Table III. Chemical Shift and Coupling Constant Data for 2-Alkyl-5-*t*-butyl-1,3-dioxanes[a] (Figure 1)

R	$J_{H_5H_4}$ 4-e	$J_{H_5H_4}$ 4-a	$-\nu_{H_2}$	$-\nu_{t\text{-Bu}}$
		trans Isomers		
CH_3	5.6	10.6	264.6	52.6
C_2H_5	4.4	11.2	252.1	52.5
$(CH_3)_2CH$	4.5	11.3	242.1	52.6
$(CH_3)_3C$	4.7	12.1	231.5	53.0
		cis Isomers		
CH_3	1.3	4.0	273.5	62.3
C_2H_5	1.1	3.9	261.9	63.1
$(CH_3)_2CH$	1.1	4.0	248.5	63.0
$(CH_3)_3C$	1.1	3.9	239.7	62.7

[a] All values in cycles per second; chemical shifts are recorded at 60 Mcps with tetramethylsilane standard in carbon tetrachloride.

the 1,3-dioxane as compared with a much larger space requirement of the axial hydrogens in cyclohexane. The small conformational energies of other 5-alkyl groups (Figure 3 and Table II, entries 5–7) are in agreement with this assumption.

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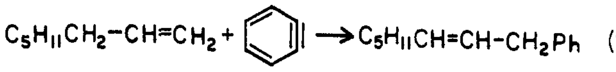
The Electronic Structure and Reactivity of Small-Ring Compounds. II. The Reaction of Bicyclobutane with Benzyne[1]

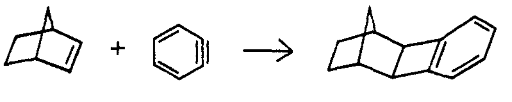
Sir:

It has been demonstrated recently that the known chemical and physical properties of bicyclobutane can be correlated with two models for the electronic structure of this molecule.[1] Although all the carbon–carbon bonds contain π character, the 1,3 bond exhibits the greatest degree of unsaturation. To demonstrate the olefinic nature of this bond further, we have investigated the course of the reaction of benzyne with bicyclobutane.

Benzyne is known to react with simple olefins, containing readily accessible allylic hydrogens, by the Alder "ene" synthesis (substitutive addition)[2-4] or, in the absence of such hydrogens, by cycloaddition (eq 1 and 2).[3,4]



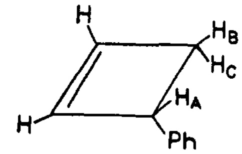
(1)



(2)

When bicyclobutane[5] is allowed to react with an equimolar amount of *o*-benzenediazoniumcarboxylate in ethylene chloride at 40–45°, a 40–60% yield of two products, in the ratio of 6–7 : 1, is obtained.

The major product was identified as 3-phenylcyclobutene (I) in the following way. Its nmr spectrum (τ values) shows five aromatic hydrogens at 2.5 ppm, two vinyl hydrogens as a singlet at 3.5 ppm, and hydrogens A, B, and C each as a double doublet at 5.8, 6.85, and 7.55 ppm, respectively, $J_{AB} = 5.0$ cps, $J_{AC} = 2.2$ cps, and $J_{BC} = 15.3$ cps.[6]



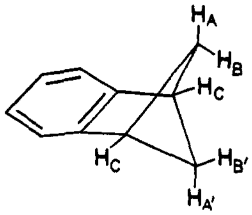
I

Catalytic hydrogenation results in the uptake of 1 equiv of hydrogen and gives a product whose nmr spectrum is consistent with the phenylcyclobutane structure, five aromatic hydrogens at 2.4 ppm, one benzylic hydrogen centered at 6.2 ppm, and six aliphatic hydrogens as a broad multiplet between 7.3 and 8.3 ppm. The infrared spectrum, which is extremely similar to that reported for this compound,[8] also supports this assignment.

Thermal rearrangement of 3-phenylcyclobutene[9] affords *trans*-1-phenyl-1,3-butadiene, whose infrared and nmr spectra are identical with those of authentic material prepared by the method of Grummitt[10] and which upon hydrogenation gives *n*-butylbenzene.

3-Phenylcyclobutene was also prepared by an independent route. Photolysis (100-w G.E. mercury lamp H100-A4/T; Pyrex filter) of *trans*-1-phenyl-1,3-butadiene initially gives a mixture of *cis*- and *trans*-phenylbutadiene, rich in the *cis* isomer, but on prolonged irradiation 3-phenylcyclobutene is formed.

The minor product from the reaction of benzyne with bicyclobutane was shown to be benzobicyclo[2.1.1]hexene (II). The mass spectrum shows the parent peak at *m/e* 130, indicating a molecular formula of $C_{10}H_{10}$.[11] The nmr spectrum shows a symmetrical four-proton A_2B_2 aromatic multiplet centered at 3.0 ppm. In addition, the bridgehead protons (H_C) appear as a triplet at 6.86 ppm, the *exo*-hydrogens (H_B) as a complex multiplet at 7.25 ppm, and the *endo*-hydrogens (H_A) as a double doublet at 7.66 ppm (Figure 1; the peaks between 7.4 and 7.5 ppm are due to an impurity).



II

The spectrum, as can be seen from Figure 1, could be reproduced rather well with the aid of a computer program using the following coupling constants:

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[1] Part I: M. Pomerantz and E. W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3070 (1966).

[2] E. M. Arnett, *J. Org. Chem.*, **25**, 324 (1960).

[3] H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

[4] J. A. Berson and M. Pomerantz, *ibid.*, **86**, 3896 (1964).

[5] We wish to thank Professor L. Friedman and Mr. J. Bayless for details of the preparation of bicyclobutane.

[6] The assignment follows that for 1,3-diphenylcyclobutene made by Masamune.[7]

[7] S. Masamune, *Tetrahedron Letters*, 945 (1965).

[8] N. A. Donskaya, V. K. Potapov, Yu. S. Shabarov, and R. Ya. Levina, *J. Org. Chem. USSR*, **1**, 1835 (1965).

[9] The thermal rearrangement was effected in a gas chromatograph with the injector temperature at 230° and the column temperature at 160°.

[10] O. Grummitt and E. I. Becker, *Org. Syn.*, **30**, 75 (1950); O. Grummitt and F. J. Christoph, *J. Am. Chem. Soc.*, **73**, 3479 (1951).

[11] We wish to thank Mr. J. Bayless for obtaining the mass spectrum.

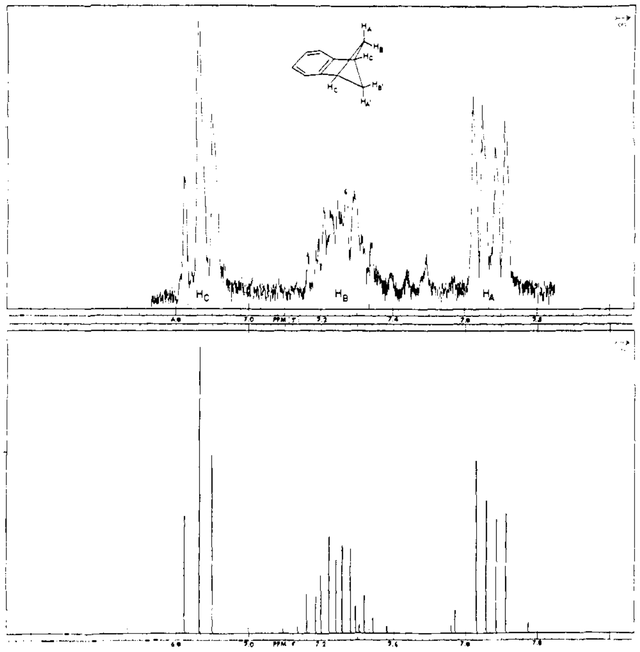
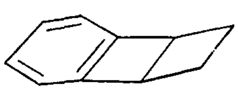


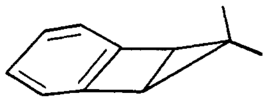
Figure 1. Observed and calculated nmr spectra of benzobicyclo-[2.1.1]hexene.

J_{BC} = 2.4 cps, J_{AB} = 4.9 cps, $J_{AA'}$ = 5.4 cps, and J_{AC} = $J_{BB'}$ = $J_{AB'}$ = 0 cps. The B hydrogens were assumed to be 25.6 cps and the C hydrogens 48.4 cps downfield from the A hydrogens. This spectrum is consistent, therefore, with the spectra of other bicyclo-[2.1.1]hexane derivatives reported by Wiberg.[12] He found that for bicyclo[2.1.1]hexane J_{AB} = 5.4 cps and $J_{AA'}$ = 6.7 cps, and for other derivatives, where nmr analysis was possible, J_{BC} varied, in most cases, between 2.6 and 3.0 cps. All other coupling constants (involving hydrogens of the A, B, and C type) were found to be zero.[13,13a]

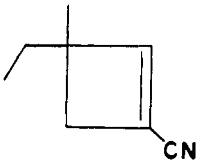
The nmr spectrum is, therefore, unique and inconsistent with all other possible structures for the adduct. The observation that this adduct (II) is stable at 100° for 6 hr also rules out structure III since compound IV, a molecule with strain comparable to that of III, apparently rearranges rapidly below 55° to the corresponding isoindene.[4]



III



IV



V

The reaction of benzyne with bicyclobutane is thus quite analagous to its reaction with olefins, consistent with the proposed electronic formulation.[1]

We cannot, at this time, speculate about the mechanism of formation of the cycloadduct, benzobicyclo-[2.1.1]hexene. It should be pointed out, however, that 1-methyl-3-cyanobicyclobutane reacts with various olefins to give cycloadducts, apparently through an intermediate diradical.[14]

The major product, 3-phenylcyclobutene, arises from a reaction that is most simply rationalized as analagous to an Alder "ene" synthesis. Reaction of 1-methyl-3-cyanobicyclobutane with ethylene has been shown to give V, the "ene" synthesis product; however, a diradical mechanism was postulated for its formation.[15] We feel that, because of the electronic resemblance of the 1,3 bond in bicyclobutane and an olefinic π bond, the mechanism for the formation of I, and probably V, is most likely similar to that for the normal "ene" synthesis. It is generally thought that the "ene" synthesis is concerted although this has not been rigorously proven.[17]

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also wish to thank Professor Donald Whitman for very helpful discussions concerning the nmr spectrum of compound II and for the use of his computer program for calculating nmr spectra.

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(12) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, 84, 1594 (1962).

(13) Since Wiberg's compounds[12] and our compound all have a plane of symmetry the spectra are independent of J_{CC} and therefore a value for this coupling constant could not be determined.

(13a) NOTE ADDED IN PROOF. The nmr spectrum of methyl benzobicyclo[2.1.1]hexene-*endo*-5-carboxylate recently reported [H. Tanida and Y. Hata, *J. Am. Chem. Soc.*, 88, 4289 (1966)] agrees extremely well with that of II.

(14) A. Cairncross and E. P. Blanchard, Jr., *J. Am. Chem. Soc.*, 88, 496 (1966).

(15) The reaction of 1-methyl-3-cyanobicyclobutane with hexafluoroacetone and bis(trifluoromethyl)dicyanoethylene gives, formally, "ene" synthesis products.[16] The highly polar nature of the reactants makes a concerted "ene" synthesis mechanism less attractive.

(16) E. P. Blanchard, Jr., and A. Cairncross, *J. Am. Chem. Soc.*, 88, 487 (1966).

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

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Received August 15, 1966

Acetolysis of the 3-Phenyl-2-norbornyl Tosylates[1]

Sir:

A priori we expected that if the intimate environment of a 2-*endo*-tosyl group in the bicyclo[2.2.1]heptane system were unchanged by substitution, then its solvolysis rate should also be unchanged relative to the parent compound. Winstein and co-workers[2] have found that the solvolysis rates of *endo*-brosylates unsubstituted at the 3 position differ from one another by a factor of less than two. However, 3,3-dimethyl substitution in *endo*-camphenyl and α-fenchyl brosylates causes rate retardations of 0.12 and 0.15, respectively. Schleyer and co-workers[3] have recently shown that 6,6-dimethyl substitution also markedly retards the acetolysis rate of a 2-norbornyl tosylate. Herein we

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(1) This research was supported in part by a grant from the National Science Foundation.

(2) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, 87, 378 (1965).

(3) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, 87, 375 (1965).