Catalytic Reduction of Ethyl 3-(3-Cyclopentenyl)-*trans*-acrylate (25). A solution of 657 mg of **25** in 10 ml of acetone was hydrogenated at 31° (744 mm) over 29 mg of prereduced 5% palladium on carbon. Hydrogen uptake ceased abruptly after 1.98 equiv had been consumed. The solution was filtered through Celite, concentrated at reduced pressure, and distilled to give 484 mg (74%) of colorless ethyl (3-cyclopentylpropionate) (**29**), bp 93–94° (11 mm), $n^{24}\text{D}$ 1.4386 [lit.[32] bp 90° (6 mm)]. Hydrolysis of 450 mg of **29** in concentrated sodium hydroxide afforded 316 mg (85%) of the corresponding acid, **34**, bp 122–123° (6 mm), $n^{24}\text{D}$ 1.4537 [lit.[32] bp 131° (6 mm), $n^{17.4}\text{D}$ 1.4594]. The corresponding anilide, mp 109.1–109.9° (needles from dilute ethanol) [lit.[32] mp 110° (needles from dilute acetic acid)], and amide, mp 120.9–121.9° (glistening plates from water) [lit.[32] mp 122°], were prepared from the crude acid chloride of **34** by standard procedures.

Catalytic Reduction of Ethyl 3-Cyclopentylpropiolate (26). A solution of 60 mg of **26** in 5 ml of acetone was exhaustively hydrogenated at 30° (742 mm) over 20 mg of 5% palladium on carbon. The solution was filtered through a Celite microplug, concentrated at reduced pressure, and freed of residual solvent by preparative vpc (butanediol succinate column, 155°) to give **29** with the same infrared spectrum as the sample prepared by reduction of **25**.

Addition of Dicyanoacetylene to 3-Methylbicyclo[1.1.0]butanecarbonitrile (31). To 765 mg (0.0103 mol) of freshly prepared **13** in 3 ml of chloroform was added 970 mg (0.0104 mol) of **31**. The mixture was tightly stoppered under nitrogen in a 15-ml flask and magnetically stirred for 5 days at room temperature with exclusion of light. Chloroform and unreacted acetylene were swept out in a slow stream of nitrogen, and unreacted **31** was removed by vacuum transfer at 0.5 mm. The black residue was dissolved in 1 ml of benzene and chromatographed on 63 g of Woelm neutral alumina, activity III. Elution with 60% benzene–40% hexane gave 129 mg (7.6%) of 3-cyano-1-methylcyclobutenyl-3-maleonitrile (**32**) as colorless crystals, mp 76–77°. One recrystallization from ether–pentane gave colorless plates, mp 77.6–78.3°, $\lambda_{\max}^{\text{ethanol}}$ 228 mμ (ε 13,500). The infrared spectrum of **32** (potassium bromide disk) showed strong absorptions at 4.42 (nitrile), 6.07 (cyclobutene), and 6.23 μ (conjugated C=C). The nmr spectrum showed peaks at τ 3.60 (singlet, 1 H), 4.29 (quartet, J = 1 cps, 1 H), 6.89 (AB quartet, J = 12.8 cps; with fine structure, 2 H), and 8.11 (doublet, J = 1 cps, 3 H).

Anal. Calcd for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.84. Found: C, 71.04; H, 4.26; N, 24.76.

Further elution of the column gave 48 mg of yellow liquid which showed three spots in addition to traces of **32** on tlc. On prolonged standing in the refrigerator this oil deposited solid material which gave 5.5 mg of white crystals, mp 146–153° after one recrystallization from ether–pentane. The 3.2-μ region of the infrared spectrum of this substance showed no olefinic protons and there was an intense C=C absorption at 6.27 μ, similar to that exhibited by **14**.

Attempts were made to increase the yield of the reaction so that the minor products could be characterized. However, prolonging the reaction time for several weeks gave no more product than was obtained in 5 days, and heating a reaction mixture to 80° in a sealed tube gave almost total decomposition. Hence the liquid mixture was not further characterized.

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Competitive Cycloaddition and Ene-Type Reactions. Mechanism of the Reaction of Bicyclo[2.1.0]pentane with Electron-Deficient Acetylenes

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Abstract: Rate studies of the addition of electron-deficient acetylene to bicyclo[2.1.0]pentane have provided data which are most consistent with the formation of a diradical intermediate. In particular, rate measurements in benzene, ethyl acetate, and acetonitrile showed a negligible solvent effect, the total change in relative rates being less than a factor of 2. More important, the product ratio was independent of solvent polarity. These results are discussed in relation to the classical cycloaddition and ene-type reactions.

Recently, we reported on the reaction of electron-deficient acetylenes with bicyclo[2.1.0]pentane, a reaction which yields both cycloaddition and ene-type products. The amazing addition of dicyanoacetylene to bicyclo[2.1.0]pentane (**1**) at room temperature[3] prompted us to carry out a detailed investigation of the mechanism of this unprecedented[4] reaction. At this time we wish to report the results of a detailed kinetic study which showed that the competitive formation of cycloaddition[5] and ene[6]-type products is mechanistically most consistent with the formation of diradical intermediates.

The reaction of dicyanoacetylene with bicyclo-[2.1.0]pentane gave 11% of 2,3-dicyanobicyclo[2.2.1]-hept-2-ene (**2a**) and greater than 58% of cyclopentenyl-3-maleonitrile[3,7] (**3a**). When dicarbomethoxyacetylene

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[1] Alfred P. Sloan Research Fellow, 1967–1969.

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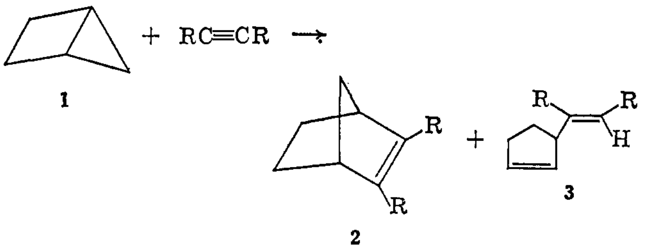
[3] P. G. Gassman and K. T. Mansfield, *Chem. Commun.*, 391 (1965); P. G. Gassman and K. T. Mansfield, *J. Amer. Chem. Soc.*, **90**, 1517 (1968).

[4] Subsequent to our initial report[3] other accounts of the thermal reaction of strained cyclopropanes with carbon–carbon multiple bonds have appeared: A. Cairncross and E. P. Blanchard, Jr., *ibid.*, **88**, 496 (1966); C. D. Smith, *ibid.*, **88**, 4273 (1966); M. Pomerantz, *ibid.*, **88**, 5349 (1966).

[5] For recent studies of cycloaddition reactions see: (a) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962); (b) C. A. Stewart, Jr., *J. Amer. Chem. Soc.*, **84**, 117 (1962); (c) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964); (d) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); (e) P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964); (f) P. D. Bartlett, *Nucleus* (Cambridge, Mass.), 251 (1966).

[6] The reaction which we are discussing is formally a "homoene" reaction. For papers relevant to the classical ene reaction see: K. Alder, F. Pascher, and A. Schmitz, *Ber.*, **76**, 27 (1943); K. Alder and H. von Brachel, *Ann.*, **651**, 141 (1962), and intervening publications.

[7] Most methods of isolation resulted in the isomerization of **3a**



a, R = C≡N
b, R = CO_2CH_3

was the electron-deficient acetylene, a reaction temperature of 100° was required for a suitable rate of reaction. The yield of products in this case was 75%, with 2,3-dicarbomethoxybicyclo[2.2.1]hept-2-ene (**2b**) constituting 24% of the reaction product, while the remaining 76% was dimethyl cyclopentenyl-3-succinate (**3b**).

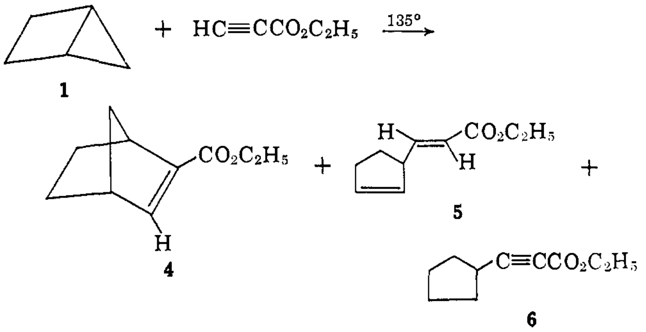
Mechanistically, the reactions described above could occur *via* either a concerted multicenter reaction or a stepwise process, with the stepwise classification being subdivided according to the formation of zwitterionic intermediates or diradical intermediates. In order to determine which of these possibilities best fits our reaction, the kinetics of the reaction of dicarbomethoxyacetylene with **1** were measured. The reaction was cleanly first order in bicyclo[2.1.0]pentane and first order in dicarbomethoxyacetylene. Table I lists the second-order rate constants in benzene, ethyl acetate, and acetonitrile. If a zwitterionic intermediate were involved in this reaction, a change of rate of 10^3 to 10^6 would be expected.[5b,8] We observed a factor of less than 2. The lack of a solvent effect practically eliminates the possibility of the formation of zwitterionic intermediates.

Table I. Second-Orde1 Rate Constants for the Reaction of Bicyclo[2.1.0]pentane with Dicarbomethoxyacetylene at 165.0 ± 0.2°

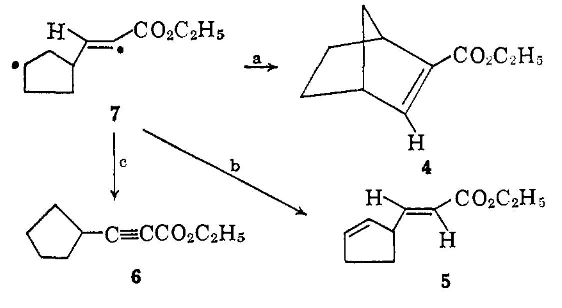
Solvent	Dielectric constant	$k \times 10^4$ l. M^{-1} sec^{-1}	k_{rel}
Benzene	2.27	1.08 ± 0.03	1.46
Ethyl acetate	6.03	0.74 ± 0.02	1.00
Acetonitrile	37.5	1.37 ± 0.03	1.85

If a concerted multicenter reaction mechanism[9] were to explain our results, 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 homoene product. The product ratio would be determined by the relative populations of these two transition states. It would be anticipated that the solvent should have at least a slight effect on the relative populations of these transition states. However, an identical product ratio of 24:76 (for **2b** and **3b**, respectively) was observed for all three solvents used in the rate studies. By comparison, if the reaction of **1** with electron-deficient acetylenes occurred *via* a radical mechanism, a single transition state would be involved in the rate-determining formation of an intermediate diradical. In subsequent fast steps the intermediate diradical would partition between the cycloadduct (combination reaction) and homoene product (intramolecular disproportionation). In simple cases the activation energies for combination and disproportionation of radicals have been found to be equal.[10] This would explain the formation of both **2** and **3** in our reaction. Furthermore, Bartlett has shown[5c–f] that intramolecular combination of a diradical is competitive with rotation about a carbon–carbon single bond (*i.e.*, has a rate constant of about 10^{-10} sec^{-1}). Competitive reactions occurring at extremely fast rates, such as radical combination and disproportionation, should have such low activation energies as to be impervious to the environment. Thus, a solvent effect would not be expected in intramolecular reactions of diradicals, which is consistent with the lack of a solvent effect on our product ratio. This is indicative of a radical mechanism for the reaction of **1** with electron-deficient acetylenes.

Additional evidence against a concerted multicenter mechanism was provided by the reaction of **1** with propiolic ester to yield **4**, **5**, and **6** in the ratio of 6:79:11.



Competitive concerted reactions would require three separate rate-determining reactions in this case. The transition state leading to **6** would be that of a 2 + 2 cycloaddition involving only σ bonds. We find this possibility somewhat unattractive. However, all of the products are readily rationalized if the intermediate diradical, **7**, is formed. This radical could close (process a) to yield **4** directly. Intramolecular hydrogen abstraction from the cyclopentane ring (process b)



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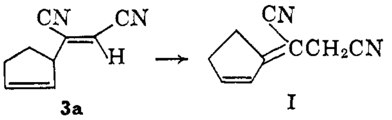
to I (*i.e.*, chromatography of the crude reaction mixture on alumina yielded 11% of **2a** and 58% of I). Pure **3a**, separated from **2a** by liquid–liquid partition chromatography, was converted to I in 97%



yield upon chromatography on alumina. Spectroscopic data showed that I was completely absent from the crude reaction mixture.

[8] J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, **84**, 2210 (1962); S. Proskow, H. E. Simmons, and T. L. Cairns, *ibid.*, **88**, 5254 (1966).

[9] Concerted formation of a 2 + 2 cycloadduct *via* a thermal reaction is forbidden on the basis of molecular orbital symmetry arguments: R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

[10] J. Kraus and J. Calvert, *ibid.*, **79**, 5921 (1957).

would give **5**. Process c would involve intramolecular hydrogen abstraction from the side chain by the cyclopentyl radical to produce **6**.

The rates of the reaction of **1** with dicyanoacetylene at 35°, dicarbomethoxyacetylene at 100°, and propiolic ester at 135° were comparable. If one considers only inductive parameters it would be anticipated that perfluoro-2-butyne should react with **1** below 100° if a concerted multicenter mechanism were involved. However, the reaction of **1** with perfluoro-2-butyne at 100° for 3 days gave only starting material. No trace of adducts could be detected by vpc. This result is most consistent with a mechanism involving formation of a diradical species in which conjugative stabilization of the intermediate radical is of considerable importance. It is inconsistent with any of the products being formed *via* a concerted multicenter reaction.

The formation of diradical intermediates in the reaction of **1** with electron-deficient acetylenes has some interesting implications in relation to the classical ene reaction. It has been proposed that the ene reaction can occur *via* zwitterionic,[11] diradical,[12] and concerted[13] multicenter mechanisms. Recently, opinion has favored a concerted mechanism for the ene reaction[13] since ene-type products have not been observed in radical cycloadditions.[5c–f] Our data appear to provide an example of competitive formation of cycloaddition and ene-type products *via* a diradical mechanism. The possibility that other ene reactions occur *via* diradical intermediates now merits serious consideration. It is possible that a spectrum of diradical reactions might exist, extending from the formation of only ene products to the formation of only 2 + 2 cycloadducts. Since the olefins which have been shown to give ene products are quite different from the olefins which yield 2 + 2 cycloadducts it seems reasonable that suitable intermediate cases have not been studied. We feel that our results represent an example of such an intermediate situation.

Experimental Section

Solvents for Kinetic Measurements. Mallinckrodt Analytical Reagent ethyl acetate was dried over anhydrous potassium carbonate, filtered, and distilled through a 40-cm Vigreux column immediately before use. A small center cut, bp 77.1°, $n^{20.5}\mathrm{D}$ 1.3716, was used. Baker Analyzed Reagent Grade benzene was distilled from sodium wire through a 40-cm Vigreux column shortly before use. A small center cut, bp 80.1°, $n^{20.5}\mathrm{D}$ 1.5007, was used. Matheson Coleman and Bell acetonitrile was dried over anhydrous magnesium sulfate, filtered, and distilled through a 40-cm Vigreux column. A small center cut, bp 81.0°, $n^{20.5}\mathrm{D}$ 1.3451, was used.

Reagents. Bicyclo[2.1.0]pentane was prepared by a modified version of Criegee's procedure.[14] Dimethyl acetylenedicarboxylate was obtained from the Aldrich Chemical Co. and was purified by distillation before use.

Kinetic Measurements. In a typical experiment, 154.8 mg of bicyclo[2.1.0]pentane, 539.3 mg of freshly distilled dimethyl acetylenedicarboxylate, and 124.4 mg of dimethyl phthalate internal standard (Eastman Kodak White Label) was accurately weighed into a tared, 5-ml volumetric flask. The mixture was then diluted to 5 ml with a weighed amount of ethyl acetate and thoroughly mixed. The density of the mixture at 165° was determined by syringing a weighed amount of this mixture into a bulb of *ca.* 1.5-ml capacity with a long capillary neck. The bulb was cooled, sealed, and equilibrated for 3 min at 165.0°. The height of the liquid in the capillary was marked and the volume of the liquid determined by filling to the mark with water. From the density at 165° determined in this manner and the known weights, the concentrations were calculated to be: bicyclo[2.1.0]pentane, 0.3691 *M;* dimethyl acetylenedicarboxylate, 0.6154 *M;* and dimethyl phthalate, 0.1039 *M.*

For a kinetic run 100 μl of the freshly prepared mixture was syringed into each of eight 70-mm tubes prepared from 3-mm o.d. Pyrex tubing. Each tube was cooled in a Dry Ice slurry for 10 sec, purged briefly with nitrogen, and sealed 10 mm above the liquid level, thus assuring negligible dead volume over the liquid at 165°. The tubes were placed in a high-temperature, constant-temperature bath at 165.0 ± 0.2°, and an accurate timer was started. Tubes were withdrawn at appropriate intervals (2000 sec in this case) and quenched by cooling. The contents were analyzed directly by vpc on the 5-ft, 0.6% PDEAS column at 133°. The runs were followed to 55–70% of completion. Analysis of a synthetic mixture gave proportionality constants for relating peak areas to per cent composition.

Since polymerization of the dimethyl acetylenedicarboxylate[15] is a minor side reaction, the plot of $[1/(b - a)] \ln [a(b - x)/b(a - x)]$ *vs.* time showed slight curvature. Thus, the rate constants listed are initial rates. In order to ensure that the reaction was first order in bicyclo[2.1.0]pentane and first order in dimethyl acetylenedicarboxylate, the concentrations of both reactants were varied. The rate constants listed in Table II demonstrated that the reaction being studied was first order in each reactant. Similar rate measurements were carried out in benzene and in acetonitrile.

Table II. Reaction of Bicyclo[2.1.0]pentane (A) with Dimethyl Acetylenedicarboxylate (B) Ethyl Acetate at 165.0 ± 0.2°

A concn, *M*	B concn, *M*	$k \times 10^5$ l. M^{-1} sec^{-1}
0.3691	0.6154	7.5
0.3630	1.1703	7.5
0.7198	0.6051	7.3

Product Studies. Product studies were carried out on the reaction of bicyclo[2.1.0]pentane with dimethyl acetylenedicarboxylate in benzene, ethyl acetate, acetonitrile, neat, and in a large excess of dimethyl acetylenedicarboxylate. The reactions were run varying lengths of time to give yields of from 5 to 75%. The reaction was investigated over the temperature range of 100–165°. Under these drastically differing conditions no variation was noted in the ratio of **2b** to **3b**. In all cases the ratio of **2b** to **3b** was 24:76, respectively, within the limits of error of determination by vpc.

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[13] H. P. Koch, *J. Chem. Soc.*, 1111 (1948); R. T. Arnold and J. F. Dowdall, *J. Amer. Chem. Soc.*, **70**, 2590 (1948); R. K. Hill and M. Rabinovitz, *ibid.*, **86**, 965 (1964); J. A. Berson, R. G. Wall, and H. D. Perlmutter, *ibid.*, **88**, 187 (1966).

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[15] For a discussion of the tetramerization of dimethyl acetylenedicarboxylate see G. LeGoff and R. B. LaCount, *Tetrahedron Letters*, 2333 (1967).