may be strongly catalyzed by sodium hydroxide, and we are exploring this possibility.

(6) National Science Foundation Postdoctorate Fellow at Purdue University, 1967–1968.

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The Electronic Structure and Reactivity of Small-Ring Compounds. III. Mechanistic Studies of the Bicyclobutane–Benzyne Reaction[1]

Sir:

We recently reported that the reaction of bicyclobutane with benzyne[1] gives 3-phenylcyclobutene and benzobicyclo[2.1.1]hex-2-ene. We wish now to report some studies on the mechanism of these reactions.

2-Deuteriobicyclobutane (I) was prepared by the method of Friedman and Wiberg[2] by the thermal decomposition of cyclopropanecarboxaldehyde *p*-tosylhydrazone in ethylene glycol-O,O-d_2 containing 0.9 equiv of the conjugate base of the solvent. The bicyclobutane I was shown by nmr spectroscopy to contain 0.83 deuterium per molecule, with 81% *endo* and 19% *exo*. That is, I had 0.67 deuterium *endo* and 0.16 deuterium *exo* at the 2 position.[3]

When I was allowed to react with benzyne, from the thermal (45°) decomposition of *o*-benzenediazoniumcarboxylate in ethylene dichloride, and the products were separated by vlpc,[4] it was determined by nmr analysis that the cycloadduct II had all of the deuterium in the *endo* position.[6,7] In addition, the "ene" synthesis product, deuterated 3-phenylcyclobutene (III), had half of the original deuterium at the 4 position *cis* to the phenyl ring.[6] The other half of the deuterium was attached to the phenyl ring, as a result of "ene" synthesis with abstraction of the deuteron. Thus, if there is an isotope effect in this reaction it must be very small (see Table I for a summary of the data).

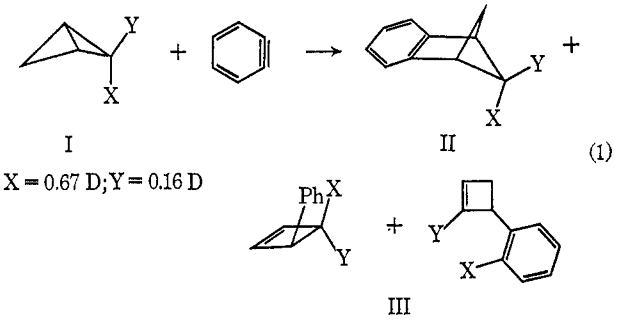
The conclusion, therefore, is that both the "ene" synthesis and cycloaddition reaction occur by bottomside attack of benzyne on bicyclobutane (eq 1). We use the term bottomside to refer to the *endo* direction. The cycloaddition reaction thus results in double inversion at the bridgeheads, whereas the "ene" synthesis gives a single inversion.

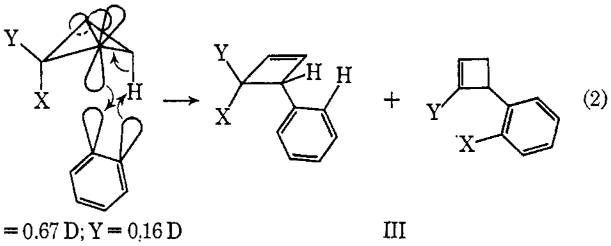
Table I

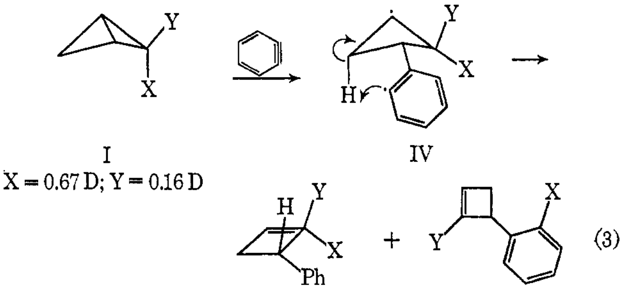
Compound	Hydrogen	Obsd nmr hydrogen ratio	Calcd ratio for bottom-side attack
Bicyclobutane (I)	Bridgehead	2.00	
	exo-2	1.84	
	endo-2	1.33	
Benzobicyclo-[2.1.1]hex-2-ene (II)	Aromatic	[a]	4.00
	Bridgehead	2.00	2.00
	exo-5	1.84	1.84
	endo-5	1.34	1.33
3-Phenylcyclo-butene (III)	Aromatic	4.66	4.66[b]
	Vinyl	1.90	1.92[b]
	Benzylic-3	1.00	1.00[b]
	trans-4	0.94	0.92[b]
	cis-4	0.67	0.66[b]

[a] Not obtained. [b] Calculated assuming no isotope effect.

One mechanistic possibility for the formation of III is a concerted reaction as indicated in eq 2. The p orbitals which are utilized[8] are in the proper orientation for such a reaction. The "ene" synthesis employing olefins has usually been assumed to be concerted,[9] but has recently, in the case of bicyclo[2.1.0]pentane, been questioned.[10] The alternative possibility in the present case would involve a diradical (IV) as pictured in eq 3.







Since the reaction of benzyne with bicyclobutane to give III involves the release of a considerable amount of strain, the reaction must be exothermic and, therefore, according to Hammond's postulate, the transition state occurs early along the reaction coordinate. A small

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(1) Part II: M. Pomerantz, *J. Am. Chem. Soc.*, **88**, 5349 (1966).

(2) F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966); J. H. Bayless, Jr., Ph.D. Thesis, Case Institute of Technology, Cleveland, Ohio, 1967; K. B. Wiberg and J. M. Lavanish, *J. Am. Chem. Soc.*, **88**, 365, 5272 (1966).

(3) To simplify the discussion this bicyclobutane will be referred to as *endo*-2-deuteriobicyclobutane.

(4) Pure II was obtained directly by vlpc; III, however, was collected with a small amount of II as contaminant. The nmr spectrum of III was obtained with an internal standard present; the solution was then heated in order to remove III by rearrangement to 1-phenyl-1,3-butadiene,[5] and finally another nmr spectrum was obtained. In this way the integrated spectrum of III was analyzed by difference.

(5) M. Pomerantz and P. M. Hartman, *Tetrahedron Letters*, 991 (1968).

(6) By "all of the deuterium" we mean all that was originally present in the *endo* position in the bicyclobutane. (The small amount of deuterium in the *exo* position was, therefore, found in the *exo* position of II and distributed between the vinyl positions and the 4 position *trans* to the phenyl group in III.)

(7) See ref 1 for nmr peak assignments.

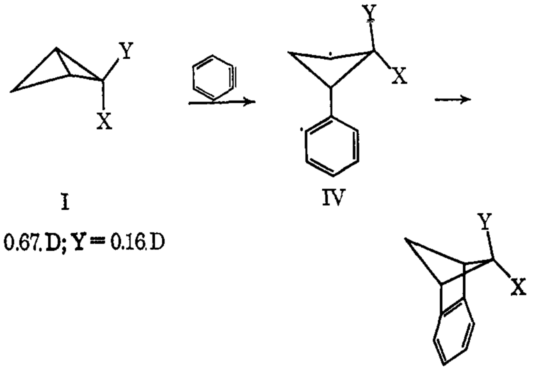
(8) M. Pomerantz and E. W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3970 (1966).

(9) J. A. Berson, R. G. Wall, and H. D. Perlmutter, *ibid.*, **88**, 187 (1966).

(10) P. G. Gassman and K. T. Mansfield, *ibid.*, **90**, 1524 (1968).

isotope effect is thus expected for the concerted reaction. Alternatively, if attack by benzyne on bicyclobutane is slow and produces diradical IV which, in turn, in a fast step, gives III, no isotope effect (or at most a small one) should be evident. Therefore, the observation of no isotope effect is consistent with both mechanisms.

The formation, by bottomside attack, of benzobicyclo[2.1.1]hex-2-ene (II) is probably best rationalized as a diradical reaction with IV again being the intermediate (eq 4). A concerted cycloaddition would be ruled out on steric grounds since the bottomside of the bicyclobutane ring is quite hindered and certainly much more hindered than the topside.[11]



I

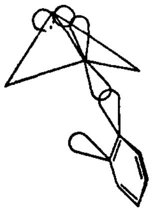
X = 0.67 D; Y = 0.16 D

IV

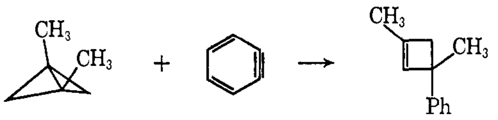
(4)

II

Thus the benzyne can come in along the axis of the p orbital of C_1 (which is bonding to C_3) and in the plane of the 1,3 bond which bisects the C_2–C_1–C_4 and C_2–C_3–C_4 angles. This would allow for a minimum of steric interactions and would produce the diradical IV. Any significant twisting of the benzyne out of the plane would mean that the free orbital of the benzyne would be closer to an *endo* hydrogen, and the "ene" synthesis should then result. The same type of diradical intermediate has recently been proposed in the bicyclopentane series.[10,12]



If the cycloadduct is indeed coming about by the mechanism indicated, the substitution of methyl groups for hydrogens on carbons 1 and 3 should produce less cycloadduct as a result of some steric compression between the 3 hydrogen on benzyne and the methyl group. Twisting of the benzyne to alleviate this strain would result in an increased amount of "ene" synthesis product. This prediction has been verified by the observation that, within the limits of nmr analysis, there is no cycloadduct produced by the reaction of 1,3-dimethylbicyclobutane with benzyne.[13] The sole product has been shown to be 1,3-dimethyl-3-phenylcyclobutene (V).

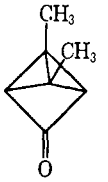


V

Structure proof for V consists of its nmr spectrum which shows five aromatic hydrogens at τ 2.81 ppm, one vinyl hydrogen as a doublet ($J = 1$ Hz) at τ 3.89 ppm, two allylic hydrogens at τ 7.49 ppm, one allylic methyl group as a doublet ($J = 1$ Hz) at τ 8.26 ppm, and the second methyl group as a singlet at τ 8.53 ppm. The infrared spectrum of V showed the double-bond stretch at 1640 cm^{-1} as compared to 1641 cm^{-1} for 1-methylcyclobutene.[14] The mass spectrum of V exhibited the parent peak (both high and low ionization potentials) at *m/e* 158, confirming the $C_{12}H_{14}$ formula.

Thermal rearrangement (160°) of 1,3-dimethyl-3-phenylcyclobutene (V) afforded three products, in the ratio 2:1:8. The major product was identified as 2-methyl-4-phenyl-1,3-pentadiene by the identity of its nmr spectrum with that reported for this compound, of unknown stereochemistry.[15] From mechanistic considerations it seems most likely that this compound is *cis*-2-methyl-4-phenyl-1,3-pentadiene since conrotatory ring opening of the cyclobutene (V) would involve less steric strain in the transition state if the methyl rather than the larger phenyl group rotated inward.

Because reaction of benzyne with bicyclobutane occurs from the bottomside, it is not surprising that attempted reaction of 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one (VI)[16] with benzyne (ethylene dichloride solvent, 84°) apparently resulted in no detectable amount of products.[17]



VI

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[11] I. Haller and R. Srinivasan, *J. Chem. Phys.*, **41**, 2745 (1964); M. D. Harmony and K. Cox, *J. Am. Chem. Soc.*, **88**, 5049 (1966).

[12] W. R. Roth and M. Martin, *Tetrahedron Letters*, 4695 (1967).

[13] If it is assumed that the cycloadduct can be separated from the "ene" synthesis product by vlpc (7 ft × 0.25 in. 20% DC 710 silicone oil on 60–80 mesh Chromosorb P column) then there is no (<1%) cycloadduct present.

[14] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1967, p 81.

[15] T. L. Jacobs and R. A. Meyers, *J. Am. Chem. Soc.*, **86**, 5244 (1964).

[16] W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, 961 (1964).

[17] Examination of the residual ketone (VI) by vlpc using an internal standard indicated only about 85% recovery. A blank reaction (same conditions as the benzyne reaction but lacking *o*-benzenediazoniumcarboxylate) showed that approximately the same amount of ketone could be recovered, the loss being due either to evaporation or to decomposition of VI.

Photolysis and Photoisomerization of Cyclooctatetraene Oxide

Sir:

Cyclooctatetraene oxide (Ib) is an interesting member of the bicyclo[6.1.0]nona-2,4,6-triene family (I) as it is