Steric and Electronic Effects in the Solvolysis of *cis*- and *trans*-Mono- and -Dihalocyclopropanes[1]

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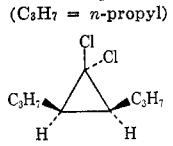
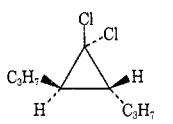
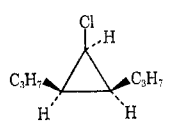
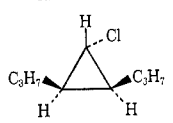
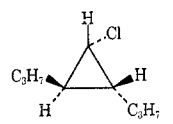
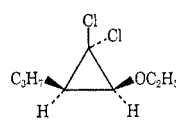
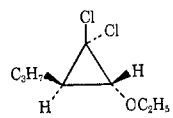
The solvolysis of five new mono- or -dichlorocyclopropanes of known -stereochemical structure (**3–7**) have been carried out in ethanol (80°) with silver nitrate under conditions identical with those previously reported for *cis*- and *trans*-1,1-dichloro-2,3-di-*n*-propylcyclopropane, and steric and electronic effects of attached substituents on rates of solvolyses have been considered.

We have previously reported[3] the rates of solvolysis of *cis*- and *trans*-1,1-dichloro-2,3-di-*n*-propylcyclopropane (**1** and **2**, respectively) at 80° in the presence of ethanolic silver nitrate. We have now determined the rates of solvolysis of the cyclopropanes **3–7**, under identical conditions, in order to obtain more quantitative data regarding the steric and electronic effects of attached substituents on the rates of solvolysis of such halocyclopropanes.

The results described in Table I are consistent with the prior conclusion that such reactions occur by rate-determining ionization of halogen,[4] followed by a concerted ring-opening process in which the groups *trans* to the leaving group rotate outward in a disrotatory manner.[5,6]

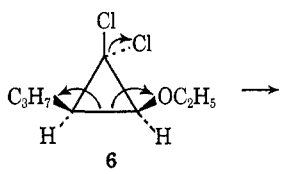
TABLE I

FIRST-ORDER REACTION RATES OF THE HALOCYCLOPROPANES AT 80.0 ± 0.2° IN THE PRESENCE OF SILVER NITRATE

Compd no.	Compd (C_3H_7 = *n*-propyl)	Rate constants, sec^{-1}	Relative rates
1		$k_1 = 1.29 \times 10^{-5}$	24.2
2		$k_2 = 5.33 \times 10^{-7}$	1
3		$k_3 < 2.17 \times 10^{-8}$	<0.04
4		$k_4 = 8.20 \times 10^{-5}$	154
5		$k_5 = 1.26 \times 10^{-6}$	2.4
6		$k_6 = 4.54 \times 10^{-4}$	852
7		$k_7 = 1.08 \times 10^{-4}$	203

Conclusions

Comparison of Solvolysis Rate of *cis*- and *trans*-Dihalocyclopropanes.—It is now established that 1,1-dihalocyclopropanes derived from *cis* olefins undergo solvolysis more rapidly than those derived from the corresponding *trans* olefins (compare k_1 with k_2 and k_6 with k_7, Table I). These results are consistent with the conclusion[3] that in *cis*-cyclopropanes such as **1** or **6** it is the halogen *cis* to the hydrogen atom that is lost preferentially (see next section). The larger difference in rates noted for the *cis–trans* isomers **1** and **2** ($k_1/k_2 = 24.2$) relative to the *cis–trans* isomers **6** and **7** ($k_6/k_7 = 4.2$) was not unexpected, since the *n*-propyl group is more bulky than the ethoxy group. Thus the difference in steric effects of H–H nonbonding interaction in **8** (eq 1) and the H–OC_2H_5 nonbonding interaction in **10** (eq 2) is less than the corresponding



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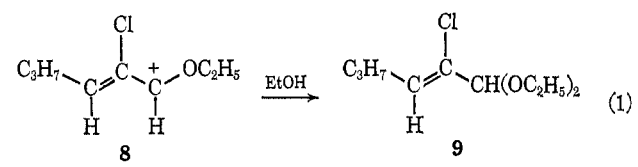
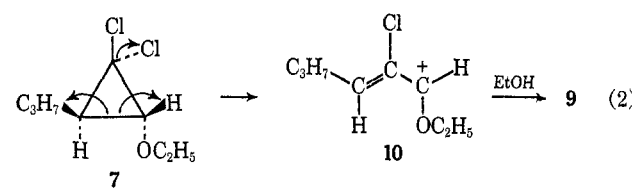


8 **9** (1)



7 **10** **9** (2)

steric interactions (H–H *vs.* H–*n*-C_3H_7) in the analogous processes involving **1** and **2**. It should be noted that both **6** and **7** gave the *trans* olefin **9** as the reaction product (see Experimental Section). This result is consistent with those previously discussed for **1** and **2**[3,7] and the conclusion[3] that solvation accompanies the ionization step such that the transition state for the reaction more closely resembles the product (**9** in this case) than the mesomeric ionic intermediate (**10**).

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(2) From the Ph.D. Thesis of K. S. Yong, The University of Minnesota, 1969.

(3) W. E. Parham and K. S. Yong, *J. Org. Chem.*, **33**, 3947 (1968).

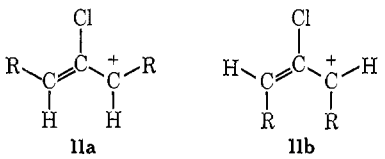
(4) W. E. Parham, H. Reiff, and P. Swartzentruber, *J. Amer. Chem. Soc.*, **78**, 1437 (1956).

(5) (a) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965); (b) C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966).

(6) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(7) L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966).

Steric Control of Loss of Halogen.—It was previously suggested[3] that loss of halogen from 1,1-dihalocyclopropanes derived from open-chain *cis* olefins (such as **1**, **6**, or large-ring *cis* cyclo olefins) involve the preferential loss of the halogen atom that is *cis* to the two hydrogen atoms on the cyclopropane ring. Such process leads to the geometrically more favorable intermediate (or transition state) **11a**, in which there is only H–H nonbonding interaction. Loss of the other halogen atom would lead to the intermediate **11b**, which is sterically less favorably because of alkyl–alkyl nonbonding interaction.



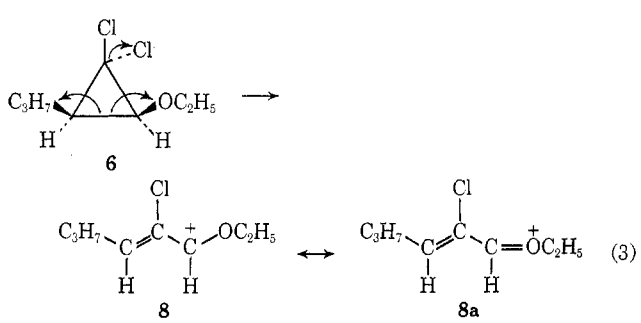
11a **11b**

This conclusion is now substantiated by results shown in Table I for the monohalocyclopropanes **3** and **4**. Isomer **4**, which would give an intermediate related to **11a**, solvolyzed quite rapidly ($k_4 = 8.20 \times 10^{-5}$ sec^{-1}) while no detectable reaction was observed after 1346 hr ($k_3 < 2.17 \times 10^{-8}$ sec^{-1}) for **3** (which would give an intermediate related to **11b**).

Effect of Rate of a Second Chlorine Atom at C-1.—Comparison of the rates of reaction of **1** with **4** (relative rates 24.2 and 154, respectively) and **2** with **5** (relative rates 1 and 2.4, respectively) established the fact that the second halogen atom in **1** and **2** inhibits the rate of solvolysis. Such retardation by the second halogen atom was expected, since the rate-determining step in such reactions is known[4] to involve ionization of halogen, and the additional halogen atom would be expected to inhibit the process by its inductive effect.

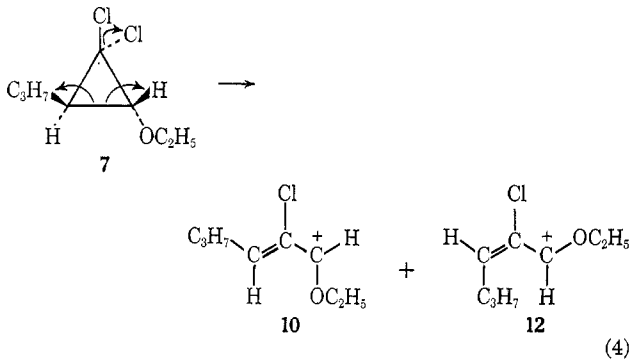
The seemingly larger difference in ratio of rates noted for the *cis* isomers **4** and **1** ($k_4/k_1 = 6.4$) than for the *trans* isomers **5** and **2** ($k_5/k_2 = 2.4$) is not unexpected, since in **1** only one halogen can leave (halogen *cis* to hydrogen). The halogen atoms in **2** are equivalent and either can leave. In effect, then, the relative rate of solvolysis of **2** is 0.5 per halogen. The overall difference in ratios of rate of reaction per halogen atom involved is therefore 6.4 and 4.8, respectively, which are comparable.

Effect on Rate of Ethoxy Group at C-2.—Rate enhancement by attached ethoxy groups, as observed for **6** and **7** compared with **1** and **2** (see Table I), were expected, since oxygen can more effectively stabilize (**8** ↔ **8a**) the carbonium ion developing in the transition state, as illustrated in eq 3.



6 **8** **8a** (3)

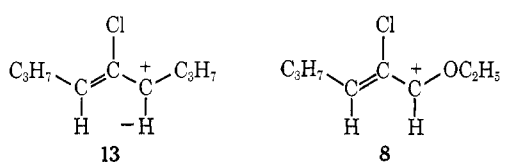
The much larger enhancement in rate observed for **7** relative to **2** ($k_7/k_2 = 203$) compared with that observed for **6** relative to **1** ($k_6/k_1 = 35.2$) is assumed to be steric in origin. Only the halogen *cis* to hydrogen can be lost from **6**, and the H–H nonbonding interaction in **8** is essentially the same as in **13** (from **1**). However, either halogen can be lost from **7**, forming **10** or **12**, respectively (eq 4). One would expect that



7 **10** **12** (4)

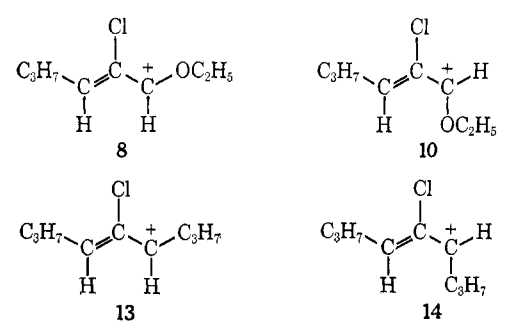
steric demands of **10** would be less than those of **12**, since the ethoxy group is smaller than *n*-propyl; the hydrogen–ethoxy steric interaction would be of less consequence in **10** than the steric interaction of *n*-propyl with H in **12** or in the related intermediate **14** derived from **2** (which also has H–*n*-propyl nonbonding interaction). Then on purely steric grounds one would expect k_7/k_2 (203) to be larger than k_6/k_1 (35.2).

Comparison of Other Electronic and Steric Effects.—If it is assumed that the magnitude of the steric effects for nonbonding H–H interaction is comparable for the intermediates **13** (from **1**) and **8** (from **6**), then



13 **8**

the ratio k_6/k_1 gives a quantitative comparison of the electronic effect of ethoxy and *n*-propyl, showing that ethoxy increases the rate of solvolysis about 35-fold relative to *n*-propyl. If it is further assumed that the magnitude of the electronic effect of the ethoxy group stabilizing **8** (from **6**) is comparable with that stabilizing **10** (from **7**) and the magnitude of the electronic effects of the *n*-propyl stabilizing **13** (from **1**) is comparable with that stabilizing **14** (from **2**), then the ratio $(k_7/k_2)/(k_6/k_1)$ (5.8) is a direct



8 **10** **13** **14**

comparison of the magnitude of the H–*n*-C_3H_7 nonbonding steric interaction with the H–OC_2H_5 nonbonding steric interaction in such disrotatory ring-expansion processes.

Experimental Section

Nuclear magnetic resonance spectra were determined using a Varian A-60 spectrometer using 20% solutions in carbon tetrachloride and tetramethylsilane as internal standard. Gas-liquid partition chromatography analyses were determined on a Beckman GC-4 and separations were carried out using a Hewlett-Packard Model 776, Prep Master Jr.

A mixture of *cis*-1-chloro-*cis*-2,3-di-*n*-propylcyclopropane (3) and *trans*-1-chloro-*cis*-2,3-di-*n*-propylcyclopropane (4) was prepared in 76% yield, bp 72–74° (28 mm), by reduction of 1[3] with tri-*n*-butyltin hydride at 68–70° for 25 hr.[8] The composition of the product as determined by glpc (silicon oil, DC-710, 20% on Chromosorb W, 0.25 in. o.d. × 60 in. at 100°) was 76% **3** and 24% **4**.

Anal. Calcd for $C_9H_{17}Cl$: C, 67.27; H, 10.67; Cl, 22.07. Found: C, 67.24; H, 10.55; Cl, 22.16.

The mixture was separated by glpc (silicon gum rubber, SD-30, 20% on Chromosorb W, 2.5 in. o.d. × 80 in. at 100°). The cyclopropane **3** showed the following data: $n^{25}D$ 1.4450; ir (neat) 3040 (cyclopropane CH), 1030, 1020 (cyclopropane), and 750–725 cm^{-1} (CCl); nmr (CCl_4) δ 3.15 (t, 1, J = 7.3 Hz, HCCl) and 1.60–0.70 ppm (m, 16). The cyclopropane **4** showed the following data: $n^{25}D$ 1.4450; ir (neat) 3030 (cyclopropane CH), 1020 (cyclopropane), and 725–718 cm^{-1} (CCl); nmr (CCl_4) δ 2.29 (d, 1, J = 3.8 Hz, HCCl) and 1.72–0.58 (m, 16).

***trans*-1-Chloro-2,3-di-*n*-propylcyclopropane** (5) was prepared in 61% yield, bp 59–62° (9.8 mm), $n^{25}D$ 1.4362, from 2[3] as described for **3** and **4**, except that a longer reduction time (45 hr) was required. The cyclopropane **5** showed the following data: ir (neat) 3030 (cyclopropane CH), 1020 and 1010 (cyclopropane), and 725–718 cm^{-1} (CCl); nmr (CCl_4) δ 2.74 (two d, 1, J = 6.5 and 4.5 Hz, HCCl) and 1.70–0.52 ppm (m, 16).

Anal. Calcd for $C_9H_{17}Cl$: C, 67.27; H, 10.67. Found: C, 67.17; H, 10.85.

***cis*-1-Ethoxy-pentene and *trans*-1-ethoxy-1-pentene**, 67% yield, bp 66–69° (114 mm), $n^{24}D$ 1.4120 (lit.[9] bp 118–119°, $n^{25}D$ 1.4107), was prepared from 1,1-diethoxypentane.[10] The mixture [*ca.* 2:1 ratio of *cis*-1-ethoxy-1-pentene and *trans*-1-ethoxy-1-pentene as determined by glpc (silicon oil, DC-710, 20% on Chromosorb W, at 80°)] was separated by a spinning-band column. The *cis* isomer, bp 114–115°, showed the following data: $n^{24}D$ 1.4120; ir (neat), 3030 (=CH), 1667, 1654 (C=C), 1250–1020 (=COC), and 725 cm^{-1} (*cis* HC=CH); nmr (CCl_4) δ 5.74 (two t, 1, J = 6.2 and 1.2 Hz, =CHO), 4.22 (two t, 1, J = 6.8 and 6.2 Hz, =CHC), 3.69 (q, 2, J = 6.7 Hz, OCH_2), 2.00 (broad q, 2, $=CCH_2$), and 1.60–0.70 ppm (m, 8). The *trans* isomer, bp 119–120°, showed the following data: $n^{24}D$ 1.4120; ir (neat) 3030 (=CH), 1672 and 1652 (C=C), 1227–1050 (=COC), and 9.28–9.16 cm^{-1} (*trans* HC=CH); nmr (CCl_4) δ 6.11 (two t, 1, J = 12.4 and 0.8 Hz, =CHO), 4.60 (two t, 1, J = 12.4 and 6.8 Hz, =CHC), 3.60 (q, 2, J = 6.8 Hz, OCH_2), 1.77 (broad q, 2, $=CCH_2$), and 1.53–0.70 ppm (m, 8).

A mixture of *cis*- and *trans*-1,1-dichloro-2-ethoxy-3-*n*-propylcyclopropane was prepared in 50% yield, bp 57–58° (4.6 mm), $n^{24}D$ 1.4482, from methyllithium, bromotrichloromethane, and *cis*,*trans*-1-ethoxy-1-pentene by a procedure similar to that previously described for other olefins.[11]

Anal. Calcd for $C_8H_{14}Cl_2O$: C, 48.75; H, 7.16. Found: C, 49.04; H, 7.23.

Pure *cis*-1,1-dichloro-2-ethoxy-3-*n*-propylcyclopropane (6) was prepared in 50% yield similarly from pure *cis*-1-ethoxy-1-pentene: bp 56–58° (4.6 mm); $n^{24}D$ 1.4489; nmr (CCl_4) δ 3.93–3.50 (m, 2, CH_2O), 3.37 (d, 1, J = 8.0 Hz), and 1.83–0.73 ppm (m, 11).

Pure *trans*-1,1-dichloro-2-ethoxy-3-*n*-propylcyclopropane (7) was prepared in 54% yield from pure *trans*-1-ethoxy-1-pentene: bp 59–61° (4.7 mm); $n^{24}D$ 1.4479; nmr (CCl_4) δ 3.93–3.47 (m, 2, CH_2O), 3.03 (d, 1, J = 4.2 Hz, OCH), and 1.83–0.73 ppm (m, 11).

***trans*-2-Chloro-1,1-diethoxy-2-hexene. A. From *cis*-1,1-Dichloro-2-ethoxy-3-*n*-propylcyclopropane.**—A mixture of 6 (7.88 g, 40 mmol), absolute ethanol (160 ml), and silver nitrate (7.14 g, 42 mmol) was heated at the reflux temperature in the absence of light in a system protected from moisture for 4 hr. Petroleum ether (bp 55–67°, 200 ml) was added to the filtered and concentrated residue, the resulting solution was washed with 5% sodium carbonate (100 ml), and the resulting mixture was dried ($MgSO_4$) and concentrated. The residue was shown by nmr to contain 78% ***trans*-2-chloro-1,1-diethoxy-2-hexene** and 22% ***trans*-2-chloro-2-hexenal.** Pure *trans*-2-chloro-1,1-diethoxy-2-hexene was obtained by fractional distillation (6-in. column packed with glass helices): yield 51%; bp 75° (3.4 mm); $n^{24}D$ 1.4400; ir (neat) 1668 and 1662 (C=C) and 1150–1050 cm^{-1} (COC); nmr (CCl_4) δ 6.00 (two t, 1, J = 7.0 and 0.8 Hz, CCH=), 4.75 (d, 1, J = 0.8 Hz, =CHO), 3.83–3.15 (m, 4, OCH_2), 2.21 (q, 2, J = 7.0 Hz, $=CCH_2$), and 1.77–0.77 ppm (m, 11). The assignment of the *trans* structure was made by analysis of the nmr spectra of the acetal and corresponding aldehyde as previously described[7] for *trans*-2-chloro-1,1-diethoxy-2-butene and *trans*-2-chloro-2-butenal.

Anal. Calcd for $C_{10}H_{19}ClO_2$: C, 58.10; H, 9.26. Found: C, 58.34; H, 9.35.

B. From *trans*-1,1-Dichloro-2-ethoxy-3-*n*-propylcyclopropane (7).—The reaction of 7 with alcoholic silver nitrate was carried our for 20 hr as described in A. Analysis of the product, yield 71%, bp 67–68° (3.5 mm), showed 87% *trans*-2-chloro-1,1-diethoxy-2-hexene and 13% *trans*-2-chloro-2-hexenal.

***trans*-2-Chloro-2-hexenal** was prepared in 97% yield, bp 60–61° (6.1 mm), $n^{24}D$ 1.4721, by hydrolysis of *trans*-2-chloro-1,1-diethoxy-2-hexene in aqueous acetone containing hydrochloric acid (1 *N*). The aldehyde showed the following data: ir (neat) 2820 and 2720 (CHO), 1706 (C=O), and 1627 cm^{-1} (C=C); nmr (CCl_4) δ 9.33 (s, 1, CHO), 6.97 (t, 1, J = 7.0 Hz, C=CH), 2.50 (q, 2, J = 7.0 Hz, $=CH_2$), 1.60 (sextet, 2, J = 7.0 Hz, CH_2CH_3), and 1.00 ppm (t, 3, J = 7.0 Hz, CH_2CH_3).

Anal. Calcd for C_6H_9ClO: C, 54.35; H, 6.84; Cl, 26.74. Found: C, 54.44; H, 7.12; Cl, 26.86.

The 2,4-dinitrophenylhydrazone of *trans*-2-chloro-2-hexenal melted at 180–181° dec (from ethanol–ethyl acetate).

Anal. Calcd for $C_{12}H_{13}ClN_4O_4$: C, 46.09; H, 4.19; N, 17.92. Found: C, 45.86; H, 4.28; N, 17.94.

Kinetic studies were conducted exactly as previously described for 1 and 2.[3] The results are shown in Table I.

Registry No.—1, 17288-68-5; 2, 22842-14-4; 3, 22842-15-5; 4, 22842-16-6; 5, 22842-17-7; 6, 22842-18-8; 7, 22842-19-9; 9, 22850-56-2; *cis*-1-ethoxy-1-pentene, 16627-08-0; *trans*-1-ethoxy-1-pentene, 16627-09-1; *trans*-2-chloro-2-hexenal, 22922-38-9; 2,4-dinitrophenylhydrazone of *trans*-2-chloro-2-hexenal, 22850-57-3.

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