The Reaction of Olefins with Bicyclo[2.1.0]pentane. The Formation of a Diradical Intermediate[1]

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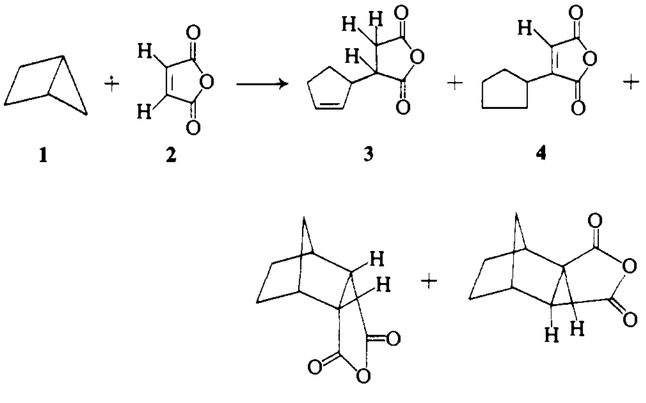
Abstract: As part of our study of the stereochemistry and mechanism of the addition of carbon–carbon multiple bonds to "bent" carbon–carbon single bonds, we have investigated the reaction of bicyclo[2.1.0]pentane (**1**) with electron-deficient olefins. Stereochemically, the addition was found to occur from below the "flap" of the bicyclo[2.1.0]pentane envelope. This was established *via* the addition of maleic anhydride to stereospecifically labeled 2,3-dideuteriobicyclo[2.1.0]pentane. Mechanistically, the addition of electron-deficient olefins was found to be a two-step process. When **1** was treated with either fumaronitrile or maleonitrile, mixtures of dicyanonorbornanes and unsaturated cyclopentylsuccinylnitriles were formed. Since the components of the mixtures were the same but the relative percentages differed, rotation about the central carbon–carbon bond (which was originally the double bond of the fumaronitrile and maleonitrile) must have occurred. The stability of both the starting materials and the reaction products to the reaction conditions required the formation of an intermediate which could experience this rotation. Solvent studies on the reaction of both fumaronitrile and maleonitrile indicate that the relative amounts of "cycloaddition" and "ene" type products are to a small degree solvent dependent.

The reaction of electron-deficient carbon–carbon multiple bonds with carbon–carbon single bonds remains one of the more fascinating aspects of the chemistry of strained ring compounds. Since our original report of the phenomenon,[1a] numerous examples of the addition of carbon–carbon multiple bonds to strained carbon–carbon single bonds have appeared.[5] Also the addition of nitrogen–nitrogen double bonds to strained carbon–carbon single bonds has been investigated.[6] In light of the relevance of these additions to the nature of strained carbon–carbon σ bonds we have carried out a detailed investigation of the stereochemistry of this reaction.[1g] This paper presents the details of our studies of the mechanism and stereochemistry of the addition of electron-deficient olefins to bicyclo[2.1.0]pentane.

In an earlier investigation of the addition of electron-deficient acetylenes to bicyclo[2.1.0]pentane (**1**), we suggested that a two-step process, involving a diradical intermediate, was the mechanistic path which was followed in the addition of acetylenes to strained rings.[1f] This proposal was based on the results of kinetic and product studies of the reaction. However, several stereochemical questions were not answered by our studies of acetylene additions. The major points of interest were (1) did the attacking carbon–carbon multiple bond approach from the top or the bottom of the bicyclo[2.1.0]pentane envelope; (2) in the addition of olefins to **1** would rotation occur about the carbon–carbon bond which was originally the double bond; (3) would the addition of olefins be solvent dependent; and (4) would the olefin orient its functional group with the cyclopropane or cyclobutane portion of **1** or would the addition be nonstereospecific.



In order to answer the first stereochemical question we investigated the reaction of **1** with maleic anhydride (**2**). When **1** and **2** were heated together for 2 days at 120° a mixture of **3**, **4**, **5**, and **6** was obtained. The yields of these products were 68.0, 17.4, 4.5, and 0.5%, respectively. Cyclopentenyl-3-succinic anhydride (**3**), *endo*-2,3-dicarboxybicyclo[2.2.1]heptane anhydride (**5**), and *exo*-2,3-dicarboxybicyclo[2.1.0]heptane anhydride (**6**) were identified by comparison with authentic samples.[7,8] The cyclopentylmaleic anhydride (**4**) was catalytically hydrogenated over 5% Pd–C to yield **7**. Hydrolysis of **7** followed by esterification with diazomethane gave **8** which was identical in all respects with an authentic sample of

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[1] Paper XI of a series on "The Chemistry of 'Bent' σ Bonds." Previous papers in the series are (a) P. G. Gassman and K. T. Mansfield, *Chem. Commun.*, 391 (1965); (b) P. G. Gassman and K. T. Mansfield, *J. Org. Chem.*, **32**, 915 (1967); (c) P. G. Gassman, *Chem. Commun.*, 793 (1967); (d) P. G. Gassman and W. E. Hymans, *ibid.*, 795 (1967); (e) P. G. Gassman and K. T. Mansfield, *J. Am. Chem. Soc.*, **90**, 1517 (1968); (f) P. G. Gassman and K. T. Mansfield, *ibid.*, **90**, 1524 (1968); (g) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **90**, 4746 (1968); (h) P. G. Gassman and G. D. Richmond, *ibid.*, **90**, 5637 (1968); (i) P. G. Gassman and G. D. Richmond, *Chem. Commun.*, 1630 (1968); (j) P. G. Gassman, A. Topp, and J. W. Keller, *Tetrahedron Letters*, in press.

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

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

[4] National Institute of Health Postdoctoral Fellow, 1967–1968.

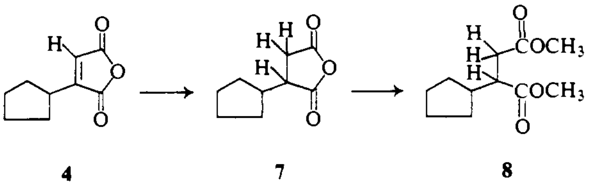
[5] A. Cairncross and E. P. Blanchard, Jr., *J. Am. Chem. Soc.*, **88**, 496 (1966); C. D. Smith, *ibid.*, **88**, 4273 (1966); M. Pomerantz, *ibid.*, **88**, 5349 (1966); H. J. Reich and D. J. Cram, *ibid.*, **89**, 3078 (1967); M. R. Rifi, *ibid.*, **89**, 4442 (1967); M. Pomerantz, G. W. Gruber, and R. N. Wilke, *ibid.*, **90**, 5040 (1968).

[6] W. R. Roth and M. Martin, *Tetrahedron Letters*, 4695 (1967).

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

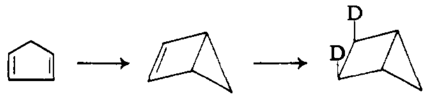
[8] D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).

dimethyl cyclopentylsuccinate.[1e] The position of the double bond in **4** was established on the basis of the nmr spectrum which showed a one-proton doublet at τ 3.67, a one-proton multiplet at 7.34, and a complex envelope at 8.34–9.00 (eight protons).

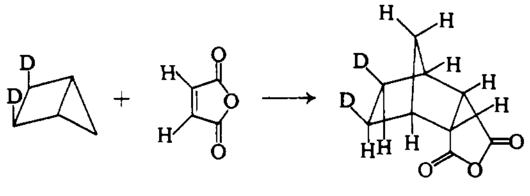


4 **7** **8**

We now could use the reaction of **1** with **2** to establish the stereochemistry of the approach of the reactants if we could prepare a stereospecifically labeled bicyclo[2.1.0]-pentane. Toward this end we photochemically converted cyclopentadiene monomer (**9**) into bicyclo[2.1.0]pentene (**10**).[9] Dideuteriodiimide reduction of **10** gave **11** with the deuterium exclusively in the *exo* position within the limits of analysis by nmr.[10] Having prepared stereochemically pure *exo,exo*-2,3-dideuteriobicyclo[2.1.0]pentane (**11**) we treated it with maleic anhydride (**2**) and selectively isolated the *endo*-anhydride **12**.

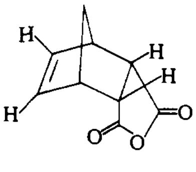


9 **10** **11**



11 **2** **12**

The stereochemistry of the deuteriums in **12** was established on the basis of both spectroscopic and chemical evidence. Chemical confirmation of the stereochemistry shown in **12** came from comparison of the infrared and nmr spectra of **12** with an authentic sample of **12** prepared by catalytic reduction of **13** utilizing deuterium gas and palladium on carbon. As with other bicyclo[2.2.1]-heptene derivatives, catalytic reduction of **13** would be expected to occur from the less hindered *exo* side of the double bond.[11] This would place the deuteriums in **12** in the *exo* positions. Spectroscopic evidence for the stereochemical assignment was based on a detailed analysis of the nmr spectra of **5** and **12**.[12] The spectrum of the nondeuterated material, **5**, shows the H_A hydrogens as an eight-peak multiplet at τ 6.49. In **12** H_A appears as a sharp quartet having lost a 2-cps long-range W-form coupling with the *exo*-hydrogens, H_E, at C-5 and C-6. The bridgehead hydrogens, H_B, of **5** appear as a broad poorly resolved eight-peak multiplet, while in **12** the pattern for these hydrogens is a sextet, the coupling of H_B with H_E having been removed. H_C and H_D appear together in a five-peak multiplet centered at τ 8.39 in both **5** and **12**. The four hydrogens H_E and H_F of **5** appeared as an AA'BB' pattern, 31 cycles wide, with superimposed bridgehead and long-range couplings, centered at τ 8.55. In **12** the H_F protons became a broad singlet at τ 8.72. The change in the nmr spectrum observed when H_E was replaced by deuterium was only consistent with the deuteriums having *exo* stereochemistry. The reaction was stereospecific within the limits of nmr spectroscopy. Because of the limits of this method of analysis less than 5% of **5** where H_F had been replaced by deuterium could have escaped detection.



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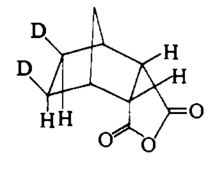

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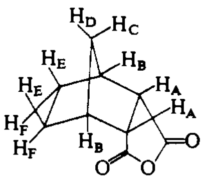

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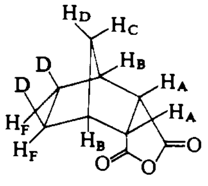

12

Since the deuteriums in **12** were unequivocally in the *exo* position, **12** must have been formed *via* attack of maleic anhydride from below the "flap" of the deuterated bicyclo[2.1.0]pentane (**11**) resulting in inversion of the "flap."

We have previously demonstrated that acetylenes add to **1** with formation of diradical intermediates.[1f] In light of this work it would appear that the initial attack by the electron-deficient carbon–carbon multiple bond involves "backside" approach on the highly strained[13] C_1–C_4 bond to yield a diradical intermediate which can undergo conversion into the observed mixture of **3**, **4**, **5**, and **6**.

In order to learn more about the diradical nature of this reaction we investigated the reaction of **1** with fumaronitrile (**14**) and maleonitrile (**15**). When **1** was treated with either **14** or **15** in tetrahydrofuran solution for 2 days at 160° a mixture of five 1:1 adducts and two 2:1 adducts was obtained. The important factor involved in these additions was that although **14** and **15** reacted with **1** to

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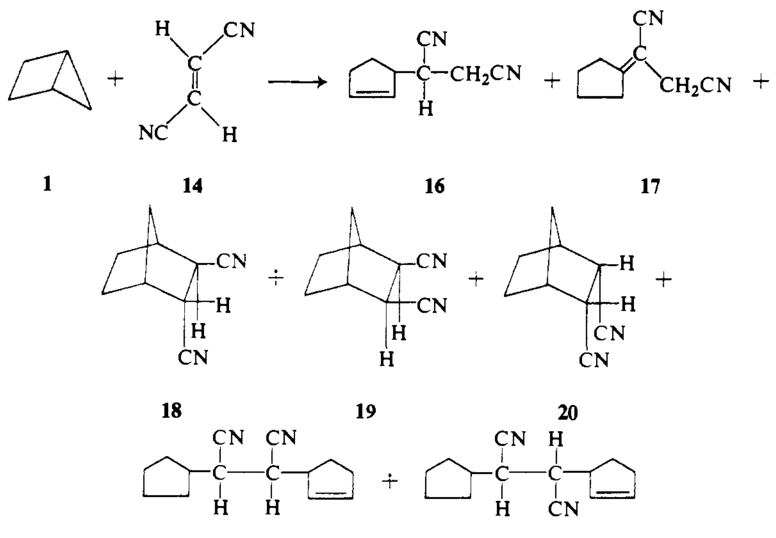
(9) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **88**, 846 (1966). We wish to thank Professor Brauman for providing us with the experimental details of the preparation of **10** and of the diprotio-diimide reduction of **10**.

(10) The nmr spectrum of bicyclo[2.1.0]pentane has been carefully analyzed. For the details of the analysis and the correction of earlier assignments see ref 1b and W. R. Roth and M. Martin, *Ann. Chem.*, **702**, 1 (1967)

(11) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

(12) For a leading reference on the analysis of spectra of bicyclo-[2.2.1]heptane derivatives see P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964); see also J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

(13) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968), have shown that cleavage of the C_1–C_4 bond of **1** releases *ca.* 48 kcal/mol.



1 14 16 17

18 19 20

21 22

give the same seven products, the ratio of the products from **14** was different from the ratio of the products from **15**.

The products obtained from the reaction of **1** with **14** were divided into two groups, the "ene" type products which were **16**, **17**, **21**, and **22**, and the "cycloaddition" type products **18**, **19**, and **20**. The combined yields of these products were 85% from **14** and 74% from **15**. The relative percentage compositions of the reaction mixtures as listed in Table I were determined *via* vpc *vs.* an internal standard. Compounds **17**, **18**, **19**, and **20** were identified by comparison with authentic samples.[1e,14,15] Compound **16** was identified by a combination of chemical and spectroscopic data. Catalytic hydrogenation of **16** over 5% Pd–C gave cyclopentylsuccinonitrile (**23**), identical in all respects with an authentic sample,[1e] thus establishing the basic structure. The nmr spectrum of **16** showed peaks at τ 3.96 (multiplet, 1 H), 4.31 (multiplet, 1 H), and 5.60–8.48 (broad envelope, 8 H). The two vinyl protons at τ 3.96 and 4.31 formed the same type of AB pattern which we had previously established as being characteristic of 3-substituted cyclopentyl derivatives.[1e] This firmly established the nature of **16**.

Both chemical analysis and mass spectral analysis established that **21** and **22** were formed from the combination of 2 equiv of **1** with 1 equiv of either **14** or **15**. Compounds **21** and **22** had different infrared and nmr spectra, but virtually identical mass spectral cracking patterns. The nmr spectra of both **21** and **22** had peaks in the vinyl region (τ 3.93 and 4.34, and 4.05 and 4.34, respectively) which were virtually superimposible on the vinyl hydrogen pattern for **16** and for other 3-substituted cyclopentenes. In addition to the two vinyl hydrogens, the spectra of both **21** and **22** integrated for 16 protons between τ 6.5 and 8.5. The identity of the mass spectral cracking patterns and the similarity of the nmr spectra indicated that **21** and **22** were diastereomers. Coupled with the fact that we have a 2:1 adduct, the spectral data were consistent with **21** and **22** having the structures shown.

As shown in Table I significant differences occur in the product ratios observed in the reaction of **1** with **14** and **15**, respectively. In addition both **14** and **15** produce mixtures of **18**, **19**, and **20**. Since the three isomeric 2,3-dicyanobicyclo[2.2.1]heptanes were obtained in the reactions of **1** with **14** and with **15**, the reaction must have proceeded *via* a mechanism which permitted rotation about the bond which originally was the olefin linkage in the fumaronitrile and maleonitrile. Since all the starting materials and all the isolated reaction products were stable under the reaction conditions an intermediate must have been formed in which this rotation could occur. The presence of such an intermediate foregoes the plausibility of any type of concerted reaction.[16] In previous studies we conclusively eliminated the possibility of zwitterionic intermediates being formed in cycloadditions to bicyclo[2.1.0]pentane.[1f] Although our earlier work involved the addition of electron-deficient acetylenes to **1** and not electron-deficient olefins, there is no reason to suspect that this minor change in addend would cause a complete change in mechanism. Hence it appears certain that the addition of olefins to bicyclo[2.1.0]pentane proceeds *via* initial formation of a diradical intermediate. In the case of fumaronitrile and maleonitrile this intermediate would be **24**. The formation of all of the observed products can be readily explained on the basis of the intermediacy of **24**. In the diradical **24**, rotation about the C_a–C_b bond would be expected to be competitive

Table I. Product Ratios from the Reactions of **1** with **14** and **15**

Compd	**1** + **14**	**1** + **15**
16	80.0	88.7
17	6.2	2.2
18	6.7	1.2
19	0.3	2.1
20	0.4	3.0
21	3.5[a]	1.0[a]
22	2.8[a]	1.7[a]

[a] The relative amounts of **21** and **22** are extremely dependent on concentration of the bicyclo[2.1.0]pentane.

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(14) A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945).

(15) J. Sauer, H. Wiest, and A. Mielert, *Ber.*, **97**, 3183 (1964).

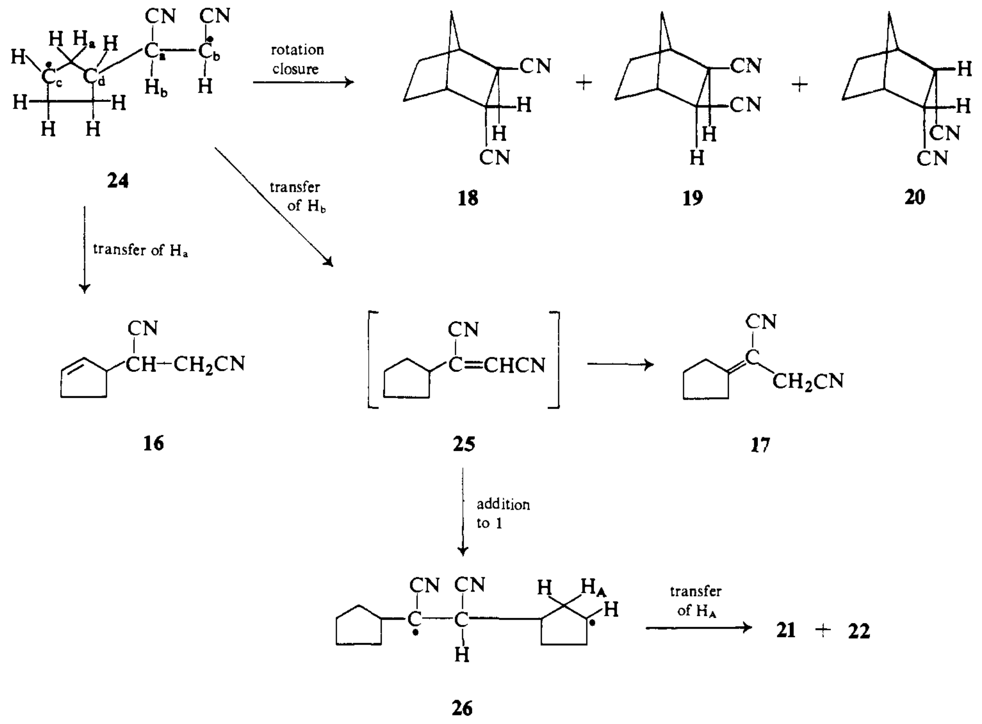
(16) Molecular orbital symmetry considerations also indicated that a concerted reaction path would not be reasonable for our additions: see R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

Table II. Effect of Solvent on the Reaction of **1** with **14**. Product Composition

	Solvent		
Product	Tetrahydrofuran	Acetonitrile	1-Butanol
16	80.0	78.8	77.7
17	6.2	5.0	8.7
18	6.7	8.4	6.3
19	0.4	0.2	0.5
20	0.7	0.4	0.7
21	3.4	1.1	2.6
22	2.8	1.9	2.9

Table III. Effect of Solvent on the Reaction of **1** with **15**. Product Composition

	Solvent		
Product	Tetrahydrofuran	Acetonitrile	1-Butanol
16	88.7	82.7	73.7
17	2.2	7.2	15.3
18	1.2	1.6	1.1
19	2.1	2.5	1.7
20	3.0	4.2	3.1
21	1.0	0.5	2.4
22	1.7	1.4	2.8



with closure of the diradical[17] to give norbornane derivatives. The different product ratios observed when fumaronitrile and maleonitrile were used as addends was completely in agreement with these expectations. On the basis of the relative ratios of **18**, **19**, and **20** we noted that starting with the *trans*-dinitrile **14**, *ca.* 10% of norbornanes formed resulted from rotation about the C_a–C_b bond. In the case where the *cis*-dinitrile **15** was the addend *ca.* 20% of rotation occurred about the same C_a–C_b bond prior to internal radical combination. The increased amount of rotation from the *cis* starting material was expected. This result alone would appear to provide definitive evidence for the formation of a diradical intermediate in the reaction of carbon–carbon multiple bonds with bicyclo[2.1.0]pentane.

The formation of **16** from **24** is very straightforward requiring only the intramolecular transfer of H_a to C_b. The formation of **17**, **21**, and **22** is more complicated and requires detailed consideration. We have previously found[1e] in the case of the reaction of propiolic ester with **1** that two different intramolecular hydrogen transfers can occur. The first type involved transfer from the ring to the addend and was the type resulting in the formation of **16**. The second type is the transfer of a hydrogen from the addend to the ring. In the case of **24** this would be the internal transfer of H_b to C_c to produce **25**. The cyclopentane derivative **25** was not found in the reaction mixture. However, this was not surprising since we had previously shown[1e] that molecules very similar to **25** undergo rapid double-bond isomerization to give tetrasubstituted double bonds such as was present in **17**. Hence, **17** would be expected if **25** were an intermediate. Another indication of the intermediacy of **25** was the formation of **21** and **22**. The intermediate **25** would be merely a mixture of monosubstituted fumaronitrile and maleonitrile. As such it would be expected to react with additional bicyclo[2.1.0]pentane (although at a slower rate than the unsubstituted dinitriles). Such a reaction would produce **26**, which *via* intramolecular transfer of H_a would yield **21** and **22**.

In line with our concern over carbon–carbon bond rotation at the diradical stage we studied the effect of changing solvents on the product ratio. Tables II and III

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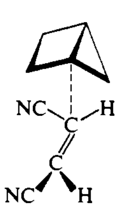
[17] P. D. Bartlett, L. K. Montgomery, and B. Siedel, *J. Am. Chem. Soc.*, **86**, 616 (1964); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964); P. D. Bartlett, *Nucleus* (Cambridge, Mass.), 251 (1966); P. D. Bartlett, *Science*, **159**, 833 (1968).

list the product ratios obtained in the reaction of **1** with fumaronitrile and maleonitrile, respectively, in tetrahydrofuran, acetonitrile, and 1-butanol. It should be noted that most of the product ratios were relatively solvent insensitive. The glaring exception to this generalization was the change in the ratio of the "ene" type products (**16** and **17**) from the reaction of **1** with **15**. Although the total amount of "ene" product only changes from 89 to 91%, the ratio of **16** to **17** changes from 40:1 in tetrahydrofuran, to 12:1 in acetonitrile, to 5:1 in 1-butanol. This order of change does not correlate with solvent polarity, but does follow the same trend as increasing solvent viscosity. This indicates to us that solvent viscosity (or some related solvent property) may be influencing the rate of rotation about the C_a–C_d bond of **24**, and in this way, may be determining the relative amounts of **16** and **17** (interestingly, no significant changes occurred in the ratio of "ene" to "cycloaddition" type products).

The increase in the amount of **17** with increasing viscosity indicates that the initial mode of attack of the electron-deficient olefin on the bicyclo[2.1.0]pentane may be one in which H_b was more readily situated for transfer to C_c than one in which H_a was properly positioned for transfer to C_b. Since the majority of the "ene" product resulted from the transfer of H_a to C_b in all the solvents investigated, it would appear that when rotation can occur freely, it prefers to occur in such a manner that the transfer of H_a is readily accomplished.

Presuming that the ratio of **19** to **20** in the reaction of **1** with maleonitrile reflects, at least to some extent,[18,19] the relative amount of orientation of the cyano groups of maleonitrile either with the cyclobutane or cyclopropane portion of **1**, we should be able to use the relative amounts of **19** and **20** as an indication of the transition states involved in the approach of **15** to **1**. There are two different types of approach which the addend, **15**, could take toward **1**. These are **27**, where the approach is "end on," and **28**, where the approach is totally from beneath the flap of the bicyclo[2.1.0]envelope. Since the group in **27** must rotate *ca.* 180° in order to form the second bond of the norbornane, **27** would be the precursor of **19** while **28** and **29** would represent possible precursors of **20**. Since we have recently shown that the addition of carbon–carbon multiple bonds to strained cyclopropanes can occur in systems where transition states similar to **28** are impossible,[1h] we prefer the transition states **27** and **29**, with **27** producing **19** and **29** yielding **20** in the reaction of **1** with **15**. Presuming that the theory of "end on" attack is correct, **29** would represent the mode of attack *ca.* 65% of the time while **27** participates *ca.* 35% of the time. It is not known at this time whether the relative amounts of **27** and **29** reflect steric or electronic differences. However, it should be noted that if the arguments used above are applied to the reaction of **1** with maleic anhydride, the transition states leading to the *exo* and *endo* adducts would be represented by **30** and **31**, respectively. In this case the ratio of **30** to **31** would be 1:9. Since the steric interactions in the addition of maleic anhydride and maleonitrile appear comparable we feel that electronic interactions may be the controlling factor.



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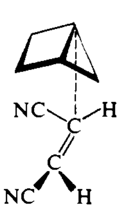

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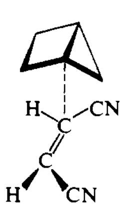

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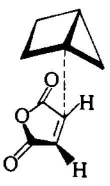

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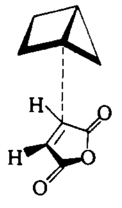

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Studies of the addition of electron-deficient carbon–carbon multiple bonds to other strained carbon–carbon single bonds are currently in progress. We also hope to determine why the ratio of **16** to **17** had considerable solvent dependence when maleonitrile was added to **1** but little effect when the addend was fumaronitrile.

Experimental Section

Reaction of Maleic Anhydride (2) with Bicyclo[2.1.0]pentane (1). Maleic anhydride (1.0 g) and bicyclo[2.1.0]pentane (1 ml) were combined in a sealed glass ampoule and heated to 120° for 2 days. The reaction was cooled, the ampoule opened, and the crude reaction mixture was analyzed by vpc using diethyl phthalate as an internal standard and 1% FS-1265 on acid-washed 80–100 Chromosorb G and 0.6% PDEAS on acid-washed 60–80 Chromosorb G as the packings in the two different columns which were used. Preparative vpc on a 10-ft 15% FS-1265 on an acid- and base-washed 60–80 Chromosorb W column at 190° gave cyclopentyl maleic anhydride (**4**), cyclopentenyl-3-succinic anhydride (**3**), *endo*-2,3-dicarboxybicyclo[2.2.1]heptane anhydride (**5**), and *exo*-2,3-dicarboxybicyclo[2.2.1]heptane anhydride (**6**). The yields were 17, 68, 4.5, and 0.5%, respectively. Compounds **3**, **5**, and **6** were identified by a comparison of their nmr and ir spectra, and vpc retention times *vs.* authentic samples prepared *via* literature procedures.[7,8]

The cyclopentyl maleic anhydride (**4**) was hydrogenated over 5% Pd–C, hydrolyzed with aqueous sodium hydroxide and esterified with diazomethane to give dimethyl cyclopentylsuccinate identical in all respects with an authentic sample.[1e] The nmr spectrum of **4** showed a one-proton doublet at τ 3.67, a multiplet at τ 7.34 (1 H)- and an eight-proton envelope in the region from τ 8.34 to 9.00.

***exo,exo*-2,3-Dideuteriobicyclo[2.1.0]pentane (11).** Cyclopentadiene monomer (16 ml) and ethanol-O-*d* (550 ml) were irradiated with a 450-W medium-pressure lamp in a quartz immersion well for 115 min below 8°. The irradiation was stopped momentarily after 1 hr to permit removal of a polymeric coating from the irradiation well. Immediately following completion of the irradiation, the total irradiation mixture was added to 130 g of potassium diazodicarboxylate in a 1-l., three-necked, round-bottomed flask immersed in an ice bath at 0° and fitted with an addition funnel, mechanical stirrer, and Dry Ice condenser. Acetic acid-O-*d* (90 ml) was added dropwise over a period of 2 hr. The gases which were not condensed by the first Dry Ice condenser were passed into a second condensing system at Dry Ice–acetone temperature. After all the acetic acid-O-*d* had been added, the reaction was stirred at 0° for an additional 3 hr. At this time the reaction mixture was warmed and the volatile reaction products were distilled from the

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(18) This presumption only requires that **18** does not arise solely from the precursor of **19**.

(19) When either maleonitrile or fumaronitrile is used as the addend two isomeric diradicals can be obtained. These would be diastereomers, since C_a and C_d are asymmetric. With maleonitrile (or maleic anhydride) as the addend, one isomer would give rise to the di-*exo* product while the other stereoisomer would give rise to the di-*endo* adduct.

solution. The distillate and the condensate in the second Dry Ice condensing system were combined to yield 20 ml of solution which was shown by vpc to consist of *ca.* 50% ethanol-O-*d* and 50% hydrocarbons. The ethanol and traces of water were removed with anhydrous calcium chloride. The cyclopentadiene present in the remaining hydrocarbon mixture was removed by treating it with maleic anhydride at room temperature. This gave 6 ml of a final hydrocarbon mixture which consisted of *exo,exo*-dideuteriobicyclo[2.1.0]pentane (**11**) (10%), dideuteriocyclopentene (50%), and tetradeuteriocyclopentane (40%). Compound **11** could be separated from this mixture by preparative vpc on a 10-ft, 15% UCON polar on Firebrick column at 25° in sufficient quantities for nmr analysis.

Addition of Maleic Anhydride to *exo,exo*-2,3-Dideuteriobicyclo[2.1.0]pentane (11). The stereospecifically deuterated sample of **11**, present to the extent of 10% in the hydrocarbon mixture described above, was used without further purification after it had been demonstrated that the presence of the deuterated cyclopentene would not adversely affect the reaction of **11** with **2**. Thus, the hydrocarbon mixture was mixed with excess maleic anhydride, sealed in a glass ampoule, and heated to 120° for 2 days. The *endo*-anhydride **12** was isolated by preparative vpc on a 10-ft, 15% FS-1265 on 60–80 Chromosorb W column. The sample of **12** which was collected was contaminated by a small percentage of the *exo*-anhydride. With allowances for the trace amount of *exo*-anhydride which was present, the nmr spectrum of **12** was identical with the nmr spectrum of an authentic sample of **12** prepared as described below.

***exo,exo*-5,6-Dideuterio-*endo*-2,3-dicarboxybicyclo[2.2.1]heptane Anhydride (12).** 5,6-Dicarboxybicyclo[2.2.1]hept-2-ene anhydride was prepared by the reaction of maleic anhydride with cyclopentadiene. This Diels–Alder adduct was catalytically deuterated with deuterium gas over 5% Pd–C catalysis to give **12**, mp 168–169° (lit.[8] mp for **5**, 167°).

Addition of Fumaronitrile (14) to Bicyclo[2.1.0]pentane (1). Fumaronitrile (65 mg) and bicyclo[2.1.0]pentane (100 mg) in 2 ml of purified tetrahydrofuran were sealed in a glass ampoule and heated to 160° for 2 days. The ampoule was opened and diethyl phenylmalonate was added (as an internal standard) to an aliquot of the reaction mixture. This was used for yield determinations *via* vpc on 3% FS-1265 on 100–120 Chromosorb G and on 3% FFAP on 45–60 Chromosorb G columns. This method of analysis indicated an 85% yield of products with the following relative percentages **16** (80.0%), **17** (6.2%), **18** (6.7%), **19** (0.3%), **20** (0.4%), **21** (3.5%), and **22** (2.8%). On a preparative scale the products were separated by vpc on a 10-ft, 15% FS-1265 on acid- and base-washed 60–80 Chromosorb W column.

Compound **16**, bp 89° (0.03 mm), had ir maxima at 4.41 and 6.17 μ. Its nmr spectrum showed a one-proton multiplet at τ 3.96, a one-proton multiplet at 4.31, and multiplets at 7.0 (3 H), 7.25 (2 H), 7.6 (2 H), and 1.9 (1 H). Catalytic reduction over 5% Pd–C gave cyclopentylsuccinonitrile, identical in all respects with an authentic sample.[1e] Comparison of the nmr spectrum of **16** with those of model compounds substantiated the identification of its structure as cyclopentenyl-3-succinonitrile.

Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.90; N, 19.16. Found: C, 73.7; H, 6.81; N, 19.4.

Compound **17**, isolated from the reaction mixture by preparative vpc was shown to be cyclopentylidenesuccinonitrile by comparison of its uv, ir, and nmr spectra with those of an authentic sample.[1e]

Compound **18**, mp 121.5–122.5° (lit.[14] mp 120–121°), was identical in all respects with an authentic sample, mp 122–123°, prepared according to the literature procedure.[14]

Compound **19** was identified by a comparison of its vpc retention time to an authentic sample[14] on three different vpc columns (SE-30, FS-1265, and FFAP).

Compound **20** was identified by a comparison of its vpc retention time to an authentic sample (60% pure) of **20** prepared by literature procedures.[15] Identical retention times were noted on the three different columns: SE-30, FS-1265, and FFAP.

In addition to the above-listed products, **21** and **22** were isolated by preparative vpc. Compound **21** was recrystallized from chloroform–hexane to give an analytical sample, mp 192–194°. The absence of strong absorption in the ultraviolet spectrum showed the absence of conjugated nitrile groups. The nmr spectrum of **21** showed the characteristic pattern previously noted[1e] for 3-substituted cyclopentenes with absorptions at τ 3.93 and 4.34. In addition the nmr spectrum integrated for 16 protons between τ 6.5 and 8.5. The mass spectrum indicated a parent peak at m/e 214 (calcd 214.3).

Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.38; H, 8.58; N, 13.10.

Compound **22**, mp 116–117°, showed no conjugation *via* ultraviolet spectroscopy. The nmr spectrum of **22** showed a characteristic 3-substituted cyclopentene pattern with absorptions at τ 4.05 and 4.34. The mass spectrum was virtually identical with that of **21**, but the infrared spectrum was different from that of **21**.

Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.39; H, 8.61; N, 12.97.

Addition of Maleonitrile (15) to Bicyclo[2.1.0]pentane (1). The addition of **15** to **1** was carried out exactly as outlined for the addition of **14** (*vide supra*). Product composition was determined by vpc and is listed in Table I.

Solvent Effects on the Addition of 14 and 15 to 1. 1-Butanol was dried over molecular sieves and distilled prior to use. Tetrahydrofuran was purified by distillation from lithium aluminum hydride and storage over molecular sieves. Analytical grade acetonitrile was used without purification. All reactions were run under identical conditions in sealed tubes at 160° for 2 days. Relative percentages were determined by vpc analysis and are listed in Tables II and III.

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