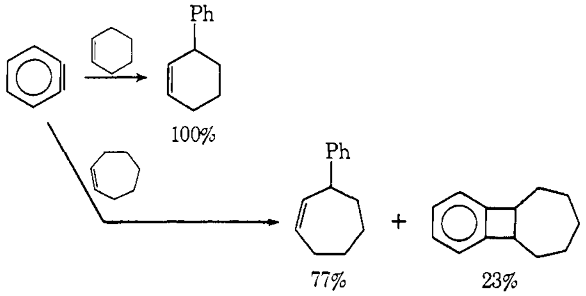
(28) C.-Y. Chen, R. J. W. LeFèvre, and K. M. S. Sundaram, *J. Chem. Soc.*, 553 (1965).

(29) H. Gunther, *Z. Naturforsch. B*, **24**, 680 (1969).

(30) M. A. Cooper, D. D. Elleman, C. D. Pearce, and S. L. Manatt, *J. Chem. Phys.*, **53**, 2343 (1970).

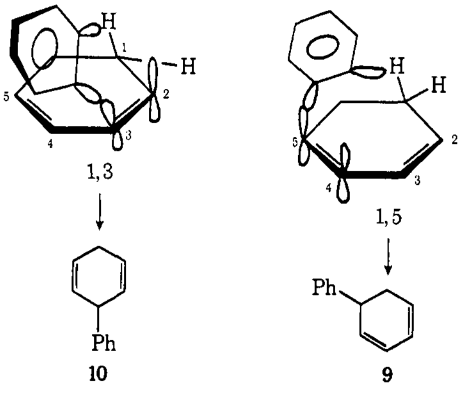
Having verified that the rate of concerted 2 + 4 benzyne reaction is sensitive primarily to the alignment of the reacting π orbitals, our preliminary assumption that a concerted ene reaction should show the same trend would seem to be strengthened. Hence, the relative ratio of ene/2 + 2 products was examined as a function of variations in angle ϕ (Figure 1). In the series cyclohexadiene, cycloheptatriene, cycloheptadiene, angle ϕ can be observed to increase from $\sim$5°, to $\sim$33°, and to $\sim$37°; and the relative ratios of ene/2 + 2 products are, respectively, $\sim$3, 0.8, and 0.07. Indeed it does seem that a simple qualitative correlation exists between ease of ene reaction and angle ϕ.

For simple olefins the same correlation is easily seen. Cyclohexene ($\phi \cong 4°$) is known to give only ene reaction,[6b] while cycloheptene ($\phi \cong 32°$) has been reported to give 77% ene and 23% 2 + 2 products.[31]

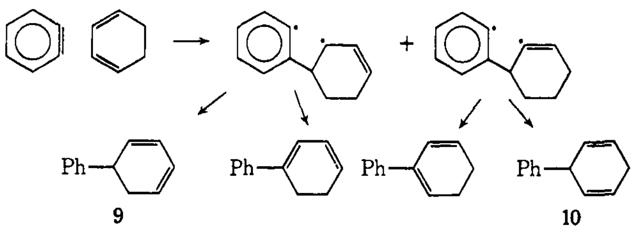


There is other circumstantial evidence in support of a concerted-like ene mechanism. Molecular models indicate that there are two approximately isoenergetic transition states leading to a concerted formation of ene products **9** and **10** from reaction of 1,3-cyclohexadiene with benzyne (in Scheme II transition states 1,3 and 1,5 are shown, and they appear to have approximately the same geometry). If a diradical mechanism, similar to that proposed by Tabushi,[13] were operating, one would expect at least *four* ene products from reaction of benzyne with cyclohexadiene. The fact that only two ene products are isolated would appear to be inconsistent with stepwise formation of intermediates, either radical or ionic (Scheme III).

SCHEME II



SCHEME III



Previous work has shown that extensive ene reaction occurs between benzyne and *trans*-1-alkoxypropene, and very little occurs with *cis*-1-alkoxypropene, while 2-alkoxypropenes give 100% ene reaction.[7a,9c] These data are consistent with a concerted ene mechanism in which there is a large steric inhibition to the requisite transition state when the alkoxy and allylic CH are cis, but none when the relative orientation is trans or geminal.

In summary,[32] the conformation of the olefin or polyolefin coreactant is of primary importance in influencing the facility of benzyne to undergo 2 + 4 or ene cycloadditions. Thus, benzyne will react with a planar 1,3-diene such as **1** principally by the 2 + 4 route, while ene reaction may predominate with substrates in which the olefinic p-π orbitals are nearly parallel to the allylic C-H bond, such as in cyclohexene. If, on the other hand, both of these conformational requirements are grossly violated, 2 + 2 cycloaddition is likely to predominate. An example of this latter situation can be seen in the exclusive formation of 2 + 2 products from the reaction of benzyne with *cis,trans*-1,3-cyclooctadiene.

Experimental Section

General.—The anthranilic acid was purified by recrystallization from water and allowed to dry before use. The *o*-aminobenzenesulfonic acid was used as received from Aldrich Chemical Co.

Pmr spectra were determined at 100 MHz on a Jeol JNM-PS-100 spectrometer, or at 60 MHz on a Varian 56/60 or a Jeol MH-60 spectrometer. Mass spectral measurements were run on a single-focusing Hatachi Perkin-Elmer RMU-6E instrument, and ir spectra were determined on a Perkin-Elmer 337 instrument.

Gas chromatographic conditions follow: A, 8 ft Carbowax (20%), 150°, 35 psi; B, 20 ft DEGS (30%), 140°, 35 psi; C, 8 ft Carbowax (20%), 126°, 50 psi. The quantitative yield determinations were obtained by vpc using 3-phenylcyclohexene as an internal standard. It was assumed that relative detector sensitivities were equivalent between the standard and hydrocarbon products.

Benzenediazonium 2-Carboxylate (BDC).—Owing to the explosive nature of this material, preparation and reaction were conducted in a special piece of glassware fashioned from a two-neck round-bottom flask to which was attached, at the opposite end, a fritted-disk Buchner funnel with a stopcock. A typical experiment involves generation of the benzenediazonium 2-carboxylate[34] with the flask tipped on its side; filtration of solvent washings was accomplished with the flask in an upright position; and the cycloaddition was conducted with the flask again tipped on its side.

BDC and Tricycloundeca-3,5-diene (1).—Benzenediazonium 2-carboxylate from anthranilic acid (2.2 g, 18.8 mmol) was decomposed with **1** (5.4 g, 36.7 mmol) in CH_2Cl_2 (100 ml) by heating in a bath at 50° for 4 hr. The dark, homogeneous solution was washed with water (2 × 100 ml) and saturated bicarbonate solution (2 × 100 ml). The organic material was dried over $MgSO_4$ and the solvent was evaporated. Pentane was added to the dark residue and the reddish solution was filtered

---

[31] L. Lombardo and D. Wege, *Tetrahedron Lett.*, 3981 (1971).

[32] Differences, which may be observed in reactions of the olefins studied here, between benzyne and other less reactive dienophiles could be principally a result of the fact that benzyne is a "hot" electrophilic species and the transition state occurs very early along the reaction coordinate. In addition, the orbital interactions of a diene with benzyne *vs.* ethylenic dienophiles are probably different, since approach of benzyne to the diene plane should be from a perpendicular direction as opposed to a parallel approach expected for ethylenic dienophiles.[33]

[33] For discussion of this latter point, see B. H. Klanderman and T. H. Criswell, *J. Org. Chem.*, **34**, 3426 (1969).

[34] L. Friedman and F. M. Logullo, *Org. Syn.*, **48**, 12 (1969).

to separate the insoluble material. The pentane was evaporated, leaving a red viscous oil. Vpc analysis, condition A, indicated only one product. Further purification by vacuum distillation gave recovered starting material, bp 33–38° (0.2 mm), and product, bp 85–95° (0.2 mm). This material was identified as **14** on the basis of spectral data (see text). The ir spectrum (in CCl_4) showed peaks at 3040 (m), 2950 (m), 2860 (m), and 1550 cm^{-1} (w).

BDC and 1,3-Cyclohexadiene.—The reaction and work-up of the reaction of benzyne derived from anthranilic acid (9.0 g, 65 mmol) with 1,3-cyclohexadiene (12.0 g, 150 mmol) was carried out by the above procedure. Chromatography of the residual oil, after pentane treatment, over neutral alumina (40 g) with hexane as eluent gave 3.7 g (36%) of hydrocarbon products. Vpc analysis, condition B, showed four products: **11** (36 min), **8** (42 min), **9** (46.5 min), **10** (51 min), in the relative amounts shown in Table I. The ir spectrum of **11** (in CCl_4) showed peaks at 2975 (m), 2925 (m), 2900 (m), 2860 (m), 1450 (w), and 1250 cm^{-1} (m).

BDC and 1,3-Cycloheptadiene.—The reaction and work-up of the reaction of benzyne derived from anthranilic acid (3.0 g, 22 mmol) with 1,3-cycloheptadiene (6.2 g, 66 mmol) was carried out by the above procedure. Vacuum distillation of the dark red oil which remained after pentane extraction gave 0.94 g (25%) of hydrocarbon products. Vpc analysis, condition C, showed three products: **15** (12.5 min), **16** (15.5 min), and an ene product (18 min) in the relative amounts shown in Table I. The products were separated by vpc collection and characterized from the data given in ref 11.

BDC and 1,3,5-Cycloheptatriene.—The reaction and work-up of the reaction of benzyne derived from anthranilic acid (3.0 g, 22 mmol) with 1,3,5-cycloheptatriene (6.0 g, 66 mmol) was carried out by the above procedure. After pentane treatment and chromatography on alumina (10 g) with hexane followed by dioxane–hexane (1:1) as eluent, vpc analysis showed two hydrocarbon products, **18** and **19** (relative yields in Table I), which were isolated by vpc collection and characterized by spectral data reported in ref 11.

BDC and 1,3,5-Cyclooctatriene.—The reaction and work-up of the reaction of benzyne derived from anthranilic acid (3.0 g, 22 mmol) with 1,3,5-cyclooctatriene (12.0 g, 66 mmol) was carried out by the above procedure. After pentane treatment, the residual oil was vacuum distilled to give two fractions: a low-boiling fraction, bp 24–30° (0.5 mm), identified as recovered cyclooctatriene (4.5 g), and a high-boiling fraction, 1.4 g, bp 80–90° (0.5 mm), shown by pmr analysis to be only one product, **20**. The product became crystalline at room temperature and was recrystallized from hexane, mp 69–70°. The ir spectrum in CCl_4 showed absorptions at 3050 (w), 2950 (m), 2875 (m), 1680 (m), 1600 (m), and 1500 cm^{-1} (m).

Benzothiadiazole and 1,3-Cyclohexadiene.—The procedure of Wittig and Hoffmann[18] for generating 1,2,3-benzothiadiazole 1,1-dioxide from *o*-aminobenzenesulfonic acid (1.44 g, 8 mmol) was followed. The benzothiadiazole was decomposed without purification with cyclohexadiene (1.9 g, 24 mmol) in CH_2Cl_2 (100 ml) at 55° for 4 hr. The work-up described above yielded 0.56 g of a yellow liquid, which was vpc-analyzed, condition B, without further purification. The net and relative hydrocarbon yields are given in Table I.

7,8-Benzobicyclo[4.2.0]octene (13). ***N*-Methylpyrrolidinium-7,8-benzobicyclo[4.2.0]octene Iodide.**—Methyl iodide (1.55 g, 10.9 mmol) was added to 1-pyrrolidino-7,8-benzobicyclo[4.2.0]-octene[6b] (1.82 g, 8.0 mmol) dissolved in absolute ethanol (25 ml), and the mixture was refluxed for 1.5 hr. At the end of this period the ethanol solution was cooled in an ice bath, but the solution remained completely homogeneous. Addition of ether (60 ml) to the cold solution resulted in the formation of an oil. The solvent was decanted, and the oil was washed with ether (2 × 50 ml). The residual solvent was evaporated to give a viscous oil (2.05 g) which was assumed to be the expected methyl iodide salt [pmr ($CDCl_3$) δ 1.0–4.2 (complicated series of multiplets), 7.1–7.9 (multiplet), and 8.1–8.4 (multiplet)].

7,8-Benzobicyclo[4.2.0]octene from Birch Reduction.—The ammonium salt obtained above (2.05 g, 5.75 mmol) along with absolute ethanol (0.26 g, 5.75 mmol) was dissolved in liquid ammonia (~50 ml). Sodium metal (0.26 g, 0.0115 g-atom) was added over a 5-min period with stirring. A blue color was formed, but it had entirely disappeared at the end of 0.5 hr and the stirring was discontinued. The ammonia was allowed to evaporate slowly. A 10% HCl solution was added to the residue and this mixture was extracted with ether. Evaporation of the ether yielded 0.37 g of a yellow-red oil; vpc analysis showed only a single peak. A pure sample was obtained by preparative vpc collection, and a pmr spectrum at 100 MHz of this material was in accord with structure **13** [δ 1.42–1.84 (multiplet), 3.49 (multiplet), 6.94–7.18 (symmetrical AA'BB' multiplet of 13 peaks), relative intensities 8:2:4].

Registry No.—**1**, 33482-87-0; **2**, 592-57-4; **3**, 4054-38-0; **4**, 544-25-2; **5a**, 1871-52-9; **5b**, 3725-28-8; **8**, 7322-46-5; **11**, 37150-32-6; **13**, 37150-33-7; **14**, 37150-34-8; **20**, 37150-35-9; benzyne, 462-80-6; *N*-methylpyrrolidinium-7,8-benzobicyclo[4.2.0]octene iodide, 37406-70-5.