Solvolysis of Cyclopropyl Halides. III. 2,3-Diphenylcyclopropyl Chlorides[1]

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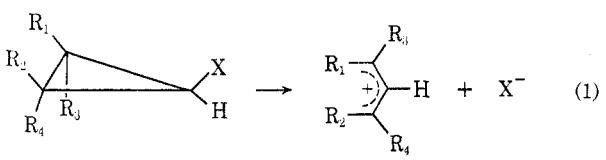
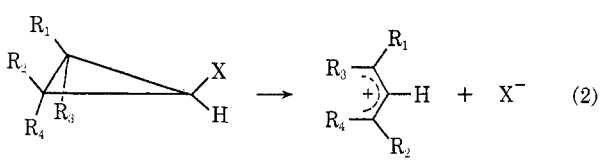
The isomeric 2,3-diphenylcyclopropyl chlorides were prepared by the addition of dichlorocarbene tc *cis*- and *trans*-stilbene followed by controlled potential electrolytic reduction. Solvolysis of *cis*-2,*cis*-3-diphenylcyclopropyl chloride, *trans*-2,*trans*-3-diphenylcyclopropyl chloride, and *cis*-2,*trans*-3-diphenylcyclopropyl chloride in acetic acid afforded as the sole product α-phenylcinnamyl acetate. The kinetic data are considered in terms of the two alternate disrotatory modes of ring opening in solvolysis.

The solvolyses of cyclopropyl derivatives proceed with concerted ring opening to form allylic products in most cases.[3] The process has been characterized as an electrocyclic transformation, the stereochemistry of which is governed by orbital symmetry considerations proposed by Woodward and Hoffmann.[4] Both kinetic[5-7] and product[8] studies are in support of this proposal. The ring-opening process involves cleavage of the 2,3 bond with rotation about the 1,2 and 1,3 bonds to bring the substituents into a coplanar configuration. The predicted stereochemistry involves a disrotatory ring opening with the substituents cis to the leaving group rotating inwardly and the substituents trans to the leaving group rotating outwardly as shown in eq 1.



(1)

Based on a consideration of steric effects in the transition state of the ring-opening process it has been suggested[5] that under certain circumstances, the disrotatory mode of ring opening may proceed with the opposite rotations, as shown in eq 2. This alternate



(2)

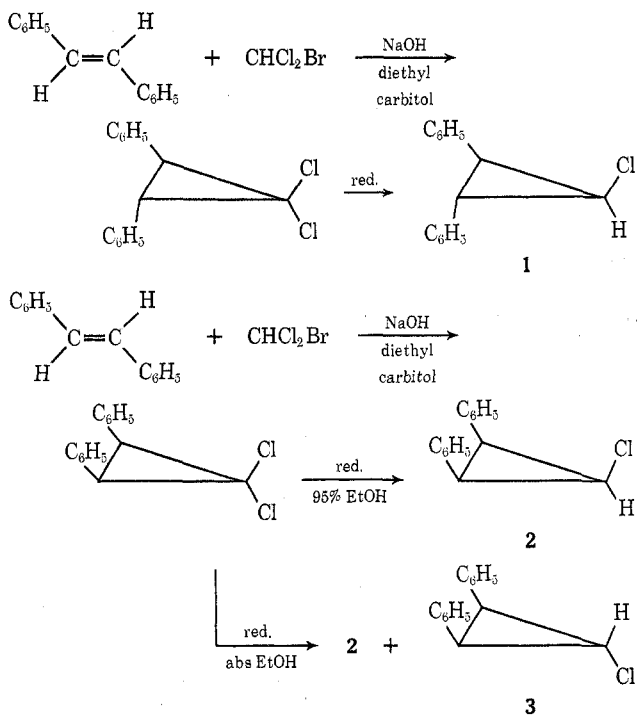
mode of disrotatory opening has been proposed for the solvolysis of *cis*-2-phenylcyclopropyl chloride.[5]

The isomeric 2,3-diphenylcyclopropyl chlorides have been prepared in order to establish the mode of ring opening in the presence of very large steric and conjugative effects.

Results

The isomeric diphenylcyclopropyl chlorides were prepared by the addition of dichlorocarbene to *cis*- or *trans*-stilbene followed by controlled-potential electrolysis of the intermediate cyclopropyl dichloride. The carbene addition to the deactivated double bond of stilbene was accomplished by generation of dichlorocarbene from the haloform and sodium hydroxide in diethylcarbitol.[9] The partial reduction of the cyclopropyl dichlorides to the monochlorides was best accomplished by controlled-potential electrolysis[10] at a massive mercury electrode in ethanol with tetraethylammonium bromide as the supporting electrolyte.

1,1-Dichloro-*trans*-2,3-diphenylcyclopropane on reduction afforded *cis*-2,*trans*-3-diphenylcyclopropyl chloride (1). 1,1-Dichloro-*cis*-2,3-diphenylcyclopropane on reduction in 95% ethanol afforded *cis*-2,*cis*-3-diphenylcyclopropyl chloride (2), whereas on reduction in ab-



(1) Presented in part: J. W. Hausser and J. T. Uchic, Abstracts, Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 1970, p 49.

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(4) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); see also R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(5) J. W. Hausser and N. J. Pinkowski, *J. Amer. Chem. Soc.*, **89**, 6981 (1967); J. W. Hausser and M. J. Grubber, *J. Org. Chem.*, **37**, 2648 (1972).

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(7) P. v. R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, **88**, 2868 (1966); P. v. R. Schleyer, Abstracts, 20th National Organic Symposium of the American Chemical Society, Burlington, Vt., June 1967, p 8; P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schollkopf, J. Paust, and K. Fellenberger, *J. Amer. Chem. Soc.*, **94**, 125 (1972); W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, **94**, 133 (1972).

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(9) G. C. Robinson, *Tetrahedron Lett.*, 1749 (1965).

(10) L. Meites, *Anal. Chem.*, **27**, 1116 (1955).

TABLE I

SOLVOLYSES OF THE ISOMERIC 2,3-DIPHENYLCYCLOPROPYL CHLORIDES IN ACETIC ACID[a]

Compd	Temp, °C	k_1, sec^{-1}	k_{rel}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
cis-2,*cis*-3-Diphenyl-	95.2	$3.59 \pm 0.08 \times 10^{-6}$	1.0	31.2	+0.8
cyclopropyl Chloride	110.1	$2.01 \pm 0.01 \times 10^{-5}$			
(2)	125.3	$9.68 \pm 0.09 \times 10^{-5}$			
trans-2,*trans*-3-Diphenyl-	40.0	$3.64 \pm 0.02 \times 10^{-5}$			
cyclopropyl Chloride	50.1	$1.23 \pm 0.02 \times 10^{-4}$			
(3)	65.1	$6.25 \pm 0.06 \times 10^{-4}$			
	95.2[b]	1.15 ± 10^{-2}	3200	23.1	−5.1
cis-2,*trans*-3-Diphenyl-	65.1	$9.20 \pm 0.06 \times 10^{-6}$			
cyclopropyl Chloride	80.4	$5.16 \pm 0.08 \times 10^{-5}$			
(1)	95.2	$2.46 \pm 0.04 \times 10^{-4}$	69	26.3	−4.1

[a] Anhydrous acetic acid with 0.04 *M* sodium acetate. [b] Extrapolated value.

solute ethanol it afforded a mixture of **2** and *trans*-2,-*trans*-3-diphenylcyclopropyl chloride (**3**).

Partial separation of **2** and **3** is possible by column chromatography. From the nmr spectrum and thin layer chromatography the only contaminant in **3** was shown to be the isomer **2**. The labile character of **3** required the utilization of freshly prepared material for the kinetic experiments. The other isomers, **1** and **2**, are stable and do not require special precautions.

The stereochemical assignments for **1–3** are based primarily on the assignment of chemical shifts and coupling constants in their nmr spectra.[11] The assignments were also consistent with the expected product distributions from the reduction.[12]

The product of solvolyses of **1–3** in acetic acid was shown to be the thermodynamically favored *trans*-α-phenylcinnamyl acetate (**4**) in all cases.[13] The starting chlorides **1–3** were recovered from the solvolysis mixture and were shown to be unchanged.

The kinetics of solvolysis of **1–3** were followed by formation of **4** as seen in the ultraviolet spectrum of the reaction mixture. The kinetics of the solvolysis of the samples of **3** containing the isomer **2** could be followed owing to the large difference in rates of **2** and **3**. The kinetics in all cases are first order in the chloride. The first-order rate constants and the activation parameters are presented in Table I.

Discussion

The relative rates presented in Table I are consistent with a disrotatory ring-opening process. Compound **3** in the disrotatory opening has both phenyl groups moving outwardly and away from each other. Compound **3** would be expected to have the fastest rate of solvolysis. Compound **1** in a disrotatory ring opening necessarily has one phenyl group moving inwardly and one phenyl group moving outwardly. The steric effect experienced by the phenyl group moving inwardly would prevent the phenyl group from assuming complete coplanarity,[14] resulting in less stabilization of the developing cation and a slower rate of solvolysis than compound **3**.

(11) J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 2249 (1962); G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962); D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963).

(12) A. J. Fry and R. H. Moore, *J. Org. Chem.*, **33**, 1283 (1968).

(13) The predicted allylic products would be expected to isomerize to the trans isomer under the reaction conditions. See V. Buss, R. Gleiter, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3927 (1971), and references cited therein.

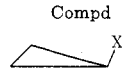
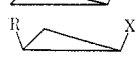
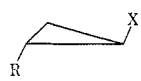
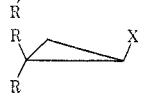
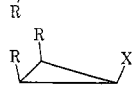
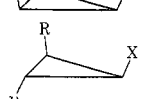
(14) A. F. Hegarty and J. E. Dubois, *Tetrahedron Lett.*, 4839 (1968); J. E. Dubois and A. F. Hegarty, *J. Chem. Soc. B*, 638 (1969).

Compound **2** in the predicted mode of disrotatory opening (eq 1) would experience severe steric compression owing to the rotation of both phenyl groups inwardly and toward each other. The rate of solvolysis of **2** by this mode must necessarily be very slow. It is for this compound that the alternate mode of ring opening would seem to have an advantage.

Additional insight into the mode of disrotatory opening for compound **2** can be gained from a consideration of the relative rates of the complete series of phenyl-substituted cyclopropyl chlorides and methyl-substituted cyclopropyl tosylates shown in Table II.

TABLE II

RELATIVE RATES OF SOLVOLYSIS OF SUBSTITUTED CYCLOPROPYL DERIVATIVES IN ACETIC ACID

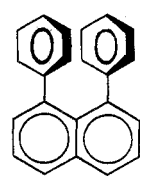
Compd	Relative rate[a] (R = C_6H_5; X = Cl)	Relative rate[b] (R = CH_3; X = OTs)
	10^{-4} [c]	0.18
	1.0[d]	1.0
	4[d]	24
	6[d]	75
	145	0.39
	10,000	81
	465,000	6700

[a] At 95°. [b] From ref 7. [c] Estimated from the rate of the tosylate given in ref 3. [d] Extrapolated from the data given in ref 5.

If the predicted mode of disrotatory ring opening (eq 1) is assumed to be operative in all cases, it would seem that compound **2** is solvolyzing much faster than expected. While **2** is slower than **1** and **3**, it is faster than the monophenyl-substituted cyclopropyl chlorides and 2,2-diphenylcyclopropyl chloride. If the corresponding *cis*-2,*cis*-3-dimethylcyclopropyl tosylate in the series of methyl-substituted cyclopropyl tosylates reported by Schleyer[7,8] is compared to **2** in the phenyl-substituted cyclopropyl chloride series, an apparent discrepancy is observed. *cis*-2,*cis*-3-Dimethylcyclopropyl tosylate shows a very minor acceleration over

the unsubstituted parent compound, suggesting that the steric effect of the methyl groups virtually cancels the inductive stabilization, whereas **2** shows a very large acceleration in spite of the substantial steric and inductive effects.

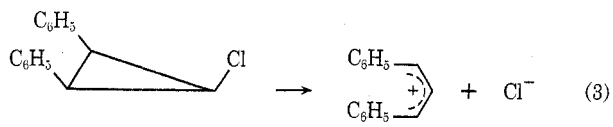
An estimate of the magnitude of the steric effect in the solvolysis of **2** can be made by a consideration of model compounds. The phenyl groups in 1,8-diphenylnaphthalene (**5**) are forced out of conjugation



5

with the naphthalene ring and assume a conformation parallel to each other.[15] The substitution on one of the phenyl groups in **5** allows resolution of optical isomers. The rate of racemization is related to the barrier for just one phenyl group to become coplanar with the naphthalene ring. The calculated barrier is 16 kcal/mol.

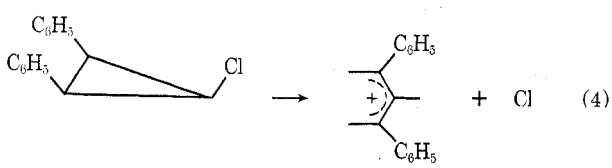
The transition state for solvolysis of **2** by the predicted mode (eq 3) of ring opening would involve ap-



(3)

proach to the same configurational requirements as **5**. While the geometry of the cation in eq 3 is not rigid as is **5**, there still should be an appreciable loss in conjugative stabilization in the transition state owing to the crowding of the phenyl groups, and in fact an inductive destabilization should result. The fact that **2** solvolyzes faster than monophenylcyclopropyl chlorides and even 2,2-diphenylcyclopropyl chloride calls into question this mode of ring opening for **2**. If the normal mode of ring opening is operative (eq 1), the acceleration must come from a very large strain in the ground state to compensate for the high strain in the transition state.

The alternate mode of disrotatory ring opening (eq 2) suggested as a possibility for *cis*-2-phenylcyclopropyl chloride appears to be the most reasonable proposal to account for the unexpectedly fast rate of solvolysis of **2**. By this mode, shown in eq 4, it is possible to generate a



(4)

degree of stability through conjugative overlap of the phenyl groups with the developing cation as the phenyl groups move outwardly and away from each other. While the favored mode (eq 1) is operative in most cases, the resulting loss of phenyl conjugation in **2**, and possibly *cis*-2-phenylcyclopropyl chloride, should make the less favored alternate mode (eq 2) more competitive. This alternate mode allows a gain in conjugation to offset the energy sacrificed in going to this mode.

The analogous methyl-substituted cyclopropyl derivatives studied by Schleyer[7,8] clearly follow the normal mode (eq 1) in all cases. This difference may lie in the fact that while the methyl group has a large steric effect, it lacks the coplanarity demand required by the phenyl group for stabilization. If the allylic cations that are kinetically formed in the solvolyses are stable at low temperatures in strong acid media it should be possible to decide on the mode of ring opening.

Experimental Section

General.—All melting points are corrected. The microanalyses were performed by Dr. Alfred Bernhardt, Max Planck Institute, Mulheim (Ruhr), Germany, and Crobaugh Laboratories, Cleveland, Ohio. Infrared spectra were recorded on a Beckman IR-20 spectrophotometer using the potassium bromide pellet technique. The ultraviolet spectra were recorded on a Cary Model 14 recording spectrophotometer. For the kinetic runs, a Beckman DU spectrophotometer was employed for absorbance measurements at 253 nm. The nuclear magnetic resonance spectra were obtained with a Varian Model A-60 spectrometer. Chemical shifts in carbon tetrachloride solution are expressed in parts per million (δ) from an internal tetramethylsilane standard.

1,1-Dichloro-*trans*-2,3-diphenylcyclopropane.—In a 100-ml flask was placed a mixture of *trans*-stilbene (0.10 mol, 18.0 g), 25 ml of diethylcarbitol, and sodium hydroxide pellets (0.40 mol, 16.0 g). The contents were vigorously stirred while the bath was heated. When the temperature approached 50°, bromodichloromethane[16] (0.15 mol, 24.6 g) was added in one portion. After 1 hr, the bath reached a maximum temperature of 79°, and then slowly dropped to 74° at the end of the 3.3-hr reaction period. The reaction mixture was poured into water, acidified with dilute hydrochloric acid, and extracted into ether (600 ml). The ether layer was washed with a dilute sodium bicarbonate solution and water, dried ($MgSO_4$), and concentrated. The diethylcarbitol was removed at 65–75° (1 mm) and the unreacted stilbene was removed at 100° (0.1 mm). The residue was transferred to a molecular still and the dichlorocyclopropane was collected as a yellow, viscous liquid, bp 85–90° (0.05–0.01 mm). Redistillation gave 13.7 g (52%) of the desired product as a viscous liquid. Crystallization could be effected from 95% ethanol, and several recrystallizations afforded a white solid: mp 39–41° (lit.[17] mp 39–40.5°); uv max (95% C_2H_5OH) 22 nm (ϵ 17,520), 254 (435), 260 (494), and 264 (382); ir (KBr) 703 (vs), 769 (s), 873 (s), and 1040 cm^{-1} (w); nmr (CCl_4) δ 3.10 (s, 2) and 7.25 ppm (s, 10).

1,1-Dichloro-*cis*-2,3-diphenylcyclopropane.—To a one-neck, 200-ml flask was added 50 ml of diethylcarbitol and sodium hydroxide pellets (0.4 mol, 16.0 g). The reaction mixture was heated to 50° and a mixture of *cis*-stilbene (0.11 mol, 20.0 g) and bromodichloromethane (0.20 mol, 32.8 g) was added in one portion. After 35 min the bath reached a maximum temperature of 80°, and the bath temperature dropped to near 50° at the end of the 2-hr reaction period. The reaction mixture was worked up in essentially the same manner as for the preparation of 1,1-dichloro-*trans*-2,3-diphenylcyclopropane. The product fraction (5.5 g, 19%) was collected at 60–70° (0.1 mm). Crystallization could be effected from 95% ethanol. Several recrystallizations from 95% ethanol gave analytically pure material: mp 56–57°; uv max (95% C_2H_5OH) 225 nm (ϵ 11,580), 253 (450), 259 (476), 262 (470), 265 (385), 267 (shoulder, 325), and 272 (shoulder, 183); ir (KBr) 708 (vs), 730 (m), 762 (s), 771 (s), 819 (vs), 1043 (m), and 1052 cm^{-1} (m); nmr (CCl_4) δ 3.16 (s, 2) and 6.77–7.25 (m, 10).

Anal. Calcd for $C_{15}H_{12}Cl_2$: C, 68.46; H, 4.60. Found: 68.20; H, 4.86.

Controlled-Potential Electrolyses.—Controlled-potential electrolysis experiments were carried out in a double-diaphraghm cell described by Meites.[10] The anode was a strip of bare silver

(15) H. O. House, W. J. Campbell, and M. Gall, *J. Org. Chem.*, **35**, 1815 (1970).

(16) M. S. Kharasch, B. M. Kuderna, and W. Urry, *ibid.*, **13**, 895 (1948).

(17) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Yick-Pui Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

wire 30–40 in. in length, while the cathode was a massive pool of metallic mercury. The reference electrode was an 8-in. length of bare silver wire isolated from the sample compartment by placing it in an immersion tube which contained the ethanolic solution of the electrolyte.

cis-2,*trans*-3-Diphenylcyclopropyl Chloride (1).—Into the electrolysis vessel was added a 0.13 *M* solution of tetraethylammonium bromide in 95% ethanol. A 1.0-g sample of 1,1-dichloro-*trans*-2,3-diphenylcyclopropane was added and the electrolysis was carried out at −1.65 to −2.0 V *vs.* the silver wire reference. When the current reading dropped to 1–2 mA, the electrolysis was stopped. The catholyte was removed and poured into water (500 ml), and the solution was refrigerated overnight. A white solid was obtained which was filtered, washed with water, and air dried to give 0.8 g (92%) of the monochlorocyclopropane, mp 62.5–63.5°. Recrystallization from 95% ethanol gave an analytical sample: mp 63–64°; uv max (95% C_2H_5OH) 222 nm (ε 19,440), 260 (697), 266 (681), and 273 (438); ir (KBr) 704 (s), 750 (s), 764 (s), and 1015 cm^{-1} (w); nmr (CCl_4) δ 2.61 (apparent d, 2), 3.40 (doublet of doublets, 1), and 7.0–7.28 ppm (m, 10).

Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.86; H, 5.78; Cl, 15.47.

cis-2,*cis*-3-Diphenylcyclopropyl Chloride (2).—The reduction of a 1.0-g sample of 1,1-dichloro-*cis*-2,3-diphenylcyclopropane was performed in the electrolysis cell. The solution of tetraethylammonium bromide in 95% ethanol was approximately 0.1 *M*. The reduction was carried out at −1.65 to −2.0 V *vs.* the silver wire reference. The catholyte was poured into 600 ml of water and refrigerated overnight. Filtration gave a solid material which was washed with water and air dried to afford 0.7 g (80%) of product. Recrystallization from 95% ethanol gave 0.5 g of colorless crystals, mp 69–71°. An analytical sample was obtained by vacuum sublimation: mp 71–72°; uv max (95% C_2H_5OH) 220 nm (shoulder, ε 13,690), 255 (433), 261 (473), 265 (shoulder, 392), and 272 (shoulder, 191); ir (KBr) 694 (s), 711 (vs), 728 (s), 778 (s), 788 (s), and 1030 cm^{-1} (w); nmr (CCl_4) δ 2.43 (d, J = 7.5 Hz, 2), 3.60 (t, J = 7.5 Hz, 1), and 6.8–7.17 ppm (m, 10).

Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.64; H, 5.86; Cl, 15.43.

trans-2,*trans*-3-Diphenylcyclopropyl Chloride (3).—A 0.7-g sample of 1,1-dichloro-*cis*-2,3-diphenylcyclopropane was reduced in the electrolysis vessel using absolute ethanol as the solvent at −1.65 to −1.9 V *vs.* the silver wire reference. The reaction period was about 2 hr. The catholyte was poured into water and extracted with ether. The ether layer was washed several times with water, dried ($MgSO_4$), and concentrated to a viscous oil consisting of a 1:3 mixture of 1-chloro-*trans*-2,*trans*-3-diphenylcyclopropane (3) and 1-chloro-*cis*-2,*cis*-3-diphenylcyclopropane (2) as determined by nmr.

Reduction of two 1-g samples of 1,1-dichloro-*cis*-2,3-diphenylcyclopropane in absolute ethanol followed by refrigeration of the oily mixtures gave, after filtration, 1.2 g of solid, mp 66–70°. On extraction of the filtrates with ether, 0.5 g of an oily material was obtained. Chromatography of the oil on neutral alumina, using low-boiling petroleum ether as the eluent, afforded about 0.1 g of liquid shown by nmr to be 1-chloro-*trans*-2,*trans*-3-diphenylcyclopropane: nmr (CCl_4) δ 2.81 (d, J = 4.5 Hz), 3.71 (t, J = 4.5 Hz), and 6.73–7.45 ppm (m).

Kinetics of 1 and 2.—A 0.020 *M* solution of the cyclopropyl chloride in acetic acid (0.040 *M* in sodium acetate) was prepared. Samples of 1.5–2.0 ml were sealed in ampoules and placed in the bath controlled to ±0.1°. The ampoules were removed and a 1-ml portion was diluted to 50 ml with 95% ethanol. A 1-ml portion of each initially diluted sample was further diluted with 9 ml of 95% ethanol and the absorbance was read at 253 nm. Since the cyclopropyl chlorides had a small absorbance at 253 nm, standard curves were necessary. Two infinity determinations were taken after 10 half-lives for each run.

Kinetics of Solvolysis of 3.—Since an isomerically pure sample of 1-chloro-*trans*-2,*trans*-3-diphenylcyclopropane was not practically obtainable, the solvolyses were performed using a mixture of 1-chloro-*cis*-2,*cis*-3- and 1-chloro-*trans*-2,*trans*,3-diphenylcyclopropane. A 0.014–0.040-g sample was dissolved in 2 ml of acetic acid (0.040 *M* in sodium acetate). About 1.0–1.5 ml of the solution was injected into a 2-ml vial capped with a rubber septum. A 50-μl Hamilton syringe was used to remove samples. At the start of a run, two 30-μl portions of the solvolysis mixture were diluted to 25 ml with 95% ethanol and the absorbance was read at 253 nm. Samples of 30 μl were removed at appropriate intervals, diluted, and read. Several infinity determinations were taken after 8 half-lives for each run.

Registry No.—1, 36611-95-7; 2, 36611-96-8; 3, 36611-97-9; 1,1-dichloro-*cis*-2,3-diphenylcyclopropane, 36611-98-0.

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Methylation of α-Chloro Ketones *via* Halohydrin Formation and Rearrangement

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A new procedure for the stereoselective introduction of an angular methyl group in two systems (1-decalone and perhydro-1-indanone) is outlined. Two monocyclic systems, cyclohexanone and 2-methylcyclohexanone, were also methylated. The sequence of reactions by which the angular methyl group was stereoselectively introduced entailed the following: the preparation of the α-chloro ketone with sulfuryl chloride, followed by its conversion to the halohydrin with methyllithium, and, lastly, transformation to the magnesium salt of the halohydrin (isopropylmagnesium bromide) followed by decomposition resulting in the production of the methylated ketone. The reaction is discussed from the synthetic and mechanistic viewpoints. The noteworthy disadvantage of the sequence is that the *trans*-methyl (angular methyl) isomers cannot be prepared; *only* the pure cis isomers can be obtained.

One of the more intriguing, challenging and seemingly endless areas of research in organic chemistry involves uncovering diverse approaches for the introduction of an angular methyl group into steroids and steroid-like systems. Still more challenging is to effect the *stereoselective* introduction of the angular methyl group into the system. To recount all the many excellent and efficacious methods and ingenious assaults at the problem is beyond the purpose and scope of this manuscript; suffice to mention some salient and excellent leading references.[2]

The rearrangement of the magnesium salts of halohydrins to ketones has long been known and its application to the synthesis of α-alkyl- and α-aryl-sub-

(1) From the Ph.D. Dissertation of A. C. Vitale, Adelphi University, 1970.

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