Cycloaddition. VIII. Ethylene as a Dienophile. A Minute Amount of 1,2 Cycloaddition of Ethylene to Butadiene

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Abstract: The product of addition of ethylene to butadiene at 175° and 6000 psi, accompanied by butadiene dimer, consists of cyclohexene (99.98%) and vinylcyclobutane (0.02%). The latter product is stable under the reaction conditions. The addition of ethylene to *trans,trans*-2,4-hexadiene under similar conditions yields stereospecifically *cis*-3,6-dimethylcyclohexene. With *cis,trans*-2,4-hexadiene at 195° and 4500 psi no detectable addition of ethylene took place in 21 hr. The four possible stereoisomeric 1,2-addition products of ethylene to the 2,4-hexadienes (**9**, **10**, **18**, and **19**) have been synthesized; they could not be detected in the direct cycloaddition product. Comparison of measured reaction rates suggests that at 175° ethylene is able to attack butadiene by a stepwise biradical mechanism, leading to 1,2 cycloaddition, about 5000 times more slowly than 1,1-dichloro-2,2-difluoroethylene.

Most olefins react thermally with conjugated dienes to give concerted 1,4 cycloaddition. However, *gem*-difluorinated olefins add stepwise to dienes by way of a biradical to give cyclobutanes (1,2 cycloaddition). The explanations[1,2] now given for these reactions suggest that both pathways should be available to all olefins. In addition to the reagents of strong preference, of which there are many examples, there should be reagents of weak preference leading to the uncommon result of mixed 1,2- and 1,4-cycloaddition products. In fact, the strongly 1,2-adding fluorinated olefins do give 1,4-cycloaddition products with conjugated systems having a cisoid geometry[3-5] and indeed have been found to do so to a small extent with butadiene itself, where it appears that about one-seventh of the product attributable to the minor cisoid diene population has the cyclohexene structure.[6]

The detailed interpretation in those cases is incomplete. Not only does a cisoid geometry in the diene favor a concerted cycloaddition mechanism, but it releases the biradical mechanism from the feature which requires it to produce cyclobutanes; if the biradical contains a *cis* allylic system, it is as well able to close to a six- as to a four-membered ring.

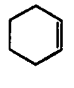
Examples from the other side, of strongly 1,4-adding reagents giving partly 1,2 addition, occur when cisoid conformation of the diene is sterically prohibited,[7] and also when the Diels–Alder product would have been antiaromatic.[8] In at least the case of ref 7, the 1,2 cycloaddition is probably by an ionic mechanism.

In addition to alterations of the normal reaction course by constraints upon the diene, it would seem that there should be reagents whose natural capacities for concerted and stepwise reactions are delicately enough balanced to show mixed products even with butadiene, and we felt that these should be sought among the known weak Diels–Alder dienophiles. One example, that of α-acetoxyacrylonitrile,[9] will be the subject of part IX of this series.[10]

It is not fully understood what determines the enormous range of reactivites in Diels–Alder reactions, but an important contributing factor is surely the π donor–acceptor complementarity between diene and dienophile, which may be effective whichever the direction of the donation.[11] Therefore, if we were to seek an example of a simple olefin giving some 1,2 cycloaddition, we might reexamine the addition of ethylene to butadiene, a slow Diels–Alder reaction in which there is no marked complementarity of the reactants.

Results

The addition of ethylene to butadiene[12] proceeded, in a steel bomb at 175° and an ethylene pressure which reached 6000 psi during the reaction, to give cyclohexene (**1**) along with the butadiene dimer, 4-vinylcyclohexene (**2**), in a ratio of 88 to 12, consistent with previous observations on this reaction.[12-14] To examine the product closely for possible minor components, its resolution on a number of vpc columns was examined and vinylcyclobutane (**6**), the suspected 1,2-addition product, was prepared by a synthetic route, characterized spectroscopically, and its behavior



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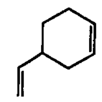

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[1] (a) K. Fukui in "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964; (b) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 87, 2046 (1965).

[2] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964).

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[4] P. D. Bartlett, G. E. H. Wallbillich, A. S. Wingrove, J. S. Swenton, L. K. Montgomery, and B. D. Kramer, *ibid.*, 90, 2049 (1968).

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[6] J. S. Swenton and P. D. Bartlett, *ibid.*, 90, 2056 (1968).

[7] C. A. Stewart, Jr., *ibid.*, 84, 117 (1962).

[8] A. T. Blomquist and Y. C. Meinwald, *ibid.*, 79, 5316 (1957); 81, 667 (1959).

[9] J. C. Little, *ibid.*, 87, 4020 (1965).

[10] P. D. Bartlett and K. E. Schueller, *ibid.*, 90, 6067 (1968).

[11] R. Huisgen, R. Grashey, and J. Sauer, in Patai, "The Chemistry of Alkenes," Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 11, pp 918–924.

[12] (a) R. V. Wheeler and W. L. Woods, *J. Chem. Soc.*, 1819 (1930); L. M. Joshel and L. W. Butz, *J. Amer. Chem. Soc.*, **63**, 3350 (1941).

[13] J. L. Skinner and C. M. Sliepcevich, *Ind. Eng. Chem., Fundam.*, 2, 168 (1963).

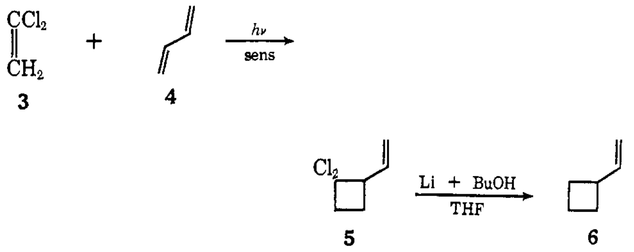
[14] D. Rowley and H. Steiner, *Discussions Faraday Soc.*, 10, 198 (1951).

Table I. Vapor Phase Chromatography Columns Used[a]

Column	Liquid phase	Solid phase	Length, ft	Outer diameter, in.	Chromatograph
A	γ-Methyl-γ-nitropimelonitrile	Chromosorb W	10	1/4	F & M 300
B	γ-Methyl-γ-nitropimelonitrile	Chromosorb W	22	1/4	F & M 300
C	γ-Methyl-γ-nitropimelonitrile	Chromosorb W	10	1/4	F & M 609
D	γ-Methyl-γ-nitropimelonitrile	Chromosorb W	22	1/8	F & M 609
E	γ-Methyl-γ-nitropimelonitrile	Chromosorb P	20	3/8	Aerograph Autoprep A-700
F	β,β'-Oxydipropionitrile	Chromosorb P	10	1/4	F & M 300
G	β,β'-Oxydipropionitrile	Chromosorb W	10	1/4	F & M 300
H	β,β'-Oxydipropionitrile	Chromosorb W	20	1/8	F & M 609
I	β,β'-Oxydipropionitrile	Chromosorb P	20	3/8	Autoprep A-700
J	Carbowax 20M	Chromosorb P	10	1/4	F & M 300
K	Carbowax 20M	Chromosorb P	20	1/4	F & M 300
L	Carbowax 20M	Chromosorb P	20	3/8	Autoprep A-700
M	Cyanosilicone grease	Chromosorb W	2	1/4	F & M 300
N	Cyanosilicone grease	Chromosorb W	2	1/8	Aerograph HyFi 600B
O	Apiezon L	Chromosorb W	6	1/4	F & M 300
P	10% Silver fluoroborate, 20% Carbowax 20M	Chromosorb W	6	1/4	F & M 300

[a] All columns are 20% by weight liquid phase on 60–80 mesh solid phase unless otherwise noted.

on the same chromatographic columns was determined. For convenient reference, Table I describes sixteen analytical and preparative columns used in the chromatographic separations in this and the following paper; the columns are referred to hereafter by letter.



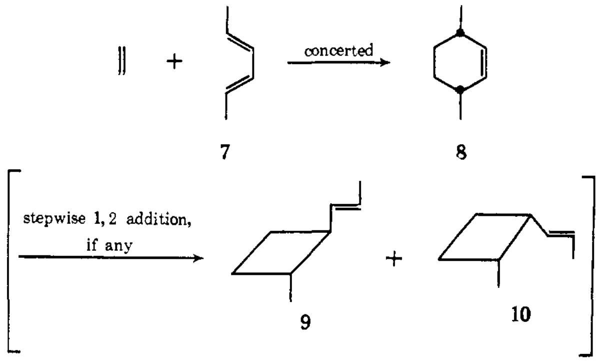
1,1-Dichloro-2-vinylcyclobutane (**5**)[15] was prepared by the photosensitized addition of vinylidene chloride to butadiene with β-acetonaphthone as sensitizer. It was characterized by ir, nmr, and mass spectra. It was reduced by the method of Bruck, Thompson, and Winstein[16] in good yield to vinylcyclobutane, whose ir and nmr spectra were identical with those published previously,[17] and whose mass spectrum showed the characteristic prominence of the butadiene ion.

On both columns D and H of Table I it was observed that vinylcyclobutane had the same retention time as a small shoulder which appeared on the butadiene peak during chromatography of the reaction product from ethylene and butadiene. It was found that the column could be made to retain butadiene selectively by the previous injection of 50 μl of a saturated solution of tetracyanoethylene in tetrahydrofuran. When the THF had come through, an analytical sample of the reaction product was injected. The chromatogram showed that the butadiene had reacted completely with the TCNE on the column and that the peak which had been a shoulder now stood alone.

In a series of experiments its area averaged 0.02% of the area of the cyclohexene peak. Synthetic vinylcyclobutane showed the same retention time on the treated as well as the untreated column. It was verified that neither the original butadiene nor the ethylene contained any impurity with this retention time.

We thus have a calibration point in the comparison of the concerted and biradical mechanisms of cycloaddition of ethylene and butadiene: the bimolecular rate constants are in the ratio of 5000 to 1.

One of the most specific criteria for distinguishing between concerted and stepwise cycloaddition is the presence or absence of stereoisomerization in such substrates as the 2,4-hexadienes. If ethylene would add to *trans,trans*-2,4-hexadiene (**7**) to give a mixture of stereoisomeric cyclobutanes (**9** and **10**) as well as the expected purely *cis*-3,6-dimethylcyclohexane (**8**), clear confirmatory evidence would be provided of a duality of mechanism.



From the reaction of ethylene with *trans,trans*-2,4-hexadiene at 185° and 4300 psi pressure, the only compounds that could be identified were starting material and *cis*-3,6-dimethylcyclohexene (**8**), the isomer unfavored thermodynamically. The isomeric *trans*-3,6-dimethylcyclohexene (**13**) was prepared by separating the mixture of elimination products of the mixed acetates (**11**), and was shown by vpc retention time to be absent in the cycloaddition product. Vapor chromatography of samples periodically taken from the catalytic hydrogenation of **8** over platinum oxide showed that its hydrogenation to *cis*-1,4-dimethylcyclohexane was accompanied by a few per cent of

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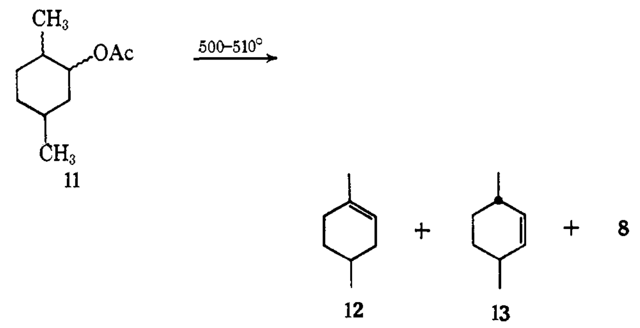
[15] N. J. Turro and P. D. Bartlett, *J. Org. Chem.*, **30**, 1853 (1965).

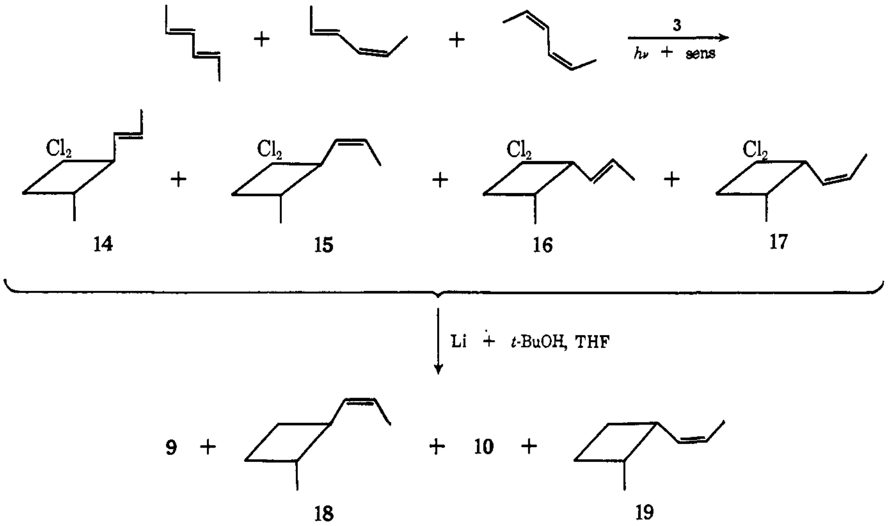
[16] P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 405 (1960).

[17] C. G. Overberger, H. Kaye, and G. Walsh, *J. Polym. Sci., Part A*, 2, 755 (1964).



isomerization to **12**, the eventual hydrogenation product including 4% of *trans*-1,4-dimethylcyclohexane.

As in the case of butadiene, the possible 1,2-cycloaddition products of ethylene to 2,4-hexadiene were synthesized by reduction of the photosensitized adducts of vinylidene chloride to a mixture of the diene isomers.



The product of photosensitized addition was separated into four components by preparative vpc, and the mixed dechlorination products were likewise separated into four components. In order of elution, both mixtures had their components in similar relative proportions. In each case the ir spectra showed that the first and third components of the mixture had *trans*-propenyl groups, while the second and fourth had *cis*-propenyl groups. The stereochemistry in the four-membered ring remains in doubt in all eight cases.

Of the 1-propenyl-2-methylcyclobutanes, **9**, **10**, **18**, and **19**, all but one (that with the longest retention time, comprising about 6% of the mixture) could be well separated from **8** by vapor chromatography. Again the deposition of tetracyanoethylene on the analytical vpc column (column D) removed 2,4-hexadiene from the ethylene–*trans,trans*-2,4-hexadiene product mixture and showed the absence of detectable amounts of the two possible 1,2 cycloadducts (**9** and **10**, with *trans* side chains[2]) in the reaction product. As little as 0.2% of one of these isomers would have been easily detected.

The fact that the biradical mechanism between ethylene and 2,4-hexadiene is too slow to yield appreciable product under these reaction conditions was confirmed in an attempted thermal reaction with the *cis,trans* isomer, whose coplanarity and Diels–Alder reaction mechanism is sharply hindered. At 195° and 4500 psi in 21 hr, no cycloadduct at all was observable by vpc on column F. The cyclobutanes **9**, **10**, **18**, and **19** were shown to be stable under the conditions of the cycloadditions.

Discussion

A comparison has been made between the reactivities of butadiene and *trans,trans*-2,4-hexadiene in 1,2 cycloaddition toward 1,1-dichloro-2,2-difluoroethylene[18] (1122). In the 1,2 mode butadiene was the more reactive by a factor of about 22. We have made a similar comparison of these dienes by a competition method toward maleic anhydride, and in this Diels–Alder reaction the *trans,trans*-2,4-hexadiene is the more reactive by a factor of 11–12. The terminal *trans* substitution of two methyl groups accordingly affects the rates of concerted 1,4 and stepwise 1,2 additions in opposite directions and the fraction of 1,2 cycloaddition might then decrease by a factor of about 200 on going from butadiene to hexadiene. In view of the very small amount of 1,2 cycloaddition in the former case, the lack of a detectable amount in the latter case appears normal. The relative rates are also those expected from the stepwise and concerted mechanisms: a reaction which must be initiated by bond formation at a substituted, rather than an unsubstituted, olefinic methylene group is retarded thereby just as is the polymerization of β-methylstyrene compared to that of styrene. On the other hand, methyl groups which do not hinder the reaction sterically are generally favorable to Diels–Alder reactions, an especially notable example being 9,10-dimethylanthracene.[19]

It is no surprise that the addition of ethylene to *trans,trans*-2,4-hexadiene is fully stereospecific, indicating a concerted mechanism. But this stereochemical evidence establishes with new experimental force the current view that the concerted mechanism does not depend upon strong differences in donor–acceptor power between diene and dienophile, but upon compatible orbital symmetries. There is no reason to doubt that the mechanism is the same with butadiene

(18) P. D. Bartlett and L. K. Montgomery, *J. Amer. Chem. Soc.*, **86**, 630 (1964).

(19) J. Sauer, D. Lang, and A. Mielert, *Angew. Chem.*, **74**, 352 (1962).

as with 2,4-hexadiene where the stereochemistry is so clear.

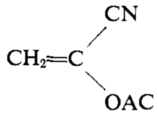
The most striking result of this study is the 0.02% of vinylcyclobutane found in the ethylene–butadiene product. Control experiments having established that this compound was not an impurity in the reactants and that it was not subject to further conversion during the bomb reaction, we may take its amount as a measure of the relative second-order rate constants of the two modes of cycloaddition between ethylene and butadiene. The total rate constant has been measured at atmospheric pressure[14] as $k_{1,4} = 3 \times 10^{10}e^{(-27,500/RT)}$ cm^3/mol sec. This corresponds to a value at 175° of 1×10^{-6} l./mol sec. Accordingly, the bimolecular rate constant for formation of vinylcyclobutane from butadiene and ethylene must be about 0.02% of 10^{-6}, or $k_{1,2} \approx 2 \times 10^{-10}$ l./mol sec. In making this estimate we choose not to correct for the effect of pressure on the rate constant,[13] since the effects upon $k_{1,2}$ and $k_{1,4}$ may be very similar and thus the uncorrected $k_{1,2}$ may be that which applies to atmospheric pressure as does our value of $k_{1,4}$.

The accurate measurements in this laboratory of the addition of 1,1-dichloro-2,2-difluoroethylene to butadiene over a temperature range were made in nitromethane as solvent and led to the equation[20]

$$\log k_2 = 6.92 - 19.14/2.3RT$$

The rate constants in nitromethane and methanol were the same at 102° and were about three times those in hexane and ether. Therefore, for order-of-magnitude purposes we may determine the rate constant at 175° between butadiene and 1122 as about 4×10^{-3} l./mol sec in nitromethane, and perhaps 2×10^{-3} in hexane. At that temperature the rate constant for 1,4 addition of these reagents is 2.3% of the 1,2 rate, or 5×10^{-5} l./mol sec. Thus we have the comparison between ethylene and 1122 toward butadiene shown in Table II, where Little's figures[9] on α-acetoxyacrylonitrile in toluene are also included.

Table II. Rate Constants at 175° for 1,2 and 1,4 Addition of Three Weak Dienophiles to Butadiene (in Bulk or Hydrocarbon Solvents)

Dienophile	$k_{1,2}$	$k_{1,4}$
$CH_2{=}CH_2$	2×10^{-10}	1×10^{-6}
$F_2C{=}CCl_2$	2×10^{-3}	5×10^{-5}
 $CH_2{=}C(CN)(OAC)$	$7 \times 10^{-6\,a}$	$3 \times 10^{-5\,a}$

[a] In toluene; data of Little.[9]

Of the two modes of cycloaddition we may reasonably assume that the 1,2 is proceeding through the same mechanism in both ethylene and 1,1-dichloro-2,2-difluoroethylene. The low solvent effect with 1122 is incompatible with a dipolar mechanism and a concerted mechanism is highly improbable on grounds of orbital symmetries. Ethylene is not more likely to react in dipolar fashion with butadiene than is 1122. The difference in rate between the two reagents corresponds to a $\Delta\Delta F^{\ddagger}$ of about 14 kcal. We have previously[2] estimated a difference in energy of formation of the biradicals from ethylene and tetrafluoroethylene of up to 16–17 kcal from destabilization of the double bond. In 1122 the destabilization term is less, but is offset by the delocalization energy of the $RCCl_2$ radical. The observed rate difference between ethylene and 1122 in 1,2 cycloaddition is therefore in line with the known factors affecting the biradical mechanism.

It appears that with respect to 1,4 cycloaddition α-acetoxyacrylonitrile and 1122 are about equally reactive toward butadiene, and about 30–50 times as reactive as ethylene. For reasons previously given, however, these three rates do not necessarily refer to the same mechanism. Work is currently under way to obtain as clear evidence on the 1,4-addition mechanism of 1122 as has here been possible with respect to ethylene.

Experimental Section

Ethylene and Butadiene.[12] Butadiene (Matheson instrument grade) (6.0 g, 0.11 mol) was poured into a 130-ml stainless steel bomb which had been cooled to −78°. The bomb was charged with ethylene (Matheson CP grade) to a pressure of 1200 psi and then heated to 175° for 36 hr. During the heating the pressure rose to 6000 psi. When it had cooled to room temperature the bomb was vented and 4.4 g of a light yellow liquid was withdrawn. Vapor phase chromatography on column C at 80° showed a little butadiene and two main product peaks present in the ratio 88:12. The retention time of the major peak was the same as that of cyclohexene and that of the minor the same as of 4-vinylcyclohexene. The products were separated by preparative vpc on column E. The main product, n^{30}D 1.4451, had infrared and nmr spectra identical with those of authentic cyclohexene, and the minor product, n^{30}D 1.4640, had infrared and nmr spectra identical with those of 4-vinylcyclohexene.

1,1-Dichloro-2-vinylcyclobutane (5). Into an irradiation vessel fitted with a Pyrex immersion well was put 1 l. of 1,1-dichloroethylene (Borden Monomer–Polymer Laboratory) and 23 g of β-acetonaphthone. The vessel was cooled to −18° and 16 g (0.30 mol) of butadiene was added. The solution was irradiated with a medium-pressure 450-W Hanovia mercury arc under nitrogen at −18° for 2 days. The polymeric deposit was then scrubbed from the walls of the well and the irradiation was resumed for 3 days. The mixture was dried over anhydrous magnesium sulfate and the 1,1-dichloroethylene was removed by flash distillation. Distillation gave 5.4 g (11% based on butadiene) of a colorless oil, bp 46° (15 mm). Vapor phase chromatography on column C at 105° showed one main peak and several impurities. The material was purified on column E at 120°.

The infrared spectrum had bands characteristic of the vinyl group at 11.01, 10.00, and 5.41 μ. The nmr spectrum showed a multiplet at τ 3.85–4.43 (1.2 H, vinyl proton), another multiplet at 4.85–5.17 (2.0 H, terminal methylene group), a quartet with fine structure at 6.61 (1.0 H, tertiary proton), and a complex multiplet from 7.17 to 8.25 (3.8 H, ring protons). The mass spectrum had a very small parent peak at *m/e* 150 but showed large peaks at *m/e* 122 and 54 due to the ions of 1,1-dichlorobutadiene and butadiene, respectively.

Anal. Calcd for $C_6H_8Cl_2$: C, 47.72; H, 5.35; Cl, 46.69. Found: C, 47.71; H, 5.34; Cl, 46.95.

Vinylcyclobutane. To a mixture of 300 ml of tetrahydrofuran, 27.0 g (0.37 mol) of *t*-butyl alcohol, and 5.0 g (0.72 g-atom) of high sodium content lithium[16] wire was added 5.8 g (0.038 mol) of 1,1-dichloro-2-vinylcyclobutane. This was stirred rapidly under nitrogen. After 5 min the reaction mixture became dark yellow; after 10 min it began to reflux spontaneously and required intermittent cooling in an ice bath. When the exothermic reaction had subsided the mixture was heated to reflux for 4 hr during which time the color became dark purple. After cooling to room temperature the mixture was poured over 1500 ml of crushed ice and was extracted with three 30-ml portions of pentane. The organic phase was washed ten times with water, dried over anhydrous sodium sulfate, and filtered. The solution was concentrated to 10 ml by distilling off pentane through a 16-in. vacuum-jacketed column

(20) J. S. Swenton, unpublished.

packed with glass helices. The residue was injected, 100 μl at a time, on column G at room temperature, and vinylcyclobutane was collected.

The infrared and nmr spectra agreed completely with those published previously[17]. The mass spectrum showed a small parent peak at *m*/*e* 82 and a large peak at 54 due to the ion of butadiene.

Analytical Vapor Phase Chromatography of the Butadiene–Ethylene Reaction Mixture. The product from ethylene and butadiene (1 μl) was injected on column D at room temperature. A tiny shoulder was seen on the butadiene peak that had the same retention time (7 min, 40 sec) as authentic vinylcyclobutane. A saturated solution of tetracyanoethylene (20 μl, from a supply kindly donated by the Du Pont Co.) in tetrahydrofuran was then injected onto the column. When the tetrahydrofuran had come through, 0.6 μl of the ethylene–butadiene product mixture was injected. The peak which had been a shoulder now stood alone and was found to have an area equal to 0.02% of the cyclohexene peak. Blank reaction mixtures in which butadiene had been heated alone or ethylene had been heated in the presence of pentane showed no peak having this same retention time. The same procedure was carried out on column H, and identical results were obtained.

The Stability of Vinylcyclobutane. Into a heavy-walled glass tube was put a mixture of vinylcyclobutane and isooctane (internal standard). An excess of butadiene was added. The tube was sealed and heated to 175° for 24 hr. Vpc analysis before and after heating showed that vinylcyclobutane was stable under the reaction conditions.

2,4-Hexadienes. 2,5-Diacetoxyhexane was prepared and pyrolyzed by Dr. Carol J. Dempster.[21] The mixture of conjugated and nonconjugated hexadienes obtained was isomerized to the desired 2,4-hexadienes by treatment with strong base. To a solution of 2.5 l. of dimethyl sulfoxide and 35 g of potassium *t*-butoxide was added 273 g (3.33 mol) of the hexadiene mixture. The black mixture was heated with stirring on a steam bath for 3 hr. After the reaction mixture had cooled to room temperature the dienes were distilled out of the flask at 1 mm pressure. The distillate was washed three times with water and dried over molecular sieves, yield 237 g (87%).

The hexadiene mixture (5.5 ml at a time) was injected into a Beckman Megachrom preparative gas chromatograph. Four sets of columns (8 ft, 5/8 in.) were arranged in parallel. Each set was made up of one column packed with 20% β,β′-oxydipropionitrile on 40–60 mesh Chromosorb P and one column packed with 35% ethylene glycol saturated with silver nitrate on 40–60 mesh Chromosorb P. The column temperature was maintained at 37° and the injector and detector temperatures at 100°. The purity of the collected hexadiene (recovery *ca.* 60%) by analytical vpc is given in Table III.

Table III

Megachrom fraction no.	Low-boiling material %	*trans*-1,3-Hexadiene, %	2,4-Hexadienes, % *trans,trans*	*cis,trans*	*cis,cis*	Other, %
Starting dienes	4.6		56	36	3.4	
1	0.2	2.2	97.2	0.4		
2			0.3	99.4	0.1	
3					90	10

***trans,trans*-2,4-Hexadiene.** The crude *trans,trans*-2,4-hexadiene obtained from the Megachrom was purified further by vpc on column I at a column temperature of 60° and a carrier gas flow rate of 100 cc/min. The diene collected contained less than 0.2% impurities.

***cis,trans*-2,4-Hexadiene.** The crude *cis-trans*-2,4-hexadiene obtained from the Megachrom was stirred overnight with maleic anhydride in acetone. The diene was steam distilled, washed several times with water, dried over anhydrous sodium sulfate, and purified by vpc on column I.

***trans,trans*-2,4-Hexadiene and Ethylene.** Into a 200-ml capacity stainless steel bomb was put 10 ml of *trans,trans*-2,4-hexadiene and a small spatula full of di-*n*-butylammonium picrate. The bomb was charged with ethylene to a pressure of 1100 psi and then heated with rocking to 185° for 17 hr, during which time the pressure rose to 4300 psi. After being cooled to room temperature the bomb was opened and 8.5 ml of a very pale yellow clear solution was withdrawn. Vapor phase chromatography on column F at room temperature showed that the product mixture contained 40% of *trans,trans*-2,4-hexadiene and 60% of a new material. The latter was collected. The infrared spectrum showed absorption at 6.09 μ. The nmr spectrum showed a doublet (J = 1 cps) for the vinyl protons at τ 4.56 (2 H) and a complex multiplet from 7.7 to 9.2 (12 H) with a sharp doublet for the methyl groups centered at 9.07.

Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 87.16; H, 12.84.

***cis,trans*-2,4-Hexadiene and Ethylene.** Into a 130-ml capacity high-pressure bomb was put 4 ml of *cis,trans*-2,4-hexadiene and a small amount of di-*n*-butylammonium picrate. The bomb was sealed and charged with ethylene to a pressure of 1100 psi and then heated with rocking to 195° for 21 hr during which time the pressure rose to 4500 psi. The bomb was cooled to room temperature. Analysis of the product by vpc on column F showed no peak due to adduct formation.

Hydrogenation of *trans,trans*-2,4-Hexadiene–Ethylene Adduct. The adduct of *trans,trans*-2,4-hexadiene and ethylene (0.2704 g, 2.45 mmol) was dissolved in 0.6 ml of glacial acetic acid. To this was added 0.02 g of platinum oxide. The mixture was hydrogenated at 760 mm and 20°: theoretical hydrogen uptake, 59.7 ml; actual uptake, 55.6 ml. The product was analyzed by vpc on column F. No starting material was present but two product peaks were seen in the ratio 9.3:90.7 in order of increasing retention time. These products had the same retention times as the two isomers of authentic 1,4-dimethylcyclohexane. The major hydrogenation product corresponded to the minor isomer of the commercial dimethylcyclohexane.

On column L the two isomers of commercial 1,4-dimethylcyclohexane were separated. The major isomer was found to have an nmr spectrum identical with that reported for *trans*-1,4-dimethylcyclohexane and the minor isomer a spectrum identical with that reported for *cis*-1,4-dimethylcyclohexane.[22] The minor isomer (0.1 ml) (containing less than 0.5% impurity) was heated in a sealed ampoule with 50 mg of 10% palladium on charcoal at 300–310° for 288 hr. Analysis by vpc showed that 78% of the starting material had been converted to the other isomer.

A mixture of 0.001 g of platinum oxide, a few drops of acetic acid and 0.967 g of the adduct of *trans,trans*-2,4-hexadiene and ethylene (**8**) was hydrogenated at room temperature and atmospheric pressure. At intervals a few drops of the solution were withdrawn from the flask through a side arm sealed by a septum cap. Analysis of the aliquots on column F showed that the initial hydrogenation product was *cis*-1,4-dimethylcyclohexane but that another peak also first appeared and then disappeared and as it disappeared some *trans*-1,4-dimethylcyclohexane was formed (Table IV).

Table IV

Aliquot no.	H_2 taken up, cc	Adduct, %	1,4-Dimethylcyclohexane, % *cis*	*trans*	New peak, %
1	0.00	100			
2	3.4	71	26		3
3	7.5	47	48	0.2	5
4	12.3	6	88	1	5
5	15.7	0	96	4	

Preparation of *trans*-3,6-Dimethylcyclohexene (13) and 1,4-Dimethylcyclohexene (12). A mixture of 60 g (0.48 mol) of isomers of 2,5-dimethylcyclohexanol, 120 g (1.2 mol) of acetic anhydride, and 60 g (0.81 mol) of pyridine was heated to 120° for 10 hr. After washing with water and saturated sodium bicarbonate solution the product was distilled: yield 62 g (76%) of a colorless oil; bp 87–94° (22 mm).

An infrared spectrum of the product showed no absorption at 5.74 μ.

The acetates were pyrolyzed at 500–510° under nitrogen. The pyrolyzate was washed with water and distilled: yield 22 g (55%); bp 112–116° (atmospheric pressure).

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[21] C. J. Dempster, unpublished.

[22] J. I. Musher, *Spectrochim. Acta*, **16**, 835 (1960).

Analysis by vpc on column G showed three products in the approximate ratio 3:2:3 in order of increasing retention time. The three products were collected from column I at 60°. On the basis of its retention time and nmr and infrared spectra the second product was shown to be identical with the major product of the reaction of *trans,trans*-2,4-hexadiene and ethylene (**8**).

On comparison of the nmr spectra of the first and third isomers, the doublet, integrating for six protons, at τ 9.08 in the nmr spectrum of the first isomer shows that both methyl groups are on saturated carbon atoms and this must therefore be *trans*-3,6-dimethylcyclohexene (**13**). A comparison of vapor phase chromatograms showed that none of this isomer (*i.e.*, <0.5%) was formed in the reaction of ethylene and *trans,trans*-2,4-hexadiene.

The singlet, integrating for three protons, at τ 8.42 and the doublet, also integrating for three protons, at τ 9.12 in the nmr spectrum of the third isomer shows that one methyl group is on an unsaturated and the other on a saturated carbon atom and that this must therefore be 1,4-dimethylcyclohexene (**12**). This has a retention time identical with that of the transient peak formed in the hydrogenation of *cis*-3,6-dimethylcyclohexene (**8**).

Photosensitized Addition of 1,1-Dichloroethylene to 2,4-Hexadiene. Into an irradiation vessel fitted with a Pyrex immersion well was put 1 l. of 1,1-dichloroethylene, 10 g (0.12 mol) of a mixture of 2,4-hexadienes, and 23 g of β-acetonaphthone. The mixture was irradiated with a medium-pressure 450-W Hanovia mercury arc under nitrogen at −18° for 1 week. Every day irradiation was interrupted while the film of polymer that had formed on the immersion well was scrubbed off and the white solid suspended in the solution was removed by filtration. The mixture was dried over anhydrous sodium sulfate and filtered, and the 1,1-dichloroethylene was removed by flash distillation. Distillation gave 7.9 g (36%) of a pale yellow oil, bp 45–58° (7 mm).

Anal. Calcd for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75; Cl, 39.58. Found: C, 53.78; H, 6.65; Cl, 39.59.

Analysis by vpc on column A at 100° showed that four products were present in the ratio 43:42:9:6 in order of increasing retention time.

The isomers **14–17** were separated and collected from column A. The infrared spectra of all four isomers showed weak absorption at 6.01 μ due to carbon–carbon double bond stretching vibrations. The spectra of the first and third isomers showed strong absorptions at 10.33 μ due to carbon–hydrogen out-of-plane deformation vibrations of a *trans* double bond. No further conclusions as to which stereoisomer is which could be drawn from the nmr spectra.

1-Propenyl-2-methylcyclobutanes (9, 10, 18, and 19). To 5.2 g (0.029 mol) of a mixture of the isomers of 1,1-dichloro-2-propenyl-3-methylcyclobutanes **14–17** and 27 g (0.37 mol) of *t*-butyl alcohol in 200 ml of tetrahydrofuran under nitrogen atmosphere was added 4.8 g (0.70 g-atom) of high sodium content lithium wire, cut into small pieces. The reaction mixture became dark yellow almost immediately; after 20 min it became very warm but did not reflux. It was then heated to reflux for 3.5 hr in which time it turned purple. The reaction mixture was cooled and poured over 800 ml of ice. When the excess lithium had reacted, the organic layer was separated. This was washed with water. An emulsion was formed so 30 ml of ether and some salt were added. The original aqueous phase was washed three times with 30-ml portions of ether. The combined organic layers were washed several times with water and dried over anhydrous magnesium sulfate. The ether was then distilled off through a 6-in. vacuum-jacketed distillation column packed with tantulum wire. Vpc analysis of the residue on column A at room temperature indicated the presence of four products having retention times consistent with those expected for C_8H_{14} hydrocarbons (they were compared with *cis*-3,6-dimethylcyclohexene) together with ether, *t*-butyl alcohol, and tetrahydrofuran. The relative amounts of the four products were very similar to the relative amounts of the four starting isomers. No starting material was found to be present. The four products were separated from the other organic compounds on column E at 90° and then from each other on column B (50-μl injections) at room temperature. The isomer having the shortest retention time was purified further by a third round of vpc, this time with 20-μl injections on column B.

The infrared spectra of the first and third showed strong absorption at 10.34 μ due to carbon–hydrogen out-of-plane deformation vibrations of a *trans* double bond. The spectra of the second and fourth showed absorption at 14.30 and 14.09 μ, respectively, due to the corresponding vibrations of a *cis* double bond.

Below are recorded the mass spectral data for each of the four isomers (A and C are **9** and **10**, B and D are **18** and **19**). To show how marked the similarity is between them the mass spectral data for another C_8H_{14} hydrocarbon, *cis*-3,6-dimethylcyclohexene (**8**), is also given. Only those fragments are listed which had a peak height equal to at least 10% of the base peak in at least one of the compounds (Table V). Exact mass determinations of the parent peak at 110 were also made for each of the four 1-propenyl-2-methylcyclobutanes (Table VI).

Table V

	% of base peak				
Mass no.	A	B	C	D	**8**
27	11.3	12.0	12.7	11.2	23.0
29	5.0	5.0	5.7	4.4	12.6
29	18.3	17.0	19.0	18.3	31.7
41	19.2	18.6	19.6	19.4	28.9
53	16.7	16.0	16.5	17.8	20.0
55	6.7	9.3	11.4	7.8	39.0
67	51.0	46.5	44.3	47.8	47.6
68	100.0	100.0	100.0	100.0	100.0
77	2.5	2.3	2.5	2.1	10.7
79	3.3	2.5	3.8	3.3	10.7
81	8.3	10.1	10.1	7.8	25.4
82	15.0	10.1	10.0	11.1	9.5
95	4.2	3.5	6.3	3.3	86.0
110	3.3	3.5	3.5	2.2	30.4

Table VI

Isomer	Found	Calcd	Error
A	110.1104	110.1095	+0.0009
B	110.1099	110.1095	+0.0004
C	110.1101	110.1095	+0.0006
D	110.1096	110.1095	+0.0001

Analytical Vapor Phase Chromatography of the *trans,trans*-2,4-Hexadiene–Ethylene Reaction Product. A vpc trace of the product mixture from *trans,trans*-2,4-hexadiene and ethylene on column D at room temperature was compared with a trace made under the same conditions of the four isomers of 1-propenyl-2-methylcyclobutane. This showed that if one or more 1,2 cycloadducts were formed in low yield in the reaction of ethylene and *trans,trans*-2,4-hexadiene, they might be hidden in the vpc by unreacted diene or product *cis*-3,6-dimethylcyclohexene (**8**).

A saturated solution of tetracyanoethylene in tetrahydrofuran (20 μl) was then injected on the column. When the tetrahydrofuran had come through, 0.6 μl of the ethylene–*trans,trans*-2,4-hexadiene product mixture was injected. The vpc trace showed no *trans,trans*-2,4-hexadiene. If more than 0.2% of one of the first three isomers of 1-propenyl-2-methylcyclobutane were present they could now have been seen, but no peaks having the correct retention time were present. The fourth isomer would still be buried under the *cis*-3,5-dimethylcyclohexene.

The Stability of 1-Propenyl-2-methylcyclobutane. The four isomers of 1-propenyl-2-methylcyclobutane were heated to 170° for 36 hr in the presence of excess *trans,trans*-2,4-hexadiene and isooctane (internal standard). Vpc analysis before and after heating showed that the cyclobutanes were stable under the reaction conditions.

Competitive Rate Ratio of *trans,trans*-2,4-Hexadiene and Butadiene with Maleic Anhydride. Into a very thin-walled glass capsule was sealed 52 mg (0.53 mmol) of maleic anhydride. This was dropped into a test tube; 713 mg (8.70 mmol) of *trans,trans*-2,4-hexadiene and 0.5 ml of acetone were added. The tube was cooled in an acetone–Dry Ice bath and 8.6 g (160 mmol) of butadiene was poured in. The tube was immediately sealed. When the contents had returned to room temperature the tube was vigorously shaken until the capsule shattered and the maleic anhydride dissolved. The tube was allowed to stand overnight at 25°. It was then opened and the volatile material was removed on a rotary evaporator. The relative amounts of the two adducts in the mixture were then determined by integrating the areas under the vinyl proton peaks in the nmr spectrum of the product mixture. The nmr spectrum of the adduct of butadiene and maleic anhydride has a quintet centered at τ 4.0 due to absorption of the ethylenic protons. The comparable absorption for the *trans,trans*-2,4-hexadiene–maleic anhydride adduct is a singlet at τ 4.22. It was found that the ratio of hexadiene adduct to butadiene adduct was 2:3. The approximate relative rate constants of *trans,trans*-2,4-hexadiene and butadiene with maleic anhydride (k_H/k_B) can then be calculated from the following equation if C_H and C_B are taken to be the areas under the vinyl proton peaks of the adducts of hexadiene and butadiene, respectively (M_B, millimoles of butadiene; M_H, millimoles of hexadiene).

$$\frac{k_H}{k_B} = \frac{C_H(M_B)}{C_B(M_H)} = \frac{(2)(160)}{(3)(8.7)} = 12$$

The same procedure was followed, this time with 730 mg (8.9 mmol) of hexadiene. C_H/C_B was found to be 1/2.7 and k_H/k_B is equal to 11.

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Cycloaddition. IX. α-Acetoxyacrylonitrile as a Dienophile. Its Concerted 1,4 Cycloaddition to 2,4-Hexadiene

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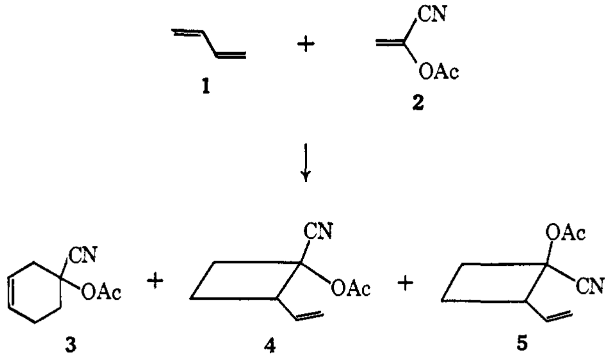
Abstract: The thermal addition of α-acetoxyacrylonitrile to *trans,trans*-2,4-hexadiene yields a 36:64 mixture of the two stereoisomers of 4-cyano-4-acetoxy-*cis*-3,6-dimethylcyclohexene (**7** and **8**). The absence of the two isomers with the methyl groups *trans* shows that this 1,4 cycloaddition occurs by a concerted mechanism. In contrast to the case of butadiene, only 0.4% of mixed cyclobutanes was present in the cycloadduct. It is concluded that in this case there is competition between a concerted Diels–Alder reaction and a less favorable stepwise mechanism leading to 1,2 cycloaddition.

In the preceding paper[1] we reported observing a minute amount of vinylcyclobutane in the product of thermal cycloaddition of ethylene to butadiene. The occurrence of any 1,2 cycloaddition, which implies a stepwise mechanism, raised the question whether such a weak dienophile as ethylene necessarily reacts concertedly in its Diels–Alder reactions, or whether some 1,4 addition might result from a branching of a biradical (stepwise) mechanism. This question could be answered for ethylene and a substituted butadiene having geometrical configuration: it was shown that the sole detectable adduct of ethylene and *trans,trans*-2,4-hexadiene was the thermodynamically unfavored *cis*-3,6-dimethylcyclohexene, establishing the mechanism as stereospecific and concerted.

A closer competition between thermal 1,2 and 1,4 cycloaddition to butadiene has been reported in the case of α-acetoxyacrylonitrile (**2**),[2] which yields from 9 to 23% of regiospecific[3] but stereorandom 1,2 adduct (**4** and **5**). The dependence of the reaction rate on solvent polarity is so small as to exclude a common *dipolar ion* intermediate for the two modes of addition. Both the small magnitude and the direction of the polar solvent effect on product composition exclude this possibility for the minor (1,2) mode of addition. On the assumption that distinctly different mechanisms, one concerted and the other by way of a biradical, should show markedly different dependence on solvent and temperature, Little[2] advocated a common mechanism for the 1,2 and 1,4 addition, involving a single intermediate with apparent allylic π bonding at the site where the eventual ring closure was to be effected.



Our recent studies have led to the view that a fairly sharp experimental distinction can be drawn between concerted reactions, which, are stereospecific, and stepwise reactions by way of a biradical, which are not.[4,5] We have applied this test to the reaction of α-acetoxyacrylonitrile with 2,4-hexadiene as the simplest homolog of butadiene that possesses configuration at both double bonds.

Results

Under conditions enabling us to duplicate one of Little's additions of α-acetoxyacrylonitrile to butadiene

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[1] Part VIII: P. D. Bartlett and K. E. Schueller, *J. Amer. Chem. Soc.*, **90**, 6071 (1968).

[2] J. C. Little, *ibid.*, **87**, 4020 (1965).

[3] A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

[4] L. K. Montgomery, K. E. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964).

[5] P. D. Bartlett, *Science*, **159**, 833 (1968).