o-Halophenols (1-X) were completely C-protonated in superacid II, while their methyl ethers (2-X) were only partially C-protonated. These data show that a hydroxy group is better in stabilizing arenium ions than an alkoxy group. Similar results have been observed in the case of other hydroxy- and alkoxybenzenium ions.[3a]

The present study of the protonation of halophenols and haloanisoles in varying superacid media also gives useful information relating to the electrophilic aromatic substitution of these compounds. The site of electrophilic attack in substitution reactions in general should parallel those observed in protonation of halophenols and haloanisoles. Kinetic *vs.* thermodynamic control can be responsible for O- or C-substitution. The former, however, is generally reversible through intermolecular displacement (exchange) reactions.[13]

Experimental Section

Materials.—All the halophenols and haloanisoles were commercially available in high purity and were used without further purification. Antimony pentafluoride (Allied Chemical Co.) was refluxed overnight while passing a stream of dry nitrogen through it. The material was then twice distilled (bp 150°). Fluorosulfuric acid (Allied Chemical Co.) was distilled (bp 160–164°) before use. Hydrogen fluoride was obtained from Baker Chemical Co. Sulfuryl chloride fluoride was obtained from Allied Chemical Co.

Preparation of Ions.—Superacid solutions were prepared by mixing antimony pentafluoride and HF or FSO_3H at −78° in Teflon bottles in the concentrations indicated. The resulting solutions were then diluted with sulfuryl chloride fluoride. Ions for nmr studies were prepared by adding 30–40 mg of the aromatic compound (dissolved in SO_2ClF) to 1 ml of the above superacid solution (at −78°). Upon warming, while stirring or shaking, a clear solution was obtained. After nmr study, solutions were quenched (as previously described)[14] and starting halophenols and haloanisoles were recovered (as indicated by nmr, ir, and glc studies) showing that no side reactions took place, other than described.

Nmr Spectra.—A Varian Associates Model A-56/60A nmr spectrometer equipped with a variable-temperature probe was used for ^1H and ^{19}F nmr spectra. Both ^1H and ^{19}F coupling constants are believed accurate to ±0.1 Hz. Unless otherwise indicated, proton chemical shifts (δ) are from an external capillary of TMS. Fluorine chemical shifts (ϕ) are from an external capillary of CCl_3F.

Registry No.—1-F, 367-12-4; 1-Cl, 95-57-8; 1-Br, 95-56-7; 1-I, 533-58-4; 2-F, 321-28-8; 2-Cl, 766-51-8; 2-Br, 578-57-4; 2-I, 529-28-2; 3-F, 372-20-3; 3-Cl, 108-43-0; 3-Br, 591-20-8; 3-I, 626-02-8; 4-F, 456-49-5; 4-Cl, 2845-89-8; 4-Br, 2398-37-0; 4-I, 766-85-8; 5-F, 371-41-5; 5-Cl, 106-48-9; 5-Br, 106-41-2; 5-I, 540-38-5; 6-F, 459-60-9; 6-Cl, 623-12-1; 6-Br, 104-92-7; 6-I, 696-62-8.

Acknowledgment.—Support of our work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health is gratefully acknowledged.

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The Copper-Catalyzed Additions of Diazo Esters to 2,4-Hexadienes

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Decomposition of ethyl diazoacetate with copper powder in the presence of *trans,trans-*, *cis,trans-*, and *cis,cis-*2,4-hexadiene afforded the eight isomeric ethyl 2-methyl-3-propenylcyclopropanecarboxylates which were separated by preparative glpc. The structures of the isomeric products were established on the basis of their spectral properties and from correlations based on thermolysis and ozonolysis results. The additions took place with a general preference for the orientation of the carboethoxy group trans to the propenyl group. The stereoselectivity of the reaction is discussed.

The addition reactions of carbenes and carbenoids have proven to be of great synthetic utility;[2,3] in particular the copper-catalyzed addition of diazoacetic ester to olefins has allowed the synthesis of numerous cyclopropanecarboxylic acids.[4] In conjunction with a study of their thermochemistry,[5] we required a series of "maximally labeled"[6] vinylcyclopropanes whose stereochemistry was known with certainty so that firm conclusions could be made on the mechanism and stereochemistry of their thermal rearrangements. With these objectives in mind we embarked on a study of the addition of alkyl diazo esters to the isomeric 2,4-hexadienes.

Results

The general procedure for the addition reactions involved adding a mixture of diazo ester in the appropriate diene to a slurry of copper powder (activated by preliminary washing with acetic acid) in the diene. Products were purified by vacuum distillation and the isomers were separated by preparative glpc. Isolated yields in the preparative runs ranged from 51 to 59%.

Product distributions (Table I) were determined by glpc analysis of the crude reaction mixture and were invariant throughout the course of the reaction, indicating that there was no product interconversion. These data are only slightly different from those ob-

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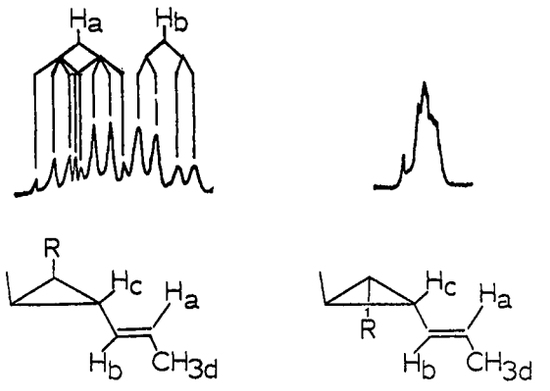
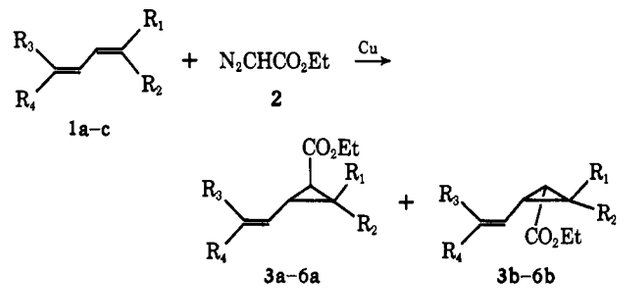


Figure 1.—The vinyl regions of the nmr spectra of **3a** and **3b** (R = CO_2Et).



1a, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
b, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
c, $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$

3a, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
4a, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
5a, $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
6a, $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$

3b, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
4b, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
5b, $R_2 = R_4 = CH_3$; $R_1 = R_3 = H$
6b, $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$

TABLE I

Reactants	Product ratios, %	
1a + **2**	**3a** (57)	**3b** (43)
1b + **2**	**4a** (17)	**4b** (10)
	5a (41)	**5b** (31)
1c + **2**	**6a** (68)	**6b** (32)

tained for the product after distillation. We attribute these differences to fractionation during distillation rather than product interconversion. A check of the starting dienes after reaction indicted that isomerization of the dienes amounted to less than 2%.

Stereochemistry.—The isomeric vinylcyclopropanes **3–6** are listed in Table II along with relevant infrared and nmr data.

TABLE II

CHEMICAL SHIFTS (τ) OF PROTONS H_a AND H_b (CCl_4, INTERNAL TMS)

Isomer	Proton absorbance, τ H_a	H_b	H_b shift, τ	$\nu_{max}^{CCl_4}$
3a	4.50	5.05		960
3b	4.53	4.53	0.52	969
4a	4.55	5.17		
4b	4.59	4.59	0.58	
5a	4.34	4.86		960
5b	4.30	4.30	0.56	962
6a	4.40	4.92		
6b	4.40	4.40	0.52	

The products may be initially broken down into three groups on the basis of their method of synthesis; *i.e.*, only **3a** and **3b** could result from addition to *trans,trans*-hexadiene, whereas **4a**, **4b**, **5a**, and **5b** could result from addition to *cis,trans*-2,4-hexadiene and **6a** and **6b** from *cis-cis*-2,4-hexadiene.

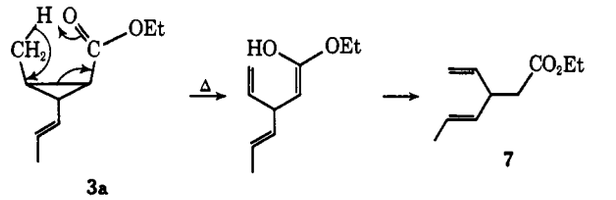
Examination of the infrared spectra allows a further simplification, since those isomers having a trans double bond (960 cm^{-1}) may be identified.[7] The isomers thus can be considered as four pairs, with one member of each pair having the carboethoxy group cis to the propenyl group (as in **3b–6b**) and the other having the carboethoxy and propenyl groups trans (as in **3a–6a**).

Examination of the vinyl region of the nmr spectra for these compounds reveals an important stereochemical correlation. For the latter group (**3a–6a**) the vinyl regions of the spectra are all similar to that of **3a** (Figure 1) showing H_a and H_b separated by *ca.* τ 0.5. This area of the spectrum is analyzable on a first-order basis and shows H_a as a doublet of quartets (J_{ab} = 15.0 Hz, J_{ad} = 6.0 Hz) at τ 4.50 and H_b as a doublet of doublets (J_{ab} = 15.0 Hz, J_{bc} = 7.5 Hz) at τ 5.05.

In contrast the vinyl regions of the nmr spectra of the former group (**3b–6b**) are similar to that shown for **3b** (Figure 1) showing H_a and H_b as a broad complex resonance centered at τ 4.53. We[5] ascribe this difference to specific deshielding of H_b by the cis carboethoxy group, a phenomenon which has been well established for the cis β hydrogens of crotonates and acyclic dienoates.[8,9] Examination of data in the literature reveals that this correlation holds for *cis*- and *trans*-(2-benzoyl)- and -(2-acetyl)vinylcyclopropanes[10] and for *cis*- and *trans*-(2-acetyl-1-methyl)vinylcyclopropane.[11] In all cases a vinyl proton (corresponding to H_b) is deshielded in the cis compound with respect to the trans compound.

Irrespective of this analysis, and especially in view of subsequent and apparently anomalous nmr results obtained on **11** (*vide infra*), it was felt that the stereochemistry of at least one pair of cis–trans isomers should be conclusively established.

Additional stereochemical evidence was furnished by thermolysis (285°, sealed tube) of **3a** and **3b**. Under these conditions[5] **3a** afforded ethyl 3-vinyl-*trans*-4-hexenoate (**7**) as a major product, whereas **3b** gave little **7**. Since this homocyclic 1,5 hydrogen



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(9) L. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 88.
(10) Y. Bahucel, F. Collonges, A. Menet, F. Pautet, A. Poncet, and G. Descotes, *Bull. Soc. Chim. Fr.*, 2209 (1971).
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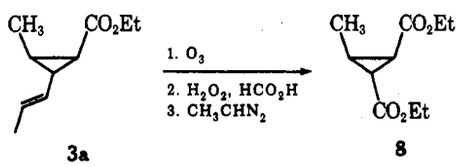
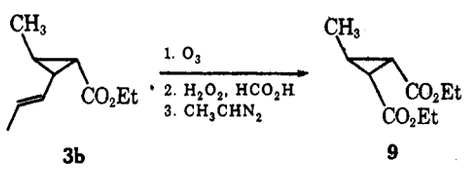
migration requires cis alkyl and carboethoxy groups,[12] the stereochemistry of **3a** should be as indicated.

Conclusive evidence on the stereochemistry of **3a** and **3b** follows from ozonolysis data. Ozonolysis of **3a** and **3b** afforded, after oxidative work-up and esterification with diazoethane, the diesters **8** and **9**, respectively. The structure of **8** and **9** are apparent



3a **8**

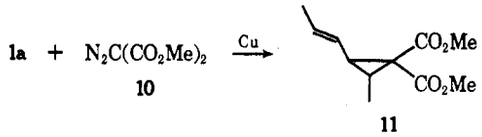


3b **9**

from their nmr spectra. Whereas the methylene groups of the ethyl esters in **9**, which has a plane of symmetry, appear as a single sharp quartet, those of **8**, which has no symmetry plane, appear as a doublet of quartets. These data conclusively establish the stereochemistry of **3a** and **3b** and, by analogy, the stereochemsitry of all of the other isomers.

That nmr analysis should not be trusted as the sole criterion for stereochemical assignments in these systems was graphically demonstrated by the results obtained from addition of methyl diazomalonate to *trans,trans*-2,4-hexadiene.

The vinyl region of the nmr spectrum of diester **11** showed H_a as a doublet of quartets at τ 4.28 (J_{ab} =



10 **11**

15.0, J_{ad} = 6.0 Hz) and H_b as a doublet of doublets at τ 4.97 (J_{ab} = 15.0, J_{bc} = 8.0 Hz). This region of the spectrum is remarkably similar to the vinyl region of **3a**, *i.e.*, the necessarily cis carboethoxy group in **11** does not deshield H_b. We believe that this is due to the preferred conformations of the cis carboethoxy groups in **3a** and **3b** with respect to **11**. For effective deshielding of the transannular vinyl proton the anisotropy of the carbonyl group is such that there must be a significant population of the s-cis conformer (Figure 2).[13] In the case of **11** the presence of the bulky geminal carboethoxy group would tend to destabilize the s-cis conformer, resulting in the virtual disappearance of the long-range deshielding as observed. A similar effect has been shown to be operative in the β-cyclopropyl acrylic esters where a distinct bathochromic shift in the ultraviolet spectrum is observed when a geminal cyclopropyl substituent is added.[13] This has been explained as being due to destabilization of the "maximum overlap" conformation in that system, a

(12) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); M. J. Jorgenson and A. F. Thacher, *Tetrahedron Lett.*, 4651 (1969); D. E. McGreer, N. W. K. Chiu, and R. McDaniel, *Proc. Chem. Soc.*, 415 (1964); R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967); W. Ando, *Tetrahedron Lett.*, 929 (1969).

(13) M. J. Jorgenson and T. Leung, *J. Amer. Chem. Soc.*, **90**, 3769 (1968).

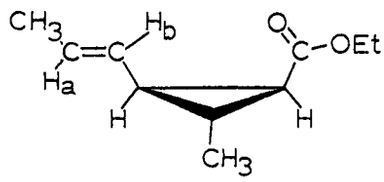


Figure 2.—The required conformation for maximum deshielding of H_a by the transannular carboxyl group.

conformation analogous to that depicted (Figure 2) for **3b**.

Discussion

There are several points that can be made concerning the product ratios in Table I. It is obvious that, in cases where there is a clear distinction, the least hindered product is always formed preferentially.[3,14] This steric discrimination is consistent with addition *via* attack of a bulky copper complex.[14,15] Thus, in the case of additions to a cis double bond to form **5a**, **6a**, **5b**, and **6b**, the anti addition product clearly predominates.

The analysis of the **3a**:**3b** and **4a**:**4b** product ratios is not so clear-cut, however, since it requires an evaluation of the steric requirements of methyl *vs.* propenyl groups. Although conformational free energies are not a direct measure of group size, they do reflect the relative steric requirements of the minimum energy orientations of various groups.[16,17] If the transition state for copper diazoacetate addition resembles one that would result from the approach of the copper complex to a planar s-trans diene, then the conformational free energies are probably reasonable values for the relative steric demands of propenyl and methyl groups in the transition state. The incoming reagent will probably experience less interaction with the planar propenyl group than with the approximately spherical methyl group.[18]

Examination of the **3a**:**3b**, and **4a**:**4b** ratios reveals that in each case the major product has cis carboethoxy and methyl groups, *i.e.*, the major product is the one that would result from the most hindered transition state, and, although the differences are small, they are not insignificant. Although the formation of hindered syn adducts is common in carbene additions, it is unprecedented in diazo ester additions, where the anti product is usually favored.[14]

A possible answer lies in a combination of opposing steric and electrostatic effects. As has been pointed out by Moss,[3] the permanent dipole in the carboethoxy group should interact in a destabilizing manner with any positive charge residing on the olefinic substituents. Since charge in the transition state (Figure 3) will preferentially delocalize into the propenyl rather than the methyl group, this electrostatic effect will

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(17) E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, **4**, 782 (1965); J. A. Hirsch in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience, New York, N. Y., 1967, p 199.

(18) The $-\Delta G°$ value for methyl is 1.70 kcal/mol.[17] The values for cis and trans propenyl groups are unknown, but they should be the same as that for the vinyl group ($-\Delta G°$ = 1.35 kcal/mol[17]), since substituents two atoms removed from the ring do not effect these values.[16]

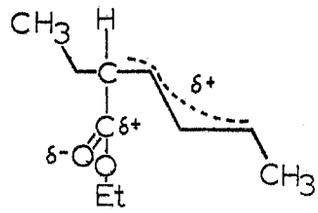

Figure 3.—A model of a possible transition state for carbenoid addition to **1a** showing electrostatic interactions. For simplicity copper has not been included.

tend to favor the cis carboethoxy–methyl arrangement. Opposing this is the slight steric preference for cis propenyl and carboethoxy groups. The result is a small but significant preference for **3a** and **4a** over **3b** and **4b**.

Our results also indicate a clear preference for addition to a cis double bond over a trans double bond. This point is graphically illustrated by comparison of the yields obtained from addition to *cis,trans*-2,4-hexadiene (**1b**). It is obvious that the products of insertion into the cis double bond (**5a** and **5b**) are the major ones. In fact **5b**, by far the most hindered product, is formed in better yield than the total yield of products from insertion into the trans double bond (*i.e.*, **4a** and **4b**). This enhanced reactivity undoubtedly reflects the higher ground-state energy of the cis alkenyl moiety.

Experimental Section

The infrared spectra were obtained on a Perkin-Elmer 337 grating infrared spectrophotometer in a 0.1-mm NaCl cell (10% in carbon tetrachloride). The nmr spectra were obtained on a Varian A-60D spectrophotometer in carbon tetrachloride solutions with tetramethylsilane as internal standard. The preparative glpc work was done on a Varian Aerograph series 90 using a thermal conductivity detector; the analytical glpc work was done on a Varian Aerograph series 1200 with flame ionization. A list of glpc columns employed follows: column A, 20% Carbowax 20M on 80/100 Chromosorb P (AW-DMCS), 15 ft × 0.25 in.; B, 15% IGEPAL (CO-880) on 80/100 Chromosorb W (AW-DMCS), 9 ft × 0.25 in.; C, 6 ft × 0.125 in. 5% IGEPAL-CO880 then 4 ft × 0.125 in. 5% XE-60 on 80/100 Chromosorb P (AW-DMCS); D, 11% Carbowax 20M and 4% DEGA on 60/80 Chromosorb W (AW-DMCS), 6 ft × 0.25 in.; E, 15% UCON 50 HB 270X on 80/100 Chromosorb W (AW-DMCS), 15 ft × 0.25 in.; F, 15% UCON 50 HB 270X on 60/80 Chromosorb W (AW-DMCS), 6 ft × 0.125 in.; G, 15% UCON 50 HB 270X on 60/80 Chromosorb W (AW-DMCS), 6 ft × 0.25 in.; H, 10% SE-30 on 100/120 Chromosorb P (AW-DMCS), 10 ft × 0.125 in.; I, 15% Carbowax 20M on 60/80 Chromosorb W (AW-DMCS), 9 ft × 0.125 in.; J, 15% silicone D. C. 550 on 60/80 Chromosorb W (AW-DMCS), 6 ft × 0.25 in.; K, 15% Carbowax 20M on 60/80 Chromosorb W (AW-DMCS), 6 ft × 0.125 in.; L, 15% Carbowax 20M on 60/80 Chromosorb W (AW-DMCS), 6 ft × 0.25 in.

Preparation of the Isomeric Ethyl 2-Methyl-3-propenylcyclopropane-1-carboxylates. A. Addition to *trans,trans*-2,4-Hexadiene (1a).—The insertion reaction was accomplished by a modification of the procedure of Musso and Biethan.[19] Into a 50-ml three-necked round-bottomed flask, fitted with a reflux condenser and addition funnel, were placed 4.5 g (0.055 mol) of **1a** and 0.2 g of finely divided activated (*via* glacial acetic acid) copper powder. The flask was flushed with nitrogen, and while the solution was stirred vigorously at reflux a mixture of 3.2 g (0.028 mol) of ethyl diazoacetate in 4.5 g (0.055 mol) of **1a** was added over a 3-hr period.

After the addition was complete, the light brown solution was filtered *via* a glass funnel to remove the copper. The filtrate was carefully distilled at atmospheric pressure to remove excess hexadiene, which was essentially pure (>98% trans,trans). The residue was distilled *in vacuo* to yield 2.7 g (57.5%), bp 68–70° (0.5 mm).

An analytical sample of the mixture was obtained by preparative glpc (column D, 110°) and submitted for analysis.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.24; H, 9.35.

This material was analyzed by glpc on column I at 125° and showed two peaks in a ratio of 43:57. Separation of the two isomers was accomplished by preparative glpc on column G (135°). The minor isomer was obtained pure by making one pass on column G and one pass on column K (135°). Similarly, the major isomer was purified by making two passes on column K (130°). The minor isomer was assigned the structure ethyl *trans*-2-methyl-*cis*-3-(*trans*-propenyl)cyclopropane-1-carboxylate (**3b**), on the basis of the following data: $\nu_{max}^{CCl_4}$ 3010, 2950, 2910, 1725, 1160, 1180, and 969 cm^{-1}; τ ~4.53 (4.39–4.70, unresolved multiplet, 2 H, vinyl), 5.94 (quartet, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 8.35 (doublet, 3 H, vinyl methyl), ~8.60 (8.20–9.00, multiplet, 6 H, cyclopropyl methyl and cyclopropyl), and 8.77 (triplet, 3 H, J = 7.0 Hz, $-COOCH_2CH_3$).

The major product was identified as ethyl *cis*-2-methyl-*trans*-3-(*trans*-propenyl)cyclopropane-1-carboxylate (**3a**) on the basis of the following data: $\nu_{max}^{CCl_4}$ 3010, 2960, 2950, 2910, 1720, 1170, and 960 cm^{-1}; nmr τ 4.50 (doublet of quartets, 1 H, J_{ab} = 15.0, J_{ad} = 6.0 Hz, vinyl H_a), 5.05 (doublet of doublets, 1 H, J_{ab} = 15.0, J_{bc} = 7.5 Hz, vinyl H_b), 5.95 (quartet, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 8.37 (doublet, 3 H, vinyl methyl), ~8.60 (8.20–9.00) (complex multiplet, 6 H, cyclopropyl and cyclopropyl methyl), and 8.77 (triplet, 3 H, J = 7.0 Hz, $-COOCH_2CH_3$).

B. Addition to *cis,trans*-2,4-Hexadiene (1b).—The procedure used was the same as above except that pure *cis,trans*-2,4-hexadiene (**1b**) was employed. The yield of product was 2.4 g (51.1%), bp 52–55° (0.8 mm).

An analytical sample of the mixture was obtained by preparative glpc (column D, 150°) and submitted for analysis.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.27; H, 9.34.

Analysis of this mixture by glpc on column C at 90° showed four peaks in a relative ratio of 14% (retention time 35 min), 8% (46 min), 27% (51 min), and 51% (60 min). The materials corresponding to these peaks were subsequently identified as isomers **4a**, **4b**, **5b**, and **5a** as follows.

The mixture (15-μl injections) was passed through column I (100°) which allowed the isolation of **4a** (**4b**, **5a**, and **5b** were collected together). A second pass on column D (120°) gave pure **4a**. The remaining material, a mixture of **4b**, **5a**, and **5b**, was passed (<15 μl) through column B (100°), which allowed the isolation of **5b** from the mixture of **4b** and **5a**. Two passes on column C (105°) gave pure **5b**. The remaining material, a mixture of **4b** and **5a**, was separated with difficulty by employing small injections (5 μl) on column E (125°). Two passes on column E and one pass on column A (110°) gave pure **5a**. Similarly, **4b** was obtained pure after two passes on column D (105°).

Isomer **4a** was identified as ethyl *cis*-2-methyl-*trans*-3-(*cis*-propenyl)cyclopropane-1 carboxylate on the following basis. The nmr spectrum showed τ 4.55 (doublet of quartets, 1 H, J_{ab} = 10.0, J_{ad} = 6.5 Hz, vinyl H_a), 5.17 (broad triplet, 1 H, J_{ab} = 10.0 Hz, J_{bc} = 10.0 Hz, vinyl H_b), 5.89 (quartet, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 8.27 (doublet of doublets, 3 H, vinyl methyl), ~8.50 (7.90–8.90, complex multiplet, 6 H, cyclopropyl methyl and cyclopropyl), 8.73 (triplet, 3 H, J = 7.0 Hz, $-COOCH_2CH_3$); ir showed $\nu_{max}^{CCl_4}$ 3020, 2970, 2950, 2930, 1730, 1170, and 700 cm^{-1}.

Isomer **4b** was identified as ethyl *trans*-2-methyl-*cis*-3-(*cis*-propenyl)cyclopropane-1-carboxylate on the following basis: nmr τ 4.59 (complex multiplet, 2 H, vinyl), 5.93 (quartet, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 8.30 (broad doublet, 3 H, vinyl methyl), ~8.50 (8.20–9.00, complex multiplet, 6 H, cyclopropyl methyl and cyclopropyl), and 8.78 (triplet, 3 H, J = 7.0 Hz, $-COOCH_2CH_3$); $\nu_{max}^{CCl_4}$ 3040, 2960, 2930, 2970, 1730, and 1180 cm^{-1}.

Isomer **5b** was assigned the structure ethyl *cis*-2-methyl-*cis*-3-(*trans*-propenyl)cyclopropane-1-carboxylate on the basis of nmr resonance at τ ~4.30 (4.20–4.50) (complex multiplet, 2 H, vinyl), 5.92 (quartet, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 8.28 (doublet, 2 H, vinyl methyl), 8.20–8.90 (complex multiplet, 6 H, cyclopropyl methyl and cyclopropyl), 8.76 (triplet, 3 H, J = 4.0 Hz, $-COOCH_2CH_3$).

(19) H. Musso and V. Biethan, *Chem. Ber.*, **97**, 2282 (1964).

The infrared spectrum of **5a** had characteristic peaks at 3010, 2980, 2960, 2940, 1735, 1160, and 962 cm^{-1}.

Isomer **5a** was identified as ethyl *trans* 2-methyl-*trans*-3-(*trans*-propenyl)cyclopropane-1-carboxylate on the following basis. The nmr spectrum exhibited absorption at τ 4.34 (overlapping quartets, 1 H, J_{ab} = 15.0, J_{ad} = 6.0 Hz, vinyl H_a), 4.86 (doublet of doublets, 1 H, J_{ab} = 15.0, J_{bc} = 8.0 Hz, vinyl H_b), 5.94 (quartet, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 7.80–9.00 (complex multiplet, 6 H, cyclopropyl methyl and cyclopropyl), 8.30 (doublet, 3 H, vinyl methyl), 8.77 (triplet, 3 H, J = 7.0 Hz, $-COOCH_2CH_3$); ir showed $\nu_{max}^{CCl_4}$ 3010, 2970, 2940, 1735, 1175, and 960 cm^{-1}.

C. Addition to *cis,cis*-2,4-Hexadiene (1c).—The yield of product was 1.6 g (59%), bp 48–50° (0.5 mm). The recovered hexadiene was pure **1c** *via* glpc.

An analytical sample of the mixture was obtained by preparative glpc (column H, 150°).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.03; H, 9.37.

Analysis of this mixture on column H (100°) showed two peaks in a relative ratio of 69:31. The two isomers were separated by preparative glpc on column E (135°). The major isomer was obtained pure after one pass on column L (105°). Similarly, the minor isomer was purified by making one pass on column L (105°).

The major isomer was assigned the structure ethyl *trans*-2-methyl-*trans*-3-(*cis*-propenyl)cyclopropane-1-carboxylate (**6a**) on the basis of the following data: $\nu_{max}^{CCl_4}$ 3025, 2970, 2935, 1730, and 1180 cm^{-1}; nmr τ 4.40 (doublet of quartets, 1 H, J_{ab} = 10.0, J_{ad} = 6.0 Hz, vinyl H_a), 4.92 (doublet of doublets, 1 H, $J_{ab} \cong$ 10.0, $J_{bc} \cong$ 10.0 Hz, vinyl H_b), 5.92 (quartet, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 8.27 (slightly split doublet, 3 H, vinyl methyl), 7.70–9.00 (complex multiplet, 6 H, cyclopropyl and cyclopropyl methyl), 8.75 (triplet, 3 H, J = 7.0 Hz, $-COOCH_2CH_3$).

Isomer **6b** was identified as ethyl *cis*-2-methyl-*cis*-3-(*cis*-propenyl)cyclopropane-1-carboxylate on the following basis: $\nu_{max}^{CCl_4}$ 3040, 2975, 2950, 2925, 1720, and 1155 cm^{-1}; nmr τ ~4.40 (4.30–4.65, unresolved multiplet, 2 H, vinyl), 5.95 (quartet, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 8.32 (doublet, 2 H, vinyl methyl), 7.80–8.90 (multiplet, 6 H, cyclopropyl and cyclopropyl methyl), and 8.77 (triplet, 3 H, J = 7.0 Hz, $-COOCH_2CH_3$).

Dimethyl *trans*-2-Methyl-3-(*trans*-propenyl)cyclopropane-1,1-dicarboxylate (11).—The general insertion procedure using 4.1 g (0.025 mol) of methyl diazomalonate[19] and 8.2 g (0.100 mol) of **1a** afforded 2.3 g (44%) of **11**, bp 69–70° (0.4 mm). Analysis by glpc showed this material to consist of one major product. The product was purified by preparative glpc (column G, 150°) and identified as dimethyl *trans*-2-methyl-3-(*trans*-propenyl)cyclopropane-1,1-dicarboxylate: nmr (CCl_4) τ 4.28 (doublet of quartets, 1 H, J_{ab} = 15.0, J_{ad} = 6.0 Hz, vinyl H_a), 4.97 (doublet of doublets, 1 H, J_{ab} = 15.0, J_{bc} = 8.0 Hz, vinyl H_b), 6.32 (slightly split singlet, 3 H, carboxymethyl), 7.50–8.30 (complex multiplet, 2 H, methyl cyclopropyl and allylic cyclopropyl), 8.33 (slightly split doublet, 3 H, J = 6.0 Hz, vinyl methyl), 8.92 (doublet, 3 H, J = 6.0 Hz, cyclopropyl methyl); $\nu_{max}^{CCl_4}$ 3010, 2975, 2940, 2920, 1725, 1435, 1290, 1210, and 965 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 61.97; H, 7.62.

Ozonolysis of Isomers 3a and 3b.—The isomers (0.50 g, 57% **3a** and 43% **3b**) were dissolved in a mixture of chloroform (10 ml) and methanol (10 ml) and cooled to −78°.

A stream of ozone from an Orec Model 03Cl Ozonator was passed through the mixture until the solution was faintly blue (~35 min). The solution was allowed to warm to room temperature and the solvents were evaporated at room temperature under reduced pressure, leaving an oil. This was dissolved in 10 ml of 90% formic acid and 10 ml of 30% hydrogen peroxide and heated gently to 60° until refluxing began. The heat was removed until the initial reaction subsided (~10 min) and then the mixture was refluxed gently for 45 min. Solvent was removed under reduced pressure, leaving an oil. A sample of 300 μl of this oil was esterified to the cyclopropane diesters **8** and **9** by the addition of diazoethane. Analysis of the esterified ether solution on column J (140°) showed two major peaks, which were subsequently identified as **8** (59%) and **9** (41%) as follows. One pass of this mixture on column J (140°) allowed separation of the two isomers. A second pass on the same column gave analytically pure **8** and **9**. The major product was identified as diethyl 3-methylcyclopropane *trans* 1,2-dicarboxylate (**8**) on the following basis: nmr τ 5.87 (doublet of quartets, 4 H, J = 7.0 Hz, $-COOCH_2CH_3$), 7.60–8.40 (complex multiplet, 3 H, cyclopropyl methine), 1.28 (triplet, 3 H, J = 7.0 Hz, $-COOCH_2CH_3$), and 1.25 (doublet, 3 H, cyclopropyl methyl); $\nu_{max}^{CCl_4}$ 2960, 2950, 1715, 1300, and 1185 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 59.78; H, 7.91.

The minor product was assigned the structure diethyl *trans*-3-methylcyclopropane-*cis*-1,2-dicarboxylate (**9**): nmr τ 4.09 (quartet, 2 H, J = 7.0 Hz, $-COOCH_2CH_3$), ~8.25 (7.85–8.40, complex multiplet, 3 H, cyclopropyl methine), 8.77 (triplet, 3 H, J = 7.0 Hz, $-COOCH_2CH_3$), and 8.82 (doublet, 3 H, cyclopropyl methyl); $\nu_{max}^{CCl_4}$ 2960, 2950, 1720, and 1175 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 59.76; H, 8.05.

Ozonolysis of 3a.—A sample of 20 μl of >95% pure **3a** was dissolved in 300 μl of ethanol–300 μl of chloroform and ozonized as before. The esterified (diazoethane) product was analyzed by glpc on column K (140°) and found to have the same retention time (coinjection) as the larger product peak in the ozonolysis of the mixture of isomers [which was subsequently identified as **8** (*vide supra*)], thus confirming the stereochemical assignments for **3a** and **3b**.

Registry No.—**1a**, 5194-51-4; **1b**, 5194-50-3; **1c**, 6108-61-8; **2**, 623-73-4; **3a**, 30626-52-9; **3b**, 30626-51-8; **4a**, 39495-86-8; **4b**, 39495-87-9; **5a**, 30634-35-6; **5b**, 30634-34-5; **6a**, 39495-90-4; **6b**, 39495-91-5; **8**, 4104-67-0; **9**, 713-51-9; **10**, 6773-29-1; **11**, 39495-94-8; copper, 7440-50-8.