

## Steric Effects in the Solvolysis of *cis*- and *trans*-13,13-Dichlorobicyclo[10.1.0]tridecane<sup>1</sup>

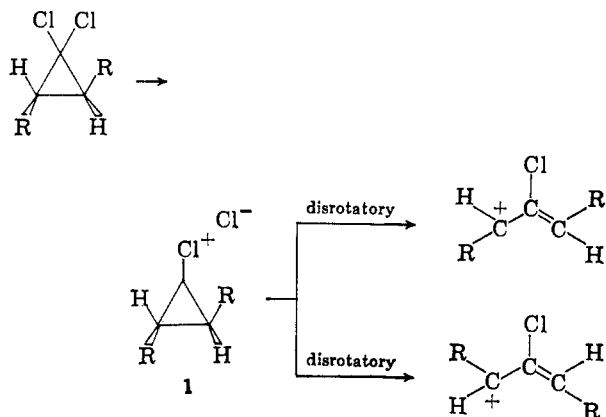
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A comparison of the ease of ring expansion of *gem*-dihalocyclopropanes derived from *cis*- and *trans*-cyclododecene, by solvolysis in the presence of silver ion, has shown that the *cis* isomer undergoes facile ring expansion while the *trans* isomer is unaffected under the reaction conditions employed. Reaction of *cis*-13,13-dichlorobicyclo[10.1.0]tridecane (**3a**) with ethanolic silver nitrate gave essentially a quantitative yield of 1-ethoxy-2-chloro-2-cyclotridecene. Reaction of **3a** with hot aqueous silver nitrate gave essentially a quantitative yield of *trans*-2-chloro-2-cyclotridecen-1-ol (**5**). The stereochemistry of **5** was determined by its reduction to *trans*-2-cyclotridecen-1-ol, and its structure was determined by oxidation to 2-chloro-2-cyclotridecen-1-ol.

Current evidence<sup>3,4</sup> indicates that *gem*-dihalocyclopropanes undergo ring expansion by ionization of a carbon-chlorine bond, with subsequent or concerted collapse of the resulting cyclopropyl cation. Such reactions involving carbonium ions are thought to occur by

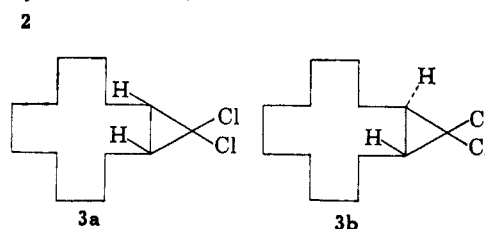


a disrotatory process<sup>5,6</sup> in which the substituent located *trans* to the leaving group rotates outward. Application of these principles has afforded a satisfactory explanation<sup>6,7</sup> for some rather impressive differences in ease of ring expansion of isomeric halocyclopropanes.

As part of our general interest in ring expansions of *gem*-dihalocyclopropanes, we wished to determine whether or not there was a marked difference in ease of ring expansion of products derived from larger ring carbocycles, and for this purpose the ring expansion of *cis*- and *trans*-13,13-dichlorobicyclo[10.1.0]tridecane was examined.

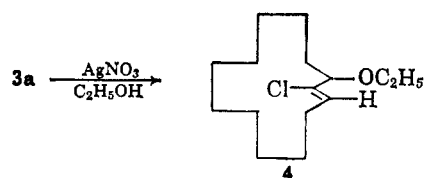
The parent hydrocarbon, cyclododecene, forms an equilibrium mixture<sup>8</sup> of *trans*-*cis* isomers in the approximate ratio 60:40, and this mixture was used to prepare a mixture of *cis*- and *trans*-13,13-dichlorobicyclo[10.1.0]tridecane (**3a** and **b**, 80% yield). Analysis of the mixture of cyclopropanes by gas-liquid partition chromatography (glpc) (by enrichment with authentic<sup>9</sup>

*cis*- and *trans*- cyclododecene →



**3b**) showed the mixture to contain **3a** and **b** in the ratio ~35:65. The nuclear magnetic resonance (nmr) spectrum of the mixture was surprisingly simple, showing methylene protons near  $\tau$  8.26 and methine protons near  $\tau$  8.82, with a ratio of 20:2.

Reaction of the mixture of *cis*- and *trans*-**3** with hot ethanolic silver nitrate<sup>3b</sup> gave 1-ethoxy-2-chloro-2-cyclotridecene (**4**) in 35% yield. Analysis of the crude



reaction mixture by glpc showed that the *cis* isomer **3a** had completely reacted and that the *trans* isomer **3b** was unchanged. Separation of the mixture by elution chromatography on alumina gave about 65% yield (essentially 100% recovery) of **3b** and a 35% yield of **4**; no **3a** was detected.

The reaction was repeated using the pure *trans* isomer **3b**. The starting cyclopropane was recovered (95%) and there was no evidence for the formation of **4**. Thus, *trans*-**3** is unaffected by ethanolic silver nitrate under the conditions employed, while *cis*-**3** undergoes complete conversion to the ring expanded product.

Molecular models suggest that both **3a** and **b** can undergo disrotatory<sup>5,6</sup> ring opening through an intermediate cyclopropyl cation; however, inspection of the probable transition states for the two cases reveals more transannular steric constraint for the *trans* isomer than for the *cis* isomer. This can be seen from the abbreviated formulas shown in eq 1 and 2. Disrotatory ring opening of the *trans* isomer (eq 1) leads to an intermediate cation in which the H and R groups are coplanar and *cis*, and thus interact sterically. Similar disrotatory ring opening of the *cis* isomer (eq 2) leads

(1) This work was supported by Grants GP-3357 and GP-6169X from the National Science Foundation.

(2) From the Ph.D. Thesis of R. J. Sperley, The University of Minnesota, 1966.

(3) (a) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Am. Chem. Soc.*, **78**, 1437 (1956); (b) P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958).

(4) W. E. Parham and E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

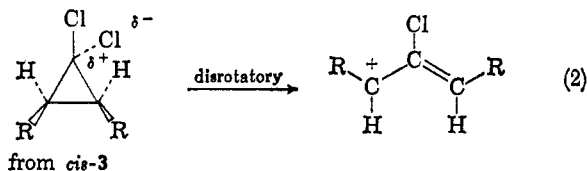
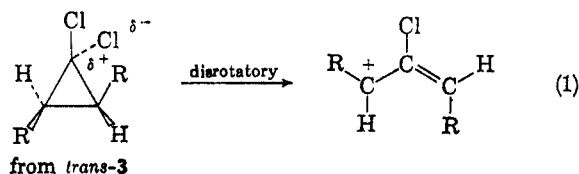
(5) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(6) (a) S. T. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965); (b) C. H. DePuy, L. G. Swnaek, J. W. Hausser, and W. Wiedman, *ibid.*, **87**, 4006 (1965).

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

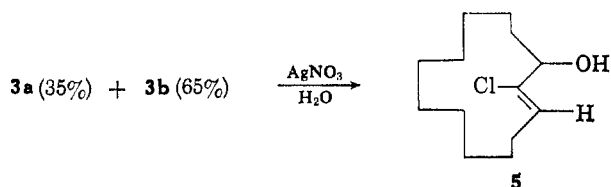
(8) M. Suoboda and J. Sicher, *Chem. Ind. (London)*, 290 (1959).

(9) J. M. Locke and E. W. Druck, *ibid.*, 1727 (1965).



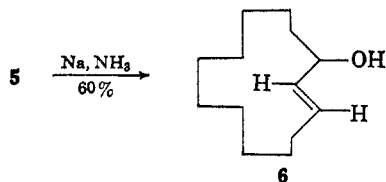
to an intermediate cation with less steric constraint in which two hydrogen atoms interact.<sup>10</sup>

Ring opening as shown in eq 2 predicts that the olefinic group in the product should have the *trans* structure. This appears to be the case. Reaction of *trans-cis*-3 (65:35) with silver nitrate in boiling dioxane-water gave a 30% yield of *trans*-2-chloro-2-cyclotridecen-1-ol (5). Analysis of the crude reaction



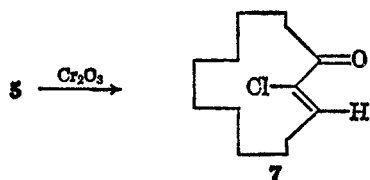
mixture by glpc showed that the *cis* isomer 3a was completely reacted and that the *trans* isomer 3b was unchanged. Separation of the mixture by elution chromatography gave about 65% *trans*-3 (100% recovery) and a 30% yield of 5.

The stereochemistry of 5 was determined by its reduction, with sodium and liquid ammonia, to *trans*-2-cyclotridecen-1-ol (6, 60% yield). The infrared



spectrum of 6 showed  $\nu_{C=C}$  at  $1663\text{ cm}^{-1}$  and strong absorption near  $980\text{ cm}^{-1}$  indicative of *trans* hydrogen out of plane bending.<sup>11</sup> Since reduction of vinyl halides with sodium and liquid ammonia is thought to be stereospecific<sup>12</sup> (retention), it was concluded that the  $C(-Cl)=C<H$  group in 5 had the *trans* configuration.

That no rearrangements had occurred during reactions of 3a with silver nitrate was established by conversion of 5, by oxidation with chromic acid, to 2-



(10) Examination of the probable transition states shown in eq 1 and 2 suggest that there may be an appreciable difference in the ease of ring expansion of *gem*-dihalocyclopropanes derived from acyclic *cis* and *trans* olefins. An evaluation of the magnitude of such differences is being made.

(11) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 24.

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

chloro-2-cyclotridecen-1-one. The 2,4-dinitrophenylhydrazone of 7 was identical with an authentic sample.<sup>13</sup>

### Experimental Section

*cis*- and *trans*-13,13-Dichlorobicyclo[10.1.0]tridecane (3a, b).—In a 500-ml three-necked flask fitted with a magnetic stirrer, reflux condenser, dropping funnel, and dry nitrogen inlet was placed cyclododecene<sup>14</sup> [86% cyclododecene, 14% cyclododecane; *cis-trans*-cyclododecene (35:65), 14.43 g, 0.075 mole], fresh sodium methoxide (14.6 g, 0.30 mole), and dry, olefin-free petroleum ether (bp 30–60°, 140 ml). The mixture was cooled (0°) and ethyl trichloroacetate (50.0 g, 0.26 mole) was added over a 30-min period. The mixture was stirred at ice-bath temperature for 4 hr and allowed to warm to room temperature and stir for an 8-hr period. Water (400 ml) was added and the mixture was extracted with petroleum ether (50 ml). The water-washed petroleum ether was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated, and the red oil (26.4 g) was chromatographed on alumina (400 g) using petroleum ether (bp 60–68°) as eluent. The product (21.4 g,  $n_D^{20}$  1.5026, obtained with 900 ml of eluent) was distilled through an 8-in. vacuum-jacketed spiral wire column to give, after a forerun, 18.44 g (85% yield) of product (bp 135–143° at 0.1 mm,  $n_D^{20}$  1.5086–1.5091). Analysis of the three fractions collected in this distillation by glpc (DC-710 at 225°) showed the first (8.85 g) to contain about 10% starting olefin and 3a and b in the ratio 35:65, the second and third fractions (9.59 g) only *cis*-cyclopropane (35%) and *trans*-cyclopropane (65%). Identification of *trans*-cyclopropane was achieved by injection of authentic<sup>15</sup> 3b.

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{22}\text{Cl}_2$ : C, 62.65; H, 8.90; Cl, 28.45. Found: C, 62.43; H, 8.81; Cl, 28.61.

The infrared spectrum of the adduct (neat) showed  $\nu_{\text{cyclopropane}}$  (1010 and  $1025\text{ cm}^{-1}$ ),  $\nu_{\text{C-Cl}}$  (823, 810, and  $790\text{ cm}^{-1}$ ). The nmr spectrum (20%  $\text{CCl}_4$ ) showed  $\text{CH}_2$  (complex near  $\tau$  8.26, wt 20) and cyclopropyl H (complex near  $\tau$  8.82, wt 2).

#### Reactions of *cis-trans*-13,13-Dichlorobicyclo[10.1.0]tridecane.

**A. With Ethanolic Silver Nitrate.**—In a 300-ml flask fitted with a magnetic stirrer and reflux condenser was placed *cis*- and *trans*-3 [*cis-trans* (35:65), 10.0 g, 0.04 mole], silver nitrate (7.7 g, 0.045 mole), and absolute ethanol (150 ml). The mixture was heated at the reflux temperature for 5 days during which time light was excluded. The mixture was cooled and filtered to give 4.1 g of purple solid and a yellow solution. The solution was diluted with water and the resulting mixture was extracted with four 100-ml portions of petroleum ether (bp 60–68°). The combined ether solution was washed with water (200 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). The oil (10.01 g) obtained from the ether solution was chromatographed on alumina (300 g) using petroleum ether (bp 60–68°) as eluent. Three fractions were obtained: (1) 5.48 g,  $n_D^{25}$  1.5087; (2) 1.42 g,  $n_D^{25}$  1.5031; and (3) 3.03 g,  $n_D^{25}$  1.4926. The fractions were analyzed by glpc (DC-710, 225°) showing 1 to be approximately 95% 3b, 2 to be 56% 3b and 44% 4, and 3 to be 100% 4. The glpc analysis showed that essentially all of the *trans*-cyclopropane was recovered unchanged, and that all of the *cis*-cyclopropane had been converted to 4.

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{27}\text{ClO}$  (fraction 3): C, 69.60; H, 10.51; Cl, 13.70. Found: C, 69.48; H, 10.43; Cl, 13.84.

The infrared spectrum (neat) of 1-ethoxy-2-chloro-2-cyclotridecene showed  $\nu_{\text{C-H}}$  ( $3050\text{ cm}^{-1}$ ),  $\nu_{\text{C=C}}$  ( $1638\text{ cm}^{-1}$ ), and  $\nu_{\text{C-OR}}$  ( $1110$  and  $1090\text{ cm}^{-1}$ ). The nmr spectrum (20%,  $\text{CCl}_4$ ) showed  $\text{CH}$  (triplet, 4.18, 4.29, 4.40  $\tau$ ,  $J = 8$  cps, wt 1),  $\text{CHOR}$  (triplet,  $\tau$  6.18, 6.28, 6.39,  $J = 6$  cps, wt 1),  $\text{OCH}_2\text{CH}_3$  (quartet,  $\tau$  6.56, 6.67, and 6.79;  $J = 7$  cps; wt 2), allylic H (multiplet,  $\tau$  7.50–8.0, wt 2),  $\text{CH}_2$  (complex singlet centered at  $\tau$  8.71, wt 18),  $\text{OCH}_2\text{CH}_3$  (triplet,  $\tau$  8.77, 8.88, 8.99;  $J = 7$  cps; wt 3).

**B. Reaction with Aqueous Silver Nitrate.**—The reaction of *cis*- and *trans*-13,13-dichlorobicyclo[10.1.0]tridecane [3.02 g, 0.012 mole, *cis-trans* (35:65)] with silver nitrate (3.66 g, 0.024 mole) in water (50 ml) and dioxane (50 ml) was carried out at the reflux temperature for 48 hr in the absence of light. The mixture was processed as described in A. The crude oil (2.96 g) was chromatographed on alumina (60 g). Elution of the column

(13) W. E. Parham and R. J. Sperley, *ibid.*, in press.

(14) Columbian Carbon Co., Princeton, N. J.

(15) Kindly supplied by J. N. Locke, The International Synthetic Rubber Co. Ltd., Brunswick House, Southampton Hants, England; cf. ref 9.

with petroleum ether (bp 60–68°) gave 2.01 g of oil which was shown by glpc analysis (DC-710, 225°) to be >95% **3b** (100% recovery). Elution of the column with diethyl ether gave an oil (0.89 g, mp 30–37°) which crystallized to give 2-chloro-2-cyclotridecen-1-ol (**5**) as a colorless solid (mp 45–46°, 0.86 g, 93% yield based on *cis-3a*) upon recrystallization from pentane-ether.

*Anal.* Calcd for C<sub>13</sub>H<sub>23</sub>ClO: C, 67.66; H, 10.04; Cl, 15.36. Found: C, 67.95; H, 10.24; Cl, 15.19.

The infrared spectrum (Nujol mull) of **5** showed  $\nu_{OH}$  (3300 cm<sup>-1</sup>),  $\nu_{C=C}$  (1658 cm<sup>-1</sup>), and  $\nu_{C-Cl}$  (845 cm<sup>-1</sup>). The nmr spectrum (15%, CCl<sub>4</sub>) showed CH=CCl (triplet,  $\tau$  4.19, 4.21, and 4.33;  $J = 7$  cps, wt 1), CHOH (triplet,  $\tau$  5.68, 5.79, and 5.90;  $J = 7$  cps, wt 1), allylic H (multiplet,  $\tau$  7.6–8.0, wt 2), COH (singlet,  $\tau$  8.08, wt 1), CH<sub>2</sub> (complex singlet centered at  $\tau$  8.73, wt 18).

**Oxidation of 2-Chloro-2-cyclotridecen-1-ol to 2-Chloro-2-cyclotridecen-1-one.**—In a 25-ml flask filtered with a magnetic stirrer was placed a solution of **5** (0.69 g, 0.003 mole) in acetone (20 ml) and the solution was cooled to 0–5°. A solution of sodium dichromate (0.298 g, 0.001 mole), water (10 ml), and concentrated sulfuric acid (0.39 g, 0.004 mole) was added dropwise with stirring. The mixture was stirred for an additional 4 hr at ice-water temperature and was then poured into water (100 ml). The resulting mixture was extracted with three 50-ml portions of ether, and the combined ether extract was washed with saturated sodium bicarbonate (10 ml), water (25 ml), and was then dried (Na<sub>2</sub>SO<sub>4</sub>). The solution was filtered and concentrated to give 0.40 g of crude 2-chloro-2-cyclotridecen-1-one. The ketone

was characterized by conversion to the 2,4-dinitrophenylhydrazone **7** [mp and mmp 131–132°,  $\lambda_{max}^{95\% \text{ alcohol}}$  371 m $\mu$  ( $\epsilon$  24,000), lit.<sup>13</sup>  $\lambda_{max}^{95\% \text{ alcohol}}$  372 m $\mu$  ( $\epsilon$  24,070)].

**Reaction of 2-Chloro-2-cyclotridecen-1-ol with Sodium and Liquid Ammonia.**—Liquid ammonia (25 ml) was added to a 100-ml flask fitted with a magnetic stirrer, Dry Ice-acetone condenser, dropping funnel, and gas inlet tube. Sodium (0.23 g, 0.01 g-atom) was added in small pieces. Upon solution of the sodium, a pentane solution of 2-chloro-2-cyclotridecen-1-ol (0.4 g, 0.0017 mole, 10 ml) was added dropwise. The mixture was stirred for 1 hr, and ammonium chloride (~10 g) and then water (50 ml) was added slowly. The mixture was extracted with ether (100 ml) and the ether extract was washed with water, aqueous sodium bicarbonate, and with water. The dried (Na<sub>2</sub>SO<sub>4</sub>) extract was filtered and concentrated. The yellow oil that was obtained (0.25 g) solidified on cooling and was recrystallized from pentane. The yield of *trans*-2-cyclotridecen-1-ol (**6**) was 0.2 g (mp 38–39°, 60% yield).

*Anal.* Calcd for C<sub>13</sub>H<sub>24</sub>O: C, 79.53; H, 12.32. Found: C, 79.80; H, 12.23.

The infrared spectrum (mull) of **6** showed  $\nu_{OH}$  (3480 cm<sup>-1</sup>),  $\nu_{C=C}$  (1663 cm<sup>-1</sup>), and  $\nu_{CH=CH}$  (*trans*) (980 cm<sup>-1</sup>). The nmr spectrum (15%, DCCl<sub>3</sub>) showed CH=CH (multiplet,  $\tau$  4.42–4.26, wt 2), allylic H (multiplet,  $\tau$  7.2–8.18, wt 3), OH (singlet,  $\tau$  8.38, wt 1), CH<sub>2</sub>,  $\tau$  8.72, wt 18).

**Registry No.**—**3a**, 5548-51-6; **3b**, 5775-08-6; **4**, 7732-06-1; **5**, 7732-07-2; **6**, 7732-09-4; **7**, 7732-08-3.

## Reactions of Enol Ethers with Carbenes. VIII. Rearrangement of the Dichlorocyclopropane Derived from 1-Ethoxycyclododecene<sup>1</sup>

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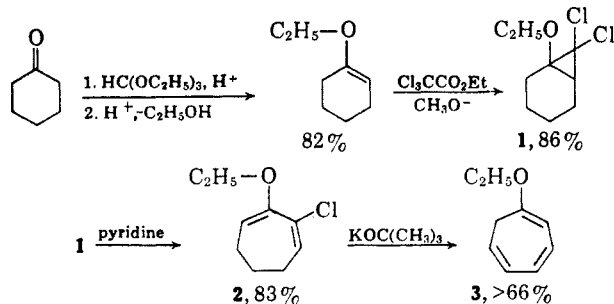
The dichlorocyclopropane prepared (96% yield) from the large-ring enol ether 1-ethoxycyclododecene (**4**) undergoes facile ring expansion to give 2-ethoxy-3-chloro-1,3-cyclotridecadiene (**6**, 87% yield). This result is in sharp contrast to the analogous cyclopropanes derived from intermediate-ring enol ethers which resist expansion and give, under more vigorous conditions, products derived by transannular processes. The stereochemistry of **6** is discussed and a variety of chemical reactions is described. A new synthesis of heterocyclic *m*-cyclophanes is reported by reaction of **6** with hydrazine, or by reaction of the derived 1-ethoxy-1-cyclotridecen-3-eyne (**13**, 74% yield from **6**) with hydrazine or 2,4-dinitrophenylhydrazine. The conversion of cyclododecanone to cyclotridecanone constitutes a new method for ring homologation.

The conversion of cyclohexanone to 1-ethoxycycloheptatriene (**3**) (Scheme I), by a process involving reaction of the intermediate **1** with hot pyridine or quinoline, was described in an earlier communication.<sup>3</sup> It was also observed that dihalocyclopropanes derived

from enol ethers of intermediate-sized rings, such as 1-ethoxycycloheptene and 1-ethoxycyclooctene, were more resistant to ring expansion and, under vigorous conditions (hot quinoline), gave products resulting from transannular reactions. It was anticipated that this reaction sequence might offer an attractive route for increasing by one the number of carbon atoms in cyclic systems of larger rings in which ring strain is diminished and transannular reactions are less likely. This has been shown to be the case, and this paper is concerned with the synthesis and reactions of 1-ethoxy-13,13-dichlorobicyclo[10.1.0]tridecane (**5**) (Scheme II) and the products derived from it by ring expansion.

1-Ethoxycyclododecene (**4**) was prepared in 78% yield by the acid-catalyzed elimination of ethanol from cyclododecanone diethyl ketal (92% yield from cyclododecanone). The data observed [nuclear magnetic resonance (nmr) and gas-liquid partition chromatography (glpc)] for this enol ether established it to be essentially one<sup>4</sup> stereoisomer (>90%), and the chemical

SCHEME I



(1) This work was supported by Grants GP-3357 and GP-6169X from the National Science Foundation.

(2) From the Ph.D. Thesis of R. J. Sperley, the University of Minnesota, 1966.

(3) W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kunel, and R. M. Dodson, *J. Am. Chem. Soc.*, **87**, 321 (1965).

(4) The parent hydrocarbon, cyclododecene, forms an equilibrium mixture of *trans-cis* isomers of about 60:40. Cf. M. Suoboda and J. Sicher, *Chem. Ind. (London)*, 290 (1959).