Synthesis, Stereochemistry, and Solvolysis of 2-Bromobicyclopropyl and Closely Related Structures

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The syntheses of *cis*- and *trans*-2-ethylcyclopropyl bromide (**10**), *cis*- and *trans*-2-vinylcyclopropyl bromide (**5**), and *cis*- and *trans*-2-bromobicyclopropyl (**8**) have been carried out and stereochemistry has been established for each isomer. The relative rates of solvolysis of each isomer (cyclopropyl bromide ≡ 1) and values for $\Delta H^{\ddagger}$ (in kilocalories per mole) and $\Delta S^{\ddagger}$ (in entropy units) are as follows: *trans* **8**, 7340, 23.9, −7.7; *cis* **8**, 379, 25.9, −8.8; *trans* **5**, 1180, 19.9, −25.8; *cis* **5**, 103, 19.3, −27.6; *trans* **10**, 361, 20.6, −22.2; *cis* **10**, 17.8, 22.4, −23.1. The *trans* to *cis* rate ratios of 11.5–20.3 are consistent with orbital symmetry considerations. The rate enhancement upon going from the 2-ethyl to the 2-cyclopropyl substituent is entirely due to a more positive $\Delta S^{\ddagger}$ and is rationalized in terms of charge delocalization into the substituent ring in the transition state.

Except for recent investigations of the solvolyses of several simple alkyl- and aryl-substituted cyclopropyl derivatives for the purpose of examining Woodward–Hoffmann predictions of the preferred stereochemistry of ring opening,[2] relatively little systematic information exists on the nature of the transition states for such reactions.

Because the cyclopropyl group has an exceptional ability to stabilize an adjacent carbonium ion,[3] its use as a substituent on a second system undergoing limiting solvolysis could lead to interesting data on transition state charge distribution. For example, unique solvolysis behavior has already been reported for 1-chlorobicyclopropyl.[4] In the following study the solvolytic behavior of *cis*- and *trans*-2-cyclopropyl, -2-vinyl, and -2-ethylcyclopropyl bromides will be reported.

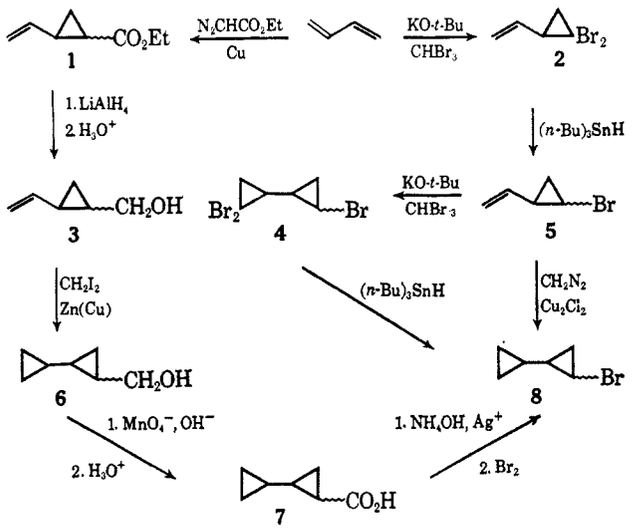
Synthesis and Stereochemistry

Various synthetic routes used for the preparation of 2-bromobicyclopropyl (**8**) and 2-vinylcyclopropyl bromide (**5**) are outlined in Scheme I.

A mixture of 68% *cis*- and 32% *trans*-2-vinylcyclopropyl bromide (**5**)[5] was conveniently converted into *cis*- and *trans*-2-bromobicyclopropyl (**8**) by the cuprous chloride catalyzed addition of diazomethane.

The over-all yield of **8** from 1,3-butadiene was 40%. It is interesting to note that the isomer distributions in **5** and **8** were essentially identical regardless of whether **5** was converted directly into **8** as previously described or by way of 2,2,2′-tribromobicyclopropyl **4**, consistent with the expected similarity in the stereochemical fate of the reaction leading from **2** to **5** with that for the reaction leading from **4** to **8**. The reduction of **2** to **5** with methylmagnesium bromide[6] gave essentially the same product isomer distribution as the tri-*n*-butyltin hydride reduction.

SCHEME I



Because of the complexity of the nmr spectrum of **5**, previous stereochemical assignments[5] were based on the observation that *cis* products predominate during the partial reduction of 1,1-dihalocyclopropanes with tri-*n*-butyltin hydride[7] (Table I), in accord with the belief that the reaction is a radical-chain process in which hydrogen is transferred from tri-*n*-butyltin

TABLE I
SELECTED DATA ON THE PARTIAL REDUCTION OF *gem*-DIHALOCYCLOPROPANES WITH TRI-*n*-BUTYLTIN HYDRIDE

Dihalocyclopropane	*cis* product, %	$\Delta\delta_{CHX}$ (*cis*–*trans*), ppm[a]
1,1-Dibromo-2,2,3-trimethylcyclopropane	80[b]	0.45
7,7-Dibromonorcarane	71.4[b]	0.61
1,1-Dibromo-2-ethylcyclopropane (**10**)	68,[c] 60[d]	0.46
2,2,2′-Tribromobicyclopropyl (**4**)	68[c]	0.42
1,1-Dibromo-2-vinylcyclopropane (**2**)	67.7[b]	0.36
7,7-Dichloronorcarane	65.5[e]	0.55

[a] Stereochemical designation refers to the halogen. [b] See ref 5. [c] This work. [d] G. L. Gloss and J. J. Coyle, *J. Amer. Chem. Soc.*, **87**, 4270 (1965). [e] See ref 2d.

(1) Taken from the Ph.D. Dissertation of L. W. B., University of Kansas, 1967.

(2) (a) P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, **88**, 2868 (1966); (b) C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966); (c) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965); (d) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965).

(3) P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966), and references cited therein.

(4) J. A. Landgrebe and L. W. Becker, *ibid.*, **89**, 2505 (1967).

(5) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(6) D. Seyferth and B. Prokai, *ibid.*, **31**, 1702 (1966).

(7) In contradiction to these observations, Cristol and DePuy[2d] have reported that the reduction of 3,3-dichlorodibenzotricyclo[3.3.2.0^{2,4}]nonadiene with triphenyltin hydride produced the *anti*-monochloride in 61% yield.

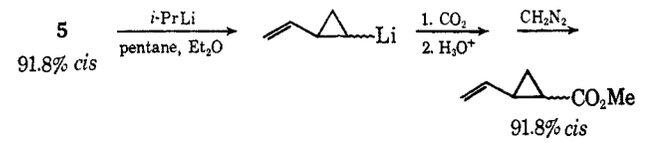
hydride to the least hindered side of a 1-halocyclopropyl radical.[8]

Although proton nmr coupling constants are useful in the assignment of stereochemistry to various substituted cyclopropyl derivatives,[5,2d] the complexity of a spectrum often precludes a straightforward determination of the appropriate values. For this reason it should be noted that the chemical shift of the proton on the halogen-bearing carbon atom for a variety of *cis*-2-substituted cyclopropyl halides (Table I) is ~0.48 ppm further downfield than that for the *trans* isomer and therefore provides a useful additional criterion for the identification of the geometric isomers.

In order to provide a more conclusive chemical proof of the stereochemistry of bromides **5** and **8**, a mixture of *cis* and *trans* **5** was related to ethyl *cis*- and *trans*-2-vinylcyclopropanecarboxylate (**1**), the stereochemistry of which had been previously established by oxidation and hydrolysis of the pure isomers to the well-known *cis*- and *trans*-1,2-cyclopropanecarboxylic acids.[9]

The copper-catalyzed decomposition of ethyl diazoacetate in the presence of 1,3-butadiene produced a 55:45 mixture of *trans* and *cis* **1** in agreement with the previously reported uncatalyzed, thermal reaction.[9,10] As expected, equilibration of the isomers with sodium ethoxide in refluxing ethanol resulted in an increase in the extent of the *trans* isomer from 55 to 91%. The ester mixture was then carefully saponified and by means of diazomethane converted into the methyl esters of the same isomeric composition.

The mixture of bromides **5** (91.8% *cis*) was then allowed to undergo halogen–metal interchange with isopropyllithium in 94% pentane, 6% diethyl ether, conditions for retention of configuration for the resulting cyclopropyllithium,[11] followed by carbonation and



treatment of the carboxylic acid with diazomethane to give a mixture of methyl *cis*- and *trans*-2-vinylcyclopropane carboxylate (91.8% *cis*) which could be directly compared (vpc) with the previously prepared sample.

A second synthetic route to **8** involved the conversion of ester **1** into 2-carboxybicyclopropyl (**7**)[12] followed by a Hunsdiecker reaction on the corresponding silver salt to give a mixture of *cis* and *trans* **8** in a ratio of 28:72. The same reaction carried out on *cis*- and *trans*-2-methylcyclopropanecarboxylic acid by Applequist and Peterson[13] produced a 34:66 ratio of the *cis* to the *trans* product.

(8) (a) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Amer. Chem. Soc.*, **84**, 3584 (1962); (b) H. G. Kuivila and E. J. Walsh, Jr., *ibid.*, **88**, 571, 576 (1966); (c) K. Sisido, S. Kozina, and K. Takizawa, *Tetrahedron Lett.*, 33 (1967).

(9) E. Vogel, R. Erb, G. Lenz, and A. A. Bothner-By, *Ann.*, **682**, 1 (1965).

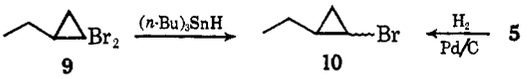
(10) I. S. Lishanskii, A. G. Zak, I. A. D'Yakonov, and T. G. Alievn, *Zh. Org. Khim.*, **1**, 1189 (1965).

(11) D. E. Applequist and A. H. Peterson, *J. Amer. Chem. Soc.*, **83**, 862 (1961).

(12) Because the Simmons–Smith reaction carried out on **3** gave inconsistent results, it was found advantageous to treat the acetate of **3** with phenyltribromomethylmercury followed by tri-*n*-butyltin hydride reduction of the *gem*-dibromocyclopropane to the acetate of **6**.

(13) D. E. Applequist and A. H. Peterson, *ibid.*, **82**, 2372 (1960).

The synthesis of *cis*- and *trans*-2-ethylcyclopropyl bromides (**10**) was accomplished by the tri-*n*-butyltin hydride reduction of 1,1-dibromo-2-ethylcyclopropane (**9**)[14] to give a 68:32 ratio of the *cis* to the *trans* isomer.



The stereochemical assignments were confirmed by a direct vpc comparison of **10** with the products of catalytic hydrogenation of **5**.

Kinetics

Solvolysis rate data were obtained in 50 vol % aqueous ethanol for *cis*–*trans* mixtures of bromides **5**, **8**, and **10** by means of the usual method for handling parallel first-order processes with a common product (see Experimental Section). In every instance the relative amounts of the *cis* and *trans* isomer present in the mixture as determined from the kinetic data were within ±0.5% of the values determined by vpc methods. Absolute and relative rate constants are tabulated in Tables II and III and the corresponding activation parameters are in Table IV.

TABLE II
SOLVOLYSIS RATES FOR 2-SUBSTITUTED CYCLOPROPYL BROMIDES IN 50 VOL % AQUEOUS ETHANOL

Substituent	Isomer	Temp,[a] °C	k,[b] sec^{-1}
Cyclopropyl (**8**)	*trans*	80.0	2.44×10^{-4}
		95.0	1.02×10^{-3}
	cis	80.0	8.38×10^{-6}
		95.0	3.93×10^{-5}
Vinyl (**5**)	*trans*	95.0	2.65×10^{-4}
		105.0	5.59×10^{-4}
	cis	95.0	2.46×10^{-5}
		105.0	5.08×10^{-5}
Ethyl (**10**)	*trans*	110.0	2.13×10^{-4}
		120.0	4.34×10^{-4}
	cis	110.0	1.01×10^{-5}
		120.0	2.21×10^{-5}

[a] Temperature variation $\leq \pm 0.1°$. [b] All rate constants were determined by the method of least squares with a probable error of $\leq \pm 1\%$. Each value represents the average of two runs with an average deviation of $\leq \pm 2\%$.

TABLE III
RELATIVE RATES OF SOLVOLYSIS OF SUBSTITUTED CYCLOPROPYL BROMIDES IN 50 VOL % AQUEOUS ETHANOL AT 130°

Substituent	k, sec^{-1}	k_{rel}
Hydrogen	2.6×10^{-6} [a]	1.0
1-Methyl	1.05×10^{-4} [a]	40.4
2,2-Propano	2.35×10^{-3} [b]	904
trans-2-Cyclopropyl (**8**)	1.91×10^{-2}	7340
cis-2-Cyclopropyl (**8**)	9.87×10^{-4}	379
trans-2-Vinyl (**5**)	3.08×10^{-3}	1180
cis-2-Vinyl (**5**)	2.67×10^{-4}	103
trans-2-Ethyl (**10**)	9.40×10^{-4}	361
cis-2-Ethyl (**10**)	4.64×10^{-5}	17.8

[a] E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 2719 (1961). [b] J. A. Landgrebe and D. E. Applequist, *ibid.*, **86**, 1536 (1964).

(14) See Table I, footnote *d*.

TABLE IV
SUMMARY OF ACTIVATION PARAMETERS FOR 2-SUBSTITUTED CYCLOPROPYL BROMIDES

Substituent	Isomer	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
Cyclopropyl (**8**)	*trans*	23.9 ± 0.8	−7.7 ± 2.2
	cis	25.9 ± 0.1	−8.8 ± 0.2
Vinyl (**5**)	*trans*	19.9 ± 0.5	−25.8 ± 1.2
	cis	19.3 ± 0.5	−27.6 ± 1.2
Ethyl (**10**)	*trans*	20.6 ± 0.9	−22.2 ± 2.2
	cis	22.5 ± 1.1	−23.1 ± 2.7

A significant solvolysis rate enhancement upon introduction of alkyl substituents into the 2 position of cyclopropyl bromide has been observed previously[15] and is entirely consistent with positive charge delocalization to the substituted position in the transition state.

In general agreement with the results for acetolyses of various di- and trimethyl-substituted cyclopropyl tosylates[2a] and 2-phenylcyclopropyl tosylate,[2b,c] the *trans* isomers of **5**, **8**, and **10** all solvolyzed 11.5–20.3 times faster (Table III, 130°) than the corresponding *cis* isomers. Thus one can visualize a slight release of nonbonded strain as the *trans* isomer approaches the transition state and a similar slight increase in strain

in the *cis* isomer.[2a] The *trans* to *cis* rate ratios for the cyclopropyl and ethyl substituents, 19.4 and 20.3, respectively, are in accord with the expected similarity in the size of the two groups.[16,17] The factor of 11.5 for the *trans*-to-*cis* rate ratio for 2-vinylcyclopropyl bromide is again consistent with the known smaller effective size of this group compared to ethyl.[18,19]

In view of the similarity of the reported σ_m values for cyclopropyl, −0.102[20] or −0.07,[21] and ethyl, −0.07,[22] as well as the similarity in size previously mentioned,[16] the rate ratio of *trans* **8** to *trans* **10**, 20.3, and that of *cis* **8** to *cis* 10, 21.3, cannot be rationalized in terms of steric or inductive differences. Charge delocalization into the cyclopropyl substituent in the transition state is clearly implied. A comparison of activation parameters (Table IV) for bromides **8** and **10** is particularly instructive. While the $\Delta S^{\pm}$ values for both *cis* and *trans* **10** are substantially negative, those for *cis* and *trans* **8** are only slightly negative. The $\Delta H^{\pm}$ values for both *cis* and *trans* **10** are actually less than those for the corresponding *cis* and *trans* **8**.

(15) See Table III, footnote *b*.

(16) Although the conformational A value for the cyclopropyl group is not known, the corresponding values for ethyl and isopropyl are 1.80 and 2.12, respectively,[17] and one would expect the value for cyclopropyl to be slightly smaller than that for isopropyl.

(17) N. L. Allinger, L. A. Freiberg, and S. E. Hu, *J. Amer. Chem. Soc.*, **84**, 2836 (1962).

(18) The conformational A value for vinyl is ~1.35.[19]

(19) R. J. Ouellette, K. Kiptak, and G. E. Booth, *J. Org. Chem.*, **31**, 546 (1966).

(20) Determined from the pK_a (5.90) of *m*-cyclopropylbenzoic acid in 50 vol % aqueous ethanol at 25.0° by Dr. Ronald H. Rynbrandt.

(21) J. Smejkal, J. Jones, and J. Furkas, *Collection Czech. Chem. Commun.*, **29**, 2950 (1964).

(22) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

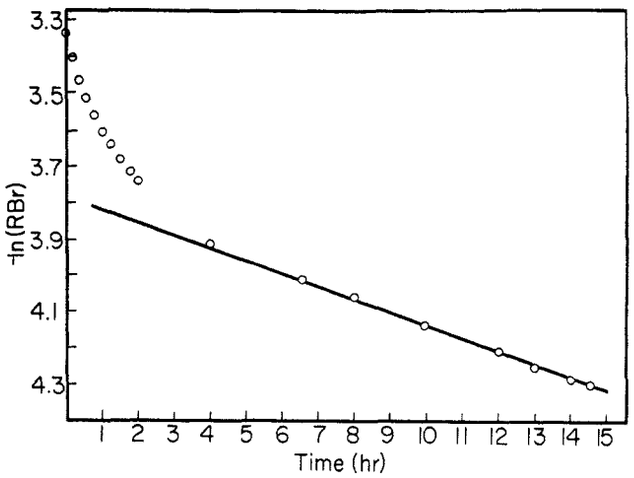


Figure 1.

Thus the increase in rate on going from the ethyl- to the cyclopropyl-substituted system is entirely due to a more positive $\Delta S^{\pm}$ in the latter system, a result which can be rationalized by assuming some degree of ring opening of the cyclopropyl substituent at the time of the transition state.

In contrast to bromides **8** are *trans*- and *cis*-2-vinylcyclopropyl bromides (**5**) which solvolyze 3.28 and 5.76 times faster than the corresponding ethyl-substituted compounds. In this case the rate difference can be attributed to the smaller $\Delta H^{\pm}$ for **5** compared with **10**, since $\Delta S^{\pm}$ for **5** is actually more negative than that for **10**. Because the σ_m for vinyl has been reported as +0.30,[23] the observed increase in rate on going from the ethyl to the vinyl substituent must be caused by favorable charge delocalization in the transition state for solvolysis of the latter system.

Further speculation on the nature of the transition states for solvolyses of **5**, **8**, and **10** must await a detailed product analysis.

Experimental Section[24]

Ethyl *cis*- and *trans*-2-Vinylcyclopropane Carboxylate (1).—Ethyl diazoacetate, generated from 0.893 mole of glycine ethyl ester hydrochloride,[25] was added dropwise (30 min) to 1,3-butadiene (400 ml, 260 g, 4.82 mol). Freshly prepared cuprous chloride[26] (1 g) was then added to the rapidly stirred solution followed by the addition of copper–bronze powder (1 g). Within 15 min, nitrogen evolution began, accompanied

(23) J. K. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, **75**, 3452 (1953)

(24) All elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo. Meeting points were taken on a Thomas–Hoover apparatus and are corrected. Boiling points are uncorrected. Infrared spectra were obtained in carbon tetrachloride solution from a Beckman IR-8 (sodium chloride optics) with a 1603-cm^{-1} peak (polystyrene *vs.* air) as a reference. Mass spectra were obtained on Nuclide Analysis Associates Model 12-90G instrument. Analyses by gas chromatography were done on an F & M Model 700 instrument (thermal conductivity) with the following columns: 20% QF-1 on 30/60 Chromosorb P (15 ft × 0.25 in.); 20% β,β'-oxydipropionitrile on 30/60 Chromosorb P (12 ft × 0.25 in.); 20% Carbowax 1540 on 30/60 Chromosorb P (12 ft × 0.25 in.); 20% Hyprose B on 30/60 Chromosorb P (12 ft × 0.25 in.); 20% tris(cyanoethoxy)propane on 30/60 Chromosorb P (12 ft × 0.25 in.); 7.6% silver nitrate, 8.4% tetraethylene glycol, and 84% 3-nitro-3-methylpimelonitrile on 80/100 Chromosorb W (9 ft × 0.25 in.). All isomeric compounds were assumed to have equal gas chromatographic sensitivity factors. Nuclear magnetic resonance spectra were obtained on a Varian A-60 or A-60-A spectrometer as solutions in carbon tetrachloride with internal tetramethylsilane standard unless otherwise specified. Chemical shifts are expressed in τ units.

(25) N. E. Searle, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, pp 424–426.

(26) R. Q. Brewester, C. A. VanderWerf, and W. E. McEwen, "Unitized Experiments in Organic Chemistry," D. Van Nostrand Co., Inc., Princeton, N. J., 1960, p 151 (procedure a).

by increased reflux rate and a gradual darkening of the solution. After 15 hr, the excess 1,3-butadiene was allowed to evaporate and the residual oil (from two runs) gave 60.0 g (0.43 mol, 24% based on glycine ethyl ester hydrochloride) of a sweet smelling liquid, bp 69–74.5° (10 mm) (lit.[9] bp 61–62° (12 mm)). Fractionation with a short Vigreux column gave 2.0 g, bp 57–69° (10 mm); 38.7 g, bp 69–72° (10 mm); and 18.5 g, bp 72–74.5° (10 mm). Vpc of the distillate before fractionation (Carbowax 1540, 115°) showed two peaks (98% of total) with relative areas of 55:45 in order of increasing retention times assigned to *trans* and *cis* isomers, respectively (see Discussion). High-boiling residue consisted mainly of diethyl fumarate and maleate.

The nmr spectrum of the mixture of isomers showed a complex multiplet at 3.90–5.25 (3 H), a quartet at 5.97 (2 H, J = 7 cps), a triplet at 8.80 (3 H, J = 7 cps), and a complex multiplet at 7.82–9.32 (4 H). The infrared spectrum showed significant absorptions at 3100 (w), 3000 (w), 1725 (s), 1640, 1380, 1175, 1165, 1034 (cyclopropyl), and 905 cm^{-1}. A mass spectrum showed a parent peak at m/e 140.

Equilibration of Ethyl *cis*- and *trans*-2-Vinylcyclopropanecarboxylate.—An isomeric mixture of ethyl 2-vinylcyclopropanecarboxylate (14.0 g, 0.10 mol, 55% *trans*) in absolute ethanol (25 ml) was added to a solution of sodium ethoxide (prepared from 0.10 g-atom of sodium) in absolute ethanol (50 ml) and the yellow solution was maintained at reflux (100 hr). Vpc analysis (Carbowax 1540, 115°) of the isolated ethyl 2-vinylcyclopropanecarboxylate showed 91% of the *trans* isomer (shorter retention time) to be present.

***cis*- and *trans*-2-Vinylcyclopropylcarbinol (3).**—Ester **1** (70.1 g, 0.50 mol, 55% *trans*) in ether (100 ml) was added to an ether slurry of lithium aluminum hydride (20.0 g, 0.53 mol) under a nitrogen atmosphere. After 1 hr at reflux, the reaction mixture was worked up in the usual manner and the product alcohol (42.0 g, 0.43 mol, 87.7%) was distilled, bp 73–74° (9.0 mm). Vpc (Carbowax 1540, 195°) indicated <1% impurity. Several vpc columns failed to separate the *cis* and *trans* isomers.

The nmr spectrum showed a complex multiplet at 4.08–5.33 (3 H), a multiplet at 6.30–6.70 (2 H), a multiplet at 8.15–9.75 (4 H), and the broad singlets (1 H) which shifted with the introduction of a trace of hydrogen chloride. The infrared spectrum showed significant absorptions at 3350, 3020, 2880, 1635, 1510, 1037 (cyclopropane), and 895 cm^{-1}. The mass spectrum showed a parent peak at m/e 98.

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: 73.17; H, 10.16.

***cis*- and *trans*-2-Vinylcyclopropylcarbinyl Acetate.**—Carbinol **3** (9.8 g, 0.10 mol) in dry ether (100 ml) which contained pyridine (7.9 g, 0.10 mol) was treated with acetyl chloride (9.0 g, 0.10 mol) in ether (25 ml) while the flask was cooled in an ice–salt bath. After 30 min, the reaction mixture was poured into water (200 ml) and the ether layer was treated in the usual manner and concentrated to give, after distillation, 10.5 g (0.075 mole, 75.6%) of colorless ester, bp 46–47° (5 mm).

Vpc (QF-1, 143°) showed two components (97%) with relative areas of 55:45 in order of increasing retention times assigned to the *trans* and *cis* isomers, respectively. The nmr spectrum of the isomeric mixture showed a complex multiplet at 4.20–5.33 (3 H, ABC pattern), a doublet at 6.13 (J = 6.8 cps) superimposed on a multiplet at 6.0–6.18 (total 2 H), a singlet at 8.04 (3 H), and a complex multiplet at 8.29–9.70 (4 H). The infrared spectrum showed absorptions at 3100 (w), 3030 (w), 1740, 1640, 1368, 1230, 1040, 1025 (cyclopropane), and 900 cm^{-1}.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.41; H, 8.39.

***cis*- and *trans*-2-Hydroxymethylbicyclopropyl (6). Simmons–Smith Method.**—Methylene iodide (300 g, 1.12 mol) was slowly added to a slurry of zinc–copper couple[27] (125 g, 1.91 g-atoms) in dry ether (300 ml) to which a few iodine crystals had been added to initiate the reaction. When the reagent had been prepared, 2-vinylcyclopropylcarbinol (28.5 g, 0.29 mole) in ether (50 ml) was added so as to maintain reflux and the mixture was stirred at reflux for 48 hr. After hydrolysis with saturated aqueous ammonium chloride (300 ml), the excess zinc was removed and the aqueous layer was extracted with ether. The residue after the ether was evaporated was allowed to remain in contact with concentrated sodium methoxide in methanol (50 ml) overnight. After an aqueous work-up the resulting oil was distilled to give 20.0 g of a colorless liquid, bp 67–68° (5 mm). Vpc (Carbowax 1540, 195°) showed a large peak (85–90%) and numerous impurity peaks. There was no separation of *cis* and *trans* isomers.

The nmr spectrum of a purified sample showed a multiplet at 5.55–6.0 (1 H), a multiplet at 6.25–6.83 (2 H), and a complex absorption at 8.3–10.0 (10 H). The infrared spectrum showed significant absorptions at 3400, 3100, 3030, 2880, 1033, and 1015 cm^{-1}.

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.80; H, 10.74.

Copper-Catalyzed Addition of Diazomethane to Olefins.—Ether (25 ml) and 50% aqueous potassium hydroxide (50 ml) were added to a 100-ml, three-necked flask (nonstandard taper) which was being magnetically stirred and cooled with an ice bath. A capillary tube was placed beneath the ether layer and attached to a nitrogen supply by Tygon tubing. The other outlet of the flask was connected to a potassium hydroxide pellet drying tower which was in turn connected to another three-necked flask with a capillary tube. As the diazomethane precursor was added to the generator, a slow stream of nitrogen was bubbled through the ether layer which carried the diazomethane through the drying tower to the reaction flask and through the capillary tube to the etherate olefin solution. This flask contained the olefin, the solvent, and the cuprous chloride and was also cooled and stirred. The reactions were monitored by vpc and nmr. It was necessary to replenish periodically the ether supply in the generator depending on the flow rate of nitrogen which carried some ether into the reaction flask. The concentration of the diazomethane in the ether layer of the generator was kept low. Usually, 1 g of the diazomethane precursor was added per 25 ml of ether and maintained as such until all the diazomethane had been used as indicated by the absence of yellow color. Depending on the amount of diazomethane passage per unit time, the color of the cuprous chloride in the reaction varied from white to black. Rapid passage caused the salt to turn black, but the black color would gradually change to white in the presence of an olefin if the rate of diazomethane passage was decreased.

***cis*- and *trans*-2-Hydroxymethylbicyclopropyl (6). Diazomethane Method.**—2-Vinylcyclopropylcarbinol (5.0 g, 0.047 mol), cuprous chloride (1 g), and absolute ether (35 ml) were treated with diazomethane as previously described. Complete conversion could be obtained only by the use of a large excess of diazomethane.

***cis*- and *trans*-2-Carboxybicyclopropyl (7).**—2-Hydroxymethylbicyclopropyl (19.0 g, 0.17 mol, 90% purity) was slowly added to a stirred cooled solution of potassium permanganate (5.0 g) and potassium hydroxide (2.0 g) in water (250 ml). Additional permanganate (1-g portions) was added until the color persisted and the excess oxidizing agent was destroyed with 95% ethanol. Water was added to bring the total volume to 750 ml and sodium bisulfite was used to reduce the manganese dioxide. Two ether extracts were discarded and the aqueous layer was acidified with 6 N hydrochloric acid and extracted with ether. Attempts to purify the crude acid product (16.0 g, 0.127 mole, 75%) by distillation resulted in considerable decomposition. The reported boiling point is 100° (4 mm).[28]

The nmr spectrum showed a singlet at −2.05 (1 H) and a complex absorption at 8.0–10.0 (10 H). The infrared spectrum showed absorptions at 3400–2300 (broad), 1670, 1425, 1035, and 1010 cm^{-1}.

***cis*- and *trans*-2-Carbomethoxybicyclopropyl** was obtained by treatment of the acid (10 g, 0.079 mol) with diazomethane in ether. The yellow oil (10.7 g, 0.076 mol, 96.3%), bp 63–64° (4 mm), gave an nmr spectrum which showed singlets at 6.36 and 6.40 (3 H) and a complex multiplet at 8.16–10.0 (9 H). The infrared spectrum showed significant absorptions at 3100, 3030, 2950, 1735, 1440, 1385, 1370, 1195, 1170, and 1148 cm^{-1}. The mass spectrum gave a parent peak at m/e 140 in addition to fragment peaks at 97, 95, 67, 58, 55, 43, 41, and 29. Vpc (Hyprose B, 135°) showed two components (99%) with relative areas 55:45 in order of increasing retention time.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.30; H, 8.57.

(27) R. S. Shank and H. Schechter, *J. Org. Chem.*, **24**, 1825 (1959).

(28) A. P. Meshcheryakov, V. G. Glukhovtsev, and N. N. Lemin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1901 (1961).

cis- and *trans*-2-Bromobicyclopropyl (8). **Hunsdiecker Method.**—The silver salt of 2-carboxybicyclopropyl was prepared from silver nitrate (14.6 g, 0.0856 mol) and the carboxylic acid (10.8 g, 0.0856 mol) by a procedurean alogous to that described by Applequist and Peterson.[13] The yield of dry salt (24 hr at 65° under vacuum) was 17.0 g (0.073 mol) or 85.4%.

The above salt was slowly added to a stirred, cooled (ice–salt bath) solution of bromine (6.9 g, 0.043 mol) in dry, alkene-free pentane (175 ml) under nitrogen, the mixture was allowed to warm to room temperature, the silver bromide was filtered, and the filtrate was evaporated to give the product (2.5 g, 0.0155 mole, 36.1%), bp 76–79° (74 mm).

The nmr spectrum showed multiplets at 7.02 and 7.38 (1 H), the latter absorption being more intense, and a complex multiplet at 8.2–10.0 (9 H). The infrared spectrum showed important absorptions at 3100, 3030, 1440, 1260, 1228, 1218, 1100, 1036, 1020, and 954 cm^{-1}. The mass spectrum showed small parent peaks at *m/e* 160 and 162 and an intense peak at *m/e* 81 ($C_6H_9^+$). The most intense peaks were at *m/e* 119 and 121 ($M^+ - c\text{-}C_3H_5$), with smaller fragments at 132 and 134. Vpc (QF-1, 70°) showed two components (98%) in the ratio 72:28 in order of increasing retention time.

Anal. Calcd for C_6H_9Br: C, 44.74; H, 5.63. Found: C, 45.05; H, 5.72.

1,1-Dibromo-2-vinylcyclopropane (2) was prepared in 60% yield by addition of dibromocarbene to 1,3-butadiene. The bp was 53–56° (10 mm) (lit.[29,30] bp 76–82° (50 mm) and 69.5–70° (26 mm)). The infrared and nmr spectra were consistent with the structural assignment.

cis- and *trans*-2-Vinylcyclopropyl Bromide (5). **Tri-*n*-butyltin Hydride Method.**—Bromides 5 were prepared in 75–80% yield by reduction of dibromide 2 with tri-*n*-butyltin hydride according to the method of Seyferth and coworkers.[5] Vpc (QF-1, 80°) indicated 30–32% of the *trans* isomer (shorter retention time). The nmr spectrum showed a complex multiplet at 4.07–5.20 (3 H), multiplets at 6.7–7.1 and 7.1–7.43 (1 H), and a complex absorption at 7.90–9.33 (4 H). The infrared spectrum showed significant absorptions at 3100, 3030, 1645, 1265, 1230, 1035, 985, and 907 cm^{-1}. The mass spectrum gave small parent peaks at *m/e* 146 and 148 and significant fragments at 67 ($C_5H_7^+$), 65, 44, 41, and 39.

Anal. Calcd for C_5H_7Br: C, 40.75; H, 4.80. Found: C, 40.59; H, 4.63.

Careful fractional distillation gave the following results: bp 60.0–62.5°, 1.2 g, 52.8% *cis*;[31] bp 62.5–65°, 3.8 g, 68.4% *cis*; bp 65.0–69.0°, 2.0 g, 75.8% *cis*; bp 69.0–76.5°, 7.0 g, 91.8% *cis* (lit.[5] bp of mixture 62–74° (90 mm)).

cis- and *trans*-2-Vinylcyclopropyl Bromide (5). **Methylmagnesium Bromide Method.**—Dibromide 5 (3.23 g, 0.022 mol) was slowly (20 min) added to a stirred solution of methylmagnesium bromide in tetrahydrofuran (14.6 ml, 1.51 *N*, 0.022 mol) under nitrogen.[6] The addition was exothermic and a second exothermic reaction occurred at the end of the 20 min together with the formation of a white precipitate. After 30 min, the mixture was hydrolyzed with water (100 ml) and extracted with ether. Vpc (QF-1, 70°) of the isolated bromides (5) indicated 70.9% of the *cis* isomer.

cis- and *trans*-2-Bromobicyclopropyl. **Diazomethane Method.**—2-Vinylcyclopropyl bromide (1.47 g, 0.01 mol, 75% *cis*) was treated with diazomethane and cuprous chloride in ether as previously described. After 90% conversion into the desired product mixture, vpc (QF-1, 70°) showed 77% of the isomer with the longer retention time. Admixture of these products with those from the Hunsdiecker procedure (vpc, QF-1 and β,β'-oxydipropionitrile) showed that they were identical but that the opposite isomer predominated.

Methyl *cis*- and *trans*-2-Vinylcyclopropanecarboxylate.—Ethyl 2-vinylcyclopropanecarboxylate (2.0 g, 0.0143 mol, 91% *trans*) was hydrolyzed with potassium hydroxide solution in the usual manner and the resulting acid was esterified with diazomethane to give the methyl ester (1.2 g, 0.0095 mol, 66.7%), bp 55.5–56.0° (10 mm). The nmr spectrum showed a complex absorption at 4.20–5.12 (3 H), a singlet at 6.34 (3 H), and a complex multiplet at 7.80–9.28 (4 H). The infrared spectrum showed significant absorptions at 3100, 2950, 1730, 1640, 1440, 1380, 1325, 1305, 1285, 1265, 1200, 1170, 980, and 905 cm^{-1}. The mass spectrum showed a parent peak at *m/e* 126 with significant fragments at *m/e* 111, 95, 67 ($M^+ - CO_2CH_3$), and 59 ($COCH_3^+$). Vpc (Carbowax 1540, 145°) showed two peaks in the ratio 91:9 in order of increasing retention times.

Stereospecific Conversion of *cis*- and *trans*-2-Vinylcyclopropyl Bromide to Methyl *cis*- and *trans*-2-Vinylcyclopropanecarboxylate.—The method of Applequist and Peterson[11] was used. A pentane solution of isopropyllithium (20 ml, 0.8306 *N*, 0.0166 mol) was cooled to 0° (N_2 atmosphere) and absolute ether (1.2 ml) was added followed by the rapid addition of 2-vinylcyclopropyl bromide (1.50 g, 0.01027 mol, 91.8% *cis*). After 5 min at 0°, the purple solution was added to finely powdered Dry Ice (100 g). Water (100 ml) was added, the mixture was allowed to warm to 25°, and hydrochloric acid was added to acidify the solution. The acid product was extracted into ether and treated with diazomethane to give 500 mg of ester. Vpc (Carbowax 1540, 145°) confirmed the identity of the ester isomers and indicated that the isomer of longer retention time was present as 91.6% of the mixture. Vpc comparison (Carbowax 1540 and Hyprose B) of the isomer mixture with a similar mixture from the treatment of ethyl diazoacetate with butadiene followed by conversion of the ethyl to the methyl ester confirmed the identity of isomers (see discussion).

cis- and *trans*-2,2,2′-Tribromobicyclopropyl (4).—2-Vinylcyclopropyl bromide (15.0 g, 0.104 mol, 32% *trans*) in dry, alkene-free pentane (100 ml) was added to a solution of potassium *t*-butoxide (prepared from 0.20 g-atom of potassium) under a nitrogen atmosphere. The mixture was stirred and cooled in an ice–salt bath while bromoform (40.0 g, 0.157 mol) was slowly added (1 hr). Stirring and cooling were continued for 12 hr, water (250 ml) was added, the aqueous layer was extracted with ether, and the ether was dried and evaporated to give the expected product (16.6 g, 0.052 mol, 50%), bp 91–95° (1.0 mm).

The nmr spectrum showed multiplets at 6.65–7.08 and 7.08–7.50 (1 H) and a complex multiplet at 7.8–9.5 (7 H). The infrared spectrum showed significant absorptions at 3030, 1425, 1260, 1150, 1035, 1008, and 685 cm^{-1}. The mass spectrum showed no parent peak but substantial fragments at *m/e* 241, 239, 237, 212, 201, 199, 197, 160, 159, 158, 157, 79, 78, and 77.

Anal. Calcd for $C_6H_7Br_3$: C, 22.60; H, 2.21; Br, 75.19. Found: C, 22.71; H, 2.21; Br, 74.98.

cis- and *trans*-2-Bromobicyclopropyl. **Tri-*n*-butyltin Hydride Method.**—Tri-*n*-butyltin hydride (25.0 g, 0.086 mol) was slowly added (2 hr) to cold (ice bath) stirred 2,2,2′-tribromobicyclopropyl (12.0 g, 0.0375 mol) under a nitrogen atmosphere. After being stirred at 25° for 70 hr, the mixture was distilled and redistilled, bp 79–82° (74 mm), to give bromide 10 (2.0 g, 0.0124 mol, 33%), identical in every respect, except isomer distribution, with the previously prepared material. Vpc (QF-1, 80°) indicated 68% of the *cis* isomer (98% over-all purity).

cis- and *trans*-2-Ethylcyclopropyl Bromide (10).—1,1-Dibromo-2-ethylcyclopropane (9) was prepared by the method of Skell and Garner[32] from bromoform, 1-butene, and potassium *t*-butoxide in an over-all yield of 52%, bp 62–64° (12 mm) (lit. bp 68–69° (30 mm)). The dibromide was reduced by tri-*n*-butylin hydride as previously described for 1,1-dibromo-2-vinylcyclopropane to give the final product (22.0 g, 0.148 mol, 74.3%), bp 105–120° (lit.[14] bp 47–52° (66 mm)). Nmr spectral data were consistent with those previously reported.[14] The mass spectrum showed parent peaks at *m/e* 148 and 150 as well as significant fragments at *m/e* 121, 119, 108, 106, 69 ($M^+ - Br$), 53, 42, and 41. Vpc indicate a *cis* to *trans* ratio of 68:32 (lit.[14] 60:40) with the two desired products representing 85% of the total product mixture. Careful fractionation gave the following results: 6.6 g, bp 100–110°, 52.4% *cis*, 27.6% impurity; 5.2 g, bp 110–114°, 57.3% *cis*, 17.8% impurity; 6.7 g, bp 114–117°, 67.5% *cis*, 4.9% impurity; 1.3 g, bp 117–117.5°, 81.9% *cis*, trace of impurity.

Anal. Calcd for C_5H_9Br: C, 40.29; H, 6.09; Br, 53.62. Found: C, 40.46; H, 6.00; Br, 53.36.

Hydrogenation of *cis*- and *trans*-2-Vinylcyclopropyl Bromide.—2-Vinylcyclopropyl bromide (1.47 g, 0.01 mol, 68% *cis*) was hydrogenated at atmospheric pressure in absolute methanol (10 ml) with palladium on charcoal (50 mg, 10%). The reaction was worked up in the usual manner after one-half the

(29) L. Skattebøl, *J. Org. Chem.*, **29**, 2951 (1964).

(30) R. C. Woodworth and P. S. Skell, *J. Amer. Chem. Soc.*, **79**, 2542 (1957).

(31) A low-boiling impurity (40%) was present.

(32) P. S. Skell and A. V. Garner, *ibid.*, **78**, 5430 (1956).

theoretical amount of hydrogen had been absorbed. Vpc analysis (QF-1, 45°) of the product mixture indicated 68% of *cis*-2-ethylcyclopropyl bromide (longer retention time). Vpc analysis of the mixture of these products with those from the previous reaction confirmed these conclusions.

***cis*- and *trans*-2-Acetoxymethylbicyclopropyl.**—2-Vinylcyclopropylcarbinyl acetate (6.0 g, 0.043 mol, 55% *trans*) was treated with phenyltribromomethylmercury[33] (24 g, 0.045 mol) in anhydrous benzene (40 ml) at reflux under nitrogen for 3 hr. Phenylmercuric bromide was filtered from the cold solution and the filtrate was evaporated to give crude product which was not further purified.

The dibromide was reduced with tri-*n*-butyltin hydride (29.1 g, 0.10 mol) over a 72-hr period by the method previously described. The product (4.0 g, 0.026 mol, 60.5%) had a bp 87–91° (3–4 mm). The nmr spectrum showed doublets at 5.9 and 6.2 (2 H, J = 7 cps) with the doublet at 5.9 further split into doublets (J = 2 cps), singlets at 8.02 and 8.04 (3 H), and a complex multiplet at 8.65–10.1 (9 H). The infrared spectrum showed significant absorptions at 3100, 3030, 1745, 1385, 1235, 1025, and 970 cm^{-1}.

***cis*- and *trans*-2-Hydroxymethylbicyclopropyl from *cis*- and *trans*-2-Acetoxymethylbicyclopropyl.**—2-Acetoxymethylbicyclopropyl (3.08 g, 0.02 mol) in ether (10 ml) was slowly added to a suspension of lithium aluminum hydride (1.14 g, 0.03 mol) in ether (25 ml) and maintained at reflux for 1 hr. After hydrolysis and work-up, 1.8 g (0.0184 mol, 80.4%) of crude product was isolated and shown by nmr and infrared spectral comparisons to be identical with the material prepared from 2-vinylcyclopropylcarbinol.

Solvolysis Procedure.—All kinetic experiments utilized a 12 × 12 in. Pyrex bath which contained *ca.* 5 gal. of oil (Cities Service, DC-915), a Lightnin Model L continuous duty stirrer, a hydrogen-jacketed thermoregulator, and a 500-W continuous-heat source which was connected to a Variac. Fine heating was controlled by a 40-W light bulb connected through a transistorized relay to the thermoregulator. The entire bath was surrounded by *ca.* 3 in. (of polyurethan foam and was covered by a 1-in. styrofoam lid.

The appropriate amount of halide was dissolved in *ca.* 50 ml of ethanol–water 50% by volume at 20.0°) and the solution (*ca.* 0.03–0.06 M in halide) was distributed among 19–20 ampoules each containing *ca.* 2.5 ml. The ampoules were sealed and placed in the bath (time started) and at appropriate time intervals ampoules were removed and quenched in ice–water. An exact aliquot (*ca.* 2 ml) was removed with a pipet calibrated with the same ethanol–water solution. The aliquot was diluted with *ca.* 10 ml of cold distilled water and the acid solution was titrated to a phenolphthalein endpoint with a sodium methoxide in methanol solution which had been standardized against potassium hydrogen phthalate. A 5-ml microburet which could be read directly to 0.01 ml was used. Infinity titrations were taken after 10 half-lives. Rate constants were determined by the method of least squares and the activation parameters were calculated from the Eyring equation. Good first-order kinetics were usually observed in ≤60% reaction.

(33) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

The data for a typical run are indicated in Table V and Figure 1 for the 50 vol % aqueous ethanol solvolysis of a mixture of 32% *trans*-2-ethylcyclopropyl bromide and 68% *cis*-2-ethylcyclopropyl bromide at 110 ± 0.1°. (There is a very rapidly solvolyzing 5% impurity present.)

TABLE V[a]

Time elapsed, min	Titrated HBr	−ln (RBr)	Time elapsed, min	Titrated HBr	−ln (RBr)
∞	0.03581	3.3301	120	0.01201	3.7389
10	0.002493	3.4025	240	0.01587	3.9156
20	0.004533	3.4656	390	0.01779	4.0171
30	0.005893	3.5100	480	0.01858	4.0623
45	0.007252	3.5165	600	0.01983	4.1373
60	0.008499	3.6010	720	0.2096	4.2108
75	0.009632	3.6436	780	0.02164	4.2578
90	0.01054	3.6788	840	0.02210	4.2903
105	0.01145	3.7154	870	0.02232	4.3068

[a] k_{cis} = 1.03 × 10^{-5} sec^{-1}.

The result of the usual analysis of the initial rate data from Table V (see Discussion) is recorded in Table VI.

TABLE VI[a]

Time elapsed, min	$(HBr)_{total} - (HBr)_{cis}$	$-\ln (RBr)_{trans}$	Time elapsed, min	$(HBr)_{total} - (HBr)_{cis}$	$-\ln (RBr)_{trans}$
∞	0.01297		75	0.00428	5.4549
20	0.00862	4.7545	90	0.00354	5.6447
30	0.00740	4.9072	105	0.00285	5.8616
45	0.00624	5.0777	120	0.00250	5.9926
60	0.00519	5.2619			

[a] k_{trans} = 2.08 × 10^{-4} sec^{-1}.

Registry No.—**1** (*cis*), 2183-89-3; **1** (*trans*), 2183-90-6; **3** (*cis*), 15135-97-4; **3** (*trans*), 15135-98-5; **4** (*cis*), 15135-99-6; **4** (*trans*), 15136-00-2; **5** (*cis*), 15136-01-3; **5** (*trans*), 15136-02-4; **6** (*cis*), 15136-03-5; **6** (*trans*), 15136-04-6; **7** (*cis*), 15136-05-7; **7** (*trans*), 15136-06-8; **8** (*cis*), 15136-07-9; **8** (*trans*), 15136-08-0; **10** (*cis*), 15136-09-1; **10** (*trans*), 15136-10-4; *cis*-2-vinylcyclopropylcarbinyl acetate, 15136-11-5; *trans*-2-vinylcyclopropylcarbinyl acetate, 15186-42-2; *cis*-2-carbomethoxybicyclopropyl, 15186-43-3; *trans*-2-carbomethoxybicyclopropyl, 15215-72-2; methyl *cis*-2-vinylcyclopropanecarboxylate, 15186-44-4; methyl *trans*-2-vinylcyclopropanecarboxylate, 7119-58-6; *cis*-2-acetoxymethylbicyclopropyl, 15186-46-6; *trans*-2-acetoxymethylbicyclopropyl, 15186-47-7.