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BICYCLO[1.1.0]BUTANE[1]

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Abstract—The chemistry of bicyclo[1.1.0]butane and some of its derivatives is reviewed. The effect of its bond angle deformation on its strain energy, its orbital hybridization, and its reactivity is discussed.

1. INTRODUCTION

As A result of our interest in obtaining a better understanding of the chemical consequences of bond angle deformation, we have made a study of substituted bicyclo[3.1.1]heptane,[3] bicyclo[2.1.1]hexane,[4] bicyclo[1.1.1]pentane[5] and bicyclo-[1.1.0]butane[6] derivatives. The bicyclobutanes are of particular interest since they are probably the most highly strained of the two-ring carbocyclic compounds. The results of a series of investigations on bicyclobutane derivatives are described below.

Several reports of the synthesis of bicyclobutane derivatives appear in the older literature.[7] However, subsequent investigations have indicated that the original structural assignments were incorrect.[8] The first authentic bicyclobutane derivative was prepared by us via the base catalyzed cyclization of methyl 3-bromocyclobutane-carboxylate.[6a] In the earlier work, sodium triphenylmethide was used as the base and a 20% yield of the ester was obtained. Currently, sodium hydride is used, and the yield has been raised to 77%. The reaction proceeds equally well when the 3-position is tertiary, for methyl 3-bromo-3-methylcyclobutanecarboxylate gives methyl 3-methylbicyclobutane-1-carboxylate in 90% yield.

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[2a] Taken in part from theses submitted by R. Ciula (1959) and G. Lampman (1964) to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree, [b] National Institutes of Health Predoctoral Fellow.

[3] K. B. Wiberg and G. Klein, *Tetrahedron Letters* No. 16, 1043 (1963).

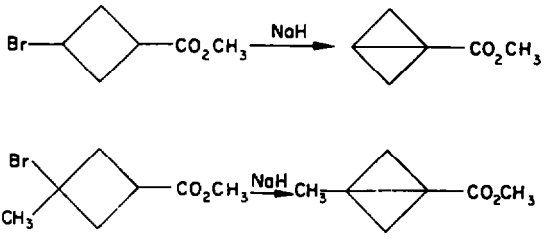
[4] K. B. Wiberg, B. J. Lowry and T. H. Colby, *J. Amer. Chem. Soc.* **83**, 3998 (1961); K. B. Wiberg and B. J. Lowry, *Ibid.* **85**, 3188 (1963).

[5] K. B. Wiberg, D. S. Connor and G. M. Lampman, *Tetrahedron Letters* No. 10, 531 (1964).

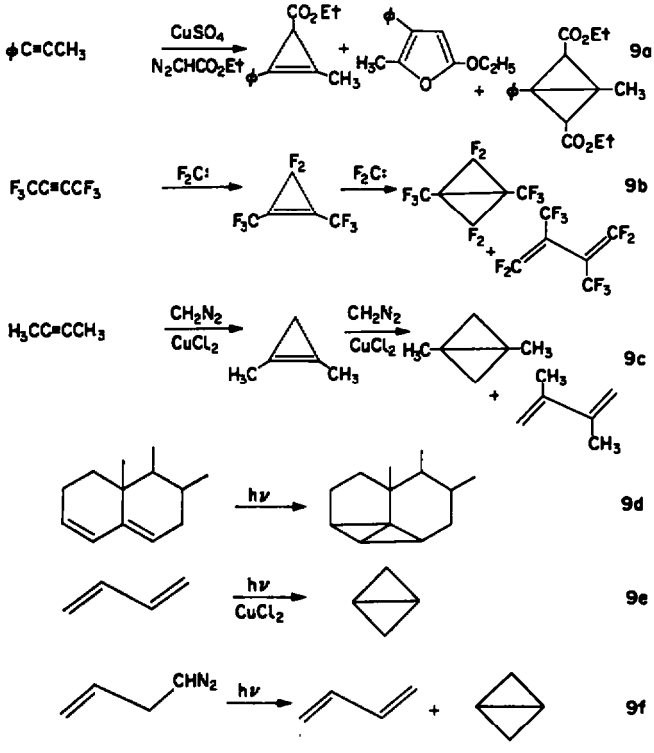
[6a] K. B. Wiberg and R. P. Ciula, *J. Amer. Chem. Soc.* **81**, 5261 (1959); [b] K. B. Wiberg and G. M. Lampman, *Tetrahedron Letters* 2173 (1963).

[7] W. H. Perkin and J. L. Simonsen, *Proc. Chem. Soc.* **21**, 256 (1905); O. Döbner and G. Schmidt, *Ber. Dtsch. Chem. Ges.* **40**, 148 (1907); N. Zelinsky and J. Gutt, *Ibid.* **40**, 4744 (1907); M. Guthzeit and E. Hartmann, *J. Prakt. Chem.* **81**, 329 (1910); R. M. Beesley and J. F. Thorpe, *Proc. Chem. Soc.* **29**, 346 (1913); *J. Chem. Soc.* **117**, 591 (1920).

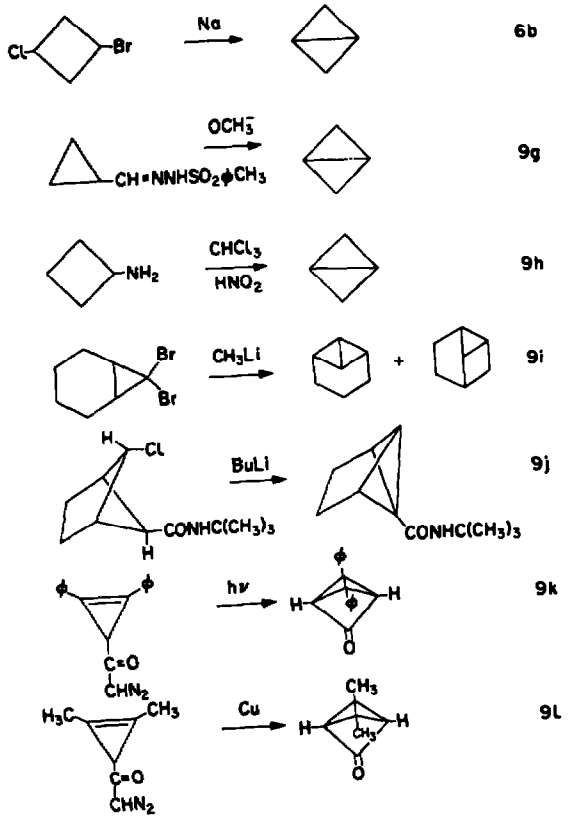
[8] W. H. Perkin and J. L. Simonsen, *Trans. Chem. Soc.* **91**, 816 (1907); R. Willstätter and J. Bruce, *Ber. Dtsch. Chem. Ges.*, **40**, 3979 (1907); C. K. Ingold, M. M. Parekh and C. W. Shoppee, *J. Chem. Soc.* 142 (1936); H. O. Larson and R. B. Woodward, *Chem. & Ind.* 193 (1959).



Recently, a number of other syntheses of bicyclobutane and its derivatives have appeared and they are summarized below:



[9a] I. A. D'yakonov and M. I. Kamendantov, *Zh. Obshch Khim.* **31**, 3881 (1961); I. A. D'yakonov, M. I. Kamendantov and V. V. Razin, *Ibid.* **33**, 2420 (1963); [b] W. Mahler, *J. Amer. Chem. Soc.* **84**, 4600 (1962); [c] W. v. E. Doering and J. F. Coburn, *Tetrahedron Letters* (1965); [d] W. G. Dauben and F. G. Willey, *Tetrahedron Letters* 893 (1962); [e] R. Srinivasan, *J. Amer. Chem. Soc.* **85**, 4045 (1963); [f] D. M. Lemal, F. Menger and G. W. Clark, *Ibid.* **85**, 2529 (1963); [g] H. M. Frey and I. Stevens, *Proc. Chem. Soc.* **144** (1964); [h] J. A. Smith, H. Shechter, J. Bayless and L. Friedman, *J. Amer. Chem. Soc.* **87**, 659 (1965); J. Bayless, L. Friedman, J. A. Smith, F. B. Cook and H. Shechter, *Ibid.* **87**, 661 (1965); [i] W. R. Moore, H. R. Ward, and R. F. Merritt, *Ibid.* **83**, 2019 (1961); [j] J. Meinwald, C. Swithenbank and A. Lewis, *Ibid.* **85**, 1880 (1963); [k] S. Masamune, *Ibid.* **86**, 735 (1964); [l] W. v. E. Doering and M. Pomerantz, *Tetrahedron Letters* 961 (1964); [m] D. M. Lemal and K. S. Shim, *Ibid.* 3231 (1964); [n] G. L. Closs and R. B. Larrabee, *Ibid.* 287 (1965).

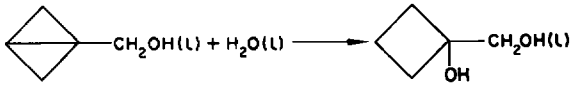

Cl
Br
Na
6b
OCH3
CH=NNHSO2φCH3
9g
NH2
CHCl3
HNO2
9h
Br
Br
CH3Li
+
9i
H
Cl
BuLi
CONHC(CH3)3
H
CONHC(CH3)3
9j
φ
φ
hν
φ
H
H
O
9k
C=O
CHN2
H3C
CH3
Cu
CH3
H
H
CH3
O
C=O
CHN2
9L
CHN2
hν
9m
H3C
CHN2
LiBr
CH3
9n
H3C
CHN2
CH3
H3C
C3H
9n

It can be seen that bicyclobutanes are now among the more readily obtainable of bicyclic ring systems. The following describes a series of observations concerning the nature of this ring system.

2. PHYSICAL PROPERTIES

Important questions concerning bicyclobutane include: what extent of rehybridization occurred in forming the necessarily bent bonds? How large a degree of thermochemical destabilization has occurred as a result of bond angle bending? What is the molecular geometry of the bicyclobutane ring? The following will attempt to answer these questions.

The thermochemical destabilization has been determined based on the observation that bicyclobutane-1-methanol was rapidly hydrated in dilute acid (see below). The heat change accompanying this reaction was measured and found to be −27·4 kcal/mole. In order to have reactant and product in the same reference state (pure liquid), the heat of solution of the product diol was determined and found to be 3·8 kcal/mole. Thus for the reaction the heat change was $\Delta H = -23{\cdot}6$ kcal/mole.



In order to compare this result with that for an unstrained system, the heat change expected for the hydration of cyclohexane to 1-hexanol was calculated from the known heat of formation of liquid cyclohexane (−37·3 kcal/mole)[10] and the heat of formation of liquid 1-hexanol (−92 kcal/mole)[11] The heat change for the reaction is then approximately 14 kcal/mole. The difference between the two is 38 kcal/mole. In order to obtain the strain energy of the bicyclobutane ring, it is necessary to add the strain energy of the cyclobutane ring which remains after the hydration (26 kcal/mole),[12] giving 64 kcal/mole as the strain energy of bicyclobutane.

It is interesting to compare this result with that obtained for bicyclo[2.1.0]pentane. Turner[13] has found the heat of hydrogenation to be −55·1 kcal/mole. The heat of hydrogenation of an unstrained single bond may be calculated from the heats of formation of cyclohexane and n-hexane,[10] and is −10·2 kcal/mole. The difference between these values is the strain energy introduced upon placing a single bond across the cyclopentane ring and is 44·9 kcal/mole. This value must be corrected for the residual strain energy in the cyclopentane ring, 6·5 kcal/mole, giving 51 kcal/mole for the strain energy of bicyclo[2.1.0]pentane.

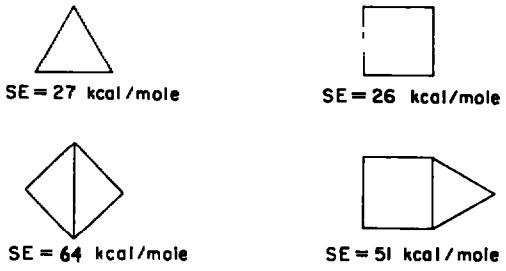
In comparing cyclopropane, cyclobutane and the two bicyclic hydrocarbons: it can be seen that the bicyclopentane has approximately the strain energy of its component parts, whereas bicyclobutane has considerably more than twice the strain energy of cyclopropane.

[10] American Petroleum Institute, Project 44, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons."

[11] *Constants of Organic Compounds* (Edited by M. Kotake) p. 565. Asakura, Tokyo (1963).

[12] Y. I. Gol'dfarb and L. I. Belen'kii, *Usp. Khem.* 214 (1960).

[13] R. B. Turner, *Kekule Symposium* 67 (1958).



Knowing the strain energy, it would now be desirable to determine the state of hybridization of the carbon-hydrogen bonds. Muller and Pritchard[14] suggested that the proton-carbon 13 spin coupling constant might be used as a direct measure of the amount of s-orbital character in the bonds. This criterion has been used by a number of authors, and Foote[15] has shown that there is also a good correlation between the bond angles and the spin coupling constants.

The spin coupling constants obtained for several compounds having bond angle deformation are given in Table 1. It can be seen that for these compounds also, there is a correlation between the angular distortion and the coupling constant. Thus, the latter increases from cyclohexane (123 c/s) to cyclobutane, cyclopropane and the bridgehead hydrogens of bicyclobutane.[16] As might be expected, the values for cyclopropane and the bridgehead position of bicyclo[1.1.1]pentane are about the same.

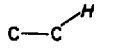
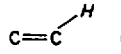
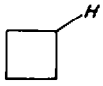
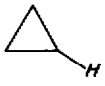
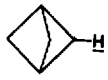
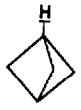
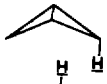
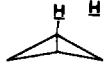
An interesting observation is that the coupling constants for the *exo-* and *endo-*methylene hydrogens of bicyclobutane differ by a substantial amount (18 c/s). If the bicyclobutane ring is considerably puckered, as suggested by Haller and Srinivasan,[17] the two *endo*-hydrogens may be close enough for a repulsive interaction to operate leading to a distortion of the bond angles involving these hydrogens. This may lead to a change in coupling constant via the same mechanism which accounts for the other changes noted in Table 1.

Recently, this criterion for determining the s-character of a bonding orbital has been questioned by Karabatsos and Orzech[18] who pointed out that the contact term was not adequate to explain their observations on the coupling constants for compounds having hetero atoms. Further, Olah *et al.* have found the C^{13}—H coupling constant to increase to as much as 382 c/s in carbonium ions.[19] In the case of hydrocarbons having similar structures, the other contributing terms might be small or relatively constant and the criterion might still be applicable.

It is possible that the criterion is not entirely satisfactory when comparing

[14] N. Muller and D. E. Pritchard, *J. Chem. Phys.* **31**, 768, 1471 (1959).
[15] C. S. Foote, *Tetrahedron Letters* 579 (1963).
[16] The values of the coupling constants for bicyclobutane were given erroneously in a previous paper (Ref. 6*b*). The coupling constants for some tricyclic compounds containing the bicyclobutane ring have been reported by Closs and Larrabee (Ref. 9*m*).
[17] I. Haller and R. Srinivasan, *J. Chem. Phys.* **41**, 2745 (1964).
[18] G. J. Karabatsos and C. E. Orzech, Jr., *J. Amer. Chem. Soc.* **86**, 3574 (1964).
[19] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre and I. J. Bastien, *J. Amer. Chem. Soc.* **86**, 1360 (1964).

TABLE 1. C^{13}-H SPIN–SPIN COUPLING CONSTANTS

Compound	J (c/s)
 (cyclohexane)	123
 (ethylene, benzene)	157
	134
	161
	144
	164
	170
	152
	202

compounds having normal bond angles with those having deformed angles. Bartell[20] has presented good evidence showing that the atoms (or perhaps better, bond orbitals) attached to a given atom give a repulsive interaction with each other. A deformation of bond angles away from one of the atoms (a hydrogen in the above cases) should result in a lower repulsive interaction and a shortening of the bond to that atom. Thus, as the bond angle distortion in the carbon framework is increased, the C—H bond length should decrease and the overlap integral between the carbon and hydrogen atomic orbitals should increase.[21] This should also result in an increase in the C^{13}—H coupling constant. Thus, although the bond deformation-coupling constant correlation is fairly well established, a further *quantitative* correlation with s-character appears premature.

It would be of interest to compare the C^{13}—H coupling constants with other

[20] L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960).

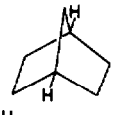
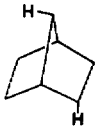
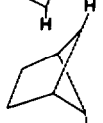
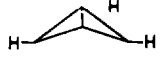
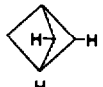
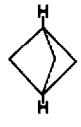
[21] This would be in accord with the reduced C—H bond length and apparent increased C—H bond dissociation energy in cyclopropane and related compounds.

phenomena that are sensitive to hybridization, such as the pK_a's of amines and of acids. 1-Aminobicyclobutane is of particular interest since the amines are more sensitive to electronic effects than are carboxylic acids. Although a number of attempts have been made to obtain the amine, these have not as yet been successful.

Methyl bicyclo[1.1.0]butane-1-carboxylate could be hydrolyzed to the anion of the acid with aqueous sodium hydroxide. Using deuterium oxide as the solvent, the anion was found to be quite stable in solution as indicated by the NMR spectrum. The basic solution was quickly acidified to pH4 and the NMR spectrum was studied as a function of time. After 5 min, a definite change was noted and after 15 min, none of the bands of the acid were found. The rapid hydration of the acid precluded its isolation.

The p*Ka* was determined via rapid titration using a pH recording titrator. After calibration with sodium acetate the pH at half neutralization for bicyclobutane-1-carboxylate was 4·53 ± 0·10. This value of pK is in good agreement with the value 4·6 reported for tricyclo[4.1.0.$0^{2,7}$]heptane-1-carboxylic acid,[22] and is significantly lower than that for cyclopropanecarboxylic acid (4·82).[23] The result is in agreement

TABLE 2. LONG RANGE PROTON SPIN–SPIN COUPLING CONSTANTS

Compound, protons	J (c/s)	Ref.
	1·5	24
	3-4	25
	7	26
	10	
	10	
	18	

[22] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.* **85**, 2022 (1963).
[23] M. Kilpatrick and J. G. Morse, *J. Amer. Chem. Soc.* **75**, 1854 (1953).
[24] R. W. King and P. E. Butler, 142*nd National Meeting*, *ACS*, Atlantic City, September (1962); Abstracts p. 84Q.
[25] J. Meinwald and Y. C. Meinwald, *J. Amer. Chem. Soc.* **85**, 2514 (1963).
[26] J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.* **83**, 2769 (1961); K. B. Wiberg, B. R. Lowry and B. J. Nist, *Ibid.* **84**, 1594 (1962).

with an increased amount of s-orbital character at the bridgehead position of bicyclobutane.

While considering NMR spectroscopy, the long range proton-proton spin coupling observed with the above compounds is of interest. Our data and those for some related compounds are summarized in Table 2. It can be seen that there is a qualitative increase in the coupling constant with a decrease in the distance between the carbons involved.

Unfortunately, the precise geometry of these compounds is not available and therefore a more quantitative treatment is premature. Making some estimates of geometry, we have observed a fair correlation between the coupling constant and the product of the C—C distance and the cosine of the angle between the two C—H bond orbitals. This will be considered in more detail later when the structural information and the coupling constants for a wider variety of compounds becomes available.[27] It is interesting to note that the long range coupling constant between the methylene protons of bicyclo[1.1.0]butane is that for bicyclo[1.1.1]pentane. In the latter, each cyclobutane ring is bent 60°, and the value for bicyclobutane based on the coupling constant should be about the same. This is in good agreement with the results of Haller and Srinivasan.[17]

As will be indicated later, bicyclobutane derivatives exhibit some properties similar to those of the corresponding alkenes. Therefore, the question of whether the bonds in the ring may interact with other unsaturated centers in electronically excited states is of interest. The UV spectrum of methyl 3-methylbicyclobutane-1-carboxylate is compared with that of methyl cyclopropanecarboxylate in Fig. 1. The remarkable increase in extinction coefficient to 7000 which is similar to that of an unsaturated ester ($\lambda_{max} = 208$ $\epsilon = 12{,}500$) indicates that this type of interaction is important.

It is not easily possible to determine from the spectrum which of the ring bonds is primarily responsible for the interaction. A suggestion may be given by the observation that when the ester is irradiated in pentane solution, a reduction product, methyl 3-methylcyclobutanecarboxylate, is obtained. The simplest hypothesis is that the central bond is involved in the photoexcitation.

3. REACTIONS OF THE CENTRAL BOND

One of the most interesting questions which may be asked concerning bicyclobutane is, "what are the relative bond dissociation energies of the central and side bonds?" It is difficult to make an apriori argument concerning this question. On one hand, cleavage of the central bond leads to a di-secondary radical whereas cleavage of the side bond would lead to a primary and a cyclopropyl radical which would probably be less favorable. On the other hand, cleavage of the central bond places two trigonal centers 1, 3 in the cyclobutane ring whereas only one trigonal center would be introduced into the cyclopropane ring if a side bond were cleaved.

[27] The structures of bicyclo[1.1.0]butane, bicyclo[1.1.1]pentane, bicyclo[2.1.1]hexane and norbornane are being determined in other laboratories via electron diffraction studies.

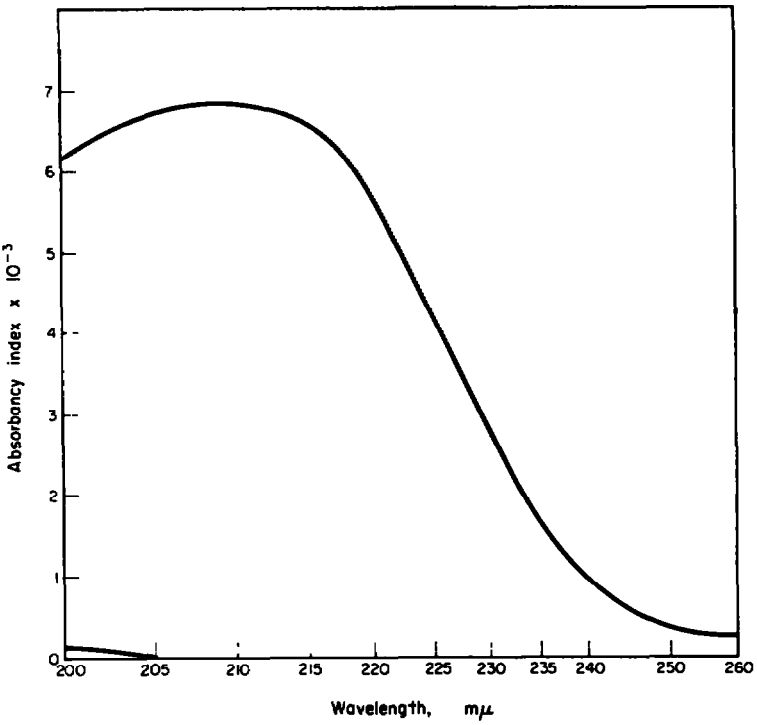
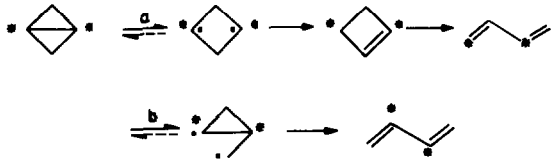


FIG. 1. Ultraviolet spectra of methyl 3-methylbicyclo[1.1.0]butane-1-carboxylate (upper curve) and methyl cyclopropanecarboxylate (lower curve).

Either mode of cleavage would leave a cyclopropyl or cyclobutyl ring and the strain energies of the two rings, in the absence of trigonal centers, are essentially the same. A possible way in which to gain information on this problem is to examine the thermal rearrangement of bicyclobutane.

The thermal rearrangement occurs at temperatures in the vicinity of 200° and gives only butadiene. The latter may be formed either directly or by a path involving cyclobutene as an intermediate. The thermal decomposition of cyclobutene to butadiene occurs at a significantly lower temperature (130–180°)[28] than the decomposition of bicyclobutane.



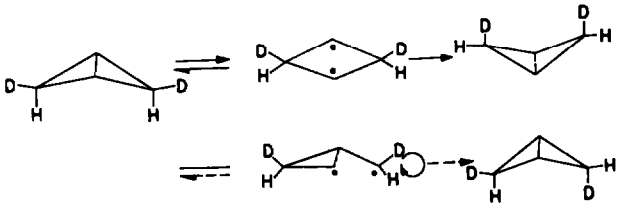
Two observations indicate that path a is not operative. Mahler[9b] has shown that perfluoro-1,3-dimethylbicyclobutane undergoes thermal isomerization to perfluoro-2, 3-dimethylbutadiene, and Doering and Coburn[9c] have shown that 1,3-dimethylbicyclobutane is converted to 2,3-dimethylbutadiene. It can be seen from the scheme

[28] W. Cooper and W. D. Walters, *J. Amer. Chem. Soc.* **80**, 4220 (1958).

given above that if cyclobutene were the intermediate, 1, 3-disubstituted butadienes should have been formed. Further, methyl substitution would probably assist path a more than path b, and thus methyl substitution should not decrease the validity of the argument as far as bicyclobutane itself is concerned. The reaction then appears to be the reverse of the photochemical ring closure observed by Srinivasan.[9c]

These data suggest that the side bond has a lower dissociation energy than the central bond. However, the conversion of the 1,3-diradical intermediate to cyclobutene requires a hydrogen migration. In the corresponding rearrangement of cyclopropane to propylene, the hydrogen migration is slower than the closure of the diradical-like intermediate.[29] If hydrogen migration to give cyclobutene were considerably slower than the recombination of the 1,3-diradical intermediate, the latter could be formed more rapidly than the cyclopropylcarbinyl diradical with essentially all of the product arising from the cyclopropylcarbinyl diradical.

A test of this possibility might be found in the thermal decomposition of *cis*-2,4-dideuterobicyclobutane. If the 1,3-diradical were formed and recombined to bicyclobutane, one would anticipate pair-wise exchange of hydrogen and deuterium. If the cyclopropylcarbinyl diradical were formed, it probably would go directly to butadiene. However, if it returned in part to bicyclobutane, one would anticipate *cis-trans* interconversion:



An examination of the type of geometrical isomerization as a function of temperature should indicate the nature of the reaction. An experiment of this type is presently being attempted.

Bicyclobutane and most of its derivatives readily undergo hydration in dilute acid solution. Using 0·0001N sulfuric acid, the rate of hydration of bicyclobutane was found to be 535 ml/hr/5 ml acid solution,[30] and the products were found to be cyclobutanol (55%) and cyclopropylcarbinol (45%). The ratio of products corresponds closely to that found by Roberts and Mazur[31] in the deamination of cyclobutylamine or of cyclopropylcarbinylamine and suggests that the hydration proceeds via a bicyclobutonium ion.

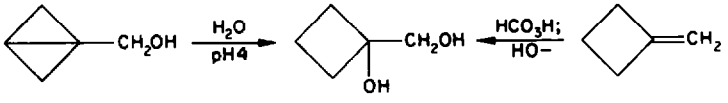
The rate of acid catalyzed hydration of cyclopropane to 1-propanol has been determined in 50–60% sulfuric acid by Baird and Aboderin[32] and has been found approximately to follow H_0. Making this assumption, the rate constant expected for pH4($H_0 = -4$) was $6{\cdot}0 \times 10^{-8}$ in the same units as above. Thus, bicyclobutane is approximately 10^{10} as reactive as cyclopropane.

[29] B. S. Rabinovitch, E. W. Schlag and K. B. Wiberg, *J. Chem. Phys.* **28**, 504 (1958).
[30] We wish to thank Dr. Richard Baird for his assistance in making this measurement.
[31] J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.* **73**, 2509 (1951).
[32] R. L. Baird and A. A. Aboderin, *J. Amer. Chem. Soc.* **86**, 252 (1964).

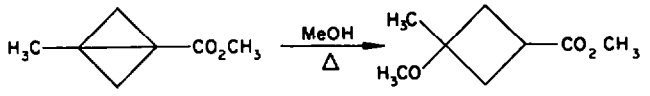
It is interesting to compare the ease of hydration of bicyclo[1.1.0]butane and bicyclo[2.1.0]pentane. The relief of strain in opening the bicyclobutane ring to a cyclopropane or cyclobutane derivative is 64–27 or 37 kcal/mole. The corresponding value for bicyclo[2.1.0]pentane giving a cyclopentane derivative is 51–6·5 or 45 kcal/mole. Thus if the overall energy change were the important factor, bicyclo[2.1.0]-pentane would be expected to be more reactive than bicyclobutane.

Whereas the bicyclobutanes are extraordinarily labile toward acid, the bicyclo-[2.1.0]pentanes are relatively unreactive. For example, LaLonde and Forney[33] found that bicyclo[2.1.0]pentane reacted only partially with glacial acetic acid at 47° for 24 hr. Bicyclobutane appears to react completely with glacial acetic acid at 25° in less than an hour. Thus, bicyclobutane is the more reactive of the two by a factor of 200 or more. It can be seen that the difference in strain relief is not reflected in the relative rates of reaction. The simplest conclusion is that bicyclobutane may give a particularly well stabilized ion on protonation (presumably the bicyclobutonium ion) whereas bicyclopentane can give no such ion.

The reaction of bicyclobutane-1-methanol with dilute acid (pH4) occurs almost instantaneously and leads to 1-hydroxycyclobutanemethanol, identical with the product derived by the hydroxylation of methylenecyclobutane.[34] The hydration of the central bond then follows Markownikoff's rule. The reaction was also carried out in deuterium oxide, and presumably the stereochemistry of the reaction could be determined from the NMR spectrum of the deuterium labeled product. However, this involves a detailed analysis of the spectrum which is not as yet available.



As might be expected the addition of alcohols across the bicyclobutane central bond is also facile. As an example, the addition of methanol across the bond in 3-methylbicyclobutane-1-carboxylate gave one of the two isomeric 3-methyl-3-methoxycyclobutane-1-carboxylates: The same compound was obtained by the acid catalyzed addition of methanol to methyl 3-methylenecyclobutane-1-carboxylate.



This reaction gave two isomers in the ratio 16:9. The product from the addition of methanol to the bicyclobutane ester corresponded to the isomer formed in larger amount in the above reaction. The stereospecificity of the addition to the bicyclo-butane ester is interesting, and an attempt is being made to determine whether it corresponds to a *cis*- or *trans*- addition.

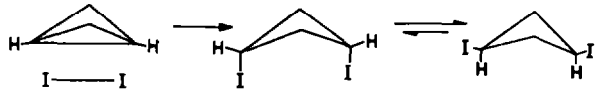
Bicyclobutane reacts readily with iodine in carbon tetrachloride leading to a mixture of the *cis*- and *trans*-1,3-diiodocyclobutanes. The configurational assignment

[33] R. T. LaLonde and L. S. Forney, *J. Amer. Chem. Soc.* **85**, 3767 (1963).
[34] J. D. Roberts and C. W. Sauer, *J. Amer. Chem. Soc.* **71**, 3925 (1949).

was based on the NMR spectra. One isomer was found to have a very simple spectrum: a high field triplet corresponding to four protons and a low field pentuplet corresponding to two protons. This must be the *trans*-isomer which presumably undergoes a rapid conformational flip leading to a spectrum corresponding to a planar structure. The other isomer must then be *cis*.

When an excess of iodine was avoided in the reaction, the product composition was 82·3% *cis*- and 17·6% *trans*- as compared to the equilibrium ratio of 63% *cis*- and 37% *trans*.[35] Iodine was shown to effect equilibration of the isomers, and thus it seems reasonable to assume that essentially all of the initially formed diiodide had the *cis*-configuration. It might be noted that *cis*-addition of iodine has also been found with 1,3-dimethylbicyclobutane.[9c] If a two step addition process were involved, such as one initiated by the addition of an iodine atom to the ring, the *cis*-product would not be expected to be found in larger amount than at equilibrium. It is known that the cyclobutane ring prefers to be planar when a trigonal center is introduced;[36] the product of the addition of an iodine atom should therefore be planar and the *trans*-diiodide would be expected to predominate on steric grounds.

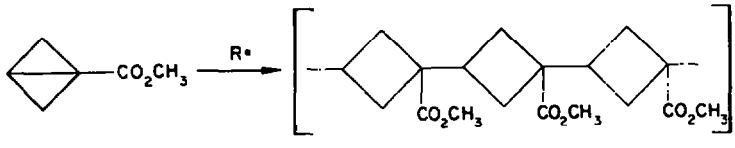
It is difficult to see how the *cis*-stereochemistry could be accounted for by other than a four-center mechanism, similar to that operative in the hydrogen-iodine reaction.[37] The predominant conformation of the *cis*-isomer has been found to be bis-pseudo-equatorial.[35]



In the addition of bromine, the product consisted of 44% *cis*- and 19% *trans*-1-.3 dibromocyclobutane, along with a cyclopropane derivative (as shown by the NMR spectrum) and an olefin in about equal amount.

The addition of chlorine was effected in the gas phase rather than in solution, and here, none of the 1,3-dichlorocyclobutane was found. Instead NMR spectrum of the product suggested that it was 2-chlorocyclopropanemethyl chloride. The data indicate that both bromine and chlorine react via different paths than does iodine, but the details of these paths require further investigation.

A facile reaction of methyl bicyclobutane-1-carboxylate is polymerization. In the absence of a free radical inhibitor, polymerization occurs readily leading to a polymer resembling a polyacrylate. The NMR spectrum showed a broad absorption centered



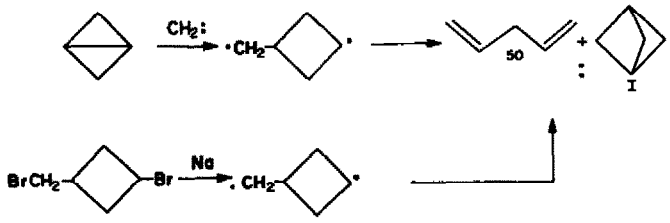
around 7·9τ and indicated neither olefinic protons or C-methyl protons. The structural inference is that the polymerization involved the central bond: The polymerization is presumably a free radical chain process since inhibitors such as t-butylcatechol

[35] The data on the equilibrium of the 1,3-dihalides will be presented separately.
[36] A. Bander, F. Tank and H. H. Günthard, *Helv. Chim. Acta* **46**, 1453 (1963).
[37] M. Bodenstein, *Z. Phys. Chem.* **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899).

effectively prevent the reaction. The facile polymerization noted with the above ester is not found either with methyl 3-methylbicyclobutane-1-carboxylate or with bicyclobutane itself.

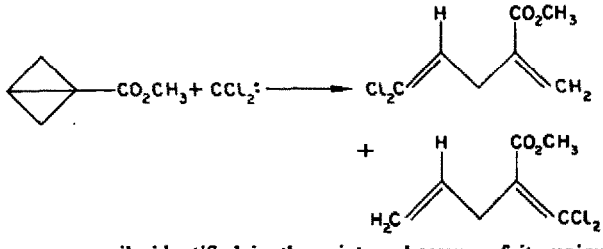
In view of the relatively high reactivity of the central bond, it seemed possible that an insertion of methylene into such a bond could be effected. Doering and Coburn[9c] attempted such a reaction using 1,3-dimethylbicyclobutane, and observed the main product to be 2,4-dimethyl-1,4-pentadiene. No bicyclo[1.1.1]pentane derivatives were formed, and via deuterium tracer experiments, they showed that bicyclo[1.1.1]pentane was not an intermediate.

An attempt was made to insert methylene into bicyclobutane itself in decalin solution at −50°. The majority of the material (80%) had a vpc retention time using a β,β′-oxodipropionitrile column which corresponded to 1,4-pentadiene, bicyclo[1.1.0]butane and bicyclo[1.1.1]pentane. Due to inadequate resolution, the analysis of the mixture was effected using the NMR spectrum and shown to consist of 21% 1,4 pentadiene, 25% dimethyl ether, 7% of an unknown compound with a sharp singlet at 7·03τ, 11% of unidentified compounds which probably included methyl substituted bicyclobutanes, 35% starting material and ~1% bicyclo[1.1.1]-pentane.[37a]



A possible interpretation of the reaction course involves a two step reaction with methylene, giving first a diradical intermediate. In view of the low yield of bicyclopentane obtained in the reaction of 3-bromocyclobutane-1-methyl bromide with sodium,[5] it is reasonable to believe that the resultant diradical would prefer fragmentation to 1,4-pentadiene over closure to bicyclo[1.1.1]pentane.

The reaction of methylene with methyl bicyclobutane-1-carboxylate was not successful, but the reaction with dichlorocarbene did lead to isolable products. The NMR spectrum indicated the presence of olefinic hydrogen and analysis indicated the presence of two chlorines. A comparison of the NMR spectra with those of methyl methacrylate and several allyl derivatives indicated that the compounds were the two possible dichlorodiolefinic esters derived by a reaction similar to the methylene reaction with bicyclobutane:



[37a] The bicyclopentane was easily identified in the mixture because of its unique NMR spectrum consisting of two sharp singlets.[5]

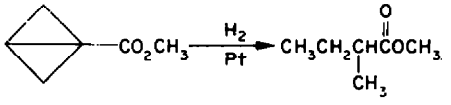
The addition of an oxygen across the central bond was also attempted using *m*-chloroperbenzoic acid. No consumption of the peroxyacid was obtained using methyl bicyclobutane-1-carboxylate. Some of the ester was recovered unchanged, and the rest was in the form of a polymer.

Although the addition of a one atom fragment across the central bond did not prove too successful, it still appeared desirable to attempt the addition of a two carbon fragment in a cycloaddition type reaction. The first attempts involved the thermal addition of ethylene to methyl 3-methylbicyclobutane-1-carboxylate for here, the parent of one of the expected products, methyl bicyclo[2.1.1]hexane-1-carboxylate, is known.[38] The major part of the reaction appeared, however, to involve the thermal cleavage of the starting ester to a substituted butadiene and no cycloaddition product was obtained. Similar results were obtained with other alkenes.

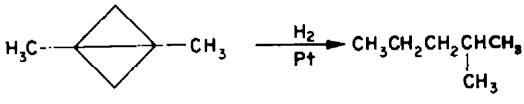
When the more reactive tetracyanoethylene was used, a color was developed immediately at room temperature. Attempts to isolate pure compounds from the reaction mixture have not as yet proven successful. The reaction with other reagents such as N-phenylmaleimide was also not successful.

The relatively strong UV absorption band for the ester suggested the possibility of a photochemically induced cycloaddition reaction. The photolysis of methyl 3-methylbicyclobutane-1-carboxylate in pentane solution was studied first. Here, the major product was methyl 3-methylcyclobutane-1-carboxylate, suggesting that the 1,3-diradical had been formed in the photochemical process, and that hydrogen abstraction from the solvent occurred. An attempt to effect the photolysis in the presence of ethylene failed, and it appeared that ethylene had been polymerized. When substituted alkenes (acetylenedicarboxylic ester, etc.) were used, it appeared that they utilized most of the light quanta and effectively protected the bicyclobutane ester against photodecomposition.

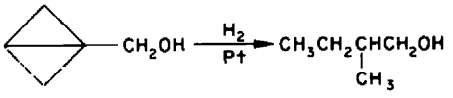
Hydrogenation of bicyclobutane derivatives invariably leads to products in which two moles of hydrogen have been incorporated:



(6a)



(9c)



The entire reaction must occur at the catalyst surface without desorption of any intermediate because both the cyclobutane and cyclopropane derivatives which might be formed would be resistant to hydrogenation under the conditions used. The hydrogenation results in the cleavage of the central bond and one of the side bonds, but it is not possible to tell from the available data which bond is cleaved first.

[38] K. B. Wiberg and B. R. Lowry, *J. Amer. Chem. Soc.* **85**, 3188 (1963).

4. REACTIONS AT THE BRIDGEHEAD

One of the most readily prepared bridgehead substituted derivatives of bicyclobutane is bicyclobutane- 1-methanol. This is formed by the reduction of the bridgehead substituted ester with LAH, and it may be isolated without difficulty provided that mixtures containing it never become acidic.

The use of triphenylphosphite and benzyl bromide has been successful in the conversion of a number of reactive alcohols to their bromides.[39] We have found it useful for the conversion of cyclopropylcarbinol to the bromide without rearrangement to cyclobutyl or allyl carbinyl bromides. When bicyclobutane-1-methanol was treated with this reagent, only 3-methylenecyclobutyl bromide was obtained. This is presumably formed via the ionization of the phosphorus containing intermediate followed by attack of bromide ion at the other side of the cyclobutane ring.

An attempt was made to prepare the corresponding tosylate using methods which have been found to be successful with other highly reactive tosylates. In each case, the only product was 3-methylenecyclobutyl tosylate. This was identified by comparison with a sample prepared from authentic 3-methylenecyclobutanol.[40] It would appear that the bridgehead methyl tosylate is remarkably reactive. The high reactivity probably results from the relief of 38 kcal of strain in going to the ring opened product.

The less reactive *p*-nitrobenzoate was prepared without difficulty. In the solvolysis of this ester in aqueous acetone, it was observed that the infinity titer corresponded to only a few percent reaction. The major product was shown to result from the hydration of the central bond, presumably catalyzed by the *p*-nitrobenzoic acid formed in the solvolysis. When an attempt was made to suppress hydration by adding a weak base, hydrolysis of the ester with carbonyl–oxygen bond cleavage became important.

A rough estimate of the rate of solvolysis could be made from the initial titrimetric points (Fig. 2). The value, 3×10^{-4} sec^{-1}, is 1000 times greater than the rate of reaction of cyclopropanemethyl *p*-nitrobenzoate. However, the majority of the latter reaction proceeds via carbonyl–oxygen cleavage, and thus the factor of 1000 is the lower limit to the increase in rate of ionization produced by going from a cyclopropane to a bicyclobutane derivative.

Attempts were made to prepare the bridgehead amide via the reaction of the bridgehead ester with ammonia. These reactions invariably failed and led to polymeric materials. The nature of the products of reaction with ammonia and with hydrazine suggest an addition of the amine across the central bond followed by other reactions such as amide formation which would lead to a polymer.

EXPERIMENTAL

Diisoamyl 3-benzyloxycyclobutane-1,1-dicarboxylate. To a hot solution of 75·9 g (3·3 g atoms) Na in 3 l. isoamyl alcohol was slowly added 720 g (4·5 moles) diethyl malonate. The condenser was replaced with a partial take-off, total reflux distilling head, and the solution was brought to the reflux temp. A mixture of isoamyl alcohol and EtOH was removed by distillation during the course of adding 396 g (1·5 mole) 1-bromo-2-benzyloxy-3-chloro-propane[41] (1·5 hr). The solution was maintained at the reflux temp for 14 hr, after which time the bulk of the isoamyl alcohol was distilled. To

[39] I. T. Harrison and B. Lythgoe, *J. Chem. Soc.* 843 (1958).
[40] E. F. Kiefer and J. D. Roberts, *J. Amer. Chem. Soc.* **84**, 784 (1962).
[41] M. Avram, D. D. Nenitzescu and M. Maxim, *Chem. Ber.* **90**, 1424 (1957).

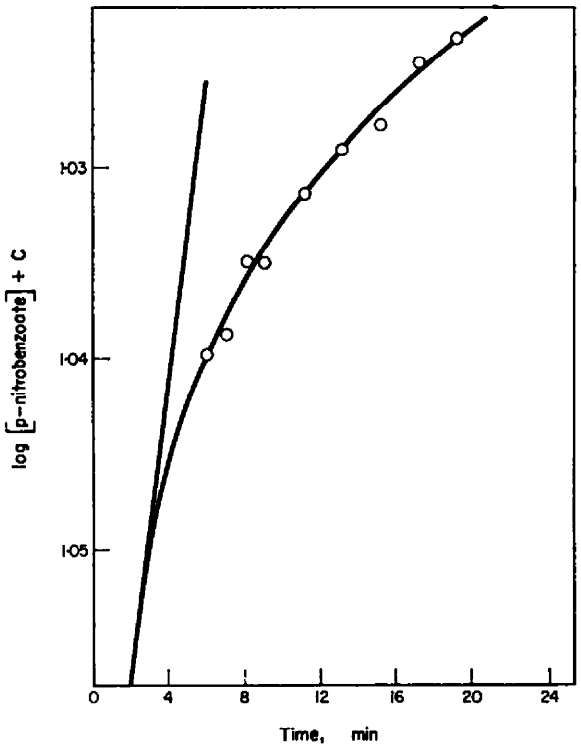


FIG. 2. Solvolysis of bicyclo[1.1.0]butane-1-methyl *p*-nitrobenzoate in 90% acetone at 118·6°.

the cool residue was added 120 ml 10% HCl, making it acidic to litmus, and then 800 ml water to bring the inorganic salts into solution. The organic layer was separated and the aqueous layer was extracted twice with ether. The organic layer and ether extracts were combined, dried over $MgSO_4$, and distilled giving 387 g (66%) of diisoamyl 3-benzyloxycyclobutane-1,1-dicarboxylate, b.p. 218–224° at 2–3 mm.

3-Benzyloxycyclobutanecarboxylic acid. To a solution of 180 g KOH in 350 ml 95% EtOH and 50 ml water was slowly added with cooling 260 g (0·666 mole) diisoamyl 3-benzyloxycyclobutane-1,1-dicarboxylate. The mixture was heated to reflux for 1·5 hr and then most of the solvent was removed under red. press. using a rotary evaporator. The residue was dissolved in water and extracted twice with 500 ml portions ether. The ether was removed and the residue was heated at 180° and 15 mm press. to effect decarboxylation. When the press. dropped, distillation gave 120 g (88%) of benzyloxycyclobutanecarboxylic acid, b.p. 146–150° at 0·1 mm.

Methyl 3-benzyloxycyclobutanecarboxylate. To a solution of 289·5 g (1·4 moles) 3-benzyloxycyclobutanecarboxylic acid, 134·4 g (4·2 moles) MeOH and 420 ml ethylene dichloride was added 4·2 ml conc. H_2SO_4. The resultant solution was heated to reflux for 16 hr. The cooled reaction mixture was washed with water, with 5% Na_2CO_3 aq, and again with water. After drying over anhydrous Na_2SO_4, distillation gave 264 g (86%) methyl 3-benzyloxycyclobutanecarboxylate, b.p. 137–145° at 2·3 mm. The NMR spectrum[42] showed bands at τ = 7·66 (m, 4), 7·10 (m, 1), 6·42 (s, 3), 6·00 (m, 1), 5·66 (s, 2), 2·75 (s, 5).

Methyl 3-hydroxycyclobutanecarboxylate. A solution of 65 g methyl 3-benzyloxycyclobutanecarboxylate in 125 ml MeOH was shaken with Pd-black (prepared from 0·5 g $PdCl_4$) under 4 atm. H_2

[42] Throughout this section the letters following the band position gives the type (s = singlet, d = doublet, m = incompletely resolved multiplet) and the number gives the relative integrated area.

for 30 hr. After filtration, distillation gave 33·8 g (89%) methyl 3-hydroxycyclobutanecarboxylate b.p. 87–93° at 2·4–2·5 mm. The NMR spectrum showed bands at τ = 7·65 (m, 4), 7·08 (m, 1), 6·37 (s, 3), 5·80 (m, 1) 5·65 (s, 1). Except for the bands due to the alkyl part of the ester group, the spectrum was the same as that of the ethyl ester prepared by Avram *et al.*[41]

3-Carbomethoxycyclobutyl benzenesulfonate. A mixture of 33·8 g (0·26 mole) methyl 3-hydroxycyclobutanecarboxylate and 44·0 g (0·25 mole) benzenesulfonyl chloride cooled in ice water was treated with 20 ml pyridine which had been dried over KOH. After standing in a refrigerator for 20 hr, 30 ml water was added, and the oil which separated was taken up in ether. The aqueous layer was extracted with ether; the organic layers were combined and washed with water, with 10% HCl aq, with 10% Na_2CO_3 aq and with water. After drying over $MgSO_4$, distillation gave 65·8 g (98%) of carbomethoxycyclobutane benzenesulfonate as a viscous oil.

Methyl 3-bromocyclobutanecarboxylate. Lithium bromide (80 g) was dried by heating to fusion. To the salt (78·7 g) was added 275 ml dry acetone and 108 g (0·40 mole) 3-carbomethoxycyclobutyl benzenesulfonate. After heating to reflux for 42 hr, most of the acetone was removed by distillation and the residue was diluted with water. The organic phase was separated and the aqueous layer was extracted with ether. The combined organic layers were dried over $MgSO_4$ and distilled giving 61·8 g (80%) of methyl 3-bromocyclobutanecarboxylate, b.p. 82–87° at 11 mm. An analysis by VPC using a diethylene glycol succinate column indicated nearly equal portions of the *cis* and *trans*-isomers; except for the ester bands, the NMR spectrum was the same as that of the ethyl ester prepared previously, for which good analytical data were obtained.[6a]

Methyl bicyclo[1.1.0]butane-1-carboxylate. To a stirred mixture of 10·1 g 52% NaH dispersion in oil, 280 ml anhydrous ether and a few mg 4-t-butylcatechol which was kept under N_2 was added 30·0 g (0·156 mole) methyl 3-bromocyclobutanecarboxylate. A granular precipitate was immediately formed and H_2 was evolved. The mixture was stirred at room temp for 3·5 days during which time a gelatinous material replaced the granular precipitate first formed. The solution was filtered and the solids were washed with dry ether. Distillation of the combined ether solution gave 13·3 g (77%) methyl bicyclo[1.1.0]butane-1-carboxylate, b.p. 39–42° at 12 mm. Except for the ester bands, the NMR spectrum was the same as that for the ethyl ester reported previously.[6a] A small amount of t-butyl catechol was added to retard polymerization. If the reaction time were decreased to 20 hr, 49% of the desired ester and 21% of starting material was isolated.

The iodo ester gave a comparable yield of the bicyclic ester. However, neither the chloroester nor the benzenesulfonate gave significant amounts of the ester, and considerable unreacted starting material was isolated in each case.

Bicyclo[1.1.0]butane-1-methanol. To 1·9 g (0·05 mole) LAH in 45 ml anhydrous ether was added dropwise with stirring 6·18 g (0·0552 mole) methyl bicyclo[1.1.0]butane-1-carboxylate in 20 ml anhydrous ether. The addition required 45 min and the solution was cooled with an ice bath. After stirring for 1·5 hr at room temp, the solution was cooled in ice and 10 ml 30% Rochelle salt solution was added dropwise. The ether solution was filtered and the solid was washed with 3 portions ether. The combined ether solution was dried over $MgSO_4$ and the ether was removed by distillation. The residue was distilled rapidly to avoid polymerization and gave 3·0 g (65%) bicyclo[1.1.0]butane-1-methanol, b.p. 46–49° at 10 mm. It slowly polymerized on standing at room temp, but at a lower temp with t-butyl catechol added it was stable indefinitely. The NMR spectrum shows bands at τ = 9·32 (s, 2), 8·72 (m, 1), 8·42 (d, 2), 6·03 (d, 2) and 5·31 (t, 1).

Hydrogenation using a Pt catalyst led to the uptake of 1·64 moles H_2 per mole alcohol. Only 2-methyl-1-butanol, identified by comparison with an authentic sample, was isolated from the reaction mixture.

Bicyclo[1.1.0]butane-1-methyl p-nitrobenzoate. To a solution of 2·15 g (25·6 mmoles) bicyclo-[1.1.0]butane-1-methanol in 100 ml dry ether was added 3·1 g (129 mmoles) NaH. The solution was stirred for 10·5 hr. More ether was added and 5·25 g (28·3 mmoles) *p*-nitrobenzoyl chloride was added in portions over a 1 hr period at 0°. The mixture was stirred at room temp for 2·5 hr. To the cooled mixture was added water, and the ether layer separated. After washing the ether layer with 3 portions 5% $NaHCO_3$ aq and with water, it was dried over Na_2SO_4 and concentrated using a rotary evaporator giving 4·16 g of an oil. Pet. ether was added, the mixture was heated to reflux and the solution was decanted from insoluble material. This was repeated several times leaving 1·3 g insoluble oil which was discarded. The pet. ether extracts were concentrated, cooled in ice, and after

scratching the sides of the vessel, 1·5 g *p*-nitrobenzoate was obtained as small yellow plates, m.p. 47·0–48·0°. Concentration of the mother liquor gave an additional 0·4 g, m.p. 45·2–46·8°. Recrystallization from pet. ether raised the m.p. to 48·0–48·6°. (Found: C, 61·6; H, 4·7; N, 6·1. Calc. for $C_{12}H_{11}O_4N$: C, 61·8; H, 4·8; N, 6·0%.)

The NMR spectrum showed bands at τ = 9·13 (s, 2), 8·49 (m, 1), 8·26 (d, 2), 5·20 (s, 2) and 1·77 (s, 4) which is consistent with the assigned structure. The material could be stored at −18° with little decomposition but at room temp, after 3 days the crystals became oily. A sample in CCl_4 in a degassed NMR tube was found to be unchanged after heating at 119° for 10 hr.

When the preparation of the ester was attempted using pyridine as the solvent, the *p*-nitrobenzoate was contaminated with a chlorine containing compound whose NMR spectrum suggested that HCl had added across the central bond.

Reaction of bicyclo[1.1.0]*butane-1-methanol with* p-*toluenesulfonyl chloride.* To a solution of 0·5 g (6·0 mmoles) bicyclo[1.1.0]butane-1-methanol in 45 ml anhydrous ether which had been cooled to −6° in an ice-salt bath was added with stirring 1·13 g (6·0 mmoles) *p*-toluenesulfonyl chloride. To the stirred, cooled solution was then added 0·95 g powdered KOH in portions over 1 hr, maintaining the temp at −6 to −3°. After stirring for 45 min at −6°, the flask was stoppered and placed in a freezer at −18° for 3·5 hr. Ice and ice water were added to the mixture, the layers were quickly separated and the aqueous layer was extracted with cold ether (1°). The ether layers were combined (5°), dried over $MgSO_4$ for 0·5 hr at −18°, and concentrated using a rotary evaporator with the flask kept in ice-bath. The oily residue was immediately dissolved in CCl_4 and the NMR spectrum taken. In addition to ether, there were bands at τ = 7·60 (s, 3), 7·20 (m, 4), 5·20 (m, 3) and 2·46 (q, 4). The spectrum was identical with that of an authentic sample of 3-methylenecyclobutyl *p*-toluenesulfonate.

The procedure used by Fang *et al.*[48] in which the alkoxide is first prepared using NaH in ether was also tried, but again only 3-methylenecyclobutyl *p*-toluenesulfonate (56%) was isolated.

Reaction of bicyclo[1.1.0]*butane-1-methanol with triphenyl phosphite and benzyl bromide.* The reaction of triphenyl phosphite with benzyl bromide was effected by the procedure of Harrison and Lythgoe. To a 100 ml 3-necked flask was added 5·9 g (0·0122 mole) of the product of the above reaction and the apparatus was set up for vacuum distillation of the volatile products into a dry ice-acetone cooled trap. Then was added 0·82 g (0·0098 mole) bicyclo[1.1.0]butane-1-methanol, and the flask was heated to 100° with stirring under red. press. (42 mm). There was obtained 0·23 g (16%) 3-methylenecyclobutyl bromide, identified by comparison with an authentic sample.[40]

Under the same conditions, cyclopropylcarbinol was converted to cyclopropylcarbinyl bromide in 69% yield.

Reaction of methyl bicyclo[1.1.0]*butane-1-carboxylate with dichlorocarbene.* A solution of 4·2 g (0·038 mole) methyl bicyclobutane-1-carboxylate and 12 ml $CHCl_3$ in 50 ml pentane was cooled to −15° using a dry ice-acetone bath. With stirring, 5·5 g (0·049 mole) sublimed potassium t-butoxide was added in small portions over a 3 hr period, maintaining the temp at −15°. Stirring was continued for 4 hr while the cooling bath came to room temp. Enough water was added to dissolve the inorganic salts. The layers were separated and the aqueous layer was extracted with pentane. The combined organic solution was dried over $MgSO_4$ and distilled giving 2·9 g unchanged reactant and a second fraction b.p. 55–59° at 0·5 mm.

VPC (XF-1150 column) showed the material to consist of 2 components in equal amount. They were separated by preparative VPC. Both gave positive tests for Cl_2 and were unsaturated to Br_2.

The NMR spectrum of the compound with the shorter retention time had bands at τ = 6·75 (d, 2) 6·24 (s, 3); 5·03 (m, 1); 4·80 (m, 1) and 4·30 (m, 1). The vinyl proton bands are similar to those of diallyl ether (τ = 4·83 (m, 1); 4·75 (m, 1); 4·12 (m, 1)) and other compounds containing the allyl group. (Found: C, 43·1; H, 4·1; Cl, 36·2. Calc. for $C_7H_8Cl_2O_2$: C, 43·1; H, 4·1; Cl, 36·3%.)

The NMR spectrum of the second compound had bands at τ = 6·84 (d, 2); 6·25 (s, 3); 4·36 (m, 1); 4·03 (t, 1) and 3·80 (m, 1). The bands at τ = 4·36 and 3·80 have the same coupling pattern as those for methyl methacrylate. (Found: C, 43·1; H, 4·2; Cl, 36·3. Calc. for $C_7H_8Cl_2O_2$: C, 43·1; H, 4·1; Cl, 36·3%.)

The data indicate the isomeric compounds to be methyl 1,1-dichloro-1,4-pentadiene-2-carboxylate and methyl 1,1-dichloro-1,4-pentadiene-4-carboxylate respectively. The IR spectra are also in accord with these structures. The total yield of the two isomers was 41%.

[48] F. T. Fang, J. K Koch. and G. S. Hammond, *J. Amer. Chem. Soc.* **80**, 563 (1958).

Reaction of methyl bicyclo[1.1.0]*butane-1-carboxylate with m-chloroperbenzoic acid.* To a solution of 1·2 g methyl bicyclo[1.1.0]butane-1-carboxylate in 20 ml $CHCl_3$ was added with stirring a solution of 3·1 g 85% *m*-chloroperbenzoic acid in 50 ml $CHCl_3$. The solution was heated to reflux for 2·5 hr under N_2 and cooled to room temp. No peroxyacid was consumed in this process. The solution was treated with 10% Na_2SO_3 aq. The organic layer was separated, washed with 10% Na_2CO_3 aq, and dried over Na_2SO_4. Distillation gave a small amount of unchanged reactant and left a viscous polymer.

Reaction of methyl bicyclo[1.1.0]*butane-1-carboxylate with tetracyanoethylene.* A solution of 0·97 g (0·0076 mole) tetracyanoethylene and 1·2 g (0·01 mole) methyl bicyclo[1.1.0]butane-1-carboxylate in 60 ml tetrahydrofuran was stirred under N_2 at room temp. Within a ½ hr, a dark red-brown color developed. After standing for another 2 hr, the solvent was removed under red. press. using a rotary evaporator leaving a dark viscous material. Attempted purification by column chromatography was not successful; the material appeared to decompose on the column. Other methods of purification were also tried, however none proved successful.

1-*Bromo-3-chlorocyclobutane.* In a 1 l. 3-necked flask equipped with a glass stirrer, addition funnel and condenser, and wrapped with Al foil to exclude light, was suspended 36·7 g (0·17 mole) of red HgO in 330 ml CCl_4. To the flask was added 30·0 g (0·222 mole) 3-chlorocyclobutanecarboxylic acid,[44] and the solution was heated to reflux with stirring. A solution of 12·6 ml (0·246 mole) Br_2 in 180 ml CCl_4 was added dropwise over a 7 min period. After a short induction period, CO_2 was evolved at a rate exceeding 200 bubbles per min. The rate of evolution slowed considerably after the Br_2 had been added, and almost stopped after 25 min. After heating for an additional 3 hr, the solution was cooled and filtered. Distillation gave 18·2 g (48%) 1-bromo-3-chlorocyclobutane, b.p. 66–68° at 30–35 mm. Using a carbowax 20 M VPC column, the *cis*- and *trans*-chlorobromides could be separated. The first peak (43%) was the *trans*-isomer as shown by its NMR spectrum: $\tau = 7{\cdot}00$ (t, 4), 5·30 (m, 2). (Found: C, 2·84; H, 3·8; Br, 46·8; Cl, 20·4. Calc. for C_4H_2BrCl: C, 28·4; H, 3·6; Br, 47·2; Cl, 20·9%.)

The third fraction (42%) was the *cis*-isomer, having an NMR spectrum: $\tau = 7{\cdot}00$ (m, 4), 5·87 (m, 2). (Found: C, 28·3; H, 3·7; Br, 47·2; Cl, 21·0. Calc. for C_4H_5BrCl: C, 28·4; H, 3·6; Br, 47·2; Cl, 20·9%.)

The second peak (15%) may be derived from an impurity in the 3-chlorocyclobutanecarboxylic acid.

Reaction of 1-*bromo-3-chlorocyclobutane with zinc* (a) *Without tetrasodium ethylenediaminetetraacetate.* A 50 ml 3-necked flask was equipped with an addition funnel, and a condenser which was connected to dry-ice cooled traps. To the flask was added 7·7 g (0·118 mole) Zn dust, 11·6 ml 95% EtOH and 1·2 ml water. The mixture was brought to reflux and 5·0 g (30 mmoles) 1-bromo-3-chlorocyclobutane was added with stirring over a 5 min period. The solution was heated for 1 hr under reflux. The product in the traps was transferred to a storage vessel using a vacuum line, and the material was gas chromatographed using a 40% nitrobenzene on firebrick column. The products were found to be 1-butene (6·6 min, 5%); 1,3-butadiene (10·4 min, 69%) cyclobutene (12·4 min, 23%) and an unidentified component (8·8 min, 3%). The NMR spectrum showed that no bicyclobutane had been formed.

(b) *With tetrasodium ethylenediaminetetraacetate.* A 500 ml 3-necked flask was equipped as above, and 41·6 g (0·10 mole) tetrasodium ethylenediaminetetraacetate dihydrate, 170 ml 95% EtOH, 75 ml water and 6·45 g (0·10 mole) Zn dust. The solution was brought to reflux and 8·5 g (0·05 mole) 1-bromo-3-chlorocyclobutane was added with stirring over a 10 min period. The solution was heated an additional 8 hr. VPC showed the presence of: 1-butene (47%); 1,3-butadiene (41%); cyclobutene (11%); and the unknown component (1%).

Bicyclo[1.1.0]*butane.* In a 300 ml 3-necked flask equipped as described above was placed 13·6 g (0·59 g atoms) Na and 150 ml dioxan (freshly distilled from the ketyl formed from benzophenone and Na). The dioxan was brought to the reflux temp, and the Na was broken into small pieces by stirring. To the boiling solution was added 20 g (0·118 mole) 1-bromo-3-chlorocyclobutane in 20 ml purified dioxan over a 1 hr period, and heating was continued for an additional 3·75 hr. There was obtained 5·76 g (90%) volatile material. Chromatography on 20% β,β'-oxydipropronitrile on 45/60

[44] W. A. Neville, D. S. Frank and R. D. Trepka, *J. Org. Chem.* **27**, 422 (1962).

chromosorb W showed cyclobutane (2·0 min, 1%); cyclobutene (2·7 min 20%) and bicyclo[1.1.0]-butane (3·8 min, 80%). The amount of cyclobutene varied between 5–20% from run to run, and the recovery after VPC was better than 80%.

The vapor press. of bicyclobutane was determined at 31 temp between −21 and 8°. A plot of log p against 1/T gave a linear relationship from which ΔH_v = 6041 cal/mole. The temp corresponding to a 760 mm vapor press. was 8·3 ± 0·2°.

Addition of halogen to bicyclo[1.1.0]*butane* (a) *Iodine*. To a 300 ml flask, wrapped to exclude light, containing 1·65 g (0·0065 mole) I_2 dissolved in 160 ml CCl_4 was added 0·0065 mole bicyclobutane using a vacuum line. The contents of the flask were warmed to 0° and maintained at this temp for 1·5 hr. The excess I_2 was removed by shaking with $NaHSO_3$ aq. The organic layer was dried over Na_2SO_4 and distilled giving 1·3 g (65%) 1,3-diiodocyclobutane, b.p. 89° at 4·5 mm. A VPC analysis using diethylene glycol succinate indicated 36% of the *trans*-isomer and 64% of the *cis* isomer.

A sample enriched in the *trans*-isomer was found to equilibrate in the presence of I_2 in CCl_4 within 9 hr. When a deficiency of I_2 was used in the addition to bicyclobutane, the product consisted of 82% *cis* and 18% *trans*-isomers.

(b) *Bromine*. To a CCl_4 solution of bicyclobutane in an NMR tube was added Br_2 in CCl_4 until the yellow color persisted. Both *cis* and *trans*-1,3-dibromocyclobutane were found to be present by a comparison of the NMR spectrum with those of authentic samples. In addition, there were bands at τ = 9·18 (m) and 8·62 (m) indicative of a cyclopropane ring and at τ3·5–5·0 indicative of olefinic hydrogens. Analysis by VPC indicated 44% *cis*-1,3-dibromocyclobutane, 19% of the *trans*-isomer, 22% of the cyclopropane derivative and 15% of the olefin.

(c) *Chlorine*. To 0·002 mole bicyclobutane in a gas reaction vessel was added 0·00195 mole Cl_2. The press. initially increased and then decreased indicating that a reaction had occurred. Analysis by VPC indicated that no 1,3-dichlorocyclobutanes had been formed (comparison with authentic samples), and the major product was one having its major band centered at 9·6 τ with a doublet at 6·73 τ. This must be a cyclopropane derivative and appears to best fit 2-chlorocyclopropanemethyl chloride.

Hydration of bicyclo[1.1.0]*butane*. To 1 ml D_2O (pH 2·3) was added 0·0021 mole bicyclobutane using a vacuum line. After standing for 1 hr at room temp, the NMR spectrum was taken and indicated 55% cyclobutanol and 45% cyclopropylcarbinol.

For the kinetic determination, the hydration was performed in apparatus used by Baird and Aboderin[22] for studying the hydration of cyclopropane. The reaction was too fast to be followed using 0·001 N H_2SO_4. However, a convenient rate was found using 0·0001 N H_2SO_4. A plot of volume of gas absorbed against time gave a good straight line with a slope of 7·12 ml/min/4 ml acid at 25° and 1 atm. For comparison with the data of Baird and Aboderin, the units were changed giving 535 ml/hr/5 ml acid at 25° and 1 atm. The rate of reaction was shown to be independent of the stirring rate under the conditions used.

Reaction of bicyclo[1.1.0]*butane with photolyzed diazomethane*. To 2·5 ml purified decalin at −50° was added 0·8 ml (0·7 g) bicyclobutane. Diazomethane generated from 4·0 g N-nitrosomethylurea was added and the solution was irradiated at −50° with two G.E. sun lamps, for 2 hr. The above process was then repeated until a total of 32 g N-nitrosomethylurea had been used. The volatile products (0·7 ml) were removed using a stream of He and collected in a liquid N_2 cooled trap. Analysis by VPC (β,β'-oxydipropionitrile) gave a peak at 4·1 min (1,4-pentadiene, dimethylether, and bicyclo-[1.1.1]pentane) and at 4·6 min (unchanged bicyclobutane). Because of inadequate resolution, the final analysis was made using the NMR spectrum giving 21% 1,4-pentadiene, 25% dimethyl ether, ~1% bicyclo[1.1.1]pentane, 35% bicyclo[1.1.0]butane, 7% of an unknown compound with a sharp singlet at 7·03 τ, and 11% of unidentified compounds which appeared to include methyl substituted bicyclobutanes.

Addition of methanol to methyl 3-methylenecyclobutanecarboxylate. Methyl 3-methylenecyclo-butanecarboxylate (1 ml) was added to 15 ml MeOH containing 2 drops conc. H_2SO_4, and the mixture was heated to reflux for 1 week. Powdered K_2CO_3 was then added and the mixture was allowed to stand overnight. Dry ether was added and the solution was filtered. After evaporation of the ether, VPC analysis using diethylene glycol succinate at 160° indicate the presence of 2 compounds in 1·8 to 1 ratio. The major product (A) had an IR carbonyl band at 1733 cm^{-1}, and NMR bands at 8·73 τ (s, 3), 6·91 τ (s, 3), 6·37 τ (s, 3), 8·14–7·46 τ (m, 5). The minor product (B) had its band at 1732 cm^{-1}, and NMR bands at 8·71 τ (s, 3), 6·90 τ (s, 3), 6·38 τ (s, 3), 8·03–7·34 τ (m, 5). These data

are in agreement with the assignment as the two isomers of methyl 3-methyl-3-methoxycyclobutanecarboxylate. (Found for B: C, 61·0; H, 9·0. Calc. for $C_8H_{14}O_3$: C, 60·7; H, 8·9. Found for A: C, 61·0; H, 9·0%.)

Addition of methanol to methyl 3-methylbicyclobutane-1-carboxylate. Methyl 3-methylbicyclobutane-1-carboxylate (0·3 ml) was added to 15 ml abs. MeOH and the solution was heated to reflux overnight. Evaporation of the MeOH under red. press. gave a colorless oil which was shown by VPC analysis to contain only one major product; it was identical with the isomer of methyl 3-methyl-3-methoxycyclobutanecarboxylate formed in larger amount in the addition of MeOH to methyl 3-methylenecyclobutanecarboxylate.