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). 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.

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

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

Paul D. Bartlett and Kathleen E. Schueller

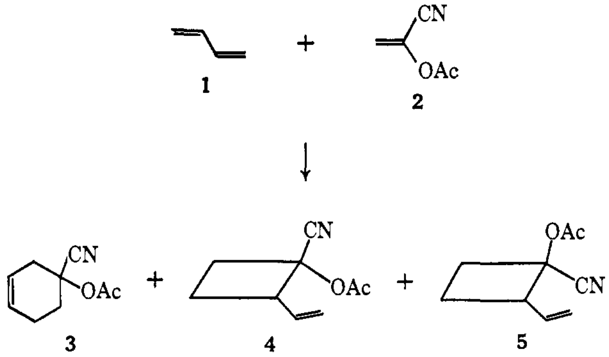
Contribution from the Converse Memorial Laboratory of Harvard University, Cambridge, Massachusetts 02138.

Received April 18, 1968

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).

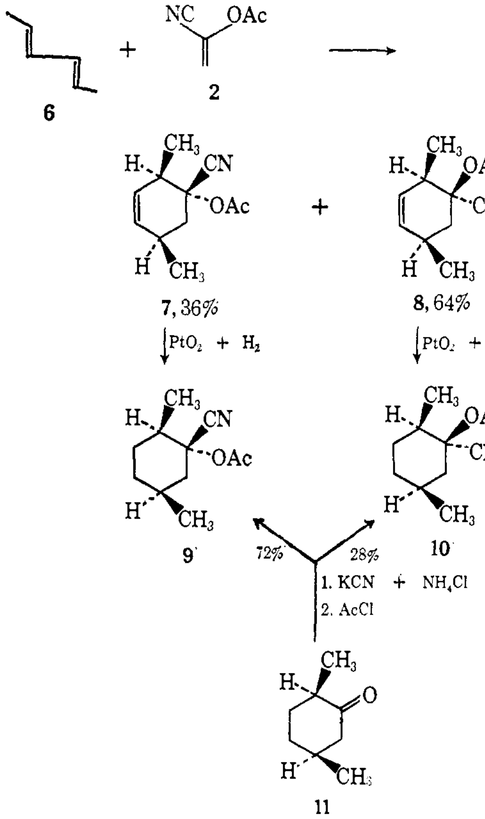
[3] A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

[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).

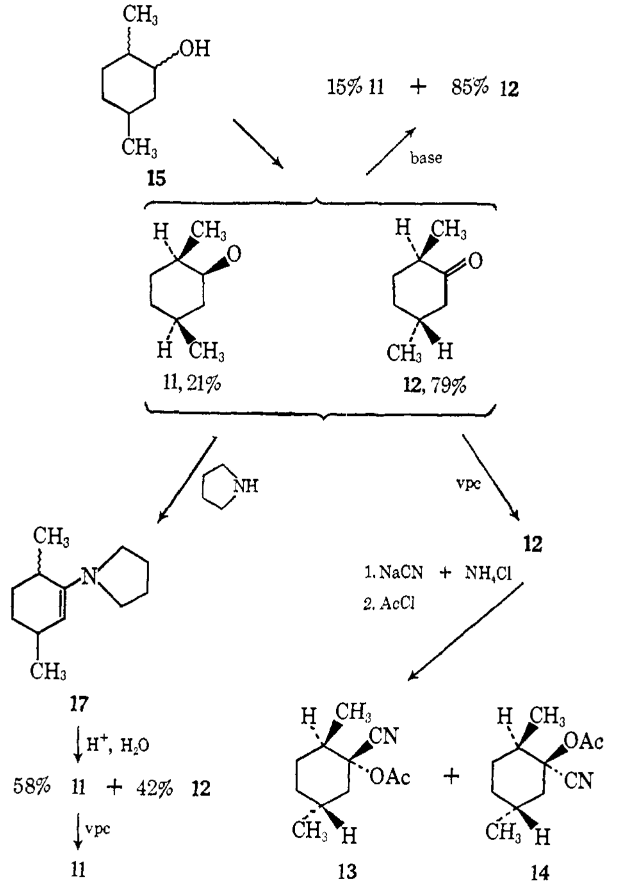
(16% 1,2 and 84% 1,4 addition), *trans,trans*-2,4-hexadiene (**6**) reacted with α-acetoxyacrylonitrile over a 48-hr period at 155° to yield a 64:36 mixture of two liquid products, accompanied by two minor fractions detected by vapor phase chromatography and amounting to only 0.3–0.4%. The two main products were shown to have the structures **7** and **8** by catalytic hydrogenation to the two cyanohydrin acetates, **9** and **10**, of *cis*-3,6-dimethylcyclohexanone (**11**) (Scheme I).

Scheme I



Chromic acid oxidation of the mixed geometrical isomers of 2,5-dimethylcyclohexanol (**15**) yielded a mixture of *cis*- and *trans*-2,5-dimethylcyclohexanones (**11** and **12**, respectively) in the ratio of 21 to 79. This mixture served as a convenient source from which to isolate the *trans*-ketone **12** by vapor chromatography. For the purpose of isolating the *cis*-ketone the pyrrolidine enamine, in which the axial conformation of the methyl group is relatively favored,[6,7] was hydrolyzed to a mixture of 58% **11** and 42% **12** (Scheme II).

Scheme II



From pure **11** and **12**, isolated by preparative vapor phase chromatography, it was possible to prepare cyanohydrin acetates without loss of the relative configurations of the methyl groups. Each ketone yielded a pair of cyanohydrin acetates. The pair **13** and **14** from the *trans*-ketone had a common feature in their nmr spectra which distinguished them from the *cis* pair, **9** and **10** (isolated by separate hydrogenation of **7** and **8**). A one-proton doublet, $J = 11$ cps, occurred in both **13** and **14**, at τ 7.24 in the major isomer (which was crystalline, mp 68.6–70.1°) and at 7.15 in the minor isomer. This signal, not distinguishable in **9** and **10**, is attributed to the tertiary axial proton adjacent to the site of the cyano and acetoxy groups and magnetically coupled to the axial proton at C_3. The corresponding proton in **9** and **10** is equatorial and not strongly coupled.

The *cis*-cyanohydrin acetates **9** and **10** proved identical *with* the two hydrogenation products of **7** and **8**. The nmr spectrum of a mixture of the two showed acetoxy methyl peaks at τ 7.91 and 7.93; these were of relative intensities 28:72 in the mixture prepared from the ketone **10**, and 64:36 in the hydrogenation product of the cycloadduct mixture.

We have no chemical evidence for the relative configurations of the cyano and acetoxy groups in the cyanohydrin acetates **9**, **10**, **13**, and **14**. However, the positions of the methyl doublets ($J = 9$ cps) in the former pair suggest that the major component is **9**, having the 2-methyl group (adjacent to CN and OAc) axial. The upfield methyl signal, presumably that of the methyl remote from the cyano and acetoxy groups, is centered at τ 9.06 in both isomers, while the other is at τ 8.81 in the major component and at τ 9.02 in the minor. Since the cyano group is more shielding than the acetoxy along its axis, but more deshielding perpendicular to its axis,[8,9] **9** would be expected on both counts to show its 2-methyl protons at lower field than **10**. This assignment is in harmony also with the slight upfield displacement of the (axial) acetoxy signal of the major cyanohydrin acetate relative to the minor.

It would follow from this assignment that in cyanohydrin formation from **11** the cyano group takes

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[6] F. Johnson and A. Whitehead, *Tetrahedron Lett.*, 3825 (1964).

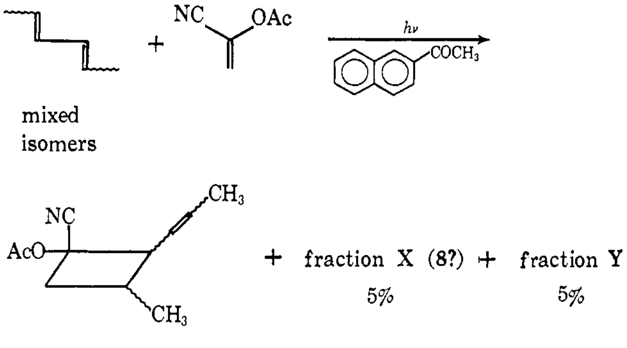
[7] H. J. Schaeffer and V. K. Jain, *J. Org. Chem.*, 29, 2595 (1964).

[8] Compare, for example, spectra numbers 140, 141, 69, 58, and 666 in the NMR Spectra Catalog, Varian Associates, 1962–1963.

[9] On the diamagnetic anisotropy of the triple bond, see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 246.

up the equatorial position by preference. Since the major configuration from cyanohydrin formation is the minor configuration in the hydrogenated cycloadduct, it follows further that in the Diels–Alder reaction of **2** and **6** the low stereoselectivity with respect to CN and OAc reflects a preferred transition state in which, if the diene and dienophile are lying in parallel planes, the CN group lies toward the conjugated system and the acetoxy group toward the methyl. Although toward cyclopentadiene the acetoxy group is more *endo* selective than the cyano, it is known that configurations of cyclopentadiene adducts are not a reliable guide to the behavior of acyclic dienes.[10]

It was clear from the vapor chromatograms of the thermal cycloadducts of α-acetoxyacrylonitrile to 2,4-hexadiene that there was no such amount of 1,2-cycloaddition as in the case of butadiene. However, there were two unidentified peaks in the chromatogram, totaling 0.3–0.4% of the whole product, which were suspected of being due to 1,2 adducts. Accordingly, a photosensitized addition of α-acetoxyacrylonitrile to the mixed isomers of 2,4-hexadiene was carried out with β-acetonaphthone as sensitizer. Since photosensitizers bring about stereoequilibration of dienes, even a fully regiospecific 1,2 adduct should contain eight stereoisomers. The vapor chromatogram showed four peaks in the approximate ratio 15:75:5:5. The composite product showed nmr signals for allylic and nonallylic methyl protons in the ratio 3.0:3.6, corresponding to chiefly 1,2-addition products. With this incomplete resolution the study of the 1,2 adducts was not carried further. It was noted, however, that two of the peaks in the vpc of the photoadduct coincided in retention time with the two unidentified peaks in the thermal product. The third component of the photosensitized product had the same retention time as the principal component of the thermal product. The inability to prepare for reference and characterize all eight 1,2 adducts meant that we could not show whether the 1,2 addition was stereospecific or not.



mixed isomers

16, 90%

Discussion

In discussing cycloaddition mechanisms the most uncomplicated point of reference is the model case of 1,2 addition of 1,1-dichloro-2,2-difluorethylene (1122) for which the following facts have been established. (1) The double bond to which the addition occurs suffers major stereochemical equilibration during the addition.[4] (2) The calculated energy requirement for biradical formation is consistent with the occurrence of such a species as a true intermediate.[4] (3) The proportion of 1,2 addition is greater than that of transoid conformation in the diene.[11–13] (4) The substitution of chlorine into the diene, of methyl at the 1 and 4 positions, and ring closure affect the reaction rate in very different ways from that of the Diels–Alder reaction.[14] (5) The effect of polar solvents on the rate is very slight, a point of similarity to the Diels–Alder reaction.[13b] (6) Photosensitized triplet cycloaddition follows the pattern of the biradical mechanism even with substrates which thermally yield stereospecific 1,4 addition.[15,16]

It is immediately clear that the stereospecific 1,4 addition of α-acetoxyacrylonitrile to 2,4-hexadiene does not occur by a branching of a biradical mechanism as we know it for 1122. Such a branching of a single mechanism would have to lead to a mixture of *cis*- and *trans*-dimethylcyclohexenes in the case of 2,4-hexadiene. The only way in which a common mechanism could operate for 1,2 and 1,4 addition with the observed stereospecificity would be by way of a "biradical" with substantial interaction between its ends, capable of leading to either 1,2 addition or 1,4 addition without loss of configuration. The way to test such a mechanism experimentally is to determine whether the 1,2 product is formed as stereospecifically as the 1,4 a test which has not yet been accomplished.

There is, however, an experimental indication that the 1,2 and 1,4 products are being formed by fundamentally different mechanisms. It was noted in the previous paper[1] that on going from butadiene to 2,4-hexadiene a typical biradical cycloaddition becomes about 20 times slower,[14] while a typical cycloaddition becomes about 20 times slower,[14] while a typical Diels–Alder reaction becomes 11–12 times faster. If α-acetoxyacrylonitrile were now yielding some 1,2 addition through a common mechanism with the Diels–Alder reaction, we might expect similar proportions of the two modes of addition in both the substituted and the unsubstituted butadienes. In fact, the proportion of 1,2 cycloaddition is about 40–50 times less with 2,4-hexadiene than with butadiene, indicating the expected differing responses of two different reaction mechanisms—one *via* a biradical and the other concerted—to substitution.

It seems at present that not only experimental but also theoretical considerations are against the common mechanism for 1,2 and 1,4 addition, even though the principle is well established that the two new bonds in a concerted cycloaddition need not form at the same rate during the passage over the transition state.

Salem,[17] from an analysis of the molecular orbital interactions in pairs of alternant hydrocarbons, has

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[10] R. Huisgen, R. Grashey, and R. Sauer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 11, p 912.

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

[12] P. D. Bartlett, A. S. Wingrove, and R. Owyang, *ibid.*, 90, 6067 (1968).

[13] (a) J. S. Swenton and P. D. Bartlett, *ibid.*, 90, 2056 (1968); (b) J. S. Swenton, unpublished results.

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

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

[16] P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Pure Appl. Chem.*, in press.

[17] L. Salem, *J. Amer. Chem. Soc.*, 90, 543, 553 (1968).

distinguished some cases in which two successive energy barriers are predicted even though the intermediate has substantial π bonding at the site where the second new bond is to be formed. One of these cases is that of symmetrical *endo* approach of two identical diene molecules to each other, the *intermediate* (between the two transition states) being σ bonded at one point and π bonded equally at two others, the whole intermediate having C_2 symmetry. This intermediate, similar to the one proposed by Woodward and Katz,[18] is considered to have attractive interaction only at those pairs of atoms which can combine to yield a 1,4 adduct, and none between the atoms C_2 of the two diene molecules. Salem's treatment excludes *concerted* 1,2 cycloaddition no less than do the rules of Hoffmann and Woodward;[19a] and since Salem's two-barrier thermal cases are thoroughly concerted,[19b] these are also excluded from leading to 1,2 cycloaddition. In terms of these theories, the only common mechanism which can lead to *both* 1,2 and 1,4 products is a completely unconcerted one, and this appears to be eliminated in the present case by the stereochemical evidence.

Experimental Section

The vpc columns referred to by letter are listed in Table I of ref 1.

α-Acetoxyacrylonitrile was prepared by the method of Nowak[20] We thank Dr. J. C. Little of the Dow Chemical Co. for an additional gift of this material.

Butadiene and α-Acetoxyacrylonitrile. The thermal addition was carried out by the method of Little.[2] The sealed tubes were heated at 165° for 24 hr.

Vpc analysis on column M at 100° showed two product peaks in the ratio 16:84 in order of increasing retention time. The products were collected from the vpc.

The infrared spectrum of the major product showed very weak absorption at 4.39 μ, strong absorption at 5.69 μ and weak absorption at 5.92–6.00 μ. The nmr spectrum showed a broad singlet at τ 4.35 (2.0 H, ethylenic protons), two broad singlets at 7.25 and 7.45 (2.0 H, allylic protons vicinal to the cyano and acetoxy groups), a broad band at 7.75 (4.0 H, methylene protons), and a sharp singlet at 7.92 (3.0 H, acetoxy methyl group).

The infrared spectrum of the minor product showed strong carbonyl absorption at 5.69 μ and weak absorption at 4.38 and 6.00 μ. The nmr spectrum showed an absorption pattern characteristic of the vinyl group from τ 3.6 to 5.1 (3.0 H). The presence of two sharp singlets at 7.92 and 7.95 indicates that both isomers of 1-acetoxy-1-cyano-2-vinylcyclobutane (**4** and **5**) are present.

Photosensitized Addition of α-Acetoxyacrylonitrile to 2,4-Hexadiene. In 20 ml of ether was dissolved 300 mg (3.7 mmol) of 2,4-hexadienes, 500 mg (4.5 mmol) of α-acetoxyacrylonitrile, and 440 mg of β-acetonaphthone. This solution was put into four Pyrex test tubes which were then degassed, sealed, and irradiated for 3 days with a 450-W Hanovia mercury arc. At the end of that time the tubes were opened and the solvent was removed on the rotary evaporator. Vpc analysis on columns M, O, and P showed that at least four products were formed in the approximate ratio 15:75:5:5 in order of increasing retention time on column P. The third had the same retention time as the major adduct of *trans,trans*-2,4-hexadiene and α-acetoxyacrylonitrile. The adducts were collected as a mixture from column P. An nmr spectrum of the mixture in CCl_4 showed peaks of approximately equal area for methyl groups on saturated (3.6 H) and methyl groups on unsaturated carbon (3.0 H), indicating that it was made up of predominantly 1,2 cycloadducts. The resonance of methyl protons on saturated carbon appeared as a broad band made up of at least four peaks centered at τ 8.15. The methyl groups on unsaturated carbon appeared as a broad doublet at 8.30.

Thermal Addition of *trans,trans*-2,4-Hexadiene (6) and α-Acetoxyacrylonitrile (2). Into a Pyrex tube was put a mixture of 3.90 g (35 mmol) of α-acetoxyacrylonitrile and 1.4 g (17 mmol) of *trans,trans*-2,4-hexadiene in 15 ml of benzene. The tube was degassed four times, sealed, and heated to 155° for 48 hr. Vapor phase chromatography of the crude product mixture on column M at 125° showed the presence of two main peaks in the ratio 64:36 in order of increasing retention time and two minor peaks, having a shorter retention time, amounting to 0.3 and 0.4% of the total product. The solvent was removed on a rotary evaporator, and the dark residue was purified by a bulb-to-bulb distillation at 0.008 mm pressure. Vapor phase chromatography on columns M, O, and P showed the retention times of the minor products to be the same as those of two of the photoadducts of α-acetoxyacrylonitrile and 2,4-hexadiene. The two main products were separated from each other and from starting material on column M at 125° using 20-μl injections.

The infrared spectrum of the major product (assigned configuration **8**) showed very weak absorption at 4.52 μ, strong absorption at 5.70 μ and weak absorption at 6.04 μ. The nmr spectrum showed broad vinyl resonance at τ 4.52 (2.0 H), a sharp singlet at 7.96 surrounded by a multiplet extending from 7.2 to 8.4 (7.3 H), and a doublet for each methyl group at 8.92 and 8.76 (5.8 H).

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.36; H, 7.82; N, 7.25. Found: C, 68.15; H, 7.70; N, 7.07.

The infrared spectrum of the minor product (assigned configuration **7**) showed strong absorption at 5.69 μ. The nmr spectrum showed ethylenic absorption at τ 4.44 (2.0 H), a sharp singlet at 7.92 surrounded by a multiplet from 6.7 to 8.6 (7.3 H), and a triplet centered at 8.97 (6.0 H) due to two overlapping doublets of the methyl groups.

When the reaction was carried out in the same way with 0.207 g (1.86 mmol) of α-acetoxyacrylonitrile and 0.203 g (2.48 mmol) of *trans,trans*-2,4-hexadiene in the absence of solvent the same peaks were seen in the vpc; their relative areas were the same as those found when the reaction was carried out in benzene.

***trans*-2,5-Dimethylcyclohexanone (12).** To a stirred mixture of 120 g (0.4 mol) of sodium dichromate and 100 g (54.3 ml, 0.97 mol) of concentrated sulfuric acid was added 74.2 g (0.58 mol) of 2,5-dimethylcyclohexanol (**13**) in three portions. After 3 min the temperature rose to 70°. The reaction mixture was cooled in ice until the temperature fell to 55°. When the ice was removed the temperature continued to fall slowly. When it reached room temperature an equal volume of ether was added. The ether layer was separated and washed three times with 200 ml of 5% sodium hydroxide. After drying over anhydrous sodium sulfate the ether was removed on a rotary evaporator and the residue was distilled. A colorless liquid, bp 52–53° (6 mm), was obtained, yield 56 g (78%). The infrared spectrum showed strong absorption at 5.83 μ. The nmr spectrum in carbon tetrachloride showed a complex multiplet from τ 7.4 to 8.8 (8 H) and a pair of doublets for the methyl groups from 8.9 to 9.2 (6 H). Vpc analysis on column K at 110° showed two isomers to be present in the ratio 79:21 in order of increasing retention time.

The major isomer was collected from column L at 110°. The infrared spectrum (neat) showed carbonyl absorption at 5.83 μ. The nmr spectrum in carbon tetrachloride showed a complex multiplet from τ 7.4 to 8.8 (8 H) and an asymmetric triplet due to the overlap of two methyl doublets centered at τ 9.03 (6 H), $n^{20}\text{D}$ 1.4436.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.15; H, 11.04.

N-(2,5-Dimethylcyclohex-6-enyl)pyrrolidine (17). To a solution of 20.4 g (0.162 mol) of a mixture of the two isomers of 2,5-dimethylcyclohexanone in 120 ml of benzene was added 26.4 g (0.372 mol) of redistilled pyrrolidine. The solution was heated under reflux and the water formed was collected in a Dean–Stark trap. After 57 hr no more water was formed so the reaction was stopped. The solvent was removed at reduced pressure and the residue distilled, bp 62.5° (1.6 mm).

***cis*-2,5-Dimethylcyclohexanone (11).** To a solution of 21 g (0.12 mol) of enamine prepared above in 400 ml of diglyme was added 15 ml of glacial acetic acid and 15 ml of water. This mixture was stirred at room temperature for 2 hr, and then extracted twice with pentane. The combined pentane layers were washed several times with water and then with bicarbonate solution. After drying over anhydrous sodium sulfate, the pentane was removed on a rotary evaporator. A pale yellow residue (7.02 g, 47%) remained. Vpc analysis on column M at 110° showed that the ratio of product ketones was 42:58 in order of increasing retention time. The isomer having the longer retention time was collected from column

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[18] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[19] (a) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965); (b) *i.e.*, bonding is established simultaneously at more than one site.

[20] R. M. Nowak, *J. Org. Chem.*, **28**, 1182 (1963).

L at 120° (0.10-ml injections). A few per cent of the other isomer was still present as an impurity so a second pass through the Autoprep was made. Now less than 1% of the other isomer was present.

The infrared spectrum (neat) showed strong carbonyl absorption at 5.85 μ. The nmr spectrum showed a complex multiplet from τ 7.4 to 8.8 (8 H) and two methyl doublets between 8.9 and 9.2 (6 H), $n^{20}\text{D}$ 1.4483.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.01; H, 11.36.

Into a test tube was put a few drops of this ketone together with a solution of sodium methoxide in methanol. The tube was sealed and heated in a steam bath for 2 hr. The tube was opened and pentane and water were added. The pentane layer was analyzed by vpc on column K at 110°. This showed that 85% of the starting ketone had been converted to the other isomer.

***trans*-2,5-Dimethylcyclohexanone Cyanohydrin.** A solution of 460 mg (3.65 mmol) of *trans*-2,5-dimethylcyclohexanone (**12**) in 3 ml of petroleum ether (bp 30–60°) was shaken vigorously for 25 min with a solution of 648 mg (9.98 mmol) of potassium cyanide and 566 mg (10.6 mmol) of ammonium chloride in 5 ml of water. The aqueous phase was separated and extracted once with petroleum ether. The combined organic layers were dried over anhydrous sodium sulfate, filtered and the solvent was removed on a rotary evaporator, yield 510 mg (91%) of a yellow oil.

The infrared spectrum showed strong absorption at 2.98 μ, and weak absorption at 4.52 μ. The carbonyl absorption at 5.83 μ had disappeared but a weak band at 5.89 μ was present. Vpc analysis on column J at 110° showed only one product peak.

1-Acetoxy-1-cyano-*trans*-2,5-dimethylcyclohexanes (13 and 14). A mixture of 400 mg (2.61 mmol) of *trans*-2,5-dimethylcyclohexanone cyanohydrin and 1.1 g (14.1 mmol) of acetyl chloride was allowed to stand 20 hr. After this time thin layer chromatography showed much unreacted cyanohydrin. A large excess of acetyl chloride was added and the mixture was allowed to stand 1 week. The excess acetyl chloride was removed on a rotary evaporator. The residue was analyzed by vpc on column M at 125°; two peaks in the ratio 80:20 in order of increasing retention time were seen. The oil was allowed to stand at 0° for several days and then was removed to room temperature. Beautiful white prisms immediately formed in the dark oil. Pentane was added and 140 mg of crystals were filtered off. A vpc trace of a solution of the crystals showed only the peak with the shorter retention time; vpc analysis of the mother liquor showed it to be enriched in the other isomer. The crystals were repeatedly recrystallized from hexane but the melting point range (68.6–70.1°) could not be narrowed, so final purification was achieved by collection from column M at 125°.

The infrared spectrum showed carbonyl absorption at 5.68 μ. The nmr spectrum showed a doublet at τ 7.24 (1.0 H, J = 11 cps) due to the tertiary proton vicinal to the cyano and acetoxy groups, a sharp singlet at 7.93 (2.9 H) for the acetoxy methyl group, a multiplet from 8.1 to 8.8 (6.1 H), and two doublets for the two methyl groups between 8.85 and 9.12 (6.0 H). Configuration **14** is assigned to this isomer.

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.77; N, 7.18. Found: C, 67.69; H, 8.78; N, 7.23.

The cyanohydrin acetates that did not crystallize were chromatographed on a short grade III alumina column and rapidly eluted with 20:80 ether–pentane. The isomer having the longer retention time (assigned configuration **13**) was collected from column M at 125°.

The infrared spectrum showed carbonyl absorption at 5.68 μ. The nmr spectrum showed a doublet at τ 7.15 (1.0 H, J = 11 cps) due to the tertiary proton vicinal to the cyano and acetoxy groups, a sharp singlet at 7.92 (3.0 H) for the acetoxy methyl, and a multiplet from 8.3 to 9.2 (13.3 H) with two doublets for the methyls at 8.87 and 9.09.

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.77; N, 7.18. Found: C, 67.59; H, 8.80; N, 7.02.

***cis*-2,5-Dimethylcyclohexanone Cyanohydrin.** A solution of 459 mg (3.65 mmol) of *cis*-2,5-dimethylcyclohexanone (**11**) in a few milliliters of petroleum ether was shaken for 0.5 hr with 648 mg (9.98 mmol) of potassium cyanide and 566 mg (10.6 mmol) of ammonium chloride in 5 ml of water. The layers were separated and the aqueous phase was extracted once with petroleum ether. The combined organic layers were dried over anhydrous sodium sulfate and filtered, and the solvent was removed on a rotary evaporator, yield 380 mg (68%). Vpc analysis on column J showed only one peak, which had a different retention time from that of the *trans*-2,5-dimethylcyanohydrins under the same conditions.

The infrared spectrum (neat) showed strong absorption at 2.99 μ and weak absorption at 4.51 μ. The carbonyl at 5.85 μ had disappeared but a weak band at 5.89 μ was present.

1-Acetoxy-1-cyano-*cis*-2,5-dimethylcyclohexanes (9 and 10). A mixture of 300 mg of *cis*-2,5-dimethylcyclohexanone cyanohydrin and a large excess of acetyl chloride was allowed to stand for 4 days. The acetyl chloride was removed on a rotary evaporator. Vpc analysis of the product on column M at 125° showed only one peak. The oil was rapidly eluted from a short grade III alumina column with 20:80 ether–pentane and was purified by collection from column M.

The infrared spectrum showed carbonyl absorption at 5.69 μ. The nmr spectrum showed two sharp acetoxy methyl peaks at τ 7.91 and 7.93 in the ratio 28:72 indicating that the material was a mixture of the two isomers of 1-acetoxy-1-cyano-*cis*-2,5-dimethylcyclohexane (**9** and **10**).

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.77; N, 7.18. Found: C, 67.49; H, 8.91; N, 7.12.

Hydrogenation of the Major Adduct of α-Acetoxyacrylonitrile and *trans,trans*-2,4-Hexadiene. A mixture of 169 mg (0.875 mmol) of the major adduct of α-acetoxyacrylonitrile and *trans,trans*-2,4-hexadiene (assigned configuration **8**) and 15 mg of platinum oxide in 5 ml of ethyl acetate was hydrogenated at 760 mm pressure and 27°. After the theoretical amount of hydrogen (21.8 ml) had been taken up, the reaction was stopped. Both vpc and nmr showed the presence of starting material. The mixture was filtered and the solvent removed at reduced pressure. The residue was chromatographed on a short grade III alumina column and rapidly eluted with 20:80 ether–pentane. The recovered material (98 mg) was returned to the hydrogenation flask with fresh catalyst. When 3.6 ml of additional hydrogen had been taken up the reaction was again stopped. Now vpc and nmr showed that reaction was complete. The product, (assigned **10**), was purified by recovery from column M at 120°.

The infrared spectrum had a weak absorption band at 4.51 μ and a strong band at 5.71 μ. The nmr spectrum showed absorption from τ 6.4 to 9.2 with a sharp singlet due to the acetoxy methyl at 7.91 (3.0 H) and two doublets due to the methyls at 8.80 (3.0 H) and 9.04 (3.0 H).

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.77; N, 7.18. Found: C, 67.58; H, 8.80; N, 7.12.

Hydrogenation of the Minor 1,4 Adduct of α-Acetoxyacrylonitrile and *trans,trans*-2,4-Hexadiene. A mixture of 135 mg (0.70 mmol) of the minor adduct of α-acetoxyacrylonitrile and *trans,trans*-2,4-hexadiene (assigned configuration **7**) and 15 mg of platinum oxide in 5 ml of ethyl acetate was hydrogenated at 769 mm pressure and 24°. After the theoretical amount of hydrogen (17.3 ml) had been taken up the reaction was stopped. The catalyst was filtered off and the solvent removed on a rotary evaporator. An nmr spectrum of the dark residue showed only about 50% hydrogenation. The product was chromatographed on a short grade III alumina column and was rapidly eluted with 20:80 ether–pentane. With fresh catalyst, 16 ml of additional hydrogen was taken up. An nmr spectrum of this product showed only 80% hydrogenation. A second chromatography resulted in material that took up 10 ml of hydrogen in the presence of fresh catalyst. The product from this hydrogenation still showed a few per cent unreacted material in an nmr spectrum. This was again chromatographed and rehydrogenated. This time 5.5 ml of hydrogen was taken up. An nmr spectrum showed that hydrogenation was complete. The product (assigned configuration **9**) was purified by collection from column M at 125°.

The infrared spectrum showed strong carbonyl absorption at 5.69 μ. The nmr spectrum showed a broad peak at τ 7.35 (1.0 H), a multiplet from 7.7 to 8.9 (10.2 H), with a sharp singlet for the acetoxy methyl at 7.93, and two overlapping doublets due to the methyls centered at 9.04 (6.0 H).

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.77; N, 7.18. Found: C, 67.75; H, 8.90; N, 7.23.

A mixture of 28% hydrogenated major and 72% hydrogenated minor 1,4 adducts of *trans,trans*-2,4-hexadiene and α-acetoxyacrylonitrile was made up. The nmr and ir spectra of this mixture were superimposable on the spectra of the mixed 1-acetoxy-1-cyano-*cis*-2,5-dimethylcyclohexanes (**9** and **10**).

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Stable Carbonium Ions. LXVIII.[1] Protonation and Ionization of Cyclopropyl Halides. Measurement of Rotational Barriers in Substituted Allyl Cations

George A. Olah and J. Martin Bollinger

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received April 6, 1968*

Abstract: Cyclopropyl halides were found to give, in fluorosulfuric acid–antimony pentafluoride–sulfur dioxide solution, either, by protonation, the corresponding halonium ions or, by ionization, substituted allylic cations, two of which exhibited temperature-dependent nmr spectra. Activation parameters were measured for these ions for rotation about the partial double bond.

We have previously reported the behavior of cyclopropanes in strong acid solutions.[2] We felt it of interest to continue these studies by examining the behavior of cyclopropyl halides in these systems as a possible pathway to both allylic cations and halonium ions.

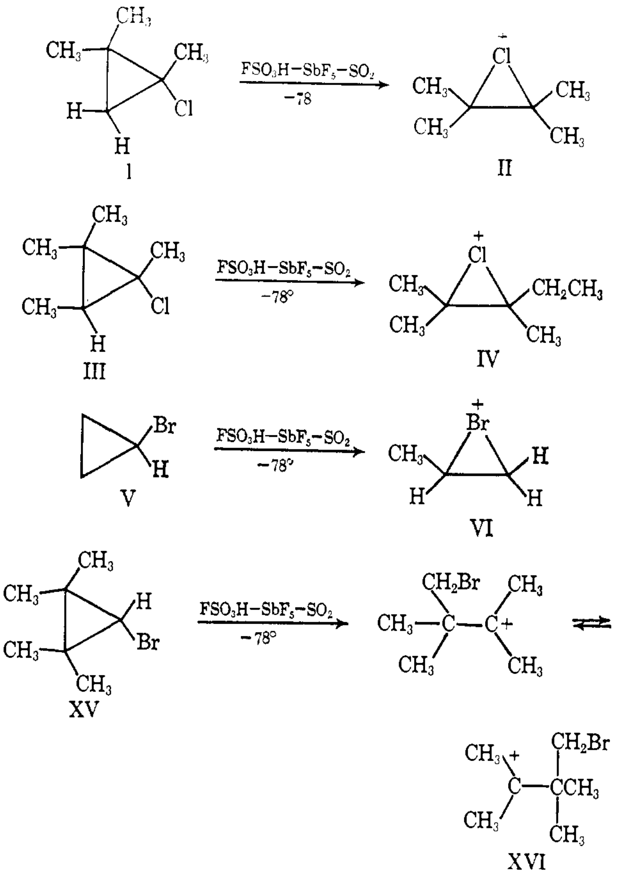
There are a large number of reports of the protolytic cleavage of cyclopropane bonds.[3] The cleavage of cyclopropanols is usually a clean reaction since the hydroxyl stabilizes positive charges.[4] Cyclopropyl halides ought to show some of the characteristics of the cyclopropanols, since halogen stabilizes positive charges in these systems.

DePuy and coworkers[5] isolated allylic products from solvolysis of cyclopropyl tosylates. Schleyer[6] has also recently reported concerted ring opening during the solvolysis of cyclopropyl tosylates. Recent reports,[7-9] on the other hand, indicate that ring opening may not always be concerted with ionization as demonstrated by the isolation of species derived from cyclopropyl cations.

We hoped to learn about the timing of the ring opening in the solvent fluorosulfuric acid–antimony pentafluoride–sulfur dioxide. According to the observations of Peterson,[10] anchimeric assistance to ionization becomes more pronounced as the nucleophilicity of the solvent decreases. This predicts that concerted ionization should take place in this extremely nonnucleophilic solvent. Unfortunately, we were unable to come to any conclusion as to whether or not the cyclopropyl halide ionizations were concerted.

Results and Discussion

Addition of the cyclopropyl halides, I, III, and V, to a solution of fluorosulfuric acid–antimony pentafluoride–sulfur dioxide at −78° resulted in protolytic cleavage of a carbon–carbon bond with formation of the halonium ions, II, IV, and VI, respectively (ions II



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