The Addition of Acetylenes to "Bent" σ Bonds

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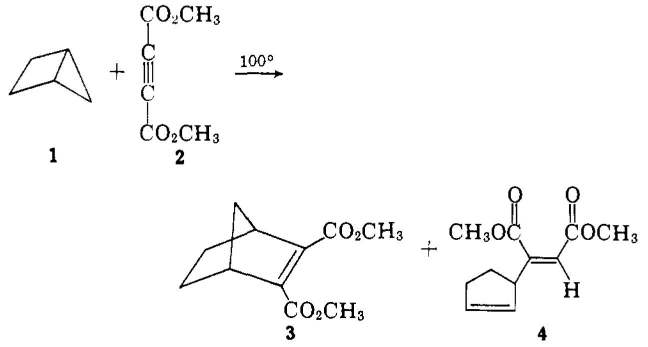
Abstract: The 1–4 bond of bicyclo[2.1.0]pentane (**1**) has been shown to be unusually reactive toward certain electron-deficient acetylenes. The combination of the acetylene and **1** in a 1:1 ratio resulted in the formation of both cycloaddition and ene-type products. For example, bicyclo[2.1.0]pentane was found to react with dicyanoacetylene at room temperature to yield 2,3-dicyanobicyclo[2.2.1]hept-2-ene and cyclopentenyl-3-maleonitrile. A similar reaction of dicarbomethoxyacetylene with **1** occurred at 100° to give products analogous to those formed with dicyanoacetylene. Propiolic ester reacted with bicyclo[2.1.0]pentane at 135° to produce 2-carbethoxybicyclo[2.2.1]hept-2-ene, ethyl 3-(3-cyclopentenyl)-*trans*-acrylate, and ethyl cyclopentylpropiolate. Under conditions where bicyclo[2.1.0]pentane was very reactive toward acetylenes, bicyclo[3.1.0]hexane was shown to be relatively inert, demonstrating the dependence of this reaction on ring strain.

In the decade since bicyclo[2.1.0]pentane (**1**) was first synthesized[3] relatively few investigations of this ring system have been described. Those investigations which have been conducted provide intriguing evidence of the dramatic change in reactivity which occurs in a σ bond when it is sufficiently strained. Indeed, bicyclo[2.1.0]pentane is an ideal subject for studies aimed at unraveling the mysteries of "bent" σ bonds, since the strain energy of the 1–4 bond of **1** is the largest yet found for a carbon–carbon σ bond. This is surprising since it might be anticipated that the 1–3 bond of bicyclo[1.1.0]butane would be more strained. However, Turner has found that hydrogenation of bicyclo[2.1.0]pentane to cyclopentane shows that the 1–4 bond of **1** has a strain energy of 47.4 kcal/mol,[4] while the strain energy of the 1–3 bond of a bicyclo[1.1.0]butane, determined from heats of hydrogenation of 1,3-dimethylbicyclo[1.1.0]butane, was calculated to be 41.3 kcal/mol.[5,6]

The unusually high strain energy of the 1–4 bond of **1** suggested that the electrons of this "bent" bond should be readily available for bond formation to appropriate electron-deficient species. This concept prompted us to investigate the reaction of bicyclo[2.1.0]pentane with electron-deficient acetylenes.

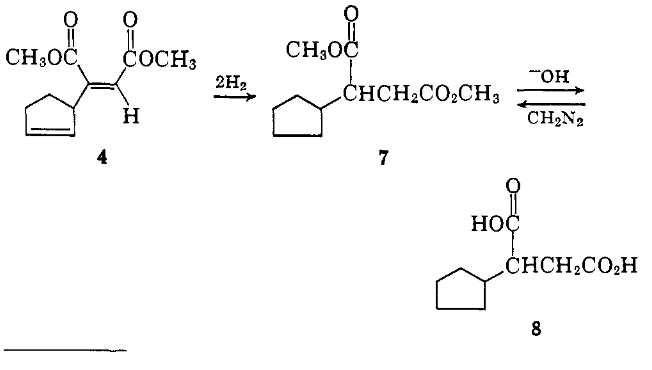
Reaction of **1** with dicarbomethoxyacetylene (**2**) at *ca.* 100° yielded a mixture of two products, each of which had a molecular formula consistent with a 1:1 adduct of **1** and **2**. The yield of the products was 75%, with the minor component **3** constituting 24% of the reaction product, while the remaining 76% was the diene **4**.

The structure of the cycloaddition-type product, **3**, was proven by independent synthesis. Reaction of cyclopentadiene (**5**) with **2** gave the known[7] Diels–Alder adduct **6**. Selective catalytic reduction of **6** over 5% palladium on carbon gave an authentic sample of **3** which was identical in all respects with the minor product obtained in the reaction of **1** with **2**.



The structure proof of the major product, **4**, was much more difficult. A problem in working with **4** was its rapid polymerization in the presence of air. Even when sealed under nitrogen, this product underwent slow deterioration to nonvolatile material.

The basic skeleton of **4** was deduced from its catalytic hydrogenation over 5% palladium on carbon. The molecule took up 2 equiv of hydrogen to give dimethyl cyclopentylsuccinate (**7**). Saponification of **7** gave the diacid, **8**, which showed no melting point depression when mixed with a sample of the known[8] material. Similarly, treatment of authentic **8** with diazomethane gave **7**, identical in all respects with the product obtained on hydrogenation of **4**.



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

[2] The Ohio State University Fellow, 1962–1963.

[3] R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957). A modified synthesis of bicyclo[2.1.0]pentane has been developed: P. G. Gassman and K. T. Mansfield, submitted for publication.

[4] R. B. Turner in "IUPAC—Theoretical Organic Chemistry—Kekulé Symposium," Butterworth & Co. (Publishers) Ltd., London, 1959, pp 67–83.

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

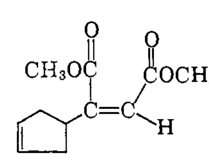
[6] One problem which exists in this comparison is the difference in bridgehead substitution between the two molecules actually hydrogenated. However, a more suitable comparison would require a knowledge of hydrogenation enthalpies for either 1,4-dimethylbicyclo[2.1.0]pentane or bicyclo[1.1.0]butane. At present these data are not available.

[7] O. Diels and K. Alder, *Ann.*, **490**, 236 (1931).

[8] K. Alder, F. Pascher, and A. Schmitz, *Ber.*, **76B**, 27 (1943).

On the premise that **4** resulted from an ene-type reaction,[9] it would be expected that one of the double bonds should be between the two carboxylate groups (*i.e.*, a maleate- or fumarate-type structure). Infrared maxima appeared at 5.72 and 5.80 μ (carbonyl absorptions), with a relatively strong olefinic stretching absorption at 6.09 μ. In addition, intense absorptions at 7.90 and 8.37 μ support a maleate or fumarate structure.[10] The ultraviolet spectrum of **4** showed strong end absorption [λ^{ethanol} 205 mμ (ϵ 15,000)] which was also consistent with a maleate- or fumarate-type structure.[11] For the present the mechanistically more reasonable maleate stereochemistry will be assumed. This assumption is based on the fact that the reaction of **1** with ethyl propiolate occurs in a *cis* manner (*vide infra*) and that intramolecular hydrogen transfer can only occur to produce *cis* addition to the acetylene.

Since the ultraviolet spectrum clearly indicated that the two double bonds in **4** were not conjugated, only two isomeric structures were possible, namely, **4** or **9**. The 4-substituted cyclopentene **9** was inconsistent with the nmr spectrum of the ene-type product. Whereas 4-substituted cyclopentenes give nmr spectra in which the vinyl protons are equivalent and the ring methylene protons are equivalent or nearly so,[12,13] the vinyl protons in our product appeared as two complex multiplets, centered at τ 4.09 and 4.32 with the higher field multiplet partially overlapping the maleate vinyl proton signal. The ring methylene appeared as complex multiplets extending from τ 7.39 to 8.51. The single tertiary proton which is doubly allylic in **4** appeared at τ 6.70. These spectral data were only consistent with structure **4**.[14]



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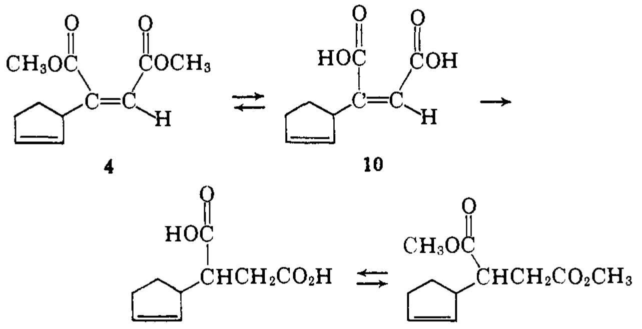
Although spectroscopic data provided substantial evidence for structure **4**, chemical proof for the position of the second double bond was obtained. Selective reduction of the conjugated double bond of **10** would yield the known[8] cyclopentenyl-3-succinic acid (**11**). In general, conjugated double bonds are easily reduced by dissolving metal reactions.[15] Arth and coworkers have demonstrated that dissolving metals can selectively reduce α,β-unsaturated acids without reducing nonconjugated double bonds. These workers also evaluated various combinations of alkali metals and proton sources for this reaction.[16]

Saponification of **4** in aqueous ethanol gave **10**, mp 180–181°. Reaction of **10** with diazomethane regenerated **4**, demonstrating that double-bond isomerization had not occurred during saponification. The diacid **10** was suspended in liquid ammonia and reduced at −70° with a large excess of potassium metal to yield 20% of **11**. Since most of the starting material, **10**, had not been reduced, the mixture of diacids was converted to the corresponding methyl esters which were separated by preparative vpc. The sample of **12** was identical in all respects with the material prepared from the known sample[8,17] of **11** upon reaction with diazomethane. Thus the structure of **4** was unequivocally established.



4 **10** **11** **12**

The reaction of **1** with **2** to yield both cycloaddition and ene-type products firmly demonstrated that strained cyclopropanes would react with carbon–carbon multiple bonds. This constituted the first published example of such a reaction.[18,19] The following sections are devoted to a discussion of our studies of the scope and limitations of the reaction of bicyclo[*n*.1.0]alkanes with substituted acetylenes.

In view of the facile reaction between bicyclo[2.1.0]pentane and dicarbomethoxyacetylene, the reaction of **1** with dicyanoacetylene (**13**) merited investigation. Dicyanoacetylene is one of the most powerful acetylenic dienophiles known, even forming Diels–Alder adducts with such unreactive "dienes" as substituted benzenes.[20] Since the cyano groups are strongly electron withdrawing, this acetylene should be quite electron deficient. Thus, it would be expected that **13** might react with **1** at a much lower temperature than that required for the corresponding reaction of dicarbomethoxyacetylene with **1**. This prediction was substantiated by the finding that **13** formed 1:1 adducts with **1** at *room temperature*.

In preliminary experiments dicyanoacetylene (**13**) was treated with excess **1** to yield a black oil which on chromatography on alumina gave 11% of 2,3-dicyanobicyclo[2.2.1]hept-2-ene (**14**), mp 42–43°, and 58% of the cyclopent-2-enylidenesuccinonitrile (**15**).

The structure of the minor product was proven by independent synthesis. Reaction of **13** with cyclopentadiene (**5**) gave 2,3-dicyanobicyclo[2.2.1]heptadiene (**16**) which on partial reduction gave the known 2,3-dicyano-

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(9) J. A. Berson, R. G. Wall, and H. D. Perlmutter, *J. Amer. Chem. Soc.*, **88**, 187 (1966).

(10) N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).

(11) J. J. Wren, *J. Chem. Soc.*, 2208 (1956), reports $\lambda_{\max}^{\text{methanol}}$ 194 mμ (ϵ 22,000) for dimethyl maleate.

(12) J. Meinwald, P. G. Gassman, and J. K. Crandall, *J. Org. Chem.*, **27**, 3366 (1962).

(13) P. K. Freeman, D. E. George, and V. N. M. Rao, *ibid.*, **28**, 3234 (1963).

(14) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, pp 51–62.

(15) A. J. Birch and H. Smith, *Quart. Rev.* (London), **12**, 17 (1958).

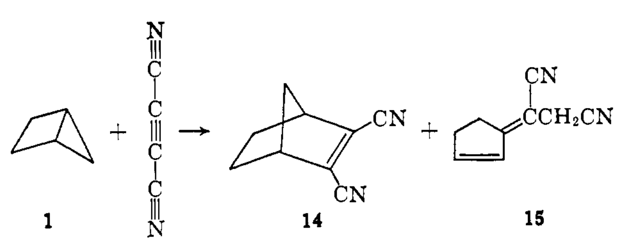
(16) G. E. Arth, G. I. Poos, R. M. Lukes, F. M. Robinson, W. F. Johns, M. Feurer, and L. H. Sarett, *J Amer. Chem. Soc.*, **76**, 1715 (1954).

(17) P. de Mayo, S. T. Reid, and R. W. Yip, *Can. J. Chem.*, **42**, 2828 (1964). We wish to thank Professor de Mayo for providing us with an authentic sample of **11**.

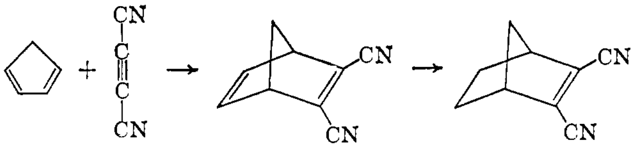
(18) For a preliminary report of part of this work see P. G. Gassman and K. T. Mansfield, *Chem. Commun.*, 391 (1965).

(19) Subsequent to our report other accounts of the thermal reaction of strained cyclopropanes with carbon–carbon multiple bonds have appeared: A. Cairncross and E. P. Blanchard, Jr., *J. Amer. Chem. Soc.*, **88**, 496 (1966); C. D. Smith, *ibid.*, **88**, 4273 (1966); M. Pomerantz, *ibid.*, **88**, 5349 (1966); M. R. Rifi, *ibid.*, **89**, 4442 (1967).

(20) C. D Weis, *J. Org. Chem.*, 27, 3520 (1962); **28**, 74 (1963); E. Ciganek, *Tetrahedron Letters*, 3321 (1967).



1 **13** **14** **15**

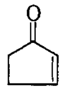


5 **13** **16** **14**

bicyclo[2.2.1]hept-2-ene (**14**) spectroscopically identical with the minor adduct obtained from **1**.[21]

The major component of the product mixture from the reaction of **1** with **13** had a uv maximum at 265 mμ (ε 17,100) indicative of extended conjugation. Thus, it was apparent that **15** was not structurally similar to the major product of the reaction of **1** with dicarbomethoxyacetylene. The infrared spectrum of **15** showed two nonequivalent nitrile absorptions, one at 4.41 μ, assigned to a nonconjugated $C\equiv N$ stretch, and one at 4.51 μ, corresponding to a conjugated nitrile absorption.

The nmr spectrum of **15** showed an AB quartet centered at τ 3.26 (two protons), a narrow multiplet at τ 6.65 (two protons), and a narrow multiplet at τ 7.23 (four protons). The two narrow multiplets showed a tendency to split; however, attempts to cleanly resolve such splitting were unrewarding. The simplicity of this spectrum was misleading, since methylenecyclopentene derivatives such as **15** would be expected to have nonequivalent cyclopentenyl methylene hydrogens as observed in such model compounds as **17**[22] and **18**.[23] However, at least one example has been noted, **19**, in which the cyclopentenyl methylenes are magnetically equivalent.[24] The ene-type product **15** would seem to constitute another example of coincidental equivalency in which protons in quite different chemical environments experience the same magnetic environment.



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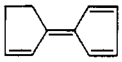

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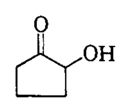

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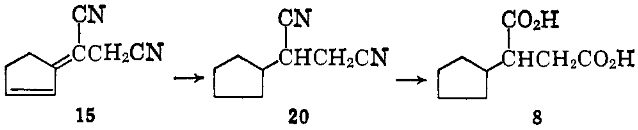
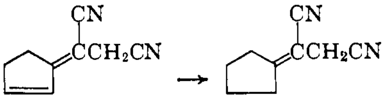
Exhaustive catalytic hydrogenation of **15** over 5% palladium on carbon gave cyclopentylsuccinonitrile (**20**). Acid-catalyzed hydrolysis of **20** gave **8**, identical in all respects with an authentic sample. Thus, the basic skeleton of **15** was proven to be the same as that of **4**. Since the uv spectrum indicated extensive conjugation, the positions of the double bonds in **15** and **4** were clearly different. Selective monoreduction of **15** gave cyclopentylidenesuccinonitrile (**21**), which still showed both conjugated and nonconjugated nitrile absorptions in the infrared at 4.47 and 4.38 μ, respectively. The shift in ultraviolet absorption from 265 to 220 mμ (ε 7700) in going from **15** to **21** was consistent with what would be expected for loss of extended conjugation.[25] The nmr spectrum of **21** was consistent with the assigned structure.



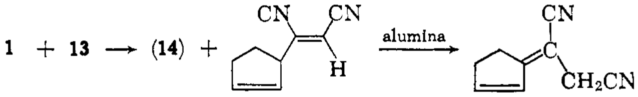
15 **20** **8**



15 **21**

Having established the structure of **15** (except for the stereochemistry about the double bond) we questioned whether **15** was a direct product of the reaction between **1** and **13** or whether an intermediate compound, **22**, might have been formed, and subsequently isomerized to **15** during the chromatographic separation. The presence of infrared absorptions in the spectrum of the crude reaction mixture which were not present in the purified products, **14** and **15**, lent credence to this proposal. In addition **15** gave a different R_f value on thin layer chromatography on silica gel than either of the components of the crude reaction mixture. Complete confirmation that **15** was not an initial reaction product was provided by the ultraviolet spectrum of the crude reaction mixture which showed absorptions at 249 (due to **14**) and 229 mμ. The absorption which **15** shows at 265 mμ was completely absent.

The ultraviolet absorption at 229 mμ in the crude reaction mixture indicated that the initial reaction product might be structurally similar to **4**. Thus, it would seem that **1** may have reacted with **13** to give **22** which rearranged to **15** on alumina. Isolation of **22** from the reaction mixture proved to be a formidable task since most procedures which would separate **14** from **22** also rearranged **22** to **15**. Liquid-liquid partition chromatography using an aqueous silver nitrate stationary liquid phase on Celatom[26] (silver nitrate–water–Celatom, 4:5:10) and eluting with 1:1 ether–pentane provided the best means of separating **14** and **22**.



22 **15**

Purified **22** showed an ultraviolet maximum at 229 mμ (ε 14,400) consistent with a monosubstituted maleonitrile.[27] The nmr spectrum of **22** was strikingly similar to that of **4**, confirming that thec yclopentene was

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[21] A. T. Blomquist and C. E. Winslow, *J. Org. Chem.*, **10**, 149 (1945), report a melting point of 36° for **14**. In agreement with their work we obtained a melting point of 34–36° for synthetic **14** obtained from the reduction of **16**. Infrared and nmr spectra of **14** from the two different routes were identical and a mixture melting point fell between those of the two samples.

[22] J. Wiemann, P. F. Casals, and S. Risse, *Bull. Soc. Chim. Fr.*, 1281 (1963).

[23] K. V. Scherer, *J. Amer. Chem. Soc.*, **85**, 1550 (1963).

[24] C. H. De Puy, C. E. Lyons, and L. B. Rodewald, *J. Chem. Eng. Data*, **11**, 102 (1965).

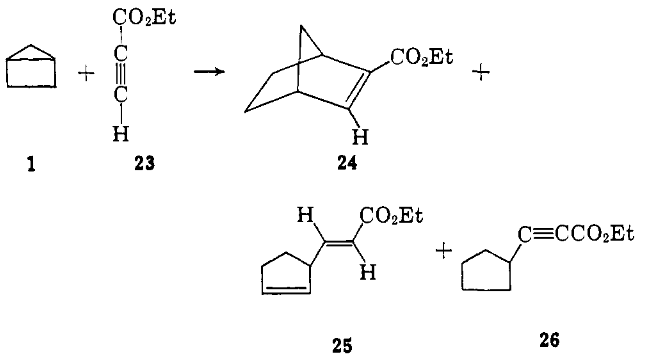
[25] A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, Inc., New York, N. Y., 1964, pp 84–85.

[26] The authors wish to thank Professor G. L. Grunewald for directions for the preparation of this column.

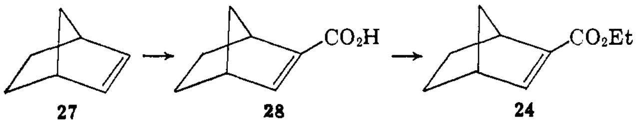
[27] R. L. Webb, S. Frank, and W. C. Schneider *J. Amer. Chem. Soc.*, **77**, 3491 (1955), report λ_{max} 220 mμ (ε 13,800) for maleonitrile.

substituted in the 3 position. When **22** was chromatographed on alumina, **15** was obtained in 97% yield.

A reaction temperature of 135–155° was required for the addition of ethyl propiolate (**23**) to **1**. Since **23** has only one electron-withdrawing group, the triple bond should be less electron deficient than the previously studied disubstituted acetylenes. Hence, the higher reaction temperature was to be anticipated. The reaction of **1** with **23** was carried out in the presence of hydroquinone in order to avoid complete polymerization of **23**. Even in the presence of hydroquinone extensive polymerization of **23** occurred, such that when equimolar quantities of **1** and **23** were treated at 135° only a 34% yield of 1:1 adducts was obtained. This adduct mixture consisted of 6% of 2-carbethoxybicyclo[2.2.1]hept-2-ene (**24**), 79% of ethyl 3-(3-cyclopentenyl)-*trans*-acrylate (**25**), and 11% of ethyl cyclopentylpropiolate (**26**). Five components constituted the remaining 4% of the reaction mixture.



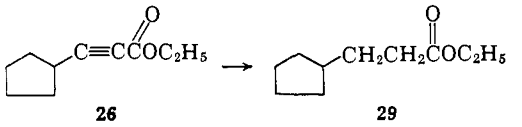
The three major components were separated and purified by preparative vpc. The structure of the cycloaddition product **24** was proven by independent synthesis. Bicyclo[2.2.1]heptene (**27**) was converted to the known[28] bicyclo[2.2.1]hept-2-ene-2-carboxylic acid (**28**) according to the procedure of Finnegan and McNees.[28] Esterification of **28** with diazoethane gave **24**, which was identical in all respects with the sample of **24** isolated from the reaction of **1** with **23**.



The structure of the major product **25** was established on the basis of spectral data and chemical conversion to known compounds. The ultraviolet spectrum of **25** showed $\lambda_{\max}^{\text{ethanol}}$ 209 mμ (ε 19,200) indicative of an α,β-unsaturated ester.[29] The presence of an α,β-unsaturated ester function was substantiated by infrared absorptions of 5.80 (conjugated ester), 6.06 (double bond conjugated with a carbonyl group), and 11.61 μ (*trans*-disubstituted olefin).[30] The nmr spectrum of **25** showed that the two vinyl hydrogens in the side chain were coupled with each other with J_{AB} = 15.4 cps, again confirming the *trans* stereochemistry in the side chain.[31] Comparison of the nmr spectrum of **25** with that of **4** showed that the cyclopentenyl rings were substituted at the same position.

Catalytic hydrogenation of **25** over 5% palladium on carbon resulted in the uptake of 2 moles of hydrogen to yield the known[32] ethyl 3-cyclopentylpropionate (**29**). Conversion of **29** to the corresponding acid, amide, and anilide gave compounds with physical constants in excellent agreement with the literature values.[32] Thus, the structure of **25** was firmly established.

The third major component of the reaction of **1** with propiolic ester was readily identified by its infrared spectrum which showed an intense acetylenic absorption at 4.43 μ and a conjugated ester absorption at 5.84 μ. The spectral data coupled with elemental analysis indicated that this third component had structure **26**. Catalytic hydrogenation of **26** gave **29**, offering conclusive confirmation of our tentative assignment.



Bicyclo[2.1.0]pentane reacted readily with the three electron-deficient acetylenes discussed above. Since **2**, **13**, and **23** were similar in many respects, having electron-withdrawing groups capable of conjugation attached to the acetylene moiety, little information about the scope of the reaction with acetylene was obtained. Hence, we desired to study other acetylenes. Diphenylacetylene and perfluoro-2-butyne were chosen as suitable examples since the former provided a conjugated acetylene which was not electron deficient, while the latter was electron deficient but not conjugated.

Diphenylacetylene, unlike the acetylene used in the previously discussed experiments, is a poor Diels–Alder dienophile. We found it to be similarly unreactive with bicyclo[2.1.0]pentane. Treatment of **1** with diphenylacetylene at 160° for 4 days gave back only starting materials. The electron deficiency of the acetylene appeared to be a critical requisite. The fact that the reactions of **1** with dicyanoacetylene at 35°, with dicarbomethoxyacetylene at 100°, and with propiolic ester at 135° occurred at comparable rates correlated this relationship between electron deficiency and reactivity.

Perfluoro-2-butyne is a powerful Diels–Alder dienophile. It is even known to react with both substituted and unsubstituted benzenes.[33] As an electron-deficient dienophile it is comparable to dicyanoacetyllene. In our reaction perfluoro-2butyne would be expected to react with **1** under much milder conditions than those required with dicarbomethoxyacetylene if the electron-withdrawing properties of the substituent were the controlling factor. Heating of **1** with perfluoro-2-butyne at 100° for 3 days gave only starting materials. No trace of adducts could be detected by vpc. It became apparent that strong electron-withdrawing substituents were not sufficient causes; resonance stabilization of the transition state must also be crucial.

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(28) R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964).

(29) Reference 25, p 80.

(30) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Metheun and Co., Ltd., London, 1958, pp 41, 45, 181, 182.

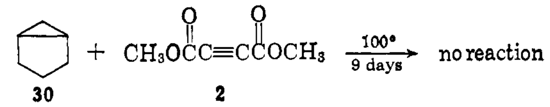
(31) L. M. Jackman "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 85.

(32) J. W. Barrett, A. H. Cook, and R. P. Linstead, *J. Chem. Soc.*, 1065 (1935); G. P. Chinsoli, *Chim. Ind.* (Milan), **41**, 513 (1959).

(33) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, **83**, 3428 (1961); see also E. Ciganek, *Tetrahedron Letters*, 3321 (1967).

Having established the characteristics of the reaction relative to the acetylene, we examined the strain requirements of the cyclopropane. Proceeding in the direction of the less strained cyclopropanes, we decided to investigate the reaction of bicyclo[3.1.0]hexane (**30**) with dicarbomethoxyacetylene. In the few comparisons of bicyclo[3.1.0]hexane and bicyclo[2.1.0]pentane which exist in the literature, **30** has been shown to be slightly less reactive than **1**. For example,[34] the reaction of mercuric acetate with **30** was carried out at 25° whereas a similar reaction of **1** occurred at 0°. Similar changes in reaction conditions were employed to effect the reaction of **30** and **1** with acetic acid,[35] lead tetraacetate, and thallium triacetate.[36]

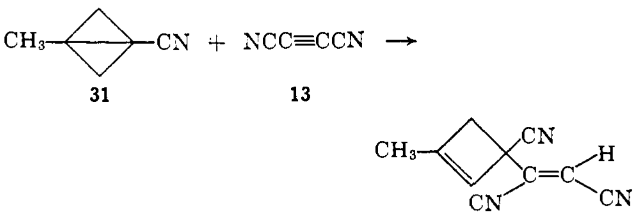
When **30** was treated with **2** for 9 days at 100°, only starting material was found. No adducts were detectable by vpc. The failure of **30** to undergo any reaction with **2** under conditions more vigorous than those required for optimum yields with bicyclo[2.1.0]pentane was indicative of the strong dependence on ring strain. In view of the lack of reactivity of **30**, the reactions of higher homologs of **1** with dicarbomethoxyacetylene were not investigated.



$$+\ CH_3O\overset{O}{\overset{\|}{C}}C{\equiv}C\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow[9\ days]{100°} \text{no reaction}$$

Since **30** failed to react with **2**, an examination of the reaction of a bicyclo[1.1.0]butane derivative was deemed desirable. As discussed earlier, the strain energy of the 1–3 bond of bicyclo[1.1.0]butane is calculated to be slightly less than the 1–4 bond of **1**. It might be anticipated that the reactivity of a derivative of bicyclo[1.1.0]butane, such as 3-methylbicyclo[1.1.0]butanecarbonitrile (**31**),[37,38] would be comparable to that of **1**. A disadvantage of the bicyclo[1.1.0]butane derivatives is their tendency to thermally dimerize and polymerize in the vicinity of 150°. In order to avoid the thermal decomposition of **31**, dicyanoacetylene was chosen as the electron-deficient acetylene.

The reaction between **31** and dicyanoacetylene was carried out at room temperature using chloroform as the solvent. Chromatography of the product mixture on activity grade III alumina gave **32** as the only identifiable product.[39] The structure of **32** was proven spectroscopically. An ultraviolet absorption at 228 mμ (ε 13,500) was very similar to that exhibited by **22**, indicating the presence of a substituted maleonitrile.[27] Infrared absorptions at 6.07 and 6.23 μ were consistent with the presence of both cyclobutene and conjugated olefin moieties The nmr spectrum showed a one-proton singlet at τ 3.60 for the vinylmaleonitrile and a one-proton quartet at τ 4.29 (J = 1 cps) for the cyclobutene proton. Since the cyclobutene proton was coupled with the three-proton doublet (J = 1 cps) at τ 8.11 the methyl group must be attached to the double bond. The ring methylene protons appeared as an AB quartet (J = 12.8 cps) centered at τ 4.29. This spectral data uniquely characterized the major product as being **32**.



At this point the scope of the reaction of cyclopropanes with acetylenes had been firmly established. Clearly, the cyclopropane had to possess considerable strain if a facile reaction was to occur under relatively mild conditions. The acetylene reacted best when it was substituted with strong electron-withdrawing groups capable of conjugative stabilization of the transition state.

A detailed study of the mechanism of additions of electron-deficient carbon–carbon multiple bonds to highly strained cyclopropanes is in progress. The findings of this mechanistic investigation will be presented in the near future.

Experimental Section[40]

Bicyclo[2.1.0]pentane (1). A modified version of Criegee's procedure[3] was used to prepare **1** in 70–80% over-all yield from cyclopentadiene.

Reaction of Dicarbomethoxyacetylene (2) with 1. A mixture of 2.93 g (0.021 mol) of **2** and 1.306 g (0.019 mol) of **1** was placed in a glass ampoule which was cooled to −70°, purged with dry nitrogen, and sealed. The ampoule was then heated at 100° for 7 days in the absence of light. The cooled reaction mixture was chromatographed on 100 g of silica gel. Elution with benzene gave back less than 0.5% of the starting acetylene, 2.31 g (57%) of dimethyl cyclopentenyl-3-maleate (**4**), and 0.71 g (18%) of dimethyl bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3**).

Combination of the chromatography fractions of **3** and distillation gave pure **3**, bp 119° (3.1 mm), $n^{24.5}\text{D}$ 1.4878, $\lambda_{max}^{ethanol}$ 236 mμ (ε 8400). This material was identical with an authentic sample of **3** prepared according to the procedure of Diels and Alder.[7]

Combination of the chromatography fractions of **4** and distillation gave an analytical sample of **4**, bp 80° (0.2 mm), $n^{24.4}\text{D}$ 1.4848. This colorless viscous liquid showed intense infrared absorptions at 5.72, 5.80, and 6.09 μ, and end absorption in the ultraviolet, $\lambda_{max}^{ethanol}$ 205 mμ (ε 15,000). The nmr spectrum of **4** showed peaks at τ 4.09 (multiplet, 1 H), 4.32 [overlapping doublet (J = 1.1 cps) and multiplet, 2 H], 6.31 and 6.38 (singlets, 3 H each), 6.70 (broad multiplet, 1 H), and 7.39–8.51 (broad envelope, 4 H).

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(34) R. Lavina, V. N. Kostin, and T. K. Ustynyuk, *Zh. Obsch. Khim.*, **30**, 359 (1960).

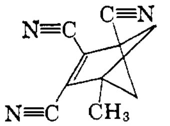
(35) R. T. LaLonde and L. S. Forney, *J. Amer. Chem. Soc.*, **85**, 3767 (1963).

(36) R. J. Ouellette, A. South, Jr., and D. L. Shaw, *ibid.*, **87**, 2602 (1965).

(37) E. P. Blanchard, Jr., and A. Cairncross, *ibid.*, **88**, 487 (1966). These workers have shown that the bridgehead substituent probably has some influence on the 1–3 bond of **31**. In this respect the reactivity of **31** might be very different from that of **1**.

(38) We wish to thank Dr. E. P. Blanchard for the sample of **31** used in our studies.

(39) Three very minor components were obtained in this reaction. One of these, mp 146–153°, had no olefinic carbon–hydrogen stretch in the infrared region of the spectrum, but did show a strong carbon–carbon olefinic absorption at 6.27 μ, indicative of a small-ring olefin. It is interesting to speculate that this minor product may have been **33**. Unfortunately, insufficient material was available for further purification and unequivocal identification.



33

(40) Melting points and boiling points are uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 137 Infracord. A Cary Model 14 recording spectrometer was used for all ultraviolet measurements. Analyses were obtained from the Scandinavian Microanalytical Laboratories, Herlev, Denmark, and from Dr. Alfred Bernhardt, Max-Planck Institute, Mulheim (Ruhr), Hohenweg, Germany.

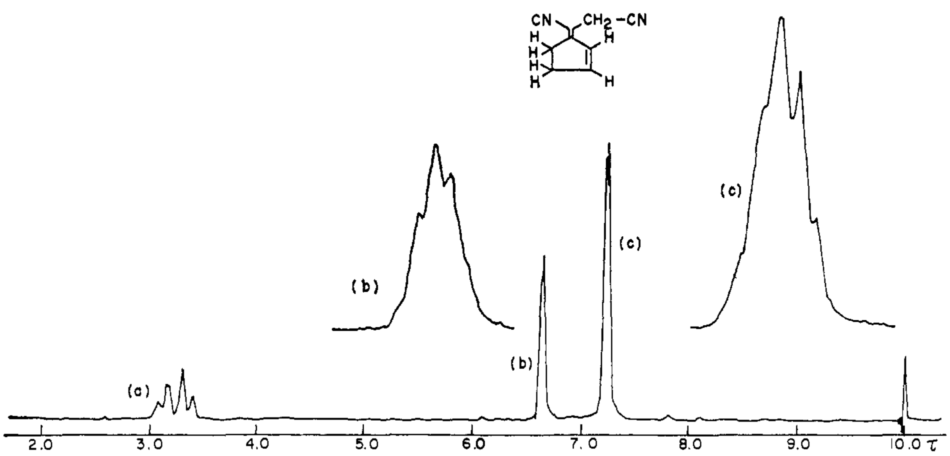


Figure 1.

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.96; H, 6.79.

Dimethyl Cyclopentylsuccinate (7). A solution of 110 mg of **4** in 8 ml of acetone was catalytically hydrogenated over 26 mg of 5% palladium on carbon at room temperature and atmospheric pressure. Hydrogen uptake ceased after 1.94 equiv of hydrogen had been consumed. The solution was filtered through a Celite microplug and the solvent was removed at reduced pressure to give 101 mg (90%) of **7**, 97% pure by vpc analysis. The material had infrared spectra and vpc retention times identical with an authentic sample prepared as described below.

Dimethyl Cyclopentylsuccinate (7). An authentic sample of **7** was prepared from the known[8] cyclopentylsuccinic acid (**8**) and diazomethane, bp 103° (1.4 mm).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.86; H, 8.36.

Hydrolysis of the Hydrogenation Product from 4. A mixture of 51 mg of dimethyl cyclopentylsuccinate from the reduction of **4** and 2 ml of 10% sodium hydroxide was refluxed for 6 hr. The cooled solution was acidified with hydrochloric acid, saturated with sodium chloride, and extracted with three 10-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and stripped to dryness to give a pale crystalline solid. One recrystallization from ether–pentane gave 25 mg of cyclopentylsuccinic acid (**8**), mp 113.5–114.7°, which gave no melting point depression on admixture with an authentic sample prepared according to the procedure of Alder and coworkers.[8]

Cyclopentenyl-3-maleic Acid (10). To 481 mg of **4** in 15 ml of ethanol was added 10 ml of 10% potassium hydroxide solution and the reaction mixture was refluxed for 24 hr in the absence of oxygen. Most of the ethanol was distilled off, and the cooled residue was washed with two 20-ml portions of ether. The aqueous solution was acidified at 0° with cold hydrochloric acid, saturated with sodium chloride, and continuously extracted with ether for 10 hr. Removal of the ether gave 490 mg of gummy yellow crystals. Trituration with cold ether afforded 225 mg of **10**, mp 180–181° dec. An analytical sample obtained by recrystallization from ether melted sharply at 182° dec.

Anal. Calcd for $C_9H_{10}O_4$: C, 59.33; H, 5.53. Found: C, 59.16; H, 5.64.

Cold diazomethane converted **10** back to **4**, demonstrating that hydrolysis had not caused any shifting of the double bonds.

Dissolving Metal Reduction of Cyclopentenyl-3-maleic Acid. To 100 ml of liquid ammonia at −70° in a three-necked, 250-ml, round-bottomed flask equipped with a mechanical stirrer and Dry Ice condenser was added 225 mg of **10**. Over a period of 15 min, 1 g of potassium metal was added in small pieces to the vigorously stirred reaction mixture. Each piece was added as the color due to the previous piece disappeared. After stirring for an additional 10 min 15 ml of dry 2-propanol was added dropwise. The stirred solution was allowed to warm for 1 hr, and 25 ml of saturated ammonium chloride solution was added dropwise. The solvent was removed, 25 ml of water was added, and the resulting solution was continuously extracted with ether for 12 hr. The ether extract was dried over anhydrous magnesium sulfate, filtered, and concentrated to yield 230 mg of yellow crystals, mp 134–154°. This mixture of compounds was converted to their corresponding methyl esters with diazomethane. The ester mixture was separated by preparative vpc on a 10 ft 20% SE-30 on 60–80 Chromosorb W column at 145°. Starting material **4** accounted for 50% of the reaction mixture. Dimethyl cyclopentenyl-3-succinate (**12**) constituted 20% of the mixture. A comparison of its infrared spectrum and vpc retention times on three different columns with an authentic sample of **12** prepared from the known[8,17] diacid **11** showed these materials to be identical.

Dicyanoacetylene (13) was prepared from acetylenedicarboxamide according to the literature procedure.[21]

Additions of Dicyanoacetylene to Bicyclo[2.1.0]pentane. A solution of 1.33 g of freshly prepared **13** was dissolved in 3.50 g of **1** in a 25-ml flask containing a small stirring bar. The flask was purged with nitrogen, sealed, and stirred magnetically at room temperature for 7.5 days in the absence of light. Unreacted starting material was swept out of the flask in a slow stream of nitrogen. The black residue was dissolved in 2 ml of benzene and chromatographed on 105 g of Woelm neutral alumina, activity III. Elution with 10% benzene in hexane gave 0.264 g (11%) of 2,3-dicyanobicyclo[2.2.1]hept-2-ene (**14**) as white plates, mp 42.3–43.1° (lit. mp 42.5°,[41] 36°, [21]) after one recrystallization from ether–pentane. Compound **14** showed $\lambda_{max}^{ethanol}$ 249 mμ (ε 9900), and infrared maxima at 4.48 and 6.31 μ. Spectral comparisons with an authentic sample firmly established the identity of **14**.

Further elution of the column with 40% benzene in hexane gave 1.52 g (58%) of cyclopent-2-enylidenesuccinonitrile, mp 55–58°. Two recrystallizations from ether–pentane gave colorless rods, mp 61.3–62.0°. The product showed $\lambda_{max}^{ethanol}$ 265 mμ (ε 17,100) and infrared absorptions at 4.41 (nitrile), 4.51 (conjugated nitrile, intense), and 6.20 and 6.35 μ (conjugated diene). The nmr spectrum in deuteriochloroform is shown in Figure 1.

Anal. Calcd for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.43. Found: C, 74.87; H, 5.81; N, 19.18.

2,3-Dicyanobicyclo[2.2.1]hepta-2,5-diene (16). The Diels–Alder adduct **16**, mp 44.7–45.1°, was prepared according to the procedure of Blomquist.[21]

2,3-Dicyanobicyclo[2.2.1]hept-2-ene (14). A solution of 345 mg of **16** in 10 ml of 95% ethanol was hydrogenated at atmospheric pressure over prereduced 5% palladium on carbon. When 1 equiv of hydrogen had been consumed the reaction was stopped, and the resulting solution was filtered through Celite. Removal of the solvent at reduced pressure gave **14**, mp 34–36° after recrystallization, as described by Blomquist.[21] Further recrystallization failed to raise the melting point. A mixture of this material and a sample, mp 42.0–42.9°, formed from the reaction of **1** with **13**, had mp 39–42°. The infrared and nmr spectra of the two samples were identical.

Catalytic Reduction of Cyclopent-2-enylidenesuccinonitrile. A solution of 240 mg (0.0016 mol) of **15** in 10 ml of acetone was hydrogenated over 6 mg of prereduced 5% palladium on carbon at 33° (745 mm) until 1.00 equiv of hydrogen had been consumed (*ca.* 20 min). The solution was filtered through a Celite microplug, concentrated, and distilled through a microcolumn to yield 209 mg (86%) of cyclopentylidenesuccinonitrile (**21**) as a colorless oil, bp 106–107° (0.20 mm), $\lambda_{max}^{ethanol}$ 220 mμ (ε 11,600). The product, which

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[41] P. Scheiner, K. K. Schmiegel, G. Smith, and W. R. Vaughan, *J. Org. Chem.*, **28**, 2960 (1963).

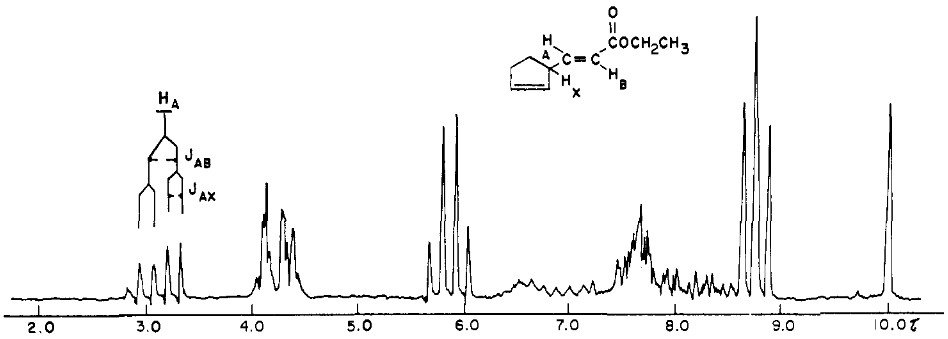

Figure 2.

was homogeneous on a 5 ft 5% SE-30 on 60–80 Chromosorb W vpc column, showed both nonconjugated (4.38 μ) and conjugated (4.47 μ) nitrile infrared absorptions, and C=C absorption at 6.08 μ. The nmr spectrum showed peaks at τ 6.74 (singlet, 2 H), 7.46 (multiplet, 4 H), and 8.16 (multiplet, 4 H).

Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.90; N, 19.16. Found: C, 74.06; H, 7.01; N, 19.13.

In a similar reduction 173 mg (0.0012 mol) of **15** in 10 ml of acetone was hydrogenated over 26 mg of prereduced 5% palladium on carbon. In 3.5 min 1 equiv of hydrogen was consumed. An additional 0.5 equiv was taken up in 2 hr. The mixture was then filtered through a Celite microplug and concentrated at reduced pressure. The 50:50 mixture of cyclopentylsuccinonitrile (**20**) (retention time 16 min) and cyclopentylidenesuccinonitrile (**21**) (retention time 34 min) was separated by preparative vpc using a 5 ft 5% SE-30 on Fluoropak column at 132°. Dinitrile **21** was identified by comparison of its infrared spectrum with the sample characterized in the previous experiment. The fully reduced product **20** showed nitrile absorption at 4.44 μ and no olefinic absorption. It was used in the next experiment without further characterization.

Hydrolysis of Cyclopentylsuccinonitrile (20). A mixture of 16 mg of **20** and 3.5 ml of concentrated hydrochloric acid was refluxed for 24 hr. The cooled solution was made alkaline with sodium hydroxide, washed with 10 ml of ether, acidified, and extracted with three 10-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated. The crystalline residue was triturated with two small portions of pentane and dried in a desiccator to give 5.7 mg of **8**, mp 112.5–115.0°, identified by infrared and mixture melting point comparison with the authentic sample prepared earlier.

Isolation of Cyclopentenyl-3-maleonitrile (22). A solution of 60 g of silver nitrate in 75 ml of distilled water was added to 300 g of Eagle-Pitcher Celatom-FW-80, and the mixture was tumbled for 12 hr in the absence of light. A 2.5 cm wide, 1 m long column was dry packed with *ca.* 200 g of this silver nitrate impregnated Celite and wrapped in aluminum foil to exclude light.[26]

The column was washed with 600 ml of 1:1 ether–pentane. Then 670 mg of a freshly distilled mixture of bicyclo[2.1.0]pentane-dicyanoacetylene adducts, bp 65–69° (0.02 mm), was chromatographed as rapidly as possible eluting with 1:1 ether–pentane to minimize decomposition of the adducts. The separation, which was monitored by ultraviolet spectroscopy, gave 88 mg of **14**, mp 40–41°, 349 mg of cyclopentenyl-3-maleonitrile (**22**), and 254 mg of yellow oil. About 60% of the yellow oil distilled between 90 and 130° (0.04 mm) to give a colorless liquid which showed ultraviolet absorptions at 229 and 265 mμ, indicating that it was a mixture of **22** and **15**.

The major product (426 mg from two runs) was rechromatographed on 150 g of silica gel, eluting with 30% ether–pentane to give, after distillation, 368 mg of **22** as a colorless liquid, bp 71° (0.03 mm), $\lambda_{\max}^{\text{ethanol}}$ 229 mμ (ε 14,400). The product showed infrared absorptions at 4.44 (conjugated CN) and 6.22 μ (conjugated olefin). The nmr spectrum of **22** showed peaks at τ 4.02 (doublet, *J* = 1.1 cps, 1 H), 3.86 (multiplet, 1 H), 4.38 (multiplet, 1 H), 6.29 (multiplet, 1 H), and 7.29–8.44 (envelope, 4 H). All of these peaks plus peaks attributable to **14** were observed in the distilled mixture of **14** and **22** before chromatography.

Anal. Calcd for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.43. Found: C, 75.18; H, 5.73; N, 19.35.

Rearrangement of Cyclopentenyl-3-maleonitrile (22) to Cyclopent-2-enylidenesuccinonitrile (15). Chromatography of 94.0 mg of **22** on 70 g of Woelm neutral alumina, activity III, gave 91.0 mg of **15**, mp 53.4–57.9°, as the only product.[42] Its infrared spectrum was the same as that of a pure sample. In a control experiment, chromatography of 89.2 mg of pure **15**, mp 61.3–61.9°, gave 86.3 mg of recovered **15**, mp 58.5–60.0°.

Reaction of Ethyl Propiolate (23) with Bicyclo[2.1.0]pentane. A mixture of 17.65 g (0.180 mol) of **23**, 12.43 g (0.183 mol) of bicyclo[2.1.0]pentane, and 0.040 g of hydroquinone was placed in a large heavy-walled glass ampoule, which was cooled to −70° and sealed under dry nitrogen. The ampoule was placed in a steel bomb and heated at 135° for 2 weeks. The cooled reaction mixture was transferred to a distillation flask and distilled through a 25-cm Vigreux column to give 10.19 g of colorless liquid, bp 97–105° (11 mm). Vpc analysis (10 ft 15% butanediol succinate on 45–60 Firebrick column, 155°) indicated an eight-component mixture. The major products were **24** (5.8%), **25** (79.6%), and **26** (10.6%), while the other five substances, which were present in from 0.25 to 1.9%, accounted for the remaining 4%. The three major products were separated at 140° on a Fischer Prep Partitioner containing a 10-ft column of 20% Dow Corning 200 Silicone Fluid. Each component was then taken up in ether, dried over anhydrous magnesium sulfate, filtered, and distilled at reduced pressure.

The first component, **24**, was identified by comparison of spectral data with an authentic sample synthesized by an independent method (*vide infra*).

The major product, **25**, bp 94° (6 mm), $\lambda_{\max}^{\text{ethanol}}$ 209 mμ (ε 19,200), showed strong infrared absorptions at 5.80 (conjugated ester), 6.06 (conjugated C=C), and a medium intensity absorption at 11.61 μ (*trans*-disubstituted ethylene). The nmr spectrum is shown in Figure 2.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.97; H, 8.61.

The third isolated component, **26**, bp 101° (7 mm), showed intense infrared absorptions at 4.43 (conjugated, disubstituted acetylene) and 5.84 μ (conjugated ester). Its nmr spectrum showed peaks at τ 5.86 (quartet, *J* = 7 cps, 2 H), 7.85 (multiplet, 1 H), 8.25 (multiplet, 8 H), and 8.72 (triplet, *J* = 7 cps, 3 H).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.24; H, 8.43.

Bicyclo[2.2.1]hept-2-ene-2-carboxylic Acid (28). Acid **28** was prepared according to the procedure of Finnegan and McNees.[28]

Ethyl Bicyclo[2.2.1]hept-2-ene-2-carboxylate (24). To 2.29 g (0.0166 mol) of **28** in 25 ml of cold ether was added a cold ethereal solution of diazoethane until nitrogen evolution ceased. The solution was boiled briefly to expel traces of diazoethane, washed with 10-ml portions of 5% sodium bicarbonate and water, dried over anhydrous magnesium sulfate, and filtered. Concentration at reduced pressure followed by distillation gave 1.250 g (45.4%) of colorless liquid, bp 73° (3 mm), which was *ca.* 95% pure by vpc. The distillate was further purified on a preparative 5-ft butanediol succinate column at 120°. The collected material was taken up in ether, dried over anhydrous magnesium sulfate, filtered, and distilled to give 895 mg of pure **24**, bp 73° (3 mm), $\lambda_{\max}^{\text{ethanol}}$ 231 mμ (ε 9500), n^{29}D 1.4767. The nmr spectrum showed peaks at τ 3.26 (doublet, *J* = 3 cps, 1 H), 5.95 (quartet, *J* = 7 cps, 2 H), 6.80 and 7.05 (broad singlets with fine structure, 1 H each), 8.2–9.2 (complex multiplet, 6 H), and 8.78 (triplet, partially obscured, 3 H).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.48. Found: C, 72.36; H, 8.36.

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[42] This product usually has mp 56–58° when the mixture of adducts is chromatographed on alumina directly.

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°, $\lambda_{\text{max}}^{\text{ethanol}}$ 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.

Acknowledgment. This research was supported by National Science Foundation Grant GP 7063 and by a grant-in-aid from The Ohio State University Development Fund.

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

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Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received November 18, 1967

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.

(2) The Ohio State University Fellow, 1962–1963.

(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**