# Electronic Structure and Reactivity of Small Ring Compounds. V. The Reaction of Some Bicyclobutanes with Various Dienophiles[1,2]

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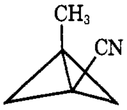
**Abstract:** The reaction of benzyne with bicyclobutane (**1**) has been shown to produce 3-phenylcyclobutene (**4**) and benzobicyclo[2.1.1]hex-2-ene (**5**) in the ratio 6:1. Both reactions occurred by attack on the bicyclobutane from the underside (endo) as shown by employing bicyclobutane-2-*endo*-$d_1$ (**9**). The cycloaddition is discussed in terms of a two-step process whereas the ene synthesis can be explained by either a two-step or a concerted reaction. Benzyne was allowed to react with 1,3-dimethylbicyclobutane (**3**) to produce only the ene synthesis product, 1,3-dimethyl-3-phenylcyclobutene (**19**). Dimethyl acetylenedicarboxylate and acrylonitrile were both observed to react with **3** at room temperature to produce the ene products **24** and **25**, whereas these dienophiles were shown not to react with bicyclobutane (**1**) even at elevated temperatures. The thermal rearrangements of **19** and **24** are also discussed.

The marked similarity between the bicyclobutane ring system, in particular the 1,3 bond, and an olefinic $\pi$ bond[8] led us to investigate further the reactions of bicyclobutanes. We initially chose to examine the reaction between bicyclobutane (**1**) and benzyne.

**1**



**2**

Benzyne was known to react with olefins lacking readily available allylic hydrogens by cycloaddition.[9] The reaction with olefins that do have available allylic hydrogens is the ene synthesis reaction (substitutive addition).[10]

Prior to our initial report[4] Cairncross and Blanchard reported on the reactions of 3-methylbicyclobutanecarbonitrile (**2**) with various olefins and butadiene.[11,12] With certain olefins the reaction with **2** resulted in cycloaddition while with other olefins ene synthesis predominated.[13] By using maleonitrile and fumaronitrile, it was demonstrated that the cycloaddition reaction involved two steps and is best rationalized as a diradical process. In addition, it was observed that when cycloaddition occurred it required heating the reactants above 100°. These observations are to be contrasted with those concerning the ene synthesis reactions. Here, only strongly electron-deficient olefins gave this reaction, and when they did it was very rapid at room temperature. Thus, heating **2** with maleonitrile, fumaronitrile, butadiene, acrylonitrile, 1-(*N*,*N*-dimethylamino)cyclopentene, and various styrenes resulted in cycloaddition, whereas the reaction of **2** with hexafluoroacetone, *sym*-dichlorotetrafluoroacetone, and 1,1-dicyano-2,2-bistrifluoromethylethylene at room temperature or below resulted in ene synthesis. The one exception appears to be the reaction of **2** with ethylene which gives both types of products at high temperature. In addition dicyanoacetylene has been shown by Gassman to react with **2** also by the ene reaction.[14]

The reaction of 1,3-dimethylbicyclobutane (**3**) with various dienophiles has also been studied by Rifi.[15] Only ene synthesis products have been observed upon reaction of **3** with maleic anhydride and hexafluoroacetone.

It should also be mentioned at this point that Gassman has demonstrated that the ene synthesis and cycloaddition reactions of bicyclo[2.1.0]pentane with various dienophiles both involve a common diradical intermediate.[16]

## Results and Discussion

When bicyclobutane[17] was allowed to react with approximately an equimolar quantity of benzyne, from *o*-benzenediazoniumcarboxylate, in ethylene chloride at 40–45°, a moderate yield of two products was obtained. Analysis by nmr spectroscopy showed the ratio of the two products to be about 6:1. The major product was identified as 3-phenylcyclobutene (**4**) and the minor one as benzobicyclo[2.1.1]hex-2-ene (**5**) in the following way. The nmr spectrum of the major

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[1] Part IV: M. Pomerantz and R. N. Wilke, *Tetrahedron Lett.*, 463 (1969).

[2] Portions of this work have appeared as preliminary communications.[1,3,4]

[3] M. Pomerantz, G. W. Gruber, and R. N. Wilke, *J. Amer. Chem. Soc.*, 90, 5040 (1968).

[4] M. Pomerantz, *ibid.*, **88**, 5349 (1966).

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[6] This work was taken in part from the Ph.D. theses of (a) R. N. Wilke, Case Western Reserve University, Cleveland, Ohio, 1971, and (b) G. W. Gruber, Case Western Reserve University, Cleveland, Ohio 1970.

[7] Texaco Corporation Fellow, 1968–1969.

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

[9] R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, pp 200–205.

[10] R. W. Hoffmann, ref 9, pp 197–199.

[11] E. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 487 (1966).

[12] A. Cairncross and E. P. Blanchard, Jr., *ibid.*, **88**, 496 (1966).

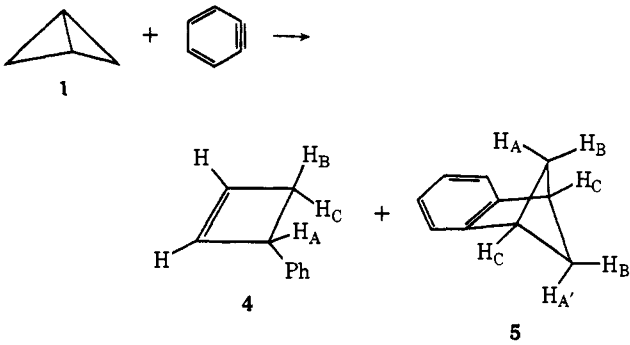
[13] For a review of the addition of dienophiles to strained rings, see P. G. Gassman, *Accounts Chem. Res.*, 4, 128 (1971).

[14] P. G. Gassman and K. T. Mansfield, *J. Amer. Chem. Soc.*, **90**, 1517 (1968).

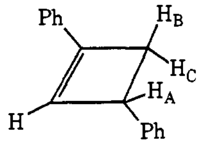
[15] M. R. Rifi, *ibid.*, **89**, 4442 (1967).

[16] For the cogent arguments and references see ref 13.

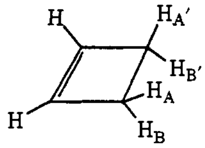
[17] We wish to thank Professor L. Friedman and Dr. J. H. Bayless, Jr., for details of the preparation of bicyclobutane; J. H. Bayless, Jr., Ph.D. Thesis, Case Institute of Technology, Cleveland, Ohio, 1967.



isomer, **4**, showed five aromatic hydrogens at $\tau$ 2.5, two vinyl hydrogens as a singlet at $\tau$ 3.5, and hydrogens A, B, and C each as a double doublet at $\tau$ 5.8, 6.85, and 7.55, respectively; $J_{AB}$ = 5.0 Hz, $J_{AC}$ = 2.2 Hz, and $J_{BC}$ = 15.3 Hz. These assignments are very much the same as those made for 1,3-diphenylcyclobutene (**6**) by Masamune.[18] In that case the vinyl hydrogen (in **6**) was at $\tau$ 3.56, the benzylic hydrogen ($H_A$) at $\tau$ 6.08, the allylic hydrogen trans to the phenyl ring ($H_B$) at $\tau$ 6.78, and the one cis ($H_C$) at $\tau$ 7.44. The coupling constants were determined as $J_{AB}$ = 4.9 Hz, $J_{AC}$ = 1.9 Hz, and $J_{BC}$ = 12.3 Hz. In addition, in cyclobutene itself (**7**), $J_{AB}$ = −12.0 Hz, $J_{AA'}$ = 4.65 Hz, and $J_{AB}$ = 1.75 Hz.[19] Thus, both the chemical shifts and coupling constants fit the cyclobutene structure (**4**) extremely well. Catalytic hydrogenation resulted in the uptake of 1 equiv of hydrogen and gave a product whose nmr spectrum showed five aromatic hydrogens at $\tau$ 2.4, one benzylic multiplet at $\tau$ 6.2, and six aliphatic hydrogens between $\tau$ 7.3 and 8.3. This is consistent with this product being phenylcyclobutane as is the infrared spectrum which is extremely similar to that reported for this compound.[20]



**6**



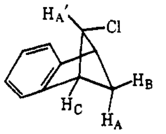
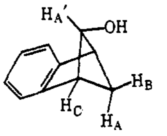
**7**

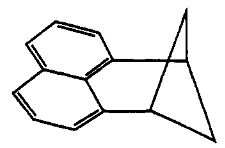
Thermal rearrangement of **4**[21] afforded *trans*-1-phenyl-1,3-butadiene whose infrared and nmr spectra were identical with those of authentic material prepared by the method of Grummitt.[22] 3-Phenylcyclobutene was also prepared independently by the photolysis of 1-phenyl-1,3-butadiene.[23]

The mass spectrum of the minor benzyne–bicyclobutane product showed the parent peak at *m/e* 130 consistent with a $C_{10}H_{10}$ molecular formula for **5**.[24] In addition the P:P + 1:P + 2 ratio was found to be 100:10.8:0.4 as compared to the calculated value of 100:10.97:0.54.

The nmr spectrum of **5** displayed a symmetrical four-proton $A_2B_2$ aromatic multiplet at $\tau$ 3.0, a triplet for the bridgehead protons ($H_C$) at $\tau$ 6.86, a complex multiplet for the exo hydrogens ($H_B$) at $\tau$ 7.25, and a double doublet for the endo hydrogens ($H_A$) at $\tau$ 7.66. Computer simulation of the spectrum was quite good using the following parameters: $J_{BC}$ = 2.4 Hz, $J_{AB}$ = 4.9 Hz, $J_{AA'}$ = 5.4 Hz, and $J_{AC}$ = $J_{BB'}$ = $J_{AB'}$ = 0 Hz and −25.6 and −48.4 Hz as the chemical shifts of the B and C hydrogens relative to the A hydrogens.[25] This spectrum not only agrees with the spectra of other bicyclo[2.1.1]hexane derivatives[26] but also with other benzobicyclohexenes[27] which have been reported subsequent to our initial observations. The chemical shifts and coupling constants in **5** are consistent with the nmr spectra of a reasonable number of substituted derivatives presented by Tanida, two of which, along with **5**, are shown in Table I. In addition *peri*-naphthobicyclo[3.1.1]heptene (**8**) shows a similar spectrum.[28]

Table I

| | Chemical shifts, $\tau$ | | | | | Coupling constants, Hz | |
|---|---|---|---|---|---|---|---|
| Compound | Aromatic | $H_A$ | $H_B$ | $H_C$ | $H_{A'}$ | $J_{AB}$ | $J_{AA'}$ |
|  | 2.97 | 7.60 | 6.28 | 6.77 | 5.88 | 6.6 | 7.4 |
|  | 3.02 | 7.64 | 6.38 | 6.98 | 5.78 | 6.2 | 6.5 |
| Benzobicyclo[2.1.1]hex-2-ene (**5**) | 3.0 | 7.66 | 7.25 | 6.86 | 7.66 | 4.9 | 5.4 |



**8**

Thus, the nmr spectrum, which shows significant long-range coupling ($H_A$–$H_{A'}$), the mass spectrum, and the observation that the molecule is stable at 100° for 6 hr led uniquely to structure **5** for the minor product.

The two reaction pathways seen here are therefore completely analogous to those of olefinic systems. Compound **5** is the result of a formal cycloaddition, while **4** is the result of an ene synthesis. The interesting point here is that both ene synthesis and cycloaddition are observed. This is, to date, only the second case where both pathways are observed in the reaction of a bicyclobutane, the other being the high-temperature reaction of **2** with ethylene.[12]

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(18) S. Masamune, *Tetrahedron Lett.*, 945 (1965).

(19) E. A. Hill and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2047 (1967).

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

(21) M. Pomerantz and P. H. Hartman, *Tetrahedron Lett.*, 991 (1968).

(22) O. Grummitt and E. I. Becker, "Organic Syntheses," Collect., Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 771; O. Grummitt and F. J. Christoph, *J. Amer. Chem., Soc.*, 73, 3479 (1951).

(23) M. Pomerantz and G. W. Gruber, *ibid.*, **93**, 6615 (1971).

(24) We wish to thank Dr. J. H. Bayless, Jr., for obtaining the mass spectrum on a General Electric analytical mass spectrometer.

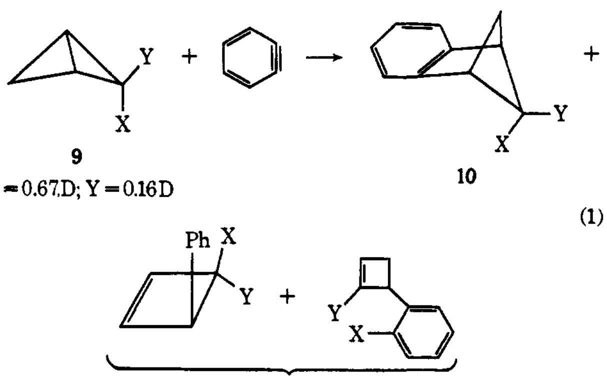
(25) The nmr spectrum of **5** as well as a computer simulation are given in ref 4. We wish to thank Professor Donald Whitman for the use of his computer program, Professor A. A. Bothner-By for the use of LAOCN III, and Mr. A. Christoph for help with some of the computations.

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

(27) Y. Hata and H. Tanida, *ibid.*, **91**, 1170 (1969).

(28) J. Meinwald and J. W. Young, *ibid.*, **93**, 725 (1971).

The mechanism of these reactions was probed by employing bicyclobutane-2-$d_1$[29] (**9**) containing 0.83 deuterium per molecule, with 67% *endo*-2-$d_1$ and 16% *exo*-2-$d_1$ and analyzed by a combination of low voltage mass spectroscopy and nmr spectroscopy.



**9**

X = 0.67D; Y = 0.16D

**10**

(1)

**11**

Reaction of **9** with benzyne (again from the decomposition of *o*-benzenediazoniumcarboxylate at 45°) in ethylene chloride, followed by vlpc purification gave the benzobicyclohexene **10** with all of the original endo bicyclobutane deuterium (0.67 D) in the endo position. The ene synthesis product, **11**, had half of the original endo bicyclobutane deuterium at the 4 position cis to the benzene ring and the other half attached to the benzene ring (eq 1).[30] Table II shows the data; the calculated nmr integrations are assuming no isotope effect. It should be pointed out that an isotope effect of 20 or 30% would probably have been within the experimental error. It is clear, therefore, that both the ene reaction and cycloaddition occur by bottomside (endo) attack of benzyne on the bicyclobutane.

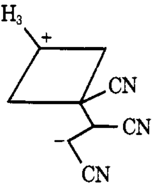
Table II

| Compound | Hydrogen | Obsd nmr hydrogen ratio | Calcd ratio for bottom-side attack |
|---|---|---|---|
| Bicyclobutane (**9**) | Bridgehead | 2.00 | |
| | *exo*-2 | 1.84 | |
| | *endo*-2 | 1.33 | |
| Benzobicyclo[2.1.1]-hex-2-ene (**10**) | Aromatic | *a* | 4.00 |
| | Bridgehead | 2.00 | 2.00 |
| | *exo*-5 | 1.84 | 1.84 |
| | *endo*-5 | 1.34 | 1.33 |
| 3-Phenylcyclobutene (**11**) | 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.

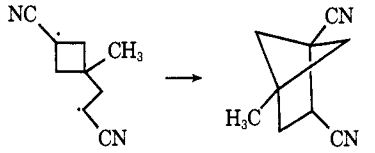
Other bicyclobutane reactions that have been shown to occur by way of bottomside (endo) attack are proton addition[31,32] and chlorine addition.[32] Blanchard and Cairncross have suggested, based on relative rate data, that the reaction of 3-methylbicyclobutanecarbonitrile (**2**) with hexafluoroacetone occurs in this way.[11] Gassman has also shown recently that the reaction of benzyne with tricyclo[4.1.0.0$^{2,7}$]heptane occurs from the underside of the bicyclobutane system.[33] In addition, the reactions of dienophiles with bicyclo[2.1.0]pentane similarly occur from the underside.[33-35]

The best rationalization for the observation of the double inversion in the cycloaddition is first, that attack is at the more readily available back lobe of the orbital employed in bridgehead–bridgehead bonding,[8,36] and second, that this initial attack produces a diradical. This is reasonable since considerable strain (>40 kcal/mol)[37] is being released. In addition, a concerted $_\sigma2_s + _\pi2_s$ reaction is sterically impossible by bottomside attack, and is symmetry forbidden.[38] Also, the cycloaddition reactions of maleonitrile and fumaronitrile with 3-methylbicyclobutanecarbonitrile (**2**) have been shown to be diradical reactions in spite of the fact that a reasonable dipolar intermediate (**12**) can be formulated.[12]

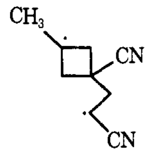


**12**

If one now accepts the diradical nature of the cycloaddition, it would appear as though the ene synthesis, at least in some cases, probably follows a different mechanistic pathway. The intermediate involved in the reaction of **2** with acrylonitrile to give **13** is best formulated as **14** rather than **15**. Using this as a model one predicts that the reaction of **2** with dicyanoacetylene would give intermediate **16** rather than **17**,



**14** **13**



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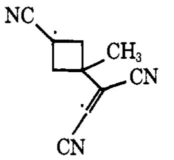

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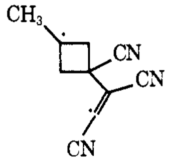

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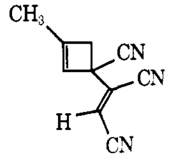

**18**

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

[30] Pure **10** was obtained directly by vlpc, whereas **11** was collected with a small amount of **10** as contaminant. The nmr spectrum of **11** was obtained using an internal standard; the solution was then heated to rearrange the phenylcyclobutene to phenylbutadiene[21] and the nmr spectrum obtained again. In this way the integrated spectrum of **11** was analyzed by difference.

[31] W. G. Dauben, J. H. Smith, and J. Saltiel, *J. Org. Chem.*, **34**, 261 (1969).

[32] K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970).

[33] P. G. Gassman and G. D. Richmond, *ibid.*, **92**, 2090 (1970); **90**, 5637 (1968).

[34] P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **91**, 1684 (1969).

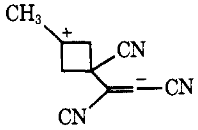
[35] W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967).

[36] J. M. Schulman and G. J. Fisanick, *J. Amer. Chem. Soc.*, **92**, 6653 (1970).

[37] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968), and references cited therein.

[38] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

if indeed diradicals are involved here. In this case, since the observed product is **18**, either **17** is involved, which does not appear to be consistent with the acrylonitrile reaction, or these two reactions involve different mechanisms. If the ene synthesis does indeed involve a mechanism different from the cycloaddition, it would either be a concerted or a dipolar pathway. Thus, the precursor of **18** might very well be **19** which is a resonance hybrid where the dipolar form contributes more than the diradical form to the structure, whereas in **14** the reverse is true. These two mechanistic possibilities for the ene synthesis cannot be distinguished at this time.

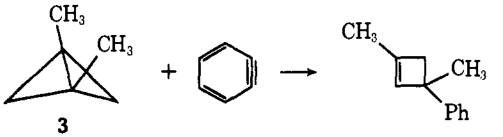


**19**

In cases involving symmetrical species such as benzyne plus bicyclobutane, the mechanistic possibilities are further limited. A two-step ene synthesis requires a common intermediate for this and cycloaddition, whereas the alternative would be a concerted ene reaction. In these cases there is no good evidence to strongly favor one or the other of the mechanisms for the ene synthesis.

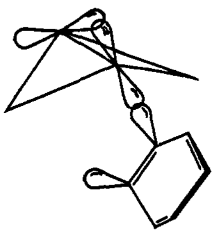
The present observation of little or no isotope effect in the production of 3-phenylcyclobutene (**11**) is consistent with either mechanistic possibility. A mechanism involving slow rate-determining formation of a diradical followed by rapid removal of a proton or deuteron should show, at most, a very small isotope effect. Since the product, 3-phenylcyclobutene, is much more stable than the starting materials, benzyne plus bicyclobutane, a concerted reaction must be exothermic. According to Hammond's postulate the transition state occurs early along the reaction coordinate which means there would be little C–H (or C–D) bond breaking in the transition state, and thus a small isotope effect is reasonable.

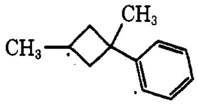
The reaction of benzyne with 1,3-dimethylbicyclobutane produced (in 41% yield) the ene synthesis product 1,3-dimethyl-3-phenylcyclobutene (**19**, eq 2).



**3** **19** (2)

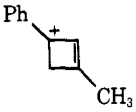
There was no cycloadduct (<3%) present as determined by nmr spectroscopy and also by vlpc (<1%, assuming we were in fact able to separate the isomers on the column employed). If the ene synthesis is a concerted reaction, we would expect less cycloadduct formed here as compared to the bicyclobutane (**1**) case. Attack to form the diradical would probably involve the benzyne attacking along the axis of the bent bond or p orbital of the bicyclobutane and the plane of the benzyne would bisect the $C_2$–$C_1$–$C_4$ angle as shown below. This would result in some steric compression between the 3-hydrogen on the benzyne and the methyl group of the bicyclobutane (**3**). Since the concerted ene synthesis reaction of **3** has about the same steric requirements as **1**, **3** produces more of this product. The alternative explanation, whereby a single intermediate diradical produces both ene product and cycloadduct, can also be made to fit the observation. In the diradical **20**, models suggest that the phenyl group is not completely free to rotate and, as a result, the preferred conformation places the radical site on the phenyl ring closer to the 2-hydrogen. Since in the diradical from bicyclobutane the phenyl can rotate more freely, it is to be expected that **20** would produce less cycloadduct than this diradical, which is what is observed.





**20**

The structure proof of **19** consists of its nmr spectrum which showed five aromatic hydrogens at $\tau$ 2.81, one vinyl hydrogen as an apparent doublet ($J = 1$ Hz) at $\tau$ 3.89, two allylic hydrogens at $\tau$ 7.49, one allylic methyl group as a doublet ($J = 1$ Hz) at $\tau$ 8.26, and the second methyl group as a singlet at $\tau$ 8.53. The infrared spectrum showed the double bond stretch at 1640 cm$^{-1}$ as compared to 1641 cm$^{-1}$ for 1-methylcyclobutene.[39] The mass spectrum of **19** exhibited the parent peak, at both high and low ionization potentials, at *m/e* 158 confirming the $C_{12}H_{14}$ formula. In addition, the P + 1 peak was 13.0% of P compared to the calculated value of 13.2%, and the base peak in the 70-eV spectrum was at 143 (P − $CH_3$) due to ion **21** which is the major ion expected from **19**.



**21**

Thermal rearrangement (160°) of **19** produced three products in the ratio of 2:1:8 (eq 3).[40] The major product was identified as 2-methyl-4-phenyl-1,3-pentadiene (**22**) by the identity of its nmr spectrum with that reported for this compound, of unknown stereochemistry.[43] From mechanistic considerations it seems most likely that this compound is (*E*)-2-methyl-4-phenyl-1,3-pentadiene since conrotatory ring opening

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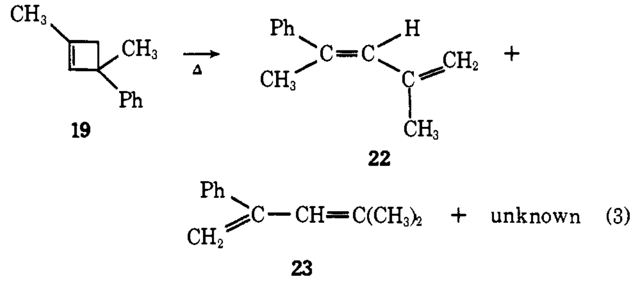
(39) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, p 81.

(40) The thermal ring opening of **19** is qualitatively slower than the ring opening of 3-phenylcyclobutene (**6**). This is to be expected since there would be more steric hindrance in the transition state for conrotatory ring opening of **19** than of **6**.[21,41,42]

(41) H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Amer. Chem. Soc.*, **87**, 3019 (1965).

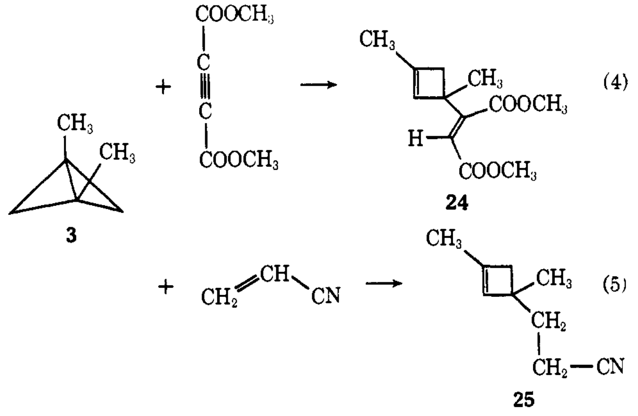
(42) R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H-A. Brune, *Chem. Ber.*, **98**, 2339 (1965).

(43) T. L. Jacobs and R. A. Meyers, *J. Amer. Chem. Soc.*, **86**, 5244 (1964).



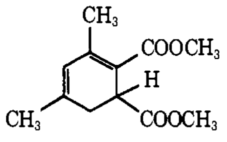
of **19** would involve less steric strain in the transition state if the methyl rather than the larger phenyl group rotated inward. The minor product (relative ratio 1) was identified as 4-methyl-2-phenyl-1,3-pentadiene (**23**) by comparison of its nmr spectrum with that reported for this compound.[43] The third compound (relative area 2) was not identified but is most likely an isomer of **22** and **23** since hydrogenation of the mixture gave a single product as determined by vlpc. Further heating of the reaction mixture partially converted **22** into **23** while the unknown compound remained unchanged. Thus **22** and the unknown are primary products from the thermal rearrangement of **19** while **23** is the result of a 1,5-sigmatropic hydrogen migration.

The reaction of 1,3-dimethylbicyclobutane (**3**) with both dimethyl acetylenedicarboxylate and acrylonitrile proceeded at room temperature and produced only the ene products (eq 4 and 5). Once again the cycloadduct was not in evidence. This was essentially what Rifi found in the reaction of **3** with maleic anhydride.[15]



Structure proof for **24** rests on the nmr spectrum which showed two methoxy groups at $\tau$ 6.17 and 6.36, one vinyl hydrogen as a singlet at $\tau$ 4.23, one vinyl hydrogen as an apparent doublet at $\tau$ 4.13 ($J$ = 1.5 Hz), two allylic hydrogens as a multiplet at $\tau$ 7.50, one allylic methyl group as a doublet ($J$ = 1.5 Hz) at $\tau$ 8.25, and the second methyl group as a singlet at $\tau$ 8.63. The infrared spectrum displayed the double bond stretch at 1640 $cm^{-1}$ and the carbonyl at 1730 $cm^{-1}$. The mass spectrum showed the parent peak at $m/e$ 224, consistent with $C_{12}H_{16}O_4$, with the ratio of $P:P + 1:P + 2$ determined as 100:13.6:*ca.* 2; the calculated ratio is 100:13.38:1.63.

Thermal rearrangement of **24** (120°) did not produce a butadiene as the observed product but instead gave a compound identified as **26** based on the following evidence. The nmr spectrum displayed a single vinyl hydrogen apparent doublet at $\tau$ 4.20 ($J$ = 1.5 Hz), one methyl singlet at $\tau$ 7.96, one methyl doublet at $\tau$ 7.67 ($J$ = 1.5 Hz), and two methoxy groups at $\tau$ 6.13 and 6.22. The allylic and methine hydrogens appeared as a multiplet at $\tau$ 7.32. The infrared spectrum showed $\nu_{C=O}$ 1725, 1705 $cm^{-1}$, and $\nu_{C=C}$ 1585 $cm^{-1}$. This compares well with 1580 $cm^{-1}$ for 1,5,5-trimethyl-1,3-cyclohexadiene.[44] The mass spectrum ($m/e$ 224) confirmed that it was an isomer of the starting cyclobutene. The ultraviolet spectrum showed $\lambda_{max}^{hexane}$ 291 nm ($\epsilon$ 8600). This is in good agreement with similar compounds shown in Table III[45] (after applying the usual correction for hexane rather than ethanol as the solvent). In addition, dehydrogenation with chloranil produced dimethyl 3,5-dimethylphthalate identified by the identity of its infrared spectrum and vlpc retention time with those of authentic material.

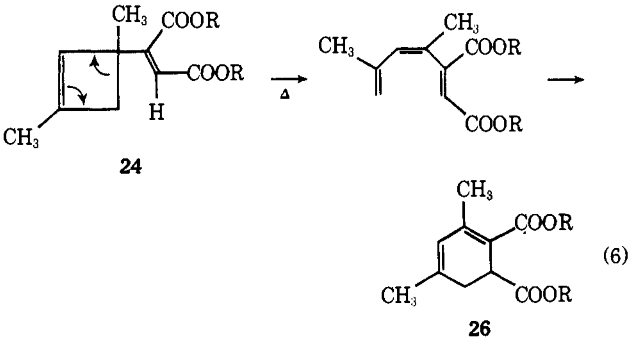


**26**

Table III

| Compound | Isomer | $\lambda_{max}^{EtOH}$, nm | $\epsilon$ |
|---|---|---|---|
| 3,5-Dimethyl-2,3-dihydrophthalic acid | *cis* | 293.5 | 7930 |
| | *trans* | 295 | 7500 |
| 3,4-Dimethyl-2,3-dihydrophthalic acid | *cis* | 298 | 6200 |
| | *trans* | 297.5 | 8000 |
| 3,6-Dimethyl-2,3-dihydrophthalic acid | *cis* | 285 | 6200 |
| | *trans* | 286 | 7000 |

A reasonable mechanism for this rearrangement is shown in eq 6. It is worthwhile pointing out that the ester groups in **24** must be cis. This follows from the nature of the constraints on the transition state in the hydrogen abstraction step for an intramolecular reaction.



The ene product from dimethylbicyclobutane and acrylonitrile (**25**) was identified by its nmr spectrum which displayed a vinyl hydrogen quartet ($J$ = 1.5 Hz) at $\tau$ 4.27, a two-proton multiplet for the $CH_2$ $\alpha$ to the ring at $\tau$ 8.18, a four proton multiplet for the two additional $CH_2$ groups at *ca.* $\tau$ 7.8, an allylic methyl doublet ($J$ = 1.5 Hz) at $\tau$ 8.34, and a saturated methyl singlet at $\tau$ 8.93. The infrared double bond stretching frequency was at 1633 $cm^{-1}$ and the parent ion in the mass spectrum at $m/e$ 135 ($C_9H_{13}N$).

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(44) Sadtler Infrared Spectrum No. 12966.

(45) V. F. Kucherov, N. Ya. Gregor'eva, and T. M. Fadeeva, *J. Gen. Chem. USSR*, 31, 2696 (1961).

Once again, as with the benzyne–dimethylbicyclobutane reaction, a definite statement about the mechanism of these ene syntheses cannot be made. The results can be rationalized with either a one- or a two-step reaction.

Other very interesting observations in bicyclobutane chemistry are that bicyclobutane itself (**1**) failed to react with acrylonitrile after 2 hr at 130° using diphenylamine as inhibitor. In addition after 8 hr at 150° without inhibitor, no adduct was observed although under these conditions the bicyclobutane was destroyed while 99% of the acrylonitrile was recovered. When **1** was heated to 120° with dimethyl acetylenedicarboxylate for 3 hr, nmr spectroscopy indicated that although the bicyclobutane was lost no adduct was formed. A possible explanation for the lack of reactivity of **1** compared to the dimethyl derivative (**3**) is first of all that **3** is about 4 kcal/mol less stable than **1**[37,46] and is therefore more reactive (assuming less than 4 kcal/mol difference in transition-state energies). In addition, for a dipolar or diradical reaction, the methyl group stabilizes the rate-determining transition state leading to the intermediate, and, in a concerted reaction, the methyl group stabilizes the developing double bond. Thus, it is not surprising that bicyclobutane (**1**) is less reactive than dimethylbicyclobutane (**3**). Any rate retardation due to steric hindrance to reaction by the methyl groups must be small compared to the other effects.

## Experimental Section

Nmr spectra were obtained on a Varian A-60 or A-60A spectrometer, mass spectra on a Varian M-66 cycloidal or a General Electric analytical mass spectrometer, infrared spectra on a Perkin-Elmer 237 or Beckman IR8 spectrometer, and ultraviolet spectra on a Cary 15 or Beckman DB spectrometer. Melting points and boiling points are uncorrected. The following 0.25-in. columns were used with a thermal conductivity instrument while the 0.125-in. columns were used with a flame ionization detector instrument: (A) 2 m × 0.25 in. 5% SE 30 on 45–60 mesh Chromosorb P; (B) 5 ft × 0.25 in 5% Carbowax 1500 on 45–60 mesh Chromosorb P; (C) 12 ft × 0.25 in. 20% TCEP on 45–60 mesh Chromosorb P; (D) 7 ft × 0.25 in. 20% Dow Corning 710 silicone oil on 60–80 mesh Chromosorb P; (E) 5 ft × 0.25 in. 20% Dow Corning 710 silicone oil on 60–80 mesh Chromosorb P; (F) 5 ft × 0.125 in. 20% Dow Corning 710 silicone oil on 60–80 mesh Chromosorb P; (G) 6 ft × 0.125 in. 15% Carbowax 20M on 80–100 mesh Chromosorb P; (H) 7 ft × 0.125 in. 5% SE-30 on 80–100 mesh Chromosorb W; (I) 10 ft × 0.25 in. 15% Carbowax 600 on 60–80 mesh Chromosorb W.

**Reaction of Benzyne with Bicyclobutane.** To a cold suspension of *o*-benzenediazoniumcarboxylate,[47] prepared from 290 mg (2.1 mmol) of anthranilic acid, in about 10 ml of ethylene chloride was added 150 μl of bicyclobutane[17] (*ca.* 100 mg, 1.9 mmol) in 2 ml of ethylene chloride. The reaction vessel was equipped with a Dry Ice cold finger and a magnetic stirrer. The mixture was stirred for 1.3 hr at 40–45°, until all of the benzyne precursor had decomposed. The ethylene chloride was distilled, at 72 mm, through a 4-cm Heli-pak column; the pot temperature was kept at 40°. Vlpc (column A at 80°) using *n*-butylbenzene as an internal standard showed the yield of the two products was *ca.* 40%. Nmr analysis showed the ratio of 3-phenylcyclobutene (**4**):benzobicyclo[2.1.1]hex-2-ene (**5**) was 6:1. The compounds were separated by preparative vlpc. Spectral data for **4** and **5** are given in the text.

**Hydrogenation of 3-Phenylcyclobutene (4).** 3-Phenylcyclobutene (10 μl, *ca.* 9 mg, 0.07 mmol) in 0.5 ml of methyl acetate was hydrogenated over prereduced $PtO_2$ in 0.5 ml of the same solvent at atmospheric pressure. Hydrogen uptake was 2.9 ± 0.5 ml; theoretical for one unsaturation is 2.6 ml. The solution was filtered and most of the solvent removed *in vacuo*. The major peak (vlpc on column B) was collected and its nmr spectrum obtained (see text).

**Ethylene Glycol-$d_2$.** Ethylene carbonate (200 g, 2.28 mol), 2 g of potassium carbonate, and 170 ml of $D_2O$ were heated to 100° in a 500-ml round-bottomed flask equipped with a reflux condenser capped with a calcium chloride drying tube. After 15 hr the excess $D_2O$ was distilled, *ca.* 1.0 g of sodium was allowed to react with the residue, and ethylene glycol-$d_2$ was distilled at 60–62° (2 mm), yield 124 g, 85% of theoretical. Nmr analysis indicated 99.6% of two deuterons.

**Bicyclobutane-*endo*-2-$d_1$ (9).**[29] Cyclopropanecarboxaldehyde *p*-tosylhydrazone (7.85 g, 33 mmol) was dissolved in 33 ml of ethylene glycol-$d_2$ which had previously been allowed to react with 0.68 g (30 mg-atoms) of sodium. The reaction flask was equipped with a magnetic stirrer and a 6-in. column packed with glass beads. This column was connected to a 2-l. filter flask containing saturated sodium sulfate solution (which had been made slightly basic by the addition of a few pellets of NaOH) where the evolved gases could be collected by displacement. The reaction flask was immersed in an oil bath at 180° while the contents were stirred rapidly. After a 2–5-min induction period about 1 l. of gas was evolved rapidly. Slow passage on this gas into a Dry Ice cooled trap gave *ca.* 0.6 ml of a colorless liquid containing (vlpc; column C at 0°) 65% of bicyclobutane, 33% of cyclobutene, and less than 2% of other compounds. Preparative vlpc afforded *ca.* 150 μl of pure bicyclobutane-2-$d_1$ (**9**) which, by mass and nmr spectroscopy, showed 0.83 deuteron per molecule of which 81% was endo and 19% exo in the 2 position. A second run gave essentially the same result.

**Reaction of Bicyclobutane-2-$d_1$ (9) with Benzyne.** This reaction was performed as described above for undeuterated bicyclobutane using 175 mg (3.2 mmol) of bicyclobutane-2-$d_1$ (**9**) and the *o*-benzenediazoniumcarboxylate from 0.48 g (3.5 mmol) of anthranilic acid.[47] Preparative vlpc, as before, provided a sample of benzobicyclo[2.1.1]hex-2-ene-$d_1$ (**10**). Nmr analysis (see text) showed 81% endo and 19% exo deuteration. Since 3-phenylcyclobutene-$d_1$ (**11**) was obtained by preparative vlpc contaminated with **10**, the deuterium analysis was as follows. *tert*-Butylbenzene was added to an nmr sample and the spectrum obtained. This mixture was then heated at 100° for 90 min to isomerize **11** to phenylbutadiene[21] and the spectrum obtained once again. This gave the integral of the **10** present and, by difference, the integral of **11**.

**1,3-Dimethylbicyclobutane (3).** To 10 g of sodium (0.44 g-atom) in 50 ml of dioxane at 90° was added 10 g (41 mmol) of 1,3-dibromo-1,3-dimethylcyclobutane[48] in about 20 ml of dioxane in a flask equipped with an addition funnel and distilling head. The mixture was then heated further, and about 15–20 ml was distilled at *ca.* 97°. Fractional distillation of this distillate through a Teflon spinning band column gave 3.2 ml (*ca.* 2.2 g; 65% yield), bp 54–56°, which was 99.5% pure dimethylbicyclobutane (**3**) as determined by nmr analysis. Other preparations not involving spinning band distillation gave **3** containing variable amounts of dioxane.

**Reaction of 1,3-Dimethylbicyclobutane (3) with Benzyne.** To a solution of 0.94 g (11.5 mmol) of 1,3-dimethylbicyclobutane (**3**) in 15 ml of ethylene chloride, in a 25-ml flask fitted with a condenser and magnetic stirrer, was added a slurry of *o*-benzenediazoniumcarboxylate (from 1.61 g, 11.8 mmol of anthranilic acid)[47] in 25 ml of ethylene chloride. The stirred mixture was heated to 40° for 1 hr and then refluxed for 15 min. Distillation of *ca.* 20 ml of the solvent removed unreacted dimethylbicyclobutane (*ca.* 50 mg). Further distillation of the solvent at 50° and 140 mm gave a residue which was taken up in 50 ml of pentane, extracted with 50 ml of dilute NaOH solution, and dried over sodium sulfate. Removal of the pentane by distillation followed by vlpc analysis (column D at 110°) showed only one peak which was not present in a blank benzyne–ethylene chloride reaction. Preparative vlpc gave pure 1,3-dimethyl-3-phenylcyclobutene (**19**); see text for spectral data. The yield by nmr analysis using benzaldehyde as internal standard was 41%.

**Thermal Rearrangement of 1,3-Dimethyl-3-phenylcyclobutene (19).** 1,3-Dimethyl-3-phenylcyclobutene (**19**, 20 μl) was heated in a Pyrex ampoule (0.15 ml) at 160° for 1 hr. Vlpc analysis (column E at 110°) showed three major peaks in the ratio of 2:1:8 in addition to a small amount of unrearranged starting material. Purification was by preparative vlpc and identification of peaks of area 1 and 8 is given in the text.

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[46] K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Conner P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

[47] F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Syn.*, **48**, 12 (1968).

[48] K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Amer. Chem. Soc.*, **87**, 3151 (1965).

About 2.0 mg of this reaction mixture was dissolved in 10 ml of ether and placed in a 15-ml three-necked flask equipped with a gas inlet, a condenser, and a magnetic stirrer. About 2 mg of $PtO_2$ was added and the solution stirred for 1 hr while $H_2$ gas was bubbled through. Only a single product was obtained as shown by vlpc on two different columns (column F at 85° and column G at 85°).

**Reaction of 1,3-Dimethylbicyclobutane (3) with Dimethyl Acetylenedicarboxylate.** A solution of *ca.* 82 mg (1 mmol) of 1,3-dimethylbicyclobutane (**3**) in 400 μl of acetonitrile and 70 μl of dioxane was placed in a 2-ml centrifuge tube equipped with a condenser. To this solution was added 135 mg (0.95 mmol) of dimethyl acetylenedicarboxylate. The solution turned yellow on standing at room temperature for 24 hr. Vlpc analysis (column E at 105°) showed the presence of only one peak in 30% yield. Preparative vlpc gave pure dimethyl (*Z*)-2-(1,3-dimethyl-2-cyclobutenyl)butendioate (**24**) identified as indicated in the text.

**Thermal Rearrangement of 24.** **24** (18 μl) was heated in a sealed ampoule (0.15 ml) at 120° for 1.5 hr. Vlpc analysis (column E at 105°) showed a single major peak in addition to one for unrearranged starting material. Preparative vlpc afforded 1,3-dimethyl-4,5-dicarbomethoxy-1,3-cyclohexadiene (**26**), identified as indicated in the text.

When 1.5 μl of **26** was heated with 0.1 g of chloranil in refluxing benzene for 3 hr, it was converted to dimethyl 3,5-dimethylphthlalate as shown by vlpc analysis (column H at 140°) and infrared spectroscopy.

**Reaction of 1,3-Dimethylbicyclobutane (3) with Acrylonitrile.** A solution of 125 mg (1.5 mmol) of **3** and 64 mg (1.2 mmol) of acrylonitrile in 190 μl of acetonitrile and 100 μl of dioxane was kept at room temperature for 24 hr in a 2-ml centrifuge tube equipped with a condenser. Vlpc (column I at 100°) indicated *ca.* 27% yield and gave pure 3-(1,3-dimethyl-2-cyclobutenyl)propanenitrile (**25**) whose spectra are given in the text.

**Acknowledgement.** We wish to thank the donors of the Petroleum Research Fund administered by the American Chemical Society (Grant 271 G) and the National Science Foundation (Grant GP-7859) for partial support of this work.

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# 1-Azabicyclobutanes. Synthesis and Reactions[1]

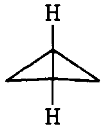
**Alfred G. Hortmann* and David A. Robertson**[2]

*Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130. Received July 27, 1971*

**Abstract:** Treatment of 2-phenylazirine with dimethylsulfonium methylide affords a 68% yield of 2-phenyl-1-azabicyclobutane (**2a**), the first authentic example of a heterocyclic bicyclobutane to be isolated and characterized. Extension of the synthesis to the preparation of **2b**, **2c**, **4a**, and **4b** is also described. Acid-catalyzed ring-opening reactions leading predominantly to products of 1,3 addition of water and methanol are described and discussed in detail for several of the azabicyclobutanes. Addition of hydrogen chloride to **2a–c** yields the 3-chloro-3-phenylazetidine hydrochlorides **7a–c** exclusively. The free amines liberated from **7a–c** rapidly and quantitatively recyclize to **2a–c** at 0°.

Since the first synthesis of a substituted bicyclobutane was reported by Wiberg and Cuila in 1959, a number of routes to this carbocyclic ring system have been developed.[3] More recently interest has been focused on the nature of the bonding in bicyclobutane (I).[4] Of particular interest is its high dipole moment (0.675 ± 0.01 $D$),[5] its unexpectedly large strain energy (64 kcal/mol),[3a] and the uv spectra of 1-carboxyl- and 1,3-diphenyl-substituted derivatives which suggest that conjugative interactions of these substituents with the bicyclic ring system can occur.[3a]

The acidity of the bridgehead protons and the $^{13}$C–H coupling constant (205 Hz)[6] associated with these hydrogens suggest that the bridgehead C–H bonds have appreciable s character. When considered with the uv data and the ability of bicyclobutanes to undergo facile 1,3 addition of water, methanol, halogens, amines, and olefins,[3a,e,f,7] these data have led a number of workers to regard the central bond of bicyclobutanes as having ethylenic or even acetylenic character;[8] the extent of the latter has been estimated from the value of the bridgehead $^{13}$C–H coupling constant,[3a,9] although the application of this parameter to strained ring systems has been questioned.[10]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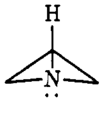

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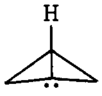

III

It was felt, at the outset of this program, that since amines are highly sensitive to electronic effects, an

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(1) For earlier reports in this series, see (a) A. G. Hortmann and D. A. Robertson, *J. Amer. Chem. Soc.*, **89**, 5974 (1967); (b) J. L. Kurz, B. K. Gillard, D. A. Robertson, and A. G. Hortmann, *ibid.*, **92**, 5008 (1970); (c) A. G. Hortmann and J. E. Martinelli, *Tetrahedron Lett.*, 6205 (1968).

(2) (a) Abstracted in part from the Ph.D. dissertation of D. A. Robertson, Washington University, 1970; (b) National Science Foundation Trainee, 1968–1969.

(3) (a) K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 185 (1968), and references cited; (b) M. R. Rifi, *J. Amer. Chem. Soc.*, **89**, 4442 (1967); (c) D. P. G. Hamon, *ibid.*, **90**, 4513 (1968); (d) W. G. Dauben and J. S. Ritscher, *ibid.*, **92**, 2925 (1970); (e) L. Skattebøl, *Tetrahedron Lett.*, 2361 (1970); (f) W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *ibid.*, 2365 (1970).

(4) J. M. Schulman and G. J. Fisanick, *J. Amer. Chem. Soc.*, **92**, 6653 (1970), and references cited.

(5) M. D. Harmony and K. W. Cox, *ibid.*, **88**, 5049 (1966); K. W. Cox M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969).

(6) K. Wuthrich, S. Meiboom, and L. C. Snyder, *ibid.*, **52**, 230 (1970).

(7) (a) E. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 487, 496 (1966); (b) K. B. Wiberg and G. Szeimies, *ibid.*, **92**, 571 (1970); (c) W. G. Dauben and C. D. Poulter, *Tetrahedron Lett.*, 3021 (1967).

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

(9) N. Muller and E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

(10) See discussion in K. B. Wiberg, G. M. Lampman, R. P. Cuila, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).