or **26** be generated and observed in the nmr, there should be two identical rather than two different methyl absorptions.

Acknowledgments. We thank Dr. Donald H. Dugre and Mr. Jon A. Kapecki for valuable consultation on the EH method and the programs employed.

Heats of Hydrogenation. VIII. Compounds with Three- and Four-Membered Rings[1]

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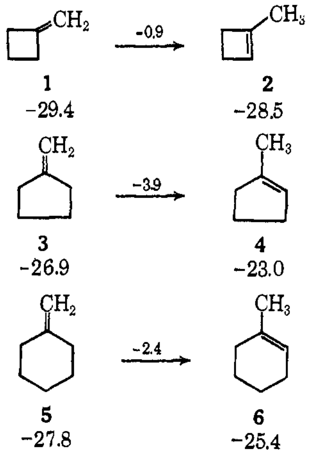
Abstract: The heats of catalytic hydrogenation of methylenecyclobutane, 1-methylcyclobutene, 1,2-dimethylcyclobutene, 1,3-dimethylenecyclobutane, 1-methyl-3-methylenecyclobutene, benzocyclobutene, bicyclo[4.2.0]-octa-2,4-diene, 1,2-dimethylcyclopropene, 1,2-dimethyl-3-carbomethoxycyclopropene, 1-methyl-2-methylenecyclopropane, ethylidenecyclopropane, bicyclo[2.1.0]pentane, 1,3-dimethylbicyclo[1.1.0]butane, and quadricyclene have been measured in solution at 25°. Total strain energies can be estimated for certain of these substances: dimethylcyclopropene, 45 kcal/mol; bicyclopentane, 54 kcal/mol; dimethylbicyclobutane, 67 kcal/mol; quadricyclene, 95 kcal/mol.

For several years we have been interested in the quantitative aspects of steric strain and have already noted a spread of more than 15 kcal/mol in the heats of hydrogenation of two *cis*-disubstituted olefins, *cis*-cyclodecene (−20.7 kcal/mol)[4] and *cis*-di-*t*-butylethylene (−36.2 kcal/mol).[5] This difference serves to emphasize the important influence of strain, both in the starting olefin (*cis*-di-*t*-butylethylene) and in the saturated reduction product (cyclodecane). The enthalpy differences of 9.2 kcal/mol between *cis*- and *trans*-cyclooctenes[4] and of 9.3 kcal/mol between *trans*- and *cis*-di-*t*-butylethylenes[5] serve as further calibration points on the scale of stress effects in highly strained systems.

In the present paper, we report the results of an investigation of the heats of hydrogenation of various small-ring compounds in which steric strain is expected to be high. The data are listed in Table I.

The first two compounds, methylenecyclobutane (**1**) and 1-methylcyclobutene (**2**), comprise a pair of *exo*–*endo* isomers which extends the data previously published for such systems[6] to the four-membered ring.[2] The heat of isomerization of methylenecyclobutane (**1**) into 1-methylcyclobutene (**2**) is −0.9 kcal/mol which is compared with values of −3.9 kcal/mol and −2.4 kcal/mol, respectively, for the corresponding five- and six-membered ring pairs.[5] Since the change in degree of double bond substitution from disubstituted to trisubstituted accounts for about 1.5 kcal/mol[7] in the heat of isomerization, the value for the isomerization of **1** into **2**, corrected for the substitution effect, is +0.6 kcal/mol. Therefore, *exo*cyclic unsaturation in four-membered ring compounds is intrinsically slightly more stable (on an enthalpy basis) than *endo* unsaturation. This situation contrasts with that demonstrated for the five- and six-ring members of the series.[6] The result is not unexpected, since the change from one to two trigonal atoms in the four-membered ring should lead to enhancement of angular strain, but the size of the effect is less than anticipated.



From its heat of combustion[8] cyclobutane is estimated to possess internal strain amounting to 26.2 kcal/mol or 6.55 kcal per methylene group[9] relative to a methylene group of the cyclohexane type as zero. If any substantial part of this strain energy arises from

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[1] Some portions of this work have been published previously in preliminary form.[2,3]

[2] R. B. Turner, "Theoretical Organic Chemistry—Papers presented to the Kekulé Symposium," Butterworths Scientific Publications, London, 1959, p 67.

[3] R. B. Turner, P. Goebel, W. von E. Doering, and J. F. Coburn, Jr., *Tetrahedron Letters*, 997 (1965).

[4] R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, 79, 4133 (1957).

[5] R. B. Turner, D. E. Nettleton, and M. Perelman, *ibid.*, 80, 1430 (1958).

[6] R. B. Turner and R. H. Garner, *ibid.*, 80, 1424 (1958).

[7] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, 57, 876 (1935).

[8] S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, 71, 261 (1952).

[9] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 189.

Table I. Heat of Catalytic Hydrogenation in Acetic Acid Solution (25°)

Compound	ΔH, kcal/mol
Methylenecyclobutane (**1**)	-29.43 ± 0.06
1-Methylcyclobutene (**2**)	-28.48 ± 0.01
1,3-Dimethylenecyclobutane (**7**)	-60.0 ± 1.0^{a}
1-Methyl-3-methylenecyclobutene (**8**)	-54.95 ± 0.11
Benzocyclobutene (**11**)	-50.32 ± 0.03
Bicyclo[4.2.0]octadiene (**12**)	-51.63 ± 0.10
1,2-Dimethylcyclobutene (**13**)	-26.37 ± 0.24
Methylmethylenecyclopropane (**14**)	-38.32 ± 0.12^{b}
Ethylidenecyclopropane (**15**)	-37.04 ± 0.15^{b}
1,2-Dimethylcyclopropene (**16**)	$-43.3 \pm 1.0^{a,b}$
1,2-Dimethyl-3-carbomethoxycyclopropene (**17**)	-40.23 ± 0.33^{b}
Bicyclo[2.1.0]pentane (**20**)	-55.14 ± 0.36
Quadricyclene (**26**)	-92.03 ± 0.49
1,3-Dimethylbicyclo[1.1.0]butane	$-40.58 \pm 0.36^{b,c}$

[a] The nature of the uncertainty in this result is discussed in the Experimental Section. [b] Heat of hydrogenation per mole of hydrogen (see Experimental Section). [c] The solvent in this case was diethyl Carbitol.

nonbonded repulsions, which might be relieved by the introduction of trigonal carbon atoms, then appreciable bond angle strain in the olefin might be undetected by the hydrogenation method. Although precise values for angular strain in the systems, methylenecyclobutane and 1-methylcyclobutene, are difficult to obtain, approximate values can be estimated in the following way.

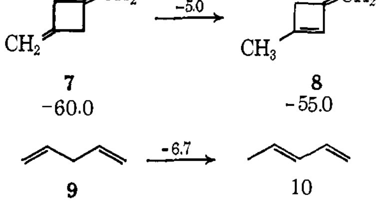
The heats of hydrogenation of methylenecyclobutane and of 1-methylcyclobutene to methylcyclobutane are, respectively, −29.4 and −28.5 kcal/mol. A tentative value of −4.0 kcal/mol is available for the vapor phase (25°) heat of formation of methylcyclobutane from the combustion data of Humphrey and Spitzer.[10] Owing to technical difficulties in the combustion experiments, the investigators expressed some lack of confidence in the accuracy of the results. The heat of formation (vapor phase, 25°) of methylcyclobutane can alternatively be calculated by the Franklin group equivalent method[11] as the sum of the enthalpy factors for three CH_2 groups, one CH group, and one CH_3 group (−26.0 kcal/mol), corrected for the strain of a four-membered ring. Since Franklin's group correction for cyclohexane relative to six acyclic methylene groups is −0.45 kcal/mol, a strain correction of +25.75 kcal/mol is taken for cyclobutane for the sake of consistency. This calculation leads to a heat of formation of −0.2 kcal/mol for methylenecyclobutane. In this treatment, the steric effect of methyl substitution is neglected. In the absence of steric properties unique to four-membered rings, this procedure is justified by the observations that the differences in heats of formation of the pairs propane–isobutane, cyclohexane–methylcyclohexane, and cyclopentane–methylcyclopentane are, respectively, −7.33, −7.56, and −7.04 kcal/mol.[12] If this latter value is taken as an approximate model for the cyclobutane–methylcyclobutane system, the calculated heat of formation, −0.8 kcal/mol for methylenecyclobutane, can be obtained from the known heat of formation of cyclobutane (+6.2 kcal/mol).

Comparison of the heats of hydrogenation obtained by Kistiakowsky and his collaborators in the vapor phase for cyclic, monounsaturated hydrocarbons with the corresponding values in solution indicates that the latter figures are less negative by about 0.5 to 1.5 kcal/mol. Therefore, we feel justified in using the solution data without correction for purposes where accuracy greater than 2–3 kcal/mol is not required. Thus, heats of formation of +25.4, +29.2, or +28.6 kcal/mol are obtained for methylenecyclobutane, depending upon which of the three values for the heat of formation of methylcyclobutane is employed. The similarly obtained heats of formation of 1-methylcyclobutene are +24.5, +28.3, and +27.7 kcal/mol.

Now the heats of formation of the strain-free assemblies of atomic groupings found in these two molecules can be calculated by the group equivalent method.[11] The results are +2.11 kcal/mol for strainless methylenecyclobutane and +0.22 for strainless 1-methylcyclobutene. The differences between these values and the heats of formation of the real molecules are defined as the total strain energy. For methylenecyclobutane this strain lies in the range 23.3–27.1 kcal/mol and for 1-methylcyclobutene in the range 24.3–28.1 kcal/mol. Irrespective of the precise values that may be assigned, it is evident that the strain energies in these molecules do not differ substantially from that in cyclobutane itself, and that no large energy increment is associated with the introduction of a second trigonal carbon atom in the four-membered ring.

Nangia and Benson[13] have noted that the low value of 32.5 kcal/mol for the activation energy of the isomerization of cyclobutene to butadiene[14] can be explained on the basis of relief of steric strain only if the strain energy in cyclobutene is very high (at least 48 kcal/mol) and much greater than that in cyclobutane. Their conclusion that strain of this magnitude is unreasonable is amply justified by the present results. The mechanism has in the meantime been shown to be concerted and not to involve an intermediate diradical as implied in the analysis of Benson and Nangia.[15]

A second molecule possessing two trigonal carbon atoms in a four-membered ring is 1,3-dimethylenecyclobutane (**7**), for which a heat of hydrogenation of −60.0 kcal/mol has been obtained.[2] This value is only 1.2 kcal/mol higher than twice the methylenecyclobutane figure (−58.8 kcal/mol), and is consistent with the hypothesis of negligible interaction involving the two double bonds.



Derivation of the heat of formation of 1,3-dimethylenecyclobutane from the heat of hydrogenation requires a value for the heat of formation of the product,

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(10) G. L. Humphrey and R. Spitzer, *J. Chem. Phys.*, 18, 902 (1950).

(11) J. L. Franklin, *Ind. Eng. Chem.*, 41, 1070 (1949).

(12) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1952.

(13) P. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **84**, 3411 (1962).

(14) W. Cooper and W. D. Walters, *ibid.*, **80**, 4220 (1958).

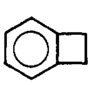
(15) R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959).

1,3-dimethylcyclobutane. Since no experimental figure is available for either *cis-* or *trans*-dimethylcyclobutane, we are forced again to rely on a calculated value, obtained by correction of the Franklin strain-free model (−32.3 kcal/mol) for the cyclobutane strain (+25.75 kcal/mol). Neglected are the effect of methyl substitution for the reasons given above and the influence of the ratio of the *cis* and *trans* isomers. The heat of formation of 1,3-dimethylcyclobutane found in this way is −6.5 kcal/mol, and the "experimental" heat of formation of 1,3-dimethylenecyclobutane is calculated to be +53.5 kcal/mol. Comparison of this figure with the Franklin stain-free value of +23.9 kcal/mol gives a total strain energy approximating 30 kcal/mol, as compared with total strain of 28.3 kcal/mol calculated for 1-methylcyclobutene by the same procedure.

1,3-Dimethylenecyclobutane is unstable with respect to 1-methyl-3-methylenecyclobutene (**8**), and some isomerization appears to proceed, albeit very slowly, in acetic acid at room temperature. The heat of hydrogenation of 1-methyl-3-methylenecyclobutene is −55.0 kcal/mol, whence the heat of isomerization of the unconjugated *exo–exo* isomer to the conjugated *exo–endo* derivative is −5.0 kcal/mol.[2,16] The conjugative interaction of the double bonds in 1-methyl-3-methylenecyclobutene as revealed by the difference between its heat of hydrogenation (−55.0 kcal/mol) and the sum of the heats of hydrogenation of 1-methylcyclobutene (−28.5 kcal/mol) and of methylenecyclobutane (−29.4 kcal/mol) is 2.9 kcal/mol, a value only slightly lower than that in butadiene (3.5 kcal/mol).[17] It is of interest to note that the heat of isomerization in an open-chain model, 1,4-pentadiene (**9**) to 1,3-pentadiene (**10**), is −6.7 kcal/mol.[18] Of the difference of 1.7 kcal/mol between the two heats of isomerization, 1.0 kcal/mol is accounted for by substitution factors. The close correspondence of these heats of isomerization leaves little room for significant strain arising from the incorporation of the third trigonal carbon atom into the four-membered ring.

We have not as yet examined a four-membered ring in which trigonal carbon atoms occupy all four positions. There are suggestions in the literature[19] that such systems may incorporate a very high degree of strain. However, experimental data which would permit a reliable estimate of the order of magnitude of such strain, uncompromised by other factors, do not appear to be available.

A particularly interesting example of a four-membered ring possessing two trigonal carbon atoms is benzocyclobutene (**11**).[20] In this case any large degree of strain might interfere with electron delocalization in the benzene ring. The heat of hydrogenation of this substance is −50.3 kcal/mol. This value is close to that obtained for *o*-xylene (−47.3 kcal/mol, vapor phase),[18] and may be compared with the heat of hydrogenation (−51.7 kcal/mol) of bicyclo[4.2.0]octadiene (**12**), from which a value for the heat of hydrogenation **11** → **12** of +1.4 kcal/mol is derived.[21] The corresponding figure for the heat of hydrogenation of benzene to cyclohexadiene-1,3 is +5.6 kcal/mol.[17] These results serve to emphasize the smallness of the effect of the strain in benzocyclobutene on aromatic resonance.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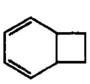
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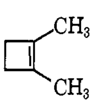

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Attention should be called to the value of −26.3 kcal/mol obtained for the heat of hydrogenation of 1,2-dimethylcyclobutene (**13**). This result for the tetrasubstituted olefin is lower than that for the corresponding trisubstituted derivative **2** by 2.2 kcal/mol. This substitution effect is somewhat larger than that reported by Kistiakowsky[17] (0.3 kcal/mol) for the system trimethylethylene–tetramethylethylene. It seems reasonable to suppose that nonbonded interactions between methyl groups in the product 1,2-dimethylcyclobutane account for the major part of this discrepancy.

Wiberg and Fenoglio have determined the heats of combustion of a number of isomers of C_4H_6, some of which overlap in interest molecules studied in this work.[22] The relevant results are shown in Table II. The total strain energy of cyclobutene found by Wiberg and Fenoglio of +28.5 kcal/mol is in good agreement with the values of +28.1 and +25.3 kcal/mol found in this work for 1-methyl- and 1,2-dimethylcyclobutene, respectively.

The interaction of a double bond with the three-membered ring is illustrated by olefins **14** and **15** which are derivatives of methylenecyclopropane and olefins **16** and **17**, derivatives of cyclopropene. With this series, the study of the effect of ring size on the relative stability of *exo* and *endo* double bonds is completed.

Methylmethylenecyclopropane and ethylidenecyclopropane were kindly provided by Professor Chesick who has investigated the temperature dependence of the rate of their interconversion.[23] Their hydrogenation is complicated by the uptake of more than 1 equiv of hydrogen. The data are handled by the assumptions that the product of absorbing 1 equiv of hydrogen is a dimethyl- or ethylcyclopropane and that the product of absorbing 2 equiv of hydrogen is *n*-pentane. The heats of formation are calculated from gas-phase group equivalent values of Franklin, a strain energy in cyclopropane of +27.1 kcal/mol (adjusted to the Franklin scale[11]), and the net interaction of the methyl groups in *cis*-1,2-dimethylcyclopropane to be 1.5

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(16) The product obtained in the platinum-catalyzed hydrogenation of 1-methyl-3-methylenecyclobutene consists of a mixture of 84% *cis*- and 16% *trans*-1,3-dimethylcyclobutanes (J. F. Coburn, Jr., Ph.D. Dissertation, Yale University, 1963). M. F. Caserio, S. H. Parker, R. Piccolini, and J. D. Roberts, *J. Am. Chem. Soc.*, 80, 5507 (1958), have shown that the reduction products of 1-methyl-3-methylenecyclobutene and of 1,3-dimethylenecyclobutane possess identical ir and nmr spectra.

(17) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, **58**, 146 (1936).

(18) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *ibid.*, **59**, 831 (1937).

(19) C. A. Coulson and W. Moffitt, *Phil. Mag.*, 40, 26 (1949); A. F. Bedford, J. G. Carey, I. T. Millar, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3895 (1962).

(20) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **78**, 500 (1956); 80, 2255 (1958).

(21) The stereochemistry of the hydrogenation products has not been investigated, and for the purposes of this discussion it is assumed that the same product is obtained from **11** and **12**.

(22) We are much appreciative of the private communication of these results with permission to cite (K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. Soc.*, in press).

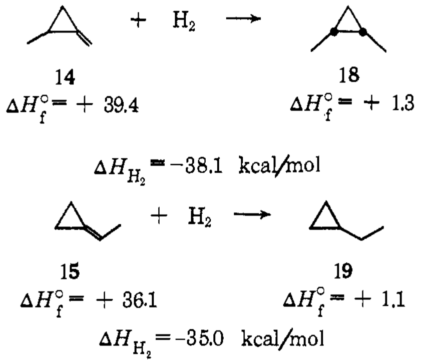
(23) J. P. Chesick, *ibid.*, **85**, 2720 (1963).

Table II. Heats of Formation and Energies of Strain for Selected Cyclic Hydrocarbons

Compound	This work		Ref 22		Ref 26	
	$\Delta H_f°$	Strain	$\Delta H_f°$	Strain	$\Delta H_f°$	Strain
Methylmethylenecyclopropane	+39.4	+38.6			+45.0	+44.2
Ethylidenecyclopropane	+36.1	+35.9			+43.0	+42.8
Methylenecyclopropane			+48.0	+41.0	+49.4	+42.4
Cyclopropene			+66.6	+52.6[a]	+61.5	+47.5
1-Methylcyclopropene			+58.2	+53.1	+55.4	+50.3
1,2-Dimethylcyclopropene	+46.4	+47.0			+49.6	+50.2
Cyclobutene			+37.5	+28.5		
1,2-Dimethylcyclobutene	+19.8	+25.3				
1-Methylcyclobutene	+28.3	+28.1				
Bicyclo[1.1.0]butane			+51.9	+63.9	+55.4	+67.4
1,3-Dimethylbicyclo[1.1.0]butane	+39.7	+68.2			+46.2	+69.3

[a] K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 3980 (1962).

kcal/mol[24,25] (*n*-pentane, $\Delta H_f° = -35.0$; *cis*-1,2-dimethylcyclopropane, $\Delta H_f° = +1.3$; ethylcyclopropane, $\Delta H_f° = +1.1$). The measured heat of hydrogenation is then employed to calculate the heat of formation of the cyclopropane derivative. Finally, the heat of hydrogenation of the double bond is calculated.



Even allowing for considerable experimental error and for the approximate nature of the calculation, it is clear that a double bond exocyclic to the cyclopropane ring is highly strained (heats of hydrogenation of methylenecyclobutane, methylenecyclopentane, and methylenecyclohexane are −29.4, −26.9, and −27.8 kcal/mol, while those of ethylidenecyclopentane and ethylidenecyclohexane are −24.9 and −26.3 kcal/mol, respectively).[6]

The strain energy of +38.6 kcal/mol found here for methylmethylenecyclopropane may be compared with the value, +41.0 kcal/mol, found by Wiberg and Fenoglio[22] for unsubstituted methylenecyclopropane (Table II). It is illustrative of the success of the calculation of Baird and Dewar[26] that they should agree so well, particularly when the value for methylenecyclopropane is tied to the unknown thermochemical values of *cis*-1,2-dimethylcyclopropane.

Chesick[23] has pointed out in his analysis of the activation energy (40.4 kcal/mol) of the thermal interconversion of methylmethylenecyclopropane and ethylidenecyclopropane that the extra strain arising from the contraction of the normal 120° bond angle of a pair of sp^2 bonds to 60° may be a relevant factor. Were the entire strain in methylmethylenecyclopropane [the difference between the heat of formation (+39.4 kcal/mol) and that calculated by the group equivalent method (+0.75 kcal/mol)] available to the transition state of the methylenecyclopropane rearrangement, the calculated activation energy of 43.4 kcal/mol (the difference between the energy of 82 kcal/mol[27] estimated for rupture of the 2,3 bond in *n*-butane and 38.6 kcal/mol) is higher than the observed value. In several other rearrangements which appear to involve bond breaking as the rate-determining step all of the strain seems not to be available for lowering the activation energy; *e.g.*, cyclopropane: $E_a = 65.1$ kcal/mol, calculated 54 kcal/mol (82 − 27.6 kcal/mol); cyclobutane: $E_a = 62.5$ kcal/mol, calculated 56 kcal/mol (82 − 26.2 kcal/mol). In fact, the closely related rearrangement of Feist's ester has been established by Ullman[28] to be concerted and does not involve a simple breaking of a bond to a diradical as is implicitly assumed in the analysis above.

1,2-Dimethylcyclopropene, prepared by the reaction of diazomethane and butyne-2,[29] is hydrogenated catalytically with the absorption of varying amounts of hydrogen to *cis*-1,2-dimethylcyclopropane and a mixture of isopentane and *n*-pentane in a ratio of 2.3:1. The observed heat of hydrogenation is reported on the basis of heat evolved per molar equivalent of hydrogen actually absorbed. On the assumption that the total amount of hydrogen absorbed could be divided into a fraction consumed in producing *cis*-1,2-dimethylcyclopropane[24,25] and another fraction consumed in producing isopentane and *n*-pentane in the ratio 2.3:1,

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(24) For want of a better number this value has been taken from the difference between the ethane barrier, 2.88 kcal/mol (K. S. Pitzer, *Discussions Faraday Soc.*, 10, 66 (1951)], and the *n*-butane barrier of 4.4 kcal/mol estimated by Pitzer [K. S. Pitzer, *Chem. Rev.*, 27, 39 (1940)].

(25) In their remarkably successful application of an approximately modified Pople SCF MO method to cyclopropanes and cyclopropenes, Baird and Dewar calculate a considerably higher strain energy for 1,2-dimethylcyclopropane (36.7 kcal/mol) than that taken by us (28.6 kcal/mol = 27.1 + 1.5).[26] Although admittedly their errors are large in terms of the use to which the results would be put in this work, it is noteworthy that their calculations assign 2.6 kcal/mol more strain to *cis*-1,2-dimethylcyclopropane than to *trans*. Definite consideration of the effect of methyl groups must obviously await the experimental determination of the heat of formation of the methyl and *cis*- and *trans*-1,2-dimethyl derivatives of cyclopropane (and, for application to other portions of this work, the corresponding cyclobutanes).

(26) N. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.*, **89**, 3966 (1967).

(27) In view of the magnitude of the uncertainties in methods presently available for the determination of the dissociation energies of the carbon–carbon bonds, we rather arbitrarily take 86 kcal/mol as the bond dissociation energy of ethane and subtract 2 kcal/mol for each element of alkyl substitution. Thus the dissociation energy in RCH_2–CH_2R is taken as 82 kcal/mol. See J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press Inc., New York, N. Y., 1962; and T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths Scientific Publications, London, 1958.

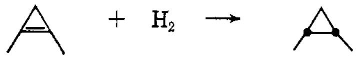
(28) F. Ullman, *J. Am. Chem. Soc.*, **82**, 505 (1960).

(29) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

the heat of formation of 1,2-dimethylcyclopropene is calculated. From this value, a heat of −45.1 kcal/mol is obtained for the hydrogenation of *cis*-1,2-dimethylcyclopropane. This value is to be compared with the heat of hydrogenation of 1,2-dimethylcyclobutene (−26.3 kcal/mol) or of tetramethylethylene (−26.6 kcal/mol in the gas phase).[30] The very large discrepancy of about 18.5 kcal/mol must be ascribed to the strain of placing a double bond within the three-membered ring. The effect is much larger than that found for placing a double bond in a four-membered ring.

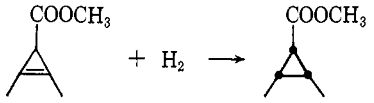
Total strain in dimethylcyclopropene can be estimated to be +47.0 kcal/mol by subtracting the heat of formation of a strain-free model (−0.60 kcal/mol calculated by the Franklin method of group equivalents) from the found heat of formation (+46.4 kcal/mol).

A related molecule, 3-carbomethoxy-1,2-dimethylcyclopropene,[29] has also been investigated. Dihydro and tetrahydro products are obtained in varying degree, so that the experimentally determined heat of absorption of 1 molar equiv of hydrogen must be translated into more usable form by the same kind of operations used before. The dihydro product is *cis,cis*-3-carbomethoxy-1,2-dimethylcyclopropane while the tetrahydro products are methyl 3-methylpentanoate and methyl 2-ethylbutanoate. In disregard of the presence of the carbomethoxy group or of a possible difference in the heat of formation of the two acyclic esters (both have the same calculated heat of formation), a heat of hydrogenation to the saturated cyclopropane derivative of −41.3 kcal/mol is obtained. This value is lower than the heat of hydrogenation of 1,2-dimethylcyclopropene (−45.1 kcal/mol) by 3.8 kcal/mol.



16 **18**

$\Delta H_{H_2} = -45.1$ kcal/mol



17 **19**

$\Delta H_{H_2} = -41.3$ kcal/mol

This difference will have to be ascribed to a raising of the energy of the *cis*-1,2-dimethylcyclopropane through a *cis* interaction larger than the 1.5 kcal/mol we have allowed[24,25] and/or to an abnormally high conjugative interaction.

The strain energy of +47.0 kcal/mol deduced in this work for 1,2-dimethylcyclopropene is less by 5.6 kcal/mol than that deduced from the heat of combustion of cyclopropene[31] (see Table II). A similar difference (6.1 kcal/mol) exists between 1,2-dimethylcyclopropene and 1-methylcyclopropene (see Table II). The values for the strain energy calculated by Baird and Dewar[26] are intermediate. Since the conjugative interaction of methyl groups with double bonds is known to vary over a wide range (0.3 kcal/mol for the fourth methyl group in tetramethylethylene to about 3.0 kcal/mol at the end of transoid butadiene) a conjugative interaction as high as 4.5 kcal/mol may not be out of the question.

Through the courtesy of Professor R. Criegee a sample of bicyclo[2.1.0]pentane (**20**)[32] was obtained for hydrogenation.[2] The material as submitted was better than 99.9% pure (gas chromatography), and was shown in Professor Criegee's laboratory to yield cyclopentane, contaminated by less than 0.06% impurity, on catalytic hydrogenation. The suggestion that bicyclopentane possesses a very high degree of strain was already on record in the observation that the substance reacts readily with iodine[32] and in the relatively low activation energy (46.6 kcal/mol) reported for its isomerization in cyclopentene.[33] The heat of hydrogenation was found to be −55.1 kcal/mol, and the heat of isomerization into cyclopentene, for which a heat of hydrogenation of −25.7 kcal/mol is available,[34] is therefore −29.4 kcal/mol. For calculations of the total strain energy of this molecule by the procedure outlined in the preceding section, the heat of formation of bicyclopentane in the gas phase at 25° is required.

20 **21** **22**

On the assumption of the essential equivalence of ΔH values obtained in solution and in the vapor phase, the necessary figure can be obtained from the known heats of formation of gaseous cyclopentene (7.9 kcal/mol[12]) or of gaseous cyclopentane (−18.5 kcal/mol[12]) and is found to be 37.3 kcal/mol. This result may then be compared with the value of −17.0 kcal/mol calculated for the vapor phase heat of formation of a strain-free C_5H_8 molecule by the Franklin method of group equivalents.[11] It follows that the strain energy in bicyclopentane approximates 54.1 kcal/mol, a result that is essentially identical with the sum (52.9 kcal/mol) of the individual strains of cyclopropane (27.1 kcal/mol) and of cyclobutane (25.8 kcal/mol) obtained from combustion measurements.[8]

The very high degree of strain associated with the bicyclopentane molecule is undoubtedly shared by several bonds and is not to be regarded as being localized in the ring fusion. For purposes of comparison with other systems an arbitrary value of 10.8 kcal per atom of carbon may be employed. It is a matter of singular interest, however, that simple cleavage of the bridge bond by catalytic hydrogenation results in the release of 48.1 kcal/mol[35] of the total strain energy of 54.1 kcal/mol.

An important outcome of the bicyclopentane investigation lies in its bearing on the thermochemistry of bond-breaking and bond-making processes. Chesick[36] has recently reported a mean energy of activation of 38.9 kcal/mol for the reversible thermal interconversion of the *cis*- and *trans*-2-methylbicyclo[2.1.0]pentanes (**23** and **24**), respectively. The energy difference between the two forms was shown to be very

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(30) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 137 (1936).

(31) K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *ibid.*, **84**, 3980 (1962).

(32) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

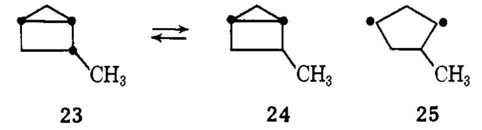
(33) M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2688 (1962).

(34) R. B. Turner, unpublished datum.

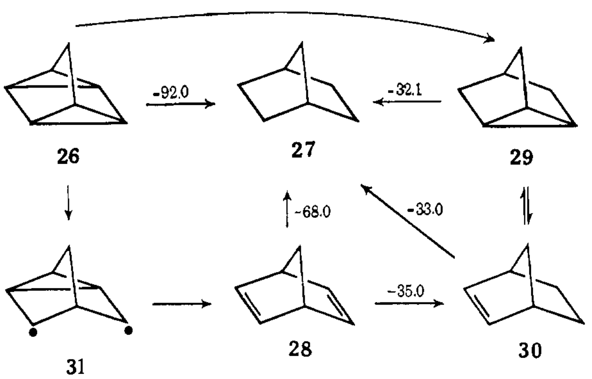
(35) Strain energy in cyclopentane derived from heat of combustion data is 6.0 kcal/mol (adjusted to the Franklin scale).

(36) J. Chesick, *J. Am. Chem. Soc.*, **84**, 3250 (1962).

small. On the assumption that the isomerization reaction passes through a planar biradical (**25**) of regular geometry, the relief of strain brought about by conversion of either **23** or **24** into **25** must be close to 50.5 kcal/mol.[37] Since the bond dissociation energy of diisopropyl to two isopropyl radicals, 78 kcal/mol,[27] is a maximum value for the bond-breaking process, the net energy change in passing from **23** or **24** to **25** must be at most 27.5 kcal/mol. Since the known activation energy (38.9 kcal/mol) is considerably greater than this value, it is clear that species **25**, if involved, must be regarded as an intermediate and not as a transition state. It follows from this analysis that bond formation in **25** to yield **23** or **24** must have an activation energy of at least 11.4 kcal/mol. The present case may be a rather special one in that considerable distortion of **25** may be required before overlap of the singly filled p orbitals can lead to significant bonding. The conclusion is, however, opposed to the general observation that radical combinations are spontaneous processes without activation energy.[27, 38]



An interesting structural relative of bicyclopentane is quadricyclene (**26**), which is reduced to bicyclo[2.2.1]-heptane (**27**) with an accompanying enthalpy change of −92.0 kcal/mol. Although the requisite data for a direct evaluation of the vapor-phase heat of formation of quadricyclene are not available, a somewhat devious estimation can be made. The heat of formation of liquid bicycloheptane has been reported as −18.0 kcal/mol by Bedford, *et al.*,[39] who give a reasonable calculation of 18.4 kcal/mol for the strain energy in this molecule. The gas-phase heat of formation of unstrained bicycloheptane obtained by the Franklin group equivalent method is −26.8 kcal/mol, which, in conjunction with the strain energy, leads to −8.4 kcal/mol for the gas-phase heat of formation of the real molecule. The heat of vaporization of +9.6 kcal/mol obtained from this calculation is reasonable when compared with known heats of vaporization of similar compounds. Taking the heat of hydrogenation of −92.0 kcal/mol as applicable in the vapor phase, the heat of formation of quadricyclene vapor is estimated to be +83.6 kcal/mol. Since the Franklin value for the heat of formation of strain-free quadricyclene is −11.5 kcal/mol, the total strain in quadricyclene becomes a very high 95.1 kcal/mol. This value is some 20% higher than the energy of a carbon–carbon bond and represents an average strain of 13.6 kcal per atom of carbon. Strain of this magnitude provides a driving force more than adequate to account for the cycloaddition reactions of quadricyclene recently observed by Smith.[40]



From the known heat of hydrogenation of bicyclo-[2.2.1]heptadiene (**28**) of −68.1 kcal/mol[41] the heat of isomerization of quadricyclene into bicycloheptadiene is found to be −24.0 kcal/mol. The rapid thermal conversion of quadricyclene into bicycloheptadiene[42] as well as the failure of bicycloheptadiene to yield quadricyclene under conditions of acid catalysis which equilibrate bicyclo[2.2.1]heptene and nortricyclene[43] are thus easily understandable in terms of thermochemical driving forces.

It is interesting to calculate the heat of hydrogenation of quadricyclene into nortricyclene (**29**). The heat of hydrogenation of bicycloheptadiene to bicycloheptene (**30**) is −35.0 kcal/mol, and the free energy change for the isomerization of bicycloheptene to nortricyclene, taken from Schleyer's equilibrium data, is −0.9 kcal/mol. These figures taken together with the heat of isomerization of quadricyclene (**26**) to bicycloheptadiene (**28**) lead to an estimated value of −59.9 kcal/mol for the heat of hydrogenolysis of one of the three-membered rings in quadricyclene. Since the heat of hydrogenolysis of a normal unstrained single bond of this degree of substitution is −7.7 kcal/mol, approximately 52.7 kcal/mol of strain are released in this single step. This is the highest such value we have yet encountered.

From data now available it is possible to calculate approximate values for the heats of formation and strain energies of bicycloheptadiene (**28**), bicycloheptene (**30**), and nortricyclene (**29**), which are included with the other derivatives of this series in Table III.

Table III. Estimated Heats of Formation and Strain Energies

Compound	ΔH_f°	E_s
Bicycloheptane (**27**)	−8.4	18.4[37]
Bicycloheptene (**30**)	24.7	22.8
Nortricyclene (**29**)	23.8	42.9
Bicycloheptadiene (**28**)	59.7	29.0
Quadricyclene (**26**)	83.6	95.0

The energetics of the quadricylene–bicycloheptadiene interconversion may now be examined. Winstein[44] has obtained a value of 35.3 kcal/mol for the enthalpy of activation of the thermal rearrangement of quadricyclene into bicycloheptadiene. If a mechanism be

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[37] This value represents the difference between the strain energy of bicyclopentane (54.1 kcal/mol) and the strain energy of the biradical **25**, which is taken as that of cyclopentene (3.8 kcal/mol), the latter figure being obtained from the heat of formation of cyclopentene (7.9 kcal/mol) and the Franklin-based heat of formation of strain-free cyclopentene (4.1 kcal/mol).

[38] The recombination of triphenylmethyl radicals is a specific exception in which activation energy is required.[27]

[39] A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963).

[40] C. D. Smith, *J. Am. Chem. Soc.*, **88**, 4273 (1966).

[41] R. B. Turner, W. R. Meador, and R. E. Winkler, *ibid.*, **79**, 4116 (1957).

[42] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

[43] P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).

[44] S. Winstein, private communication.

assumed in which the rate-determining formation of the biradical **31** is followed by collapse to bicycloheptadiene in an activationless process, the minimum activation energy calculated for the transformation of **26** into **28** is 26 kcal/mol (78, bond dissociation energy,[27] minus 52, approximate relief of strain energy). The discrepancy between this minimum value and the experimental figure is thus nearly the same as that found in the bicyclopentane case. By use of Winstein's activation energy (35.3 kcal/mol) and the heat of isomerization (−24.0 kcal/mol) obtained in this investigation, and with the further unsupported assumption that the forward thermal and the reverse photochemical[42] reactions proceed through the same transition state, an activation energy of 59.3 kcal/mol may be assigned to the photochemical conversion of bicycloheptadiene into quadricylene. The value is reasonable for triplet excitation. For further discussion of the photosensitized interconversion of these isomers, the reader is referred to the comments of Hammond, *et al.*[45]

The smallest bicyclic system, bicyclo[1.1.0]butane, has attracted much attention recently by the surprising variety of methods by which it can be synthesized and by the remarkable acidity of its bridgehead hydrogen atoms. Fundamental to an ultimate understanding of the chemical and physical properties of the ring system is knowledge of its total strain energy.[3,46] Since hydrogenation leads to known products, this reaction can be used to obtain an insight into the strain. 1,3-Dimethylbicyclo[1.1.0]butane, the specific molecule studied, has been prepared from butyne-2 by biscyclopropanation with diazomethane in the presence of cuprous chloride and tributyltin chloride as an inhibitor.[46] The molecule is so sensitive to acid that diethyl Carbitol must be used as solvent in place of the customary acetic acid. The hydrogenation is inconveniently slow but fast enough to allow satisfactory thermochemical measurements. The amount of hydrogen absorbed varies from run to run and always exceeds 1 molar equiv. Gas chromatographic analysis of a typical run showed that 2-methylpentane (63%) is the major product and that *cis*-1,3-dimethylcyclobutane and *trans*-1,3-dimethylcyclobutane are formed in a ratio of about 6:1. The thermochemical results are reported in terms of the heat evolved per molar equivalent of hydrogen absorbed. The heat of formation of 1,3-dimethylbicyclo[1.1.0]butane is calculated by subtracting the total molar heat of hydrogenation from the sum of the partial molal heats of formation of the products. Its heat of formation is found in this manner to be +39.7 kcal/mol. The difference between the heat of formation and the calculated heat of formation of 1,3-dimethylcyclobutane is the heat of hydrogenation of the central 1,3 bond and is equal to −45.7 kcal/mol. The heat of hydrogenation of a comparable unstrained bond would be −3.8 kcal/mol. The total strain in the molecule is estimated from the difference between the found heat of formation and that calculated for a strain-free model by the Franklin method of group equivalents. This strain of 68.2 kcal/mol is enormously high and averages about 17 kcal/mol for each of the four carbon atoms required to bear it. The value agrees satisfactorily with that found by Wiberg and Fenoglio for bicyclobutane[22] and is amazingly close to that calculated by Baird and Dewar (see Table II).[26] The geometrical situation is such that there is no one bond the breaking of which can relieve all this strain. Thus, breaking the 1,3 bond leaves a four-membered ring and relieves 43.6 kcal/mol, whereas breaking a 1,2 bond leaves a three-membered ring and relieves 42.2 kcal/mol. In this respect bicyclobutane is not as dramatic as bicyclopentane, in which almost all of the strain can be relieved by breaking one single bond.[3]

Experimental Section

Materials. Samples of methylenecyclobutane (**1**), 1-methylcyclobutene (**2**), 1,3-dimethylenecyclobutane (**7**), and 1-methyl-3-methylenecyclobutene (**8**) were kindly provided by Professor J. D. Roberts and were hydrogenated in the calorimeter without further purification. The specimen of 1,3-dimethylenecyclobutane was contaminated by 10.0% 1-methyl-3-methylenecyclobutene, and the hydrogenation results were corrected accordingly. The dimethylene compound showed evidence of a very slow reaction after solution in the calorimeter, but prior to introduction of the catalyst, as indicated by comparison of the first rating period in the run and in the calibration stage. We interpret this phenomenon as a slow isomerization of the substance into 1-methyl-3-methylenecyclobutane promoted by the acetic acid solvent. The extent of reaction was insufficient to compromise the validity of the results, but under the circumstances the experimental figure of −60.03 ± 0.08 kcal/mol is reported as −60.0 ± 1.0 kcal/mol.

Benzocyclobutene (**11**) was prepared[20] as described by Cava and Napier. The material was subjected to preparative vapor chromatography on an SE-30 column, and the purity of the collected material was confirmed by ultraviolet, infrared, and nmr measurements. Hydrogenation proceeded with the quantitative absorption of 3 mol of hydrogen.

Methylmethylenecyclopropane (**14**) and ethylidenecyclopropane (**15**) were prepared and submitted for calorimetric examination by Professor John P. Chesick. Both samples were reduced with accompanying hydrogenolysis and with irregular hydrogen uptake. In two runs, compound **14** absorbed 1.256 and 1.363 molar equiv of hydrogen with heats of hydrogenation per mole of hydrogen of −38.19 and −38.44 kcal, respectively. Similarly, compound **15** absorbed 1.554 and 1.582 molar equiv of hydrogen in two runs, which yielded ΔH values of −35.89 and −36.19 kcal/mol of H_2, respectively.

The bicyclo[2.1.0]pentane (**20**) employed in this investigation was a sample specially prepared and purified in the laboratories of Professor R. Criegee, Karlsruhe.

A crude sample of quadricyclene was obtained through the courtesy of Drs. W. G. Dauben and R. Cargill. The material was purified by preparative vapor phase chromatography, and the purity of the hydrogenation specimen was checked by nmr spectroscopy.

Calorimetric Measurements. Heats of hydrogenation were measured in the apparatus, and by the general procedure, previously described.[47] The solvent consisted of 225 ml of prereduced acetic acid, except in the case of dimethylbicyclobutane where diethyl Carbitol was employed.[48] Samples of olefins sufficient to provide for an uptake of approximately 3 mmol of hydrogen were introduced in evacuated, sealed ampoules, and the hydrogenation reaction was initiated by breaking an ampoule containing approximately 100 mg of PtO_2 catalyst, which had previously been calibrated with respect to hydrogen absorption and heat evolution. The values reported in Table I represent averages of duplicate runs except in the case of quadricyclene in which three runs were carried out.

1,2-Dimethylcyclopropene. In a procedure based on that of Doering and Mole,[29] butyne-2 (100 ml) and *n*-heptane (50 ml) were placed in a reaction vessel fitted with an inlet tube from a generator of diazomethane and a condenser of the cold-finger type filled with Dry Ice and surrounded by a larger flask through which acetone at

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[45] G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964).

[46] W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Letters*, 991 (1965).

[47] R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

[48] *Cf.* R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *ibid.*, **79**, 4127 (1957).

−50° was circulated by pumping. Diazomethane was transferred into the reacting solution by a stream of nitrogen from a generator consisting of a two-necked flask cooled in ice and containing 100 g of 45% potassium hydroxide and 20 ml of decalin. N-Nitroso-N-methylurea was added slowly in such a manner that 30 g decomposed in a 3-hr period. After each transfer of diazomethane, irradiation with a pair of GERS sunlamps was carried on until decomposition was complete. The alternating procedure of addition of diazomethane and photolysis was carried out six times until 194 g of N-nitroso-N-methylurea had been consumed.

Fractional distillation of the reaction mixture [butyne-2 (75%); 1,2-dimethylcyclopropene (19.6%); and pentyne-2 (3.5%)] through a Helipak column (1.4 × 60 cm) at atmospheric pressure afforded 7.8 ml of 1,2-dimethylcyclopropene (99.9% purity by glpc), bp 38.8°. From the immediately preceding and following fractions (8.0 ml of 50% purity) further pure material was isolated by glpc (9-ft column) (1 in. i.d.) fitted with 40–60 mesh Firebrick containing 15% by weight of Dow Corning 550 silicone oil. Pure material showed two singlets at δ 1.99 and 0.70 ppm in the nmr.

Catalytic hydrogenation of 248 mg of 1,2-dimethylcyclopropene in 25 ml of glacial acetic acid containing 100 mg of prereduced platinum oxide was effected at 27° (957 mm). After 10 hr, 110 ml of hydrogen (1.23 molar equiv) had been absorbed. Vacuum distillation removed the hydrocarbons which consisted of *cis*-1,2-dimethylcyclopropane (77%) and a mixture of pentanes (23%) consisting of 2.3 parts of isopentane and 1 part of *n*-pentane, determined by glpc.

Certain technical difficulties were encountered in the calorimetric hydrogenation of this substance. Thermal response in the initial rating period suggested a very slow isomerization to methylmethylenecyclopropane in the acetic acid solvent (a similar phenomenon was observed with 1,3-dimethylenecyclobutane). The rate of hydrogen uptake became exceedingly slow at the end, presumably owing to catalytic hydrogenation of product dimethylcyclopropane. However, hydrogen absorption terminated within the usual time limits, possibly because of coagulation of the catalyst. Neither isomerization prior to introduction of the catalyst nor hydrogenolysis of the product can account for more than a very small fraction of the *n*-pentane obtained. We are therefore inclined toward the belief that at least this substance is formed by relatively rapid platinum-catalyzed isomerization of the starting material into methylmethylenecyclopropane followed by hydrogenolysis. The effect of these difficulties on the observed heat of hydrogenation (42.74 kcal/mol of H_2 with an uptake of 1.308 molar equiv and 43.88 kcal/mol of H_2 with an uptake of 1.290 molar equiv) is calculated to be negligible, but suggests that the uncertainty is possibly larger than the ±0.57 kcal/mol obtained from these experiments. Although hydrogen absorption trailing was observed with methylmethylenecyclopropane and ethylidenecyclopropane, these substances were stable in acetic acid.

1,3-Dimethylbicyclo[1.1.0]butane. Into the same type of reaction vessel employed in the preparation of 1,2-dimethylcyclopropene, there was placed 20 mg of cuprous chloride, 20 ml of butyne-2, and 1 ml of tributyltin chloride. Over a period of 4 hr, a total of 30.5 g of N-nitroso-N-methylurea was decomposed and the resultant diazomethane bubbled into the reaction mixture *via* a nitrogen stream. The reaction mixture was stirred throughout and kept at 0°. The progress of the photolysis was followed by glpc every hour. After the diazomethane transfer was completed and the decomposition was over, the contents were centrifuged to remove the catalyst and analyzed by glpc on a 2-m column of 15% Dow Corning silicone oil 710 on 40–60 Firebrick: 1,2-dimethylcyclopropene (2.4%), 1,3-dimethylbicyclo[1.1.0]butane (2.6%), 2,3-dimethylbutadiene-1,3 (1.2%), and butyne-2 (93.8%).

Concentration to about 15% of purity was effected by distillation through a 3-ft glass spiral column to remove much of the butyne-2 and then rapidly distilled under vacuum (100 mm) to separate from polymers and tin compounds. This material was then fractionally distilled through a Helipak column (60 × 1.5 cm i.d.) with ice-cooled condenser. Pure 1,3-dimethylbicyclo[1.1.0]butane had bp 54.3°. From immediately preceding and following fractions, additional pure material (>99.7%) was obtained by glpc: ir (neat), 3005 (s), 2947 (s), 2925 (s), 2895 (s), 2860 (s), 2793 (w), 2738 (w), 1470 (s), 1440 (m), 1385 (m), 1375 (m), 1265 (s), 1215 (w), 1093 (s), 1065 (sh), 1020 (m), 970 (s), 805 (m), 730 (w), and 600 (w) cm^{-1}; nmr, a singlet of relative area 6.0 at δ 1.34 ppm, a singlet (2) at 0.97 ppm, and a broad singlet (2) at 0.49 ppm.

Hydrogenation of 84 mg of 1,3-dimethylbicyclo[1.1.0]butane in 15 ml of diethyl Carbitol, freshly distilled from sodium metal, was effected with 28 mg of prereduced platinum oxide at 28° (761 mm). After 4 hr, 38.1 ml of hydrogen had been absorbed corresponding to 1.51 molar equiv. The product was separated from solvent by vacuum distillation, analyzed by glpc, and found to consist of 2-methylpentane (63%), *cis*-1,3-dimethylcyclobutane (32%), and *trans*-1,3-dimethylcyclobutane (5%). The two dimethylcyclopropanes were identified by comparison of their ir and nmr spectra with those of samples obtained by hydrogenation of 1-methyl-3-methylenecyclobutane (*vide infra*).

Catalytic Hydrogenation of 1-Methyl-3-methylenecyclobutene. A mixture of 30 mg of platinum oxide and 10 ml of diethyl Carbitol (freshly distilled from sodium metal) was prereduced with hydrogen and treated with 96 mg of 1-methyl-3-methylenecyclobutene in 5 ml of diethyl Carbitol. Hydrogenation at 23° (763 mm) over a period of 2.25 hr led to the uptake of 58.8 ml of hydrogen (2.03 molar equiv). Distillation from the solvent and separation by glpc afforded *cis*- (83%) and *trans*- (17%) 1,3-dimethylcyclobutanes. Pure *cis*-1,3-dimethylcyclobutane has an ir spectrum (neat): 2970–2910 (s), 2870 (s), 2858 (s), 1460 (s), 1435 (sh), 1380 (s), 1333 (s), 1238 (m), 1132 (m), and 945 (m) cm^{-1}; an nmr spectrum consisting of a doublet at δ 1.00 ppm (J = 5 cps) and an unresolved multiplet centered at 2.2 ppm.

Pure *trans*-1,3-dimethylcyclobutane has an ir spectrum (neat): 2965–2905 (s), 2865 (s), 2852 (s), 1450 (s), 1425 (sh), 1373 (s), 1324 (s), 1240 (s) and 975 (s) cm^{-1}; an nmr spectrum consisting of a doublet at δ 1.10 ppm (J = 7 cps), a triplet at 1.7 ppm (J = 7 cps), and a quintuplet at 7.7 ppm (J = 7 cps).

1,2-Dimethyl-3-carbomethoxycyclopropene. Following the procedure of Doering and Mole,[29] 1,2-dimethyl-3-carbomethoxycyclopropene was obtained in 37% of theory from 60 g of butyne-2 and a total of 67 g of methyl diazoacetate, added in small portions and irradiated to completion each time before addition of the next portion. For hydrogenation this material was further purified by glpc on a silicone column. The ir showed absorptions at 3020 (w), 2955 (m), 2924 (m), 2854 (w), 2845 (w), 1917 (w), 1728 (s), 1432 (m), 1344 (m), 1244 (m), 1194 (s), 1177 (s), 1136 (m), 1036 (m), 1027 (m), 986 (m), 953 (w), 906 (w), 831 (w), 708 (m), and 678 (w).

Hydrogenation with 150 ml of platinum oxide (previously reduced in 160 ml of acetic acid) of 501 mg of 1,2-dimethyl-3-carbomethoxycyclopropene in a total of 175 ml of glacial acetic acid resulted in the uptake of 1.10 molar equiv of hydrogen. Filtered and concentrated by distillation of acetic acid through a 35-cm Helipak column, the residue was neutralized with saturated aqueous sodium bicarbonate solution, extracted four times with ether, and dried over anhydrous magnesium sulfate. Concentration of the ether solution by fractional distillation afforded material which was analyzed by glpc on a 4-m column of 40–60 mesh Firebrick containing 15% Dow Corning 710 silicone oil at 116° and 10 psi hydrogen. The product consisted of *cis*-1,2-dimethyl-*cis*-3-carbomethoxycyclopropene (89%),[29] methyl 3-methylpentanoate (7%), and methyl 2-ethylbutanoate (4%), all identified by comparison of infrared spectra with those of authentic materials. Methyl 3-methyl-*trans*-3-pentenoate was prepared by the method of Wagner[49] and hydrogenated to methyl 3-methylpentanoate, bp 41–44° (17 mm). Methyl 2-ethylbutanoate was prepared by esterification of 2-ethylbutanoic acid with diazomethane, bp 39–40° (21 mm).

Acknowledgments. M. Pomerantz expresses his gratitude for the award of fellowships by the Woodrow Wilson Fellowship Foundation (1959–1960), the Leeds and Northrup Company (1960–1962), and the National Science Foundation (1962–1963). This work was supported by the National Science Foundation in the form of Research Grants 11378 to Yale University and GP203 to Rice University. We wish to thank the National Science Foundation for Grant 22689 to Yale University for the purchase of the Varian A-60 analytical nmr spectrometer.

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(49) R. B. Wagner, *J. Am. Chem. Soc.*, **71**, 3214 (1949).