30 min. The catalyst was filtered, and the solution was stripped, leaving a solid, 8.4 g (100% yield). Nmr peaks were present at δ 0.08 (s), 1.75 (s), and 2.60 (s) in the ratio of 6:1:4. A sharp-melting material (69-70°) was obtained by trituration of the diamine with warm water, followed by distillation from KOH, bp 110° (10 mm), and sublimation from barium oxide. *Anal.* Calcd for $C_{10}H_{22}N_2$: C, 70.6; H, 12.9; N, 16.5. Found: C, 70.4; H, 12.9; N, 16.6 (Dumas method).

Registry No.—I (R = CH_2Ph), 17288-10-7; II (R = Me), 17288-11-8; II (R = CH_2Ph), 17322-87-1; III (R = Me), 17288-12-9; III (R = CH_2Ph), 17288-13-0; IV, 17288-14-1.

Steric Effects in the Solvolysis of *cis*- and *trans*-1,1-Dichloro-2,3-dipropylcyclopropane[1]

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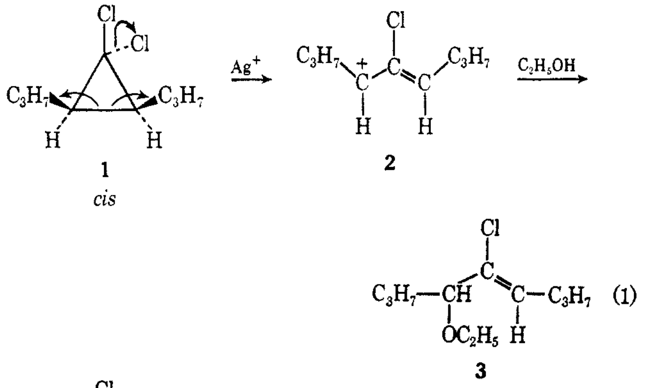
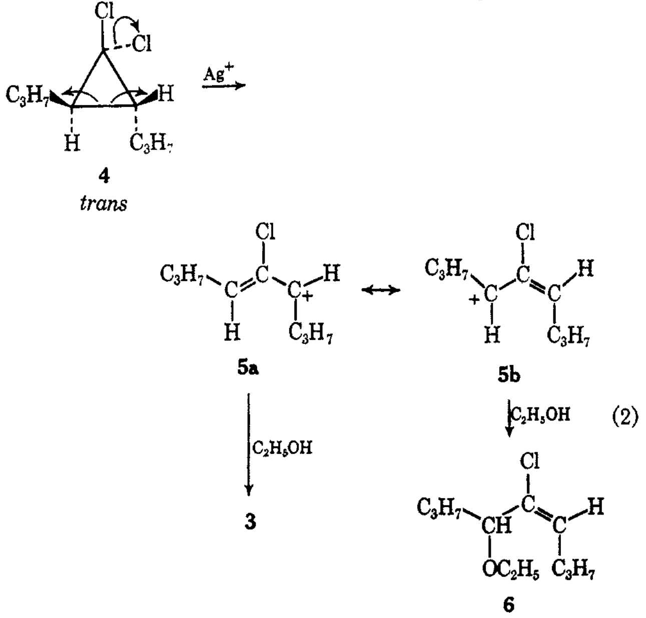
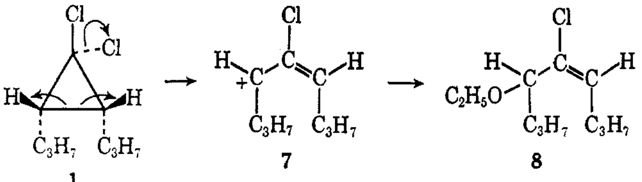
We have investigated the rates of solvolysis of the isomeric cyclopropanes **1** and **4** (eq 1 and 2), derived from *cis*- and *trans*-octene-4, at 80° in the presence of ethanolic silver nitrate. This method of ring opening of dihalocyclopropanes was first described by Skell and Sandler[2] and the scope of reaction has recently been extended by Sandler.[3] The observed difference in rates ($k_{cis} = 1.29 \times 10^{-5}$ sec^{-1}, $k_{trans} = 5.33 \times 10^{-7}$ sec^{-1}, $k_{cis}/k_{trans} = 24.2$) and the fact that both reactions gave only the *trans* chloro ether **3** are consistent with the combined data provided by (a) prior studies of mechanism of such ring-opening reactions,[2-5] (b) the work of DePuy[6] and coworkers concerning ring opening accompanying solvolysis of cyclopropyl tosylates, (c) the selection rules of Woodward and Hoffmann[6,7] for electrocyclic reactions, and (d) the relative rates of ring opening of the corresponding dichlorocyclopropanes derived from *cis*- and *trans*-propenyl ethyl ether[5] and from *cis*- and *trans*-cyclododecene.[8]



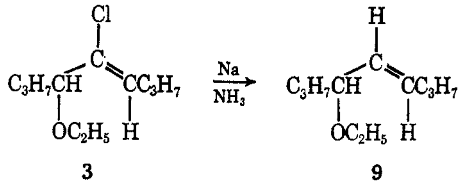


If these processes occur, as is now assumed,[6,7] by a process in which the groups *trans* to the leaving group rotate outward in a disrotatory manner, then it follows that the chlorine atom *cis* to hydrogen in **1** is lost preferentially. This is expected, since loss of the chlorine in **1** *cis* to alkyl, as shown in eq 3, would give a less favorable intermediate (or transition state) **7** in which



(3)

the two alkyl groups interact sterically. Such a process would lead to the *cis*-chloro ether **8** which is not observed. The more rapid rate of reaction of the *cis* isomer **1**, relative to the *trans* isomer **4**, is consistent with results previously described for the dihalocyclopropanes derived from *cis*- and *trans*-cyclododecene[8] and from *cis*- and *trans*-propenyl ethyl ether;[5] the results are those expected by considering steric demands of the intermediates (or transition states) comparable to **2** and **5**. The stereochemistry of the chloro ether **3** was determined by its reduction, with sodium in liquid ammonia, to *trans*-6-ethoxynonene-4 (**9**). The



infrared spectrum of **9** showed $\nu_{C=C}$ at 1662 cm^{-1} and strong absorption at 975 cm^{-1} indicative of *trans* hydrogen out of plane bending.[9] Since reduction of vinyl halides with sodium and liquid ammonia is known to be stereospecific,[10] with retention, it was concluded

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(1) This work was supported by the National Science Foundation Grant GP-6169X.

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

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(10) M. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Amer. Chem. Soc.*, **73**, 3329 (1951).

that the -CCl=CH- group in **3** has the *trans* configuration.

The formation of only the *trans*-chloro ether **3** from the *trans*-cyclopropane **4** is perhaps more surprising than its formation from **1**, since the proposed intermediate mesomeric ion **5** is asymmetric and could lead to either **3** or to **6** by solvolysis. Some pertinent arguments for the related preferential formation of a single *trans* olefin from *trans*-1,1-dichloro-2-ethoxy-3-methylcyclopropane have been discussed by Skattebøl.[5] We would like to suggest that the ring-opening process is accompanied by solvent attack concerted with ionization, so that the transition state for the process more closely resembles the product **3** than the ion **5**. It is apparent from steric considerations that such an intermediate leading to *trans* **3** would be sterically more favorable than one with the two bulky groups *cis*, leading to **6**.

The preferential loss of chlorine *cis* to hydrogen that occurs with dichlorocyclopropanes derived from *cis* olefins such as *cis*-octene-4 and *cis*-cyclododecene, is not general for cyclopropanes derived from small-ring olefins, such as cyclohexene. It is well known[11] that steric requirements prevent formation of smaller ring *trans* olefins, and requires formation of the *cis* olefin (analogous to eq 3). The rate of elimination of hydrogen chloride from the 1,1-dichlorocyclopropane derived from cyclohexene was studied by Cristol and coworkers[11] in acetic acid at 124.6°; the observed rate constant was 4.5×10^{-7} sec^{-1}.

Experimental Section

***cis*-1,1-Dichloro-2,3-dipropylcyclopropane** (1) was prepared from octene-4[12] (96% *cis* and 4% *trans*), sodium methoxide[13] (from a fresh bottle), and ethyl trichloroacetate by a procedure essentially identical with that described for the reaction with cyclododecene.[8] The chromatographed product was distilled to give an 89% yield of **1**: bp 77–80° (9 mm); $n^{25}D$ 1.4568. The product was shown by glpc (silicon oil, DC-710, 20% on Chromosorb W) to be **1** contaminated by ~4% of **4**.

Anal. Calcd for $C_9H_{16}Cl_2$: C, 55.39; H, 8.27. Found: C, 55.39; H, 8.43.

***trans*-1,1-Dichloro-2,3-dipropylcyclopropane** (4) was prepared as described for **1**. The cyclopropane was obtained pure in 82% yield, bp 131–136° (86 mm), $n^{25}D$ 1.4520.

Anal. Calcd for $C_9H_{16}Cl_2$: C, 55.39; H, 8.27; Cl, 36.34. Found: C, 55.54; H, 8.35; Cl, 36.08.

***trans*-5-Chloro-6-ethoxy-4-nonene** (3). **A. From 4.**—A mixture of **4** (7.81 g, 0.04 mol), absolute ethanol (150 ml), and silver nitrate (7.70 g, 0.045 mol) was heated at the reflux temperature for 48 hr. The cooled mixture was filtered and alcohol was removed (rotatory evaporator). The residue was extracted with petroleum ether (350 ml, bp 55–67°) and washed with two 50-ml portions of water, and the resulting solution was dried ($MgSO_4$) and concentrated. The residue (7.35 g) was chromatographed on alumina (150 g) using petroleum ether as eluent. The first fraction (6.25 g) was recovered **4** (80% recovery). The second compound eluted, and the only product detected, was *trans*-5-chloro-6-ethoxy-4-nonene (**3**, 0.97 g, 12% yield, $n^{25}D$ 1.4420). The ether **3** showed the following spectral data: ir, $\nu_{C=C}$ (1625 cm^{-1}), ν_{C-O-C} (1117 and 1092 cm^{-1}); nmr (20% in CCl_4), C=**CH** (triplet, τ 4.40, J = 7 cps, wt 1), **H_2C**—O—**CH** (complex, τ 6.28–7.08, wt 3), C=C—**CH_2** (quartet, τ 7.81, J = 7 cps, wt 2), and **CH_2** and **CH_3** (complex, τ 8.27–9.18, wt 15).

Anal. Calcd for $C_{11}H_{21}OCl$: C, 64.53; H, 10.34. Found: C, 64.84; H, 10.04.

B. From 1.—The reaction of **1** (7.81 g) with ethanolic silver nitrate was carried out as described for **4**. There was obtained recovered starting material (1.16 g, $n^{25}D$ 1.4471) and *trans*-5-chloro-6-ethoxy-4-nonene (5.27 g, 64% yield, $n^{25}D$ 1.4421). A small third fraction (0.82 g) was obtained which was principally **3**; the small impurity was not characterized. The nonene **3** was identical (ir and nmr spectroscopy and glpc, silicon oil, DC-710, 20% on Chromosorb W) with the product obtained in A, above.

Kinetic Experiments.—The cyclopropane **4** (1.9513 g, 0.0100 mol) was diluted to the mark in a 50-ml volumetric flask with purified ethanol.[14] Approximately 0.0015 mol (0.2548 g) of silver nitrate was placed quantitatively in each of a number of 50-ml, round-bottom flasks wrapped with tin foil. Three pieces of clean boiling chips and 5 ml of stock cyclopropane solution were added to each flask which were fitted with condensers and drying tubes wrapped with aluminum foil. The flasks were placed in an oil bath maintained at 80.8 ± 0.2°. The flasks were removed successively at intervals from 12 to 525 hr and the contents were cooled quickly with an ice bath. In each case, the mixture was transferred quantitatively to a 250-ml volumetric flask and diluted to the mark with 0.1 *N* potassium nitrate solution containing 0.05% of gelatin. Aliquots of these solutions were pipetted and titrated with 0.1000 *N* standard potassium chloride solution using an amperometric method.[15]

The resulting rate constant was $k_{trans} = 5.33 \times 10^{-7}$ sec^{-1}.

By a similar procedure the rate of reaction of **1** was found to be $k_{cis} = 1.29 \times 10^{-5}$ sec^{-1}. The ratio of k_{cis}/k_{trans} was 24.2.

***trans*-6-Ethoxynonene-4** (9).—The reduction of **3** (0.641 g, 0.003 mol) was carried out essentially as described for a similar reduction of 2-chloro-2-cyclotridecen-1-ol.[8] The product, collected at 57–70° at 32 mm (80% yield), contained no starting material as determined by glpc (silicon oil, DC 710, 20% on Chromosorb W, 3/4 in. × 80 in. column at 100°) and was nearly pure **9**. A sample collected from the glpc described above showed the following properties: ir, $\nu_{C=C}$ (1662 cm^{-1}), ν_{C-O-C} (1115, 1090 cm^{-1}), and $\nu_{CH=CH\,(trans)}$ (975 cm^{-1}). The nmr spectrum (20% in CCl_4) showed C=**CH** (multiplet, τ 4.22–5.00, wt 2), **H_2O**—O—**CH** (multiplet, τ 6.27–7.08, wt 3), C=C—**CH_2** (quartet, τ 7.97 J = 7 cps, wt 2), and **CH_2** and **CH_3** (complex, τ 8.28–9.27, wt 15).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.38; H, 12.97.

Registry No.—**1**, 17288-67-4; **3**, 17322-88-2; **4**, 17288-68-5; **9**, 17288-69-6.

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[12] Obtained from Chemical Samples Co., Columbus, Ohio.

[13] Obtained from Mallinckrodt Chemical Works, St. Louis, Mo.

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Oligomerization Catalysts. III. Cyclocodimerization of Conjugated Dienes with Acetylenic Hydrocarbons Catalyzed by Iron(0) Complexes. Synthesis of 1,2-Diphenyl-1,4-cyclohexadiene

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In the first two communications of this series[1,2] we described bis(cyclooctatetraene)iron ($Fe(COT)_2$), a new π complex of zerovalent iron, and the activity of this catalyst, which promotes both the oligomerization of butadiene to 1,3,6,10-*n*-dodecatetraene and to 1,5-cyclooctadiene and the codimerization of butadiene with ethylene to *cis*-1,4-hexadiene.

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[2] A. Carbonaro, A. L. Segre, A. Greco, C. Tosi, and G. Dall'Asta, *J. Amer. Chem. Soc.*, **90**, 4453 (1968).