The Thermal Addition of Carbon–Carbon Multiple Bonds to Strained Carbocyclics

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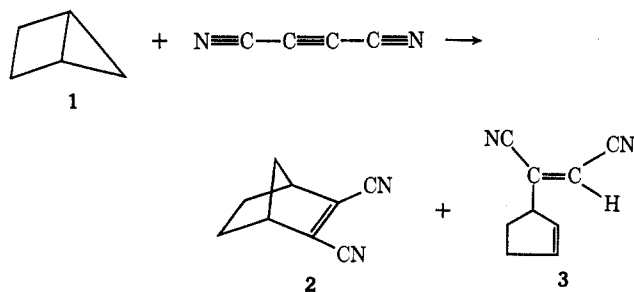*Department of Chemistry, The Ohio State University, Columbus, Ohio 43210*

The many similarities which exist in the chemical and physical properties of olefins and small carbocyclic rings have intrigued chemists for decades. In particular, cyclopropane, with 27.6 kcal/mole of strain energy, parallels propene in many of its chemical reactions. Both undergo hydrogenation to give propane. Both add hydrogen bromide. Both are protonated by strong mineral acids. Moreover, the vinylic hydrogens of
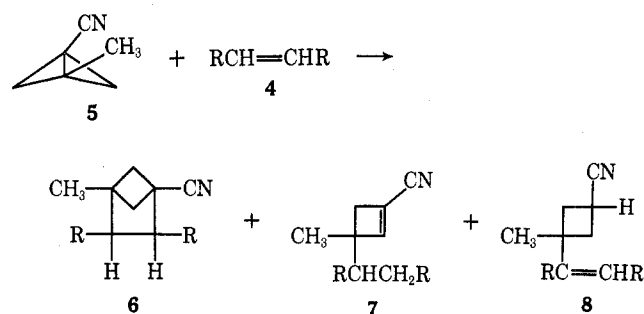
propene are similar in acidity to the hydrogens of cyclopropane. It seems apparent that the correspondence of the chemical properties of propene to those of cyclopropane is a function of the strain incorporated in the three-membered ring, since larger rings, such as cyclopentane, bear little resemblance to cyclopropane in their chemical behavior.

Since the strain inherent in a cyclopropyl ring causes this system to have unique properties, any increase in this strain due to the incorporation of the cyclopropyl moiety into a bicyclic molecule would be expected to magnify the unusual characteristics of the cyclopropyl ring. Thus, we would expect the bent σ bonds of highly strained polycyclic molecules to be unusually reactive and to have properties characteristic of carbon–carbon double bonds. In certain circumstances we might expect that strain effects could make a carbon–carbon single bond more reactive than a normal carbon–carbon double bond. It is the purpose of this Account to review a type of reaction in which a carbon–carbon single bond takes on the characteristics of a highly reactive π bond: the thermal addition of carbon–carbon multiple bonds to the σ bonds of highly strained carbocyclics.

Although olefin dimerizations have been known for many years, it was only recently that examples of the thermal addition of carbon–carbon multiple bonds to strained carbocyclic σ bonds began to appear in the literature. The first example of such a cycloaddition was reported in 1965 by Gassman and Mansfield, who noted that bicyclo[2.1.0]pentane (1) reacted spontaneously with dicyanoacetylene at room temperature to produce a mixture of 2 and 3.[1] Early in 1966 Blan-


chard and Cairncross published their independent discovery of the addition of a variety of olefins of general formula 4 to derivatives of bicyclo[1.1.0]butane typified by 5.[2] These workers found that, at temperatures in excess of 150°, 4 reacted with 5 to give "cycloaddition" products[3] represented by 6 and "ene-type" prod-

ucts[3] of general formulas 7 and 8. The complementary efforts of the Du Pont group[2] and The Ohio State University group[1] have provided the basis for a critical evaluation of the scope and mechanism of this curious addition reaction.

Mechanism and Stereochemistry

Cairncross and Blanchard were the first to carry out a thorough study of the addition of olefins to bicyclo[1.1.0]butanes.[2] They found that 3-methylbicyclo[1.1.0]butanecarbonitrile (5) reacted with butadiene, acrylonitrile, maleonitrile, fumaronitrile, ethylene, styrene, p-methoxystyrene, and 1-(N,N-dimethylamino)-cyclopentene to form 1:1 adducts. In all cases the cycloaddition-type products were derivatives of 4-methylbicyclo[2.1.1]hexane-1-carbonitrile (6). On the basis of the observations that 5 reacted with acrylonitrile to produce 9 and with fumaronitrile or maleonitrile
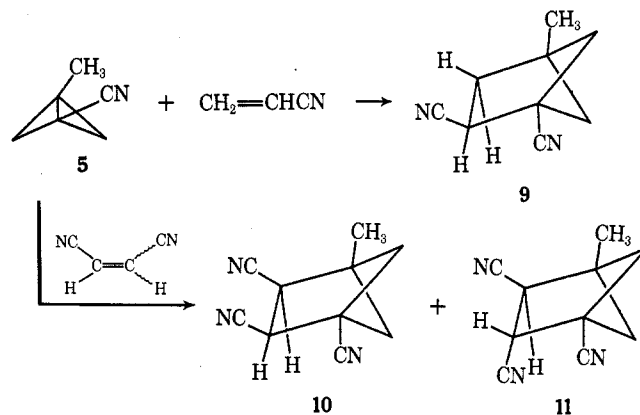
to give a mixture of 10 and 11, these workers tentatively suggested that the rate-determining step in the addition of olefins to 5 was the formation of a diradical intermediate. The validity of this hypothesis was confirmed by Gassman and coworkers (vide infra).

Certain characteristics of the addition of carbon–carbon multiple bonds to strained carbocyclics merit discussion prior to a detailed consideration of the mechanism. The occurrence of this reaction is significantly dependent on ring strain. Whereas derivatives of bicyclo[1.1.0]butane and bicyclo[2.1.0]pentane react

(1) P. G. Gassman and K. T. Mansfield, Chem. Commun., 391 (1965); P. G. Gassman and K. T. Mansfield, J. Amer. Chem. Soc., 90, 1517 (1968).

(2) A. Cairncross and E. P. Blanchard, Jr., ibid., 88, 496 (1966).

(3) For the remainder of this Account the term "cycloaddition products" will refer to those products which can formally be considered to result from a metathesis involving four carbon centers. In this transformation a carbon–carbon σ bond and a carbon–carbon π bond are destroyed and two new carbon–carbon σ bonds are created. In current terminology this transformation could be classified as a $\sigma2 + \pi2$ cycloaddition.[4]

The term "ene-type product" will refer to those products which result from the cleavage of the carbon–carbon σ bond and a carbon–hydrogen σ bond and the formation of a carbon–carbon σ bond and

a carbon–hydrogen σ bond. In some cases a carbon–carbon π bond is broken and a new carbon–carbon π bond is formed. In most, but not all, cases this process results in the transfer of a hydrogen from the strained ring system to the side chain of the ene-type product.

(4) For a detailed discussion of symmetry-allowed cycloaddition reactions see R. B. Woodward and R. Hoffmann, Angew. Chem., Int. Ed. Engl., 8, 781 (1969). It should be noted at this point that a $\sigma2_s + \pi2_s$ cycloaddition is a symmetry-forbidden thermal process.

Table I

Relationship between Ring Strain and Rate of Cycloaddition of Dicarbomethoxyacetylene

Compd	Strain energy relief on cleavage of central bond[a]	Rate of reaction
(structure) 12	~41	Rapid
(structure) 1	~47	Rapid
(structure) 13	~32–34[b]	No reaction

[a] Kilocalories per mole. [b] For recent discussions of strain in polycyclic alkanes see: (a) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968); (b) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1962 (1969); (c) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970); (d) S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *ibid.*, **92**, 3109 (1970); and (e) N. C. Baird, *Tetrahedron*, **26**, 2185 (1970).

with dicyanoacetylene at room temperature, relatively unstrained cyclopropanes such as are present in bicyclo-[6.1.0]nonane require temperatures in the vicinity of 200° for reaction.[5] In terms of relief of ring strain, Table I shows that bicyclo[1.1.0]butane (**12**) and bicyclo[2.1.0]pentane (**1**) react readily with dicarbomethoxyacetylene under conditions where bicyclo[3.1.0]-hexane (**13**) fails to react. The relief of ring strain which accompanies the cleavage of the central bond of **12** and **1** is probably *ca.* 7–15 kcal/mole greater than that for the similar cleavage of the central bond of **13**.[6] This indicates that the overall reaction is extremely sensitive to the strain energy of the polycyclic alkane.

The occurrence of the addition reaction is also dramatically dependent on the electronic character of the carbon–carbon multiple bond. Table II shows that the rate of reaction of bicyclo[2.1.0]pentane (**1**) with various acetylenes is dependent on the electron-withdrawing power of the substituent on the acetylene[1,7] As the electron-withdrawing power of the substituents was decreased, the conditions required for reaction became more vigorous, up to the point where diphenylacetylene failed to react, even after several days at 160°.

In general, we can consider three possible mechanistic routes for the addition of electron-deficient acetylenes to strained carbocyclics: (a) a two-step process involving initial formation of a zwitterionic intermediate followed by either ring closure or proton transfer, (b) competitive concerted ene-type and cycloaddition reactions, and (c) a two-step process involving formation of a diradical followed by either ring closure or hydrogen atom transfer. In order to distinguish among these possibilities, a detailed study of the addition of electron-deficient carbon–carbon multiple bonds to **1** was made.[7,8]

(5) P. G. Gassman and J. Seter, unpublished work.
(6) See Table I, footnote b.
(7) P. G. Gassman and K. T. Mansfield, *J. Amer. Chem. Soc.*, **90**, 1524 (1968).
(8) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **90**, 4746 (1968); **91**, 1684 (1969).

Table II

Temperatures Required for Comparable Rates of Reaction of 1 with Acetylenes of the Type RC≡CR′

R	R′	Temp required, °C
CN	CN	30
CO_2CH_3	CO_2CH_3	100
$CO_2CH_2CH_3$	H	135
C_6H_5	C_6H_5	No reaction after prolonged periods at 160°

An initial mechanistic investigation involved a study of the effect of solvent polarity on the rate of the reaction of **1** with dicarbomethoxyacetylene. The reaction was cleanly first order in both bicyclo[2.1.0]pentane and dicarbomethoxyacetylene. The second-order rate constants listed in Table III show that there is a negligible solvent effect on the rate of reaction. We observed a rate change of only 1.27 in going from benzene as the least polar solvent to acetonitrile as the most polar solvent. These solvents differ by about 35 in dielectric constant. If a zwitterionic intermediate, such as **14**, were involved in this reaction, a change of rate of 10^3 to 10^6 would be expected.[9,10] The lack of a significant solvent effect is strong evidence against the intermediacy of a zwitterionic intermediate.

(structure 14)

14
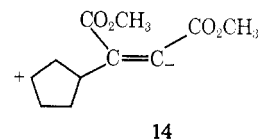
If the formation of cycloaddition and ene-type products from the reaction of **1** with dicarbomethoxyacetylene were to occur *via* competing concerted reactions, two different transition states would be required in the rate-determining step, one for the formation of the cycloadduct and one for the formation of the ene-type product. The relative populations of these two transition states would then determine the product ratio. It would be anticipated that there should be some solvent effect and some temperature effect on the relative populations of these two transition states. However, the ratio of ene product to cycloaddition product remained unchanged within the limits of detection by vpc in the three solvents used in the kinetic study and over a temperature range of 65°. These findings provided a preliminary indication that the two products observed were not arising *via* two competing concerted reactions.

More definitive evidence against a mechanism involving concerted reactions was provided by a study of the reactions of **1** with fumaronitrile and maleonitrile. As shown in Chart I, **1** reacts with both fumaronitrile and maleonitrile to give a mixture of seven products.[8] With maleonitrile (**15a**) the ratio of **16**:**17**:**18** was 1:2:3.

(9) C. A. Stewart, Jr., *ibid.*, **84**, 117 (1962); J. K. Williams, D. W. Wiley, and B. C. McKusick, *ibid.*, **84**, 2210 (1962); S. Proskow, H. E. Simons, and T. L. Cairns, *ibid.*, **88**, 5254 (1966).
(10) This prediction presumes that the formation of the intermediate is the rate-determining step. The clean first-order dependency on both reagents supports this assumption.

Table III

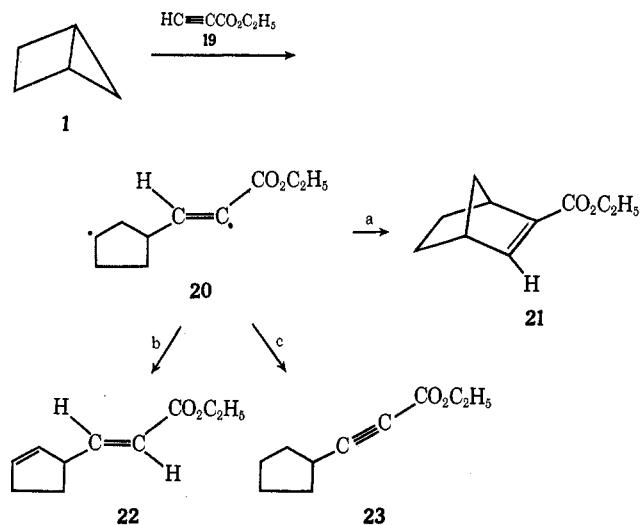**Second-Order Rate Constants for the Reaction of Bicyclo[2.1.0]pentane with Dicarbomethoxyacetylene at 165.0 ± 0.2°**

Solvent	Dielectric constant	$k \times 10^4$ 1. M^{-1} sec^{-1}	k_{rel}
Benzene	2.27	1.08 ± 0.03	1.46
Ethyl acetate	6.03	0.74 ± 0.02	1.00
Acetonitrile	37.5	1.37 ± 0.03	1.85

Chart I

15a, X = C≡N; Y = H
b, X = H; Y = C≡N

16   17

18
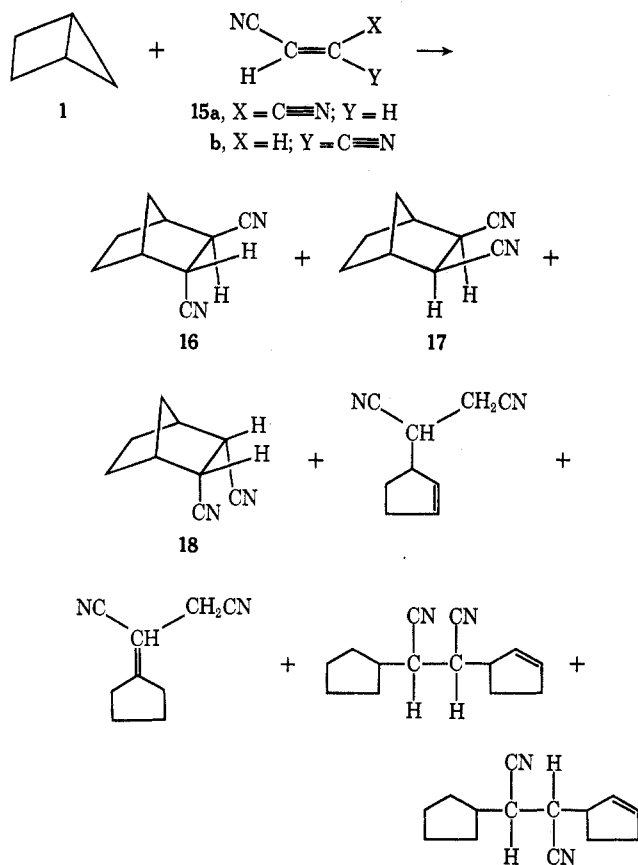
With fumaronitrile (**15b**) the ratio was 22:1:1.3. Since **15a, 15b, 16, 17,** and **18** were stable under the reaction conditions, the formation of **16** from the reaction of **1** with **15a** and the formation of **17** and **18** from the addition of **15b** to **1** required the formation of a discrete intermediate in which rotation could occur about the bond which originally was the olefinic linkage in **15a** and **15b**. The existence of such an intermediate foregoes the plausibility of competing concerted reactions.[11]

The exclusion of the possibility of a zwitterionic intermediate and the incompatibility of competing concerted

Chart II

reactions with the observed data indicated that an intermediate other than a zwitterion must have been formed. The logical candidate for such a role is a diradical. Diradicals have been firmly established as intermediates in the additions of olefins such as 1,1-dichloro-2,2-difluoroethylene to olefins and dienes.[12] Diradical intermediates appear to be equally well suited to explain the addition of olefins and acetylenes to strained carbocyclic rings.

The role of a diradical intermediate is outlined for the reaction of propiolic ester (**19**) with **1** in Chart II. The addition of **19** to **1** should yield the diradical **20**. Closure of the diradical would give the cycloaddition product **21** as indicated by process a. Two types of hydrogen-transfer processes can occur, as indicated by routes b and c, to yield two different ene-type products. Transfer of a hydrogen from the ring to the side chain would give **22**, while transfer of a hydrogen from the side chain to the ring would produce **23**.

The lack of solvent polarity and temperature effects on the product ratio obtained in the reaction of **1** with dicarbomethoxyacetylene is also readily explained on the basis of the formation of a diradical in the rate-determining step. A single transition state would be involved in the rate-determining formation of an intermediate diradical.[13] In subsequent fast steps the diradical would partition itself between cycloadduct formation (radical recombination) and formation of ene-type product (intramolecular radical disproportionation). In simple cases the activation energies for radical combination and radical disproportionation have been found to be comparable.[14] This explains the formation of both cycloadduct and ene-type products in our reaction. Furthermore, Bartlett and coworkers[12]

(11) Starting with the cis isomer, **15a**, we observed ca. 17% rotation in the formation of the dicyanonorbornanes, while with the trans isomer, **15b**, we observed ca. 10% rotation.[3] In a similar study in the bicyclo[1.1.0]butane series Cairncross and Blanchard[2] observed the loss of ca. 26% stereopurity in the products formed from both **15a** and **15b**. This indicates to us that the closure of the intermediate, leading to the bicyclo[2.2.1]heptane derivatives, in our series occurs faster than the closure of the intermediate leading to the bicyclo[2.1.1]hexane derivatives in the work of Cairncross and Blanchard.[2] The decreased lifetime of our intermediate relative to that of Cairncross and Blanchard is probably related to the smaller strain energy which must be overcome in the formation of the bicyclo[2.2.1]heptane nucleus relative to that involved in the formation of the bicyclo[2.1.1]hexane skeleton.

(12) For a discussion and leading references see P. D. Bartlett, *Science*, 159, 833 (1968); P. D. Bartlett, *Nucleus (Cambridge, Mass.)*, 251 (1966); and P. D. Bartlett and G. E. H. Wallbillich, *J. Amer. Chem. Soc.*, 91, 409 (1969).

(13) Since diradical formation would involve little, if any, change in the polarity of the reactants, the effect of solvent polarity on the rate-determining step would be negligible.

(14) J. Kraus and J. Calvert, *J. Amer. Chem. Soc.*, 79, 5921 (1957).

have shown that intramolecular combination of a diradical is competitive with rotation about a carbon–carbon single bond (*i.e.*, has a rate constant of *ca.* 10^{-10} sec^{-1}). Reactions which occur at extremely fast rates, such as competitive diradical combination and disproportionation, should have such low activation energies as to be relatively independent of the environment. As a result, the ratio of cycloaddition to ene-type products obtained from the reaction of **1** with dicarbomethoxyacetylene *via* a diradical intermediate should be essentially unchanged by solvent polarity and temperature. Thus, our results appear to be uniquely consistent with the initial formation of a diradical intermediate.

We have noted above that acetylenes which are electron deficient due to the presence of electron-withdrawing substituents work best in our reaction. Since the rate-determining step appears to involve the formation of a diradical, it might be anticipated that the substituent on the acetylene should be both electron withdrawing and capable of stabilizing an adjacent radical through conjugation. The failure of perfluoro-2-butyne (**24**) to react with **1** gave credence to this hypothesis. The trifluoromethyl groups of **24** are strongly electron withdrawing and **24** is comparable to dicyanoacetylene as a dienophile. The failure of **24** to react with **1** demonstrated that the requirements of a "tanycyclophile"[15] were quite different from those of a dienophile. Additional evidence for the formation of a diradical intermediate in these reactions was provided by the reaction of **1** with 1,1-dichloro-2,2-difluoroethylene (**25**) to give 5% of **26** and 31% of **27**.[16] The formation of **27** and **26** could be readily accounted for if **28** were
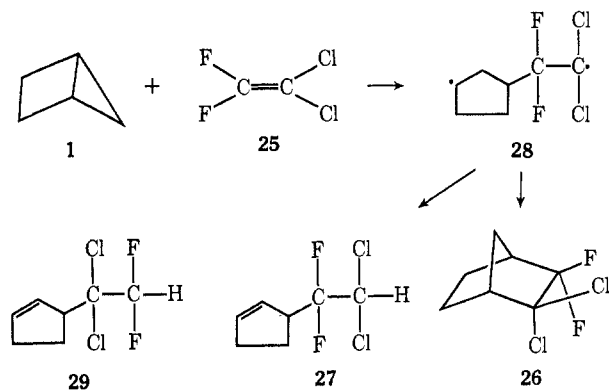

the initially formed intermediate. Chlorine is far superior to fluorine as a radical-stabilizing substituent.[12] In this regard the absence of **29** and the formation of **27** indicated the intermediacy of the diradical **28**, with the radical center situated at the more stable position next to the two chlorines.

The major mechanistic question which remains to be discussed concerns the stereochemical approach of the

reacting species to each other. Since bicyclo[2.1.0]pentane has an envelope shape, the question is whether the approach of the tanycyclophile is from above or below the flap of the envelope. The addition of maleic anhydride (**30**) to *exo,exo*-2,3-dideuteriobicyclo[2.1.0]pentane (**31**) provided a definitive answer to this stereochemical question. When **31** and **30** were heated together at 120° for 2 days, **32** was obtained as one of four
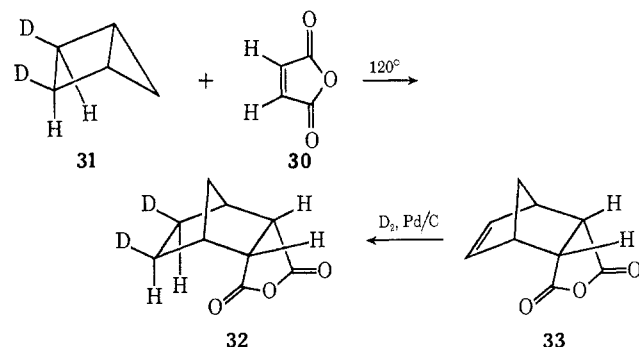
products.[8] None of the isomer with the two deuteriums in the endo position could be detected. This required that the attacking olefin approach **31** from the underside of the flap, resulting in an inversion of this bridge relative to the deuterium labels.[17] The stereochemistry of the isotopic label was firmly established *via* both nmr spectroscopy and synthesis of an authentic sample by reduction of **33**.

The effect of steric hindrance to attack of derivatives of both bicyclo[2.1.0]pentanes and bicyclo[1.1.0]butane by tanycyclophiles was elucidated by Gassman and Richmond.[19] The bicyclo[1.1.0]butane derivative, **34**, has the inside of the flap hindered by a trimethylene bridge while the bicyclo[2.1.0]pentane derivative, **35**, has the inside of its flap unsymmetrically hindered by

an ethano bridge. The addition of benzyne to **34** occurred readily to give a 61% yield of a single 1:1 adduct which was shown to be **36**. Mechanistically, the formation of **36** could occur *via* attack of benzyne on the inside of the flap to form the diradical **37**, followed by hydrogen atom transfer to give **38** and closure of the 1,3-dirad-

(15) In general the author is opposed to the needless coining of trivial names. Unfortunately, he can think of no better way of categorizing those carbon–carbon multiple bonds containing compounds which attack strained rings than to call them "tanycyclophiles" (from the Greek for strained ring seeking).
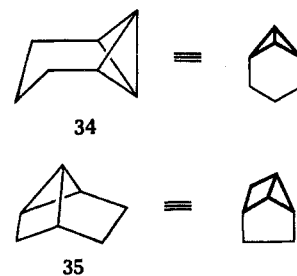
(16) P. G. Gassman and K. T. Mansfield, unpublished work.

(17) W. R. Roth and M. Martin (*Tetrahedron Lett.*, 4695 (1967)) have demonstrated that nitrogen–nitrogen double bonds also attack derivatives of **1** from the underside of the flap. The attack of carbon–carbon multiple bonds on the inside of the flap of bicyclo[1.1.0]butanes has also been postulated by Cairncross and Blanchard[2] and demonstrated by Pomerantz and coworkers.[18]

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

(19) P. G. Gassman and G. D. Richmond, *ibid.*, **90**, 5637 (1968); P. G. Gassman and G. D. Richmond, *Chem. Commun.*, 1631 (1968); P. G. Gassman and G. D. Richmond, *J. Amer. Chem. Soc.*, **92**, 2090 (1970).
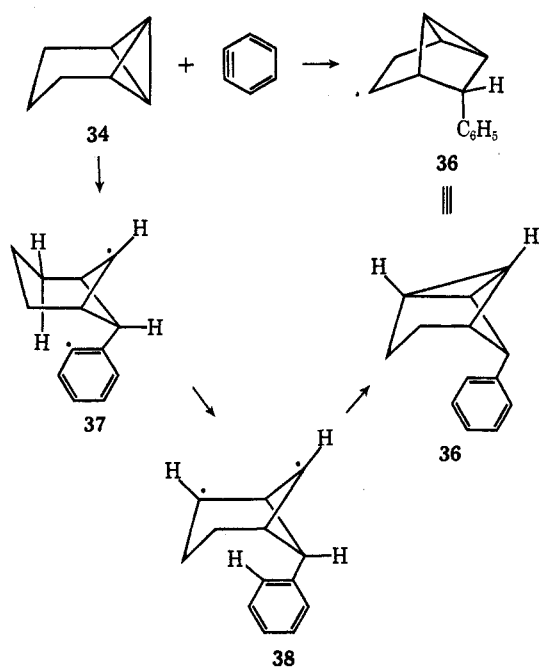
ical **38** to yield **36**.[20] Similarly, **35** added dicyano-acetylene to give the adduct **39**. The formation of **39** is readily explained in terms of the initial generation of the diradical[20] **40** followed by hydrogen atom transfer to give **41** and ring closure. It should be noted that attack again occurred from the inside of the flap of **35** in
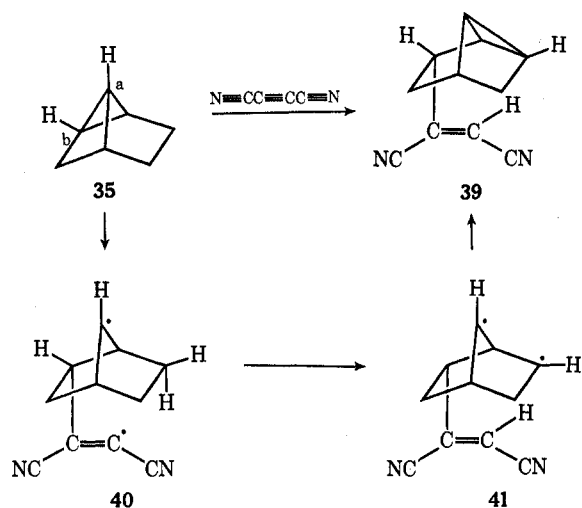
spite of the hindrance to approach provided by the ethano bridge. However, the sensitivity of the reaction to steric hindrance was indicated by the absence of products derived from initial attack at position a of **35** which was slightly more hindered than position b.

In terms of the overall mechanism, we view this reaction as a displacement reaction in which the carbon–carbon multiple bond initially attacks the back lobe of the bent central carbon–carbon σ bond to displace an orbital containing one electron (*i.e.*, the displacement of a carbon radical). The rapid appearance of dark blue colors on the addition of dicyanoacetylene to **1** and

the observation of complex esr signals would seem to support this hypothesis.

An approximate order of reactivity for tanycyclophiles was able to be constructed as a result of our studies. This order in terms of declining tanycyclophilicity is: dicyanoacetylene $\cong$ tetracyanoethylene > dicarbomethoxyacetylene > maleic anhydride $\cong$ fumaronitrile $\cong$ maleonitrile > 1,1-dichloro-2,2-difluoroethylene $\gg$ benzyne $\gg$ perfluoro-2-butyne and diphenylacetylene. The last three reagents fail to react with derivatives of **1** under normal reaction conditions.

Applications

Following the original reports of the addition of carbon–carbon multiple bonds to strained carbocyclics,[1,2] several groups of workers investigated applications of this reaction. Pomerantz was the first to utilize the concept of this reaction in his addition[21] of benzyne to bicyclo[1.1.0]butane to obtain a 6:1 mixture of **42** and **43**. In an extension of this work it was reported that
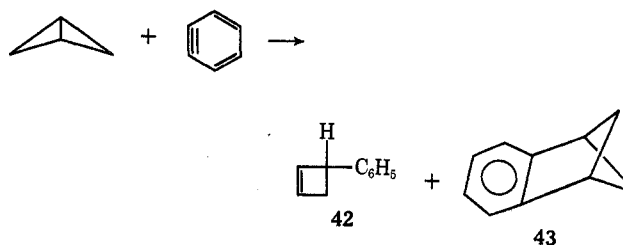
44 failed to react with benzyne[18] but did react with dicarbomethoxyacetylene to give, among other products, **45**.[22] The formation of **45** can be explained in terms of
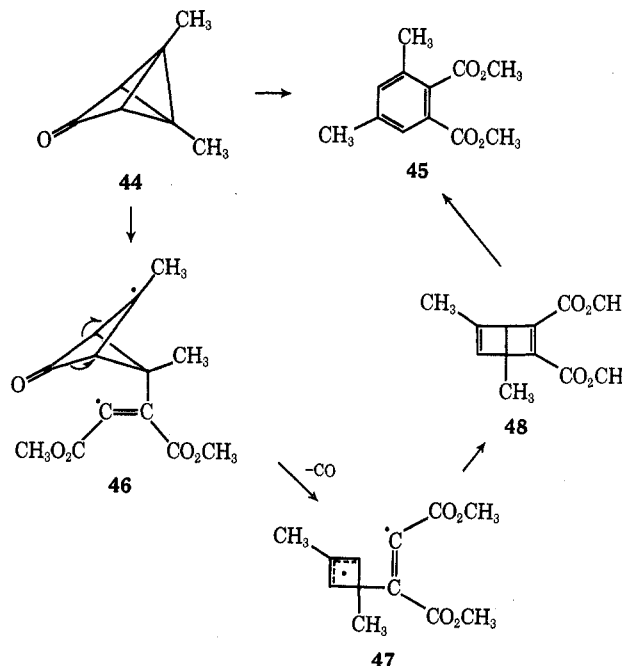
attack on the inside of the flap of the bicyclo[1.1.0]-butane portion of **44** to give the diradical **46**. Loss of carbon monoxide from **46** could give the allylic radical **47** which would give **48** on closure. An alternate possi-
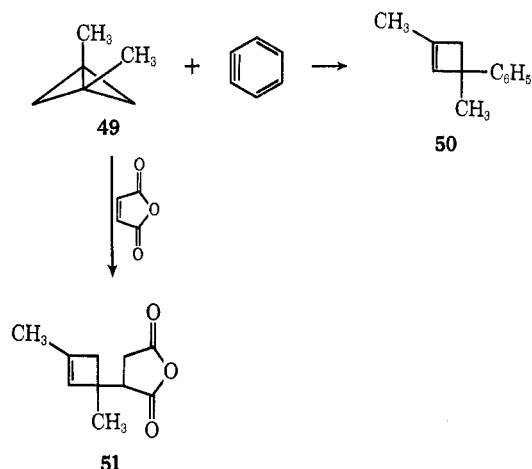
(20) A concerted $_\pi 2 + _\sigma 2 + _\sigma 2$ reaction could also be invoked as a possible mechanism in this particular reaction: R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(21) M. Pomerantz, *ibid.*, **88**, 5349 (1966); M. Pomerantz and E. W. Abrahamson, *ibid.*, **88**, 3970 (1966).

(22) M. Pomerantz and R. N. Wilke, *Tetrahedron Lett.*, 463 (1969).

bility would be the direct formation of **48** from **46**. Valence isomerization of **48** would give **45**.

In a related case, the reaction of **49** with benzyne[18] gave only **50**. Similarly, Rifi found[23] that **49** reacted with maleic anhydride to give only **51**. An obscure ex-

ample of a simple cycloaddition to a complex bicyclo[2.1.0]pentane derivative was recently described as the "intramolecular trapping of a 1,3-diradical."[24] On close examination, this intramolecular addition of the cyclobutene double bond of **52** to the central bond of the bicyclo[2.1.0]pentane moiety of **52** appears to be little more than another example of the well-established addition of carbon–carbon multiple bonds to bent σ bonds. Although this cycloaddition might appear to involve attack of the carbon–carbon multiple bond on
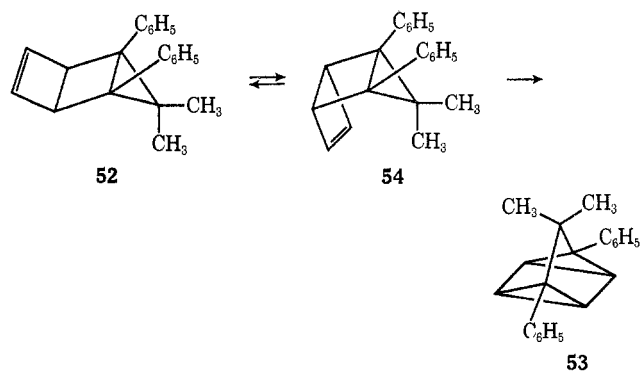
the top side of the bicyclo[2.1.0]pentane flap, it is the opinion of this reviewer that insufficient data have been presented for a determination of the direction of attack. Flap inversion of bicyclo[2.1.0]pentane derivatives fused to other rings at the 3,4 positions is known[25,26] to occur at temperatures as low as 40°. Thus, it seems

likely that rapid interconversion of **52** and **54** should occur at the temperatures used in this reaction. Formation of **53** could then occur *via* the expected attack of the cyclobutene carbon–carbon multiple bond of **54** on the backside of the bicyclo[2.1.0]pentane flap.

Related Thermal Cycloadditions

Smith reported an intriguing cycloaddition of a carbon–carbon multiple bond to the highly strained σ bond of quadricyclane (**55**) in 1966.[31] In this reaction, **55**
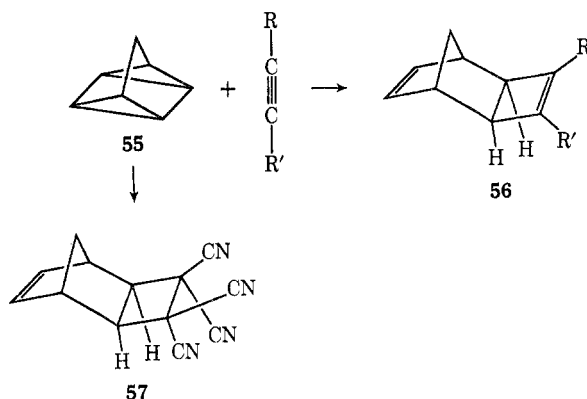
added dicyanoacetylene, dicarbomethoxyacetylene, and methyl propiolate to give compounds of the general formula **56**. Similarly, **55** added tetracyanoethylene to
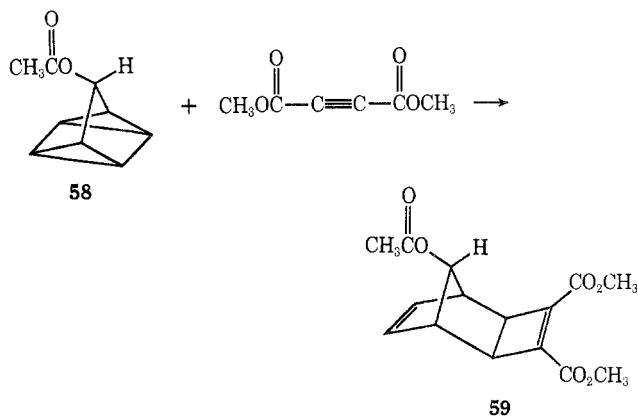
give **57** in high yield. The stereoselectivity of this reaction was illustrated by the addition of dicarbomethoxyacetylene to **58** which produced greater than 95% of **59**. Several substituted quadricyclanes were subjected to cycloaddition conditions by Prinzbach and coworkers.[32] They found that quadricyclanes of the general formula **60** added electron-deficient acetylenes of the general formula **61** to yield **62**. The nature of X was varied sig-

(23) M. R. Rifi, *J. Amer. Chem. Soc.*, **89**, 4442 (1967).

(24) L. A. Paquette and L. M. Leichter, *ibid.*, **92**, 1765 (1970).

(25) K. Mackenzie, W. P. Lay, J. R. Telford, and D. L. Williams-Smith, *Chem. Commun.*, 761 (1969).

(26) This inversion need not involve the intermediacy of a diradical. Although it has been generally suggested that breakage of the central carbon–carbon bond occurs in the first step leading to the inversion of the flap of the bicyclo[2.1.0]pentane nucleus, the author knows of no compelling evidence in support of this hypothesis. In principle, this inversion could occur *via* a planar bicyclo[2.1.0]-pentane in which the bridgehead carbons remain tetravalent. The recent synthesis of molecules containing pyramidal carbon[27,28] indicates the feasibility of the inversion of highly strained polycyclics *via* planar tetracoordinate carbon.[29,30]

(27) K. B. Wiberg and G. J. Burgmaier, *Tetrahedron Lett.*, 317 (1969); P. G. Gassman, J. Keller, and A. Topp, *ibid.*, 1093 (1969); K. B. Wiberg, unpublished work. We wish to thank Professor Wiberg for informing us of his results prior to publication.

(28) The term "pyramidal carbon" refers to a tetracovalent carbon which is bonded to four nuclei, all of which are located on one side of a plane passing through the tetravalent carbon.

(29) For a recent discussion of planar tetracoordinate carbon see R. Hoffmann, R. W. Alder, and C. F. Wilcox, Jr., *J. Amer. Chem. Soc.*, **92**, 4992 (1970).

(30) The author wishes to acknowledge stimulating discussions with T. J. Atkins which led to the development of this concept.
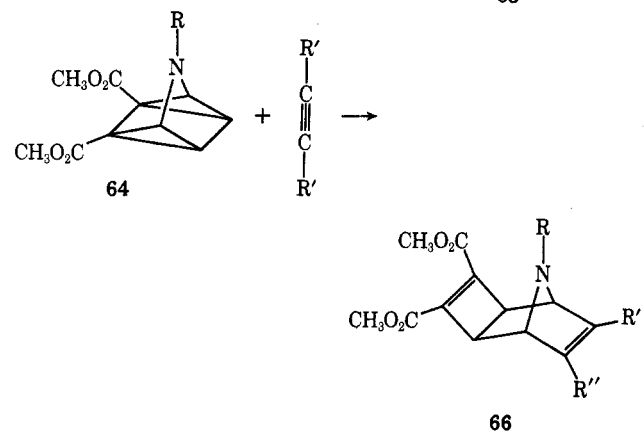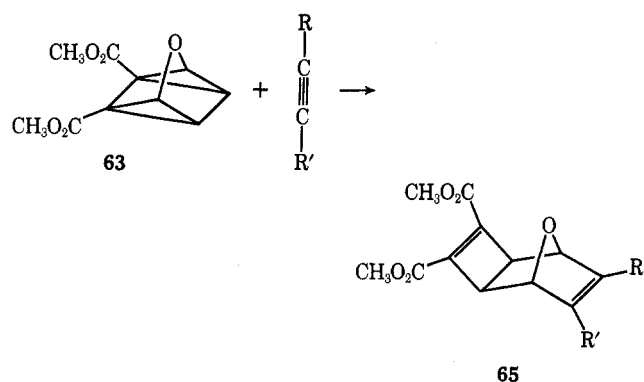
(31) C. D. Smith, *J. Amer. Chem. Soc.*, **88**, 4373 (1966).

(32) H. Prinzbach and J. Rivier, *Angew. Chem., Int. Ed. Engl.*, **6**, 1069 (1967); H. Prinzbach, *Pure Appl. Chem.*, **16**, 17 (1968).
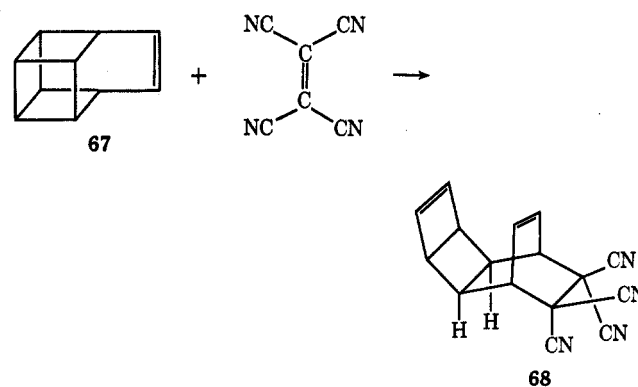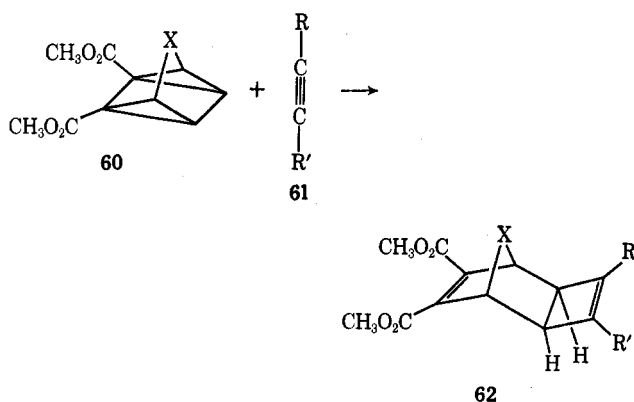
nificantly from CH_2, through $C(CH_3)_2$, $C=C(CH_3)_2$, $C=CHC_6H_5$, and $C=C(C_6H_5)_2$, to $C=O$.

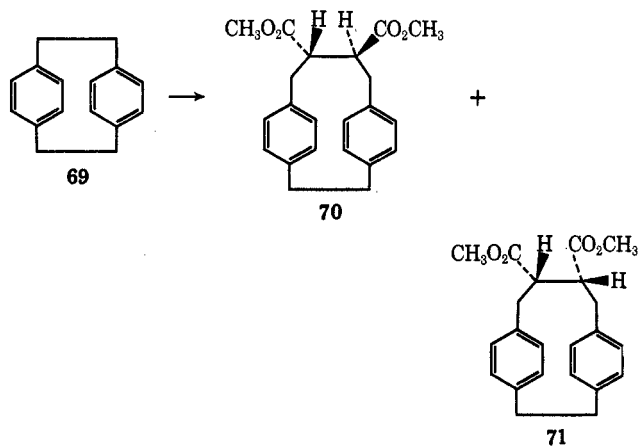In applying the Smith type of cycloaddition to 3-oxaquadricyclanes and 3-azaquadricyclanes (63 and 64, respectively), Prinzbach and coworkers found a new mode of addition in that the heterocyclic strained systems gave 65 and 66, respectively.[33] This involves attack of the acetylenes at the carbons adjacent to the heteroatom in an overall $2 + 2 + 2$ cycloaddition. In an analogous reaction, 67 adds electron-deficient olefins, as shown for the addition of tetracyanoethylene to give 68.[34] The additions described by Smith, Prinzbach, and LeGoff differ considerably from additions to simple bicyclo[2.1.0]pentanes and bicyclo[1.1.0]butanes. Whereas the latter are symmetry-forbidden thermal processes, the former are symmetry-allowed thermal $_\pi 2_s + _\sigma 2_s + _\sigma 2_s$ additions.

A unique addition of a carbon–carbon multiple bond to a strained σ bond was described for paracyclophane (69) which added either dimethyl fumarate or dimethyl maleate to give a mixture of 70 and 71. The authors suggested[35] that 69 underwent homolytic cleavage of the strained carbon–carbon σ bond to form the p,p'-di-methylenebibenzyl diradical. Addition of this diradical to the unsaturated ester would give a new diradical, at which stage rotation could occur followed by a radical combination step to give a mixture of 70 and 71. It has not been definitively established whether the unsaturated diester reacted directly with 69 to give the immediate precursor of 70 and 71 or whether the p,p'-dimethylenebibenzyl diradical is involved in the reaction as suggested.

Derivatives of the somewhat less strained tricyclo-[3.2.1.0²,⁴]oct-6-ene skeleton undergo thermal intramolecular cycloaddition.[36,37] The conversion of 72 into 73 was achieved at 190° in the case of 72a[36] and at 60° for 72b.[37,38] Similarly, 74 was postulated[35] as an inter-

(33) H. Prinzbach, R. Fuchs, R. Kitzing, and H. Achenbach, *Angew. Chem., Int. Ed. Engl.*, **7**, 727 (1968).

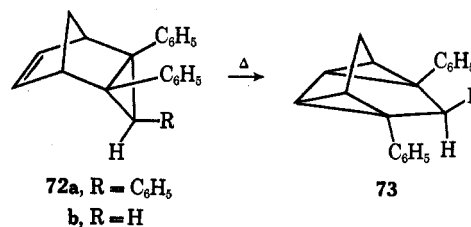(34) E. LeGoff and S. Oka, *J. Amer. Chem. Soc.*, **91**, 5665 (1969).

(35) H. J. Reich and D. J. Cram, *ibid.*, **89**, 3078 (1967).

(36) H. Prinzbach and H.-D. Martin, *Helv. Chim. Acta*, **51**, 438 (1968); H. Prinzbach, W. Eberbach, M. Klaus, and G. v. Veh, *Ber.*, **101**, 4066 (1968).

(37) D. T. Longone and D. M. Stehouwer, *Tetrahedron Lett.*, 1017 (1970).
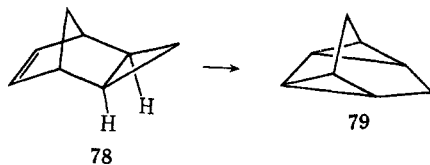
(38) The stereochemistry of the cyclopropane ring (and of the phenyl groups) was not specified for 72b.

mediate in the reaction of **75** with **76** to give **77**. Presumably, the thermal intramolecular cycloaddition required for the conversion of **74** into **75** occurs at relatively low temperatures.


75   **76**

74

77
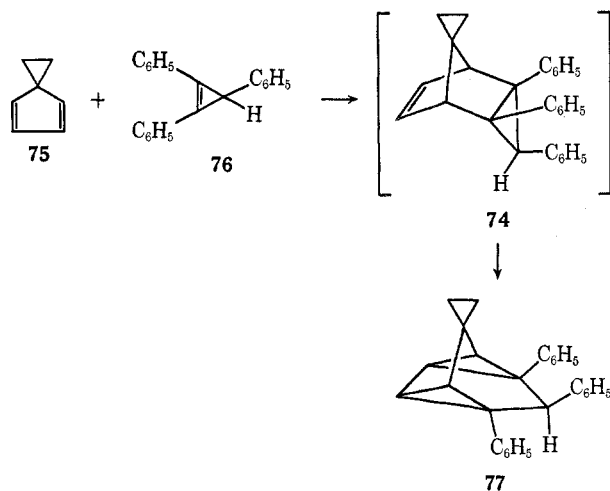
Metal-Catalyzed Additions

Metal-catalyzed intermolecular additions of carbon–carbon multiple bonds to strained carbocyclics are yet to be observed. However, intramolecular reactions of this type are known. Rhodium on carbon and various coordination complexes of rhodium readily transform **78** into **79**.[39,40] Some mechanistic details of this reaction have been reported.[39]

78   **79**

A related curiosity involves the conversion of **1** into **80** in the presence of maleic anhydride and rhodium dicarbonyl chloride dimer.[41] Although it has been

1

80   **81**
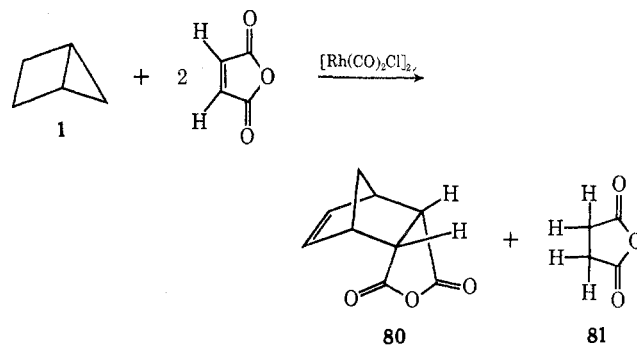
found[41] that **1** is rapidly isomerized to cyclopentene in the presence of the catalyst and that cyclopentene reacts with maleic anhydride in the presence of the catalyst to yield a mixture of **80** and **81**, we have yet to establish all the details of this particular set of reactions.

Summary

The addition of electron-deficient carbon–carbon multiple bonds to strained carbocyclics has been shown to be a general reaction. Mechanistic evidence indicates that the rate-determining step involves the formation of a diradical in the simple $_\pi 2 + _\sigma 2$ additions.

(39) T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 2405 (1969); **91**, 6519 (1969).

(40) H. C. Volger, H. Hogeveen, and M. Gaasbeek, *ibid.*, **91**, 218 (1969).

(41) P. G. Gassman, J. T. Lumb, and T. J. Atkins, unpublished work.

Additions and Corrections

Volume 4, 1971

Paul G. Gassman: The Thermal Addition of Carbon–Carbon Multiple Bonds to Strained Carbocyclics.

Page 135. Add to reference 34: "Recent studies

have shown that what appears to consist of a formal symmetry-allowed thermal $_\pi2_s + _\sigma2_s + _\sigma2_s$ addition to **67** is a stepwise process in which the tetracyanoethylene is *not* involved in the rate-determining step: H. H. Westberg, E. N. Cain, and S. Masamune, *ibid.*, **91,** 7512 (1969)."