Dichloro-2-methylpropane was identified from the infrared and mass spectra of glpc-trapped material.

Codimerization of Methallyl Chloride and Allyl Acetate.—The products were analyzed by glpc using a Ucon P/firebrick column (6 mm o.d. × 1.5 m long) programmed from 40 to 200° at 6°/min with a helium flow rate of 60 cc/min. The retention times of the various components are allyl chloride (2.7 min), methallyl chloride (4.5 min), allyl ether (6.5 min), allyl acetate (9.1 min), MAC dimer (24 min), codimer (27.4 min), B:A:B trimer (43.7 min), A:B:B trimer (47.5 min), and A:A:B trimer (52.8 min). The various products were identified in the same manner as described above. The codimer exhibited an infrared spectrum with $\nu_{max}^{CS_2}$ 3050 (sh), 2950 (s), 1745 (vs) (C=O), 1650 (w) (C=C), 1380 (m), 1365 (m), 1230 (vs) (C—O), 1030 (s) (C—O), 980 (w), 890 (m) (C=CH_2), 830 (w), 740 (sh), 725 (w), and 690 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 154 (M − HCl), 130 (1 Cl, M − $C_2H_4O_2$), 95 (130 − Cl), 43 ($C_2H_3O^+$). The A:A:B trimer exhibited an infrared spectrum with $\nu_{max}^{CS_2}$ 2900 (s), 1745 (vs) (C=O), 1380 (m), 1365 (m), 1225 (vs) (C—O), 1035 (s) (C—O), 980 (w), 895 (w) (C=$CH)_2$, 735 (w), and 695 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 230 (1 Cl, M − $C_2H_4O_2$), 170 [1 Cl, M − 2-($C_2H_4O_2$)], 157 (1 Cl, M − $C_2H_4O_2$ and $C_3H_5O_2$), 135 ($C_{10}H_{15}^+$), 121 (157 − HCl), 96 ($C_7H_{12}^+$), 43 ($C_2H_3O^+$). The A:B:B trimer exhibited an infrared spectrum with $\nu_{max}^{CS_2}$ 3050 (w), 2900 (s), 1745 (vs) (C=O), 1650 (w) (C=C), 1385 (m), 1370 (m), 1225 (vs) (C—O), 1035 (s) (C—O), 892 (m) (C=CH_2), 840 (w), 775 (w), 740 (m), and 725 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 245 (1 Cl, M − Cl), 207 (2 Cl, M − $C_3H_5O_2$), 184 (1 Cl, M − $C_2H_4O_2$ and HCl), 96 ($C_7H_{12}^+$). The B:A:B trimer exhibited an infrared spectrum with $\nu_{max}^{CS_2}$ 2900 (s), 1745 (vs) (C=O), 1385 (m), 1370 (m), 1290 (w), 1225 (vs) (C—O), 1030 (s) (C—O), 980 (w), 890 (sh), 870 (m), 840 (m), 780 (w), 740 (m), 735 (w), and 700 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 245 (1 Cl, M − Cl), 220 (2 Cl, M − $C_2H_4O_2$), 207 (2 Cl, M − $C_3H_5O_2$), 182 (2 Cl, M − C_2H_3O and C_4H_7), 171 (1 Cl, M − $C_3H_5O_2$ and HCl), 95 ($C_7H_{11}^+$). Allyl chloride was identified by comparison of the infrared spectrum of the glpc-trapped sample with the authentic material (Shell Chemical Co.). Allyl ether was identified by comparison of the infrared spectrum of the glpc-trapped sample with the authentic material in the Sadtler Catalog.[13]

Codimerization of Methallyl Chloride and Vinyl Acetate.—The products were analyzed by glpc using a SE-30/firebrick column (6-mm o.d. × 1.5 m long) programmed from 40 to 225° at 6°/min with a helium flow rate of 60 cc/min. The retention times of the various components are vinyl acetate (4.3 min), methallyl chloride (6.5 min, programming started), codimer (29 min), MAC dimer (31.5 min), and B:A:B trimer (42.1 min). The codimer exhibited an infrared spectrum with $\nu_{max}^{CS_2}$ 3050 (w), 2950 (sh), 2920 (m), 1740 (s) (C=O), 1650 (w) (C=C), 1380 (m), 1225 (vs) (C—O), 1085 (w), 1035 (s) (C—O), 935 (m), 895 (s) (C=CH_2), and 740 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 127 (M − CH_2Cl), 116 (1 Cl, M − $C_2H_4O_2$), 81 ($C_6H_9^+$), 43 ($C_2H_3O^+$). The B:A:B trimer exhibited an infrared spectrum with $\nu_{max}^{CS_2}$ 3050 (w), 2925 (m), 1740 (s) (C=O), 1640 (w) (C=C), 1360 (m), 1230 (s) (C—O), 1020 (m) (C—O), 893 (C=CH_2), and 740 (w) cm^{-1}; and mass spectrum with the following selected fragment ions, *m/e* 211 (2 Cl, M − C_4H_7), 206 (2 Cl, M − $C_2H_4O_2$), 157 (1 Cl, M − $C_2H_4O_2$ and CH_2Cl), 81 ($C_6H_9^+$), 43 ($C_2H_3O^+$).

Acknowledgments.—The author wishes to thank R. E. Thorpe for obtaining and interpreting the mass spectra and to express appreciation for helpful discussions with F. F. Rust.

(13) "Sadtler Catalog," Sadtler Research Laboratories, Philadelphia, Pa., 1959.

Stereochemistry of the Opening of Cyclopropanols[1]

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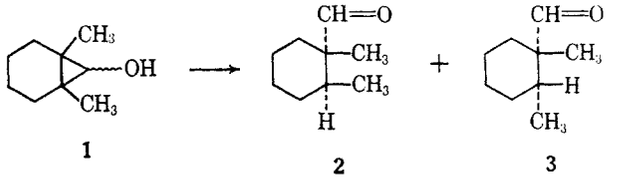
The stereochemistry of base-catalyzed opening of *endo*- and *exo*-7-hydroxy-1,6-dimethyl[4.1.0]bicycloheptane (1) was examined using potassium *t*-butoxide in *t*-butyl alcohol (both gave >90% retention) and ethylene glycol and its sodium salt (40 and 70% inversion). These results are consistent with those from previously reported electrophilic substitutions at carbon, implying that the three-membered ring does not introduce a significant novel mechanistic feature into the ring opening.

Nickon has reported that the conversion of 1-hydroxynortricylene to 2-norbornanone leads to >94% incorporation of an *exo*-deuterium atom at C-6 when various bases and deuterated solvents are used to effect the reaction.[2] This result of predominant inversion of stereochemistry at C-6 is unusual in that it does not conform to the pattern of stereochemical results obtained by Cram in his more general studies of electrophilic substitution at carbon, with carbon as a leaving group, using the same solvent systems.[3] In particular, Nickon observes predominant inversion and Cram predominant retention, with potassium *t*-butoxide in *t*-butyl alcohol. Nickon's result can be attributable either to a special feature of 1-hydroxynortricylene or to a special feature of cyclopropanols in general. That it is not the latter is clear from our results: we find that the stereochemistry of opening of *endo*- and *exo*-7-hydroxy-1,6-dimethyl[4.1.0]bicycloheptane (1) is in accord with the pattern observed by Cram,[3] namely, predominant retention (1 → 2) with potassium *t*-butoxide in *t*-butyl alcohol and much inversion (1 → 3) with ethylene glycol and its sodium salt. The only other study of the stereochemistry of cyclopropanol opening has been carried out by DePuy who finds predominant inversion in the opening of 1-methyl-*trans*-2-phenylcyclopropanol,[4] using only one medium,



1 2 3

(1) This investigation was supported in part by Petroleum Research Fund Grant 1116-A4. Acknowledgment is also made of National Science Foundation Grant G 19108 which contributed to the purchase of the nmr spectrometer used in this research.

(2) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 3713 (1963).

(3) For references and a summary of these studies, see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 138–158.

(4) C. H. DePuy and F. W. Breitbeil [*J. Am. Chem. Soc.*, **85**, 2176 (1963)] described their compound as *cis*-1-methyl-2-phenylcyclopropanol.

sodium hydroxide in dioxane–water (1:1), a system which would be expected to lead to substantial inversion[5] if the cyclopropanol opening were a normal example of electrophilic substitution at carbon.

Preparative Work.—Diazoacetic ester was added to 1,2-dimethylcyclohexene; the product was saponified. The *exo*-carboxylic acid, mp 137–139.5°, was obtained by crystallization of the crude product from alcohol. The *endo* isomer, mp 120.5–122°, was finally obtained pure by conversion of the mother liquors to a mixture of S-benzylisothiuronium salts, crystallization, and subsequent regeneration of acid from purified salt. Stereochemical assignments to the two acids were readily made on the basis of observed differences in the nmr chemical shifts in carbon tetrachloride and benzene solutions of the methyls *cis* and *trans* to the carboxyl group, according to the method already described.[6]

Both acids were treated with methyllithium, the ketonic products subjected to Baeyer–Villiger oxidation, and the resulting cyclopropyl acetates isolated by preparative gas chromatography (gc). The retention of stereochemical integrity of the *endo* and *exo* series was evident from the different gc retention times of the two acetates and from the different nmr chemical shifts of the cyclopropyl hydrogens, τ 6.71 and 6.42 for *endo* and *exo* acetates, respectively.

Both acetates were saponified to the corresponding cyclopropanols without opening of the three-membered ring as determined by infrared and nmr spectral data and reconversion of the products to starting acetates. Although both cyclopropanols were white crystalline solids, handling led to rapid deterioration; they were, therefore, not purified but prepared from the acetates as needed and used immediately.

In order to analyze the stereochemistry of opening of **1**, authentic samples of **2** and **3** were prepared from the known corresponding carboxylic acids, to which stereochemistry has been assigned on the basis of derivation of the *cis*-dimethyl isomer from the Diels–Alder reaction of butadiene and tiglic acid.[7] The acids were converted to acylaziridines which were then reduced with lithium aluminum hydride; the resulting aldehydes were isolated by preparative gc. *cis*-Dimethyl aldehyde **2** was obtained 97% and the *trans* isomer **3** 89% pure as determined by capillary gc on a 150-ft Ucon Polar column which clearly resolved the two and was used in subsequent analyses.

Cyclopropanol Opening.—Only two solvent systems with base were examined because of the limited availability of the cyclopropanols: *t*-butyl alcohol *ca.* 1 *M* in potassium *t*-butoxide and ethylene glycol *ca.* 1 *M* in its sodium salt. A small amount of *p*-dichlorobenzene was added to each reaction mixture to provide an internal standard for following the reaction by nmr spectrometry. The reaction in *t*-butyl alcohol was followed by observing the growth of the area of the aldehydic proton relative to the area of the aromatic protons of *p*-dichlorobenzene. The reaction in ethylene glycol was followed less well by observing the change of the methyl region with time. All reactions were carried out at 57° and run through several half-lives before work-up. No further change was visible in the nmr spectrum of the reaction mixture in *t*-butyl alcohol after 100 half-lives, thereby demonstrating that the system as a whole did not deteriorate appreciably with time and that *p*-dichlorobenzene was stable under the reaction conditions. In the absence of base, but otherwise under the same reaction conditions, it was found that *exo* **1** was undecomposed; *i.e.*, no thermal or induced[8] decomposition competed with base-catalyzed opening. The product from each run was analyzed by capillary gc with the results shown in Table I.

TABLE I

BASE- AND ACID-CATALYZED OPENING OF *endo* AND *exo* **1**

Compd **1**	Medium	**2** (retention)	**1** (inversion)	% unidentified
endo	$(CH_3)_3COK$ in $(CH_3)_3COH$	99	1	0
exo		96	4	0
exo		96	4	4
endo	$HOCH_2CH_2ONa$ in $HOCH_2CH_2OH$	60	40	5
exo		29	71	9
exo		31	69	2
endo	HCl in H_2O–$CH_3OCH_2CH_2OCH_3$ (1:6, v/v)	98	2	0
exo		94	6	4
exo		92	8	1

Samples of *endo* and *exo* **1** were also opened with acid catalysis, 0.2 *M* hydrochloric acid in aqueous dimethoxyethane, and the products from each run were analyzed by capillary gc, with the results also shown in Table I.

Discussion

The results of the base-catalyzed opening of **1** are in accord with Cram's over-all stereochemical pattern of electrophilic substitution at carbon[3], predominant retention in *t*-butyl alcohol, and substantial inversion in ethylene glycol, and it can be concluded that there is no evidence for a novel mechanism operating *via* the unusual properties of the cyclopropane ring.

The qualitative agreement with Cram's results suggests that the opening is SEl. If this is so, then the rupture of the three-membered ring provides sufficient driving force for generating even tertiary aliphatic carbanions under mild conditions. It also follows, at least in ethylene glycol, that the tertiary carbanion does not hold its pyramidal configuration but inverts faster than it is protonated.

Our results differ from Cram's in detail in that ours show a dependence on the configuration of the leaving group: in *t*-butyl alcohol *endo* and *exo* **1** give 99 and 96% retention, respectively; in ethylene glycol, 60 and 30%. Cram found *identical* stereochemical results on cleaving the two diastereomeric pairs of 1,2-diphenyl-2-methyl-1-butanol and 2,3-diphenyl-3-methoxy-2-butanol[9] although no equilibration of diastereomers was found. We suggest that the difference arises from the formation of the two possible cyclohexane chairs in different amounts from the isomeric starting materials, the chairs being protonated individually (with a rate close to diffusion controlled at $\Delta pK_a = \sim 30$)[10] faster than they interconvert ($E_a = \sim 11$ kcal).[11]

(5) See ref 3, pp 144 and 161.
(6) P. S. Wharton and T. I. Bair, *J. Org. Chem.*, **30**, 1681 (1965).
(7) See G. Stork and I. Borowitz, *J. Am. Chem. Soc.*, **82**, 4307 (1960).
(8) See C. H. DePuy, G. M. Dappen, and J. W. Hauser [*ibid.*, **83**, 3156 (1961)] and ref 4, footnote 7.
(9) D. J. Cram, F. Hauck, K. R. Kopecky, and W. D. Nielsen, *ibid.*, **81**, 5767 (1959).
(10) See ref 3, pp 4, 14, and 19.
(11) See F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 145 (1964); F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *ibid.*, 146 (1964).

Both *endo* and *exo* **1** were opened by acid with predominant retention of stereochemistry, in agreement with the findings of Nickon[2] and DePuy.[4] The formation of minor products (2 and 7%) from *endo* and *exo* **1**, respectively, with a retention time corresponding to *trans*-dimethyl aldehyde **3** is interesting but cannot be considered to be mechanistically significant until their identities are unambiguously established.[12]

Experimental Section

Melting points were taken in capillary tubes in a Thomas–Hoover melting point apparatus and are uncorrected. Capillary gc data were obtained using a 150-ft Ucon Polar capillary column with a Perkin-Elmer Model 154 unit, flame ionization detector and Disc integrator. Preparative gc was carried out with a 5 ft × $^3/_8$ in. column of 10% Carbowax 20M on Chromosorb P and an Aerograph A-90-P2 unit. Infrared, ultraviolet, and nmr spectra were recorded using Perkin-Elmer Infracord Model 137, Cary Model 11, and Varian A-60 spectrometers, respectively. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

1-Methyl-*trans*-2-methylcyclohexanecarboxaldehyde. "*cis*-Dimethyl Aldehyde" (2).[13]—To 0.800 g of crude 1-methyl-*trans*-2-methylcyclohexanecarboxylic acid[7,14] was added a solution of 1.0 g of oxalyl chloride in 10 ml of benzene. After several days the benzene and excess oxalyl chloride were removed and the residue was subjected to short-path distillation from an oil bath at 90–110°, yielding 0.635 g (72%) of acid chloride. Treatment with aniline gave, after work-up and crystallization, an anilide, mp 114.5–116° (for authentic anilide lit.[7,14] mp 114–116 and 115–117°).

To a reaction vessel cooled in an ice–salt bath and containing 0.500 g (11.6 mmoles) of ethylenimine and 1.20 g (11.9 mmoles) of triethylamine in 10 ml of anhydrous ether was added 2.00 g (11.5 mmoles) of acid chloride obtained from another run. The mixture was stirred for 30 min and then filtered. The collected salt was washed with several portions of dry ether; the washings were added to the original filtrate. To this combined solution, cooled in an ice–salt bath, was added with stirring 8 ml (3.44 mmoles) of 0.43 *M* lithium aluminum hydride in ether over a period of 10 min. After an additional 20 min, 5 ml of 5 *N* sulfuric acid was added with stirring and cooling and the mixture was worked up. The crude product showed two major components on gc analysis, 54% at 3.8 min and 32% at 9.7 min. Material corresponding to the later peak was collected and found to be the expected primary alcohol. Material corresponding to the earlier peak was collected and found to be aldehyde, 3.71 and 5.82 μ, which consisted of one major component (97%) when subjected to capillary gc. An analytical sample was obtained by short-path distillation.

Anal. Calcd for $C_9H_{16}O$: C, 77.14; H, 11.43. Found: C, 77.36; H, 11.65.

The aldehyde deteriorated rapidly in solution or on exposure to the air. Samples were, therefore, stored in sealed ampoules under nitrogen at 5°.

1-Methyl-*cis*-2-methylcyclohexanecarboxaldehyde. "*trans*-Dimethyl Aldehyde" (3).—Carbonylation of a mixture of 2,3-dimethylcyclohexene and 2-methyl-1-methylenecyclohexane[15] and conversion of the resulting acids to their methyl esters with ethereal diazomethane yielded a three-component mixture as observed for the similar carbonylation of 1,2-dimethylcyclohexanol.[14] Material corresponding to the gc peak at 13.5 min (13%) was collected and shown to be the *cis*-dimethyl ester. Material corresponding to the peak at 10.7 min (84%) was collected and found to contain only one major component (98%) by capillary gc. A portion of this ester was saponified; the resulting acid was converted to its acid chloride with oxalyl chloride. Treatment of the chloride with aniline gave, after work-up and crystallization, white needles of an anilide showing dimorphism, mp 85.5–86.5 and 94.0–95.5° (only single melting points of 88–89 and 81.4–82.6° were reported[7,14] for the authentic anilide by previous workers).

Further runs yielded chloride which was treated successively with ethylenimine and lithium aluminum hydride as described for the *cis* series. The crude product showed two major components on gc analysis, 78% at 4.6 min and 18% at 14.3 min. Material corresponding to the later peak was collected and found to be the expected primary alcohol. Material corresponding to the earlier peak was collected and found to be aldehyde, 3.71 and 5.82 μ, which consisted of one major component (89%) by capillary gc. Samples were stored in sealed ampoules under nitrogen at 5°.

***endo*- and *exo*-1,6-Dimethylbicyclo[4.1.0]heptane-7-carboxylic Acids.**—1,2-Dimethylcyclohexene[15] (40 g, 0.36 mole), bp 134–136°, and 8 g of powdered copper were placed in a reaction vessel equipped with magnetic stirrer, a dilution head[16] attached to a pressure-equalized dropping funnel, and a condenser attached to a gas-measuring apparatus. The reaction vessel was heated in an oil bath at 160–190° so that the olefin boiled vigorously, and a solution of 70 g (0.61 mole by volumetric assay) of ethyl diazoacetate[17] in 60 g (0.55 mole) of 1,2-dimethylcyclohexene was added slowly over 10 hr. After the theoretical amount of nitrogen had been evolved the reaction flask was cooled and its contents were filtered through glass wool to remove the suspended solids. Distillation of the filtrate yielded, after foreruns of excess olefin and a mixture of diethyl fumarate and maleate, 75.3 g (63% based on diazo acetate used) of product, bp 105–125° (20 mm).

***exo* Acid.**—A portion (57 g) of this product was saponified in a solution of 300 ml of ethanol and 50 ml of water containing 45 g of 85% potassium hydroxide, heated to reflux for 24 hr. The solution was cooled, acidified with dilute hydrochloric acid, and filtered, yielding 15 g of solid, mp 130–136°. Two crystallizations from aqueous ethanol gave white needles of the *exo* acid, mp 137–139.5°, from which an analytical sample, mp 137–138.5°, was obtained by sublimation.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.55; H, 9.58.

Esterification of the acid with ethereal diazomethane and distillation of the product yielded the methyl ester as a colorless liquid showing a single peak on capillary gc and nmr chemical shifts (CCl_4) at τ 6.45 (3 H) and 8.77 (6 H). The methyl singlet at τ 8.77 was displaced to 8.67 in benzene solution.

***endo* Acid.**—The original filtrate obtained after acidifying the saponification mixture was diluted with water; further solid acid was obtained. Attempts to obtain pure *endo* acid from this solid by crystallization from various solvents were unsuccessful. Therefore, a portion (24 g, 0.137 mole) of the solid acid, mp 81–91° (containing *endo* and *exo* acids in a 3:1 ratio according to capillary gc on a small sample converted to methyl esters), was neutralized to phenolphthalein with 5% aqueous sodium hydroxide. To this solution was added a soluton of 29.5 g (0.146 mole) of benzylisothiourea hydrochloride in 75 ml of hot 95% ethanol. The resulting white precipitate was collected, washed with water, partially dried, and then crystallized from 350 ml of ethanol, yielding 14.5 g of white needles, mp 132.5–135° dec. Recrystallization gave 7.0 g, mp 136–138.5° dec. A portion of this salt (3.0 g) was treated with 60 ml of 10% sodium hydroxide solution. After 1 hr 970 mg of iodine was added and the mixture was extracted several times with ether. The aqueous layer was acidified and the mixture was extracted with ether. The ether layer was washed with sodium thiosulfate solution and the acid was recovered from the ether layer, 1.6 g, mp 119.5–121° after softening at 113°. Crystallization from ethanol gave 937 mg of white needles of the *endo* acid, mp 120.5–122.0°, from which an analytical sample, mp 120.5–121.5°, was obtained by sublimation.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.66; H, 9.53.

Esterification of the acid with ethereal diazomethane and distillation of the product yielded the methyl ester as a colorless liquid showing a single peak on capillary gc and nmr chemical shifts (CCl_4) at τ 6.42 (3 H) and 8.83 (6 H). The methyl singlet at τ 8.83 was displaced to 9.07 in benzene solution.

(12) For a recent discussion of the protonation of cyclopropanes, see R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964).

(13) General procedure: H. C. Brown and A. Tsukamoto, *ibid.*, **83**, 4549 (1961).

(14) H. O. House and W. F. Gilmore, *ibid.*, **83**, 3980 (1961). Note the different nomenclature in ref 7.

(15) G. S. Hammond and T. D. Nevitt, *ibid.*, **76**, 4121 (1954).

(16) K. B. Wiberg, "Laboratory Techniques in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 218.

(17) *Org. Syn.*, **36**, 25 (1956).

exo-**7-Acetoxy-1,6-dimethylbicyclo[4.1.0]heptane.**[18]—To a solution of 5.0 g (29.8 mmoles) of *exo* acid, mp 137–139°, in 100 ml of anhydrous ether, was added with stirring 160 ml of a solution of methyllithium in ether containing 59.6 mmoles of total base as determined by titration. After 5 min the reaction mixture was worked up, yielding 1.75 g of recovered starting material, mp 136–139°, and 3.34 g of neutral product. The small amount of less volatile tertiary alcohol (2.87 μ) contaminating the product was removed by distillation through a spinning-band column at oil pump pressure which gave 2.08 g of ketone (65% based on unrecovered acid): bp 29–30° (0.2 mm); λ_{max}^{film} 5.92 μ; $\lambda_{max}^{95\%\ EtOH}$ 210 mμ (ϵ 6800); τ (CCl_4) 7.89 (3 H) and 8.80 (6 H).

To a slurry of 2.00 g (12.0 mmoles) of ketone and 26 g of dibasic sodium phosphate in 80 ml of methylene chloride was added, with stirring, a solution of peroxytrifluoroacetic acid prepared by adding, with stirring, 1.0 ml (37 mmoles) of 90% hydrogen peroxide and 6.2 ml (44 mmoles) of trifluoroacetic anhydride to 15 ml of ice-cooled methylene chloride. Work-up gave 1.50 g of crude product which was first subjected to short-path distillation (oil bath 105–140°) and then preparative gc. Material corresponding to the major peak (85%) at 6.7 min was collected: λ_{max}^{film} 5.73 μ; τ (CCl_4) 6.42 (1 H) 8.00 (3 H), 9.03 (6 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.53; H, 9.89. Found: C, 72.76; H, 10.07.

Conversion of the cyclopropyl acetate to cyclopropanol was effected by using freshly distilled solvents for each run (including work up). Typically, a solution of 37 mg of acetate in a mixture of 2.5 ml of methanol and 1.5 ml of 0.3 *N* sodium hydroxide solution was allowed to stand at room temperature for 50 min under nitrogen. Water (10 ml) was then added and the mixture was extracted with three 3-ml portions of pentane. The combined extracts were washed with 2 ml of water and then dried over sodium sulfate. Evaporation of solvent left a white solid showing hydroxylic (2.8 and 2.9 μ) but no carbonyl absorption; τ ($CDCl_3$) 6.93 (1 H), 8.07 (1 H), 8.98 (1 H, singlet superimposed on complex absorption).

The white solid from one run was treated with excess acetic anhydride in pyridine. Work-up, using carbon tetrachloride as solvent, gave a solution showing the same nmr absorption as starting acetate. Capillary gc of the concentrated solution showed, apart from solvent, only one peak with a retention time corresponding to that of starting acetate.

endo-**7-Acetoxy-1,6-dimethylbicyclo[4.1.0]heptane** was similarly prepared[18] from *endo* acid, mp 120–122°; 1.450 g of the acid yielding 0.800 g of crude ketone which showed only weak hydroxyl absorption in the infrared spectrum. A portion (589 mg) of this crude ketone was subjected to Baeyer–Villiger oxidation, giving 549 mg of crude product which showed on gc two major peaks in the ratio 6:1 at 5.7 and 9.3 min. Material corresponding to the peak at 5.7 min was collected and shown to be unresolved on capillary gc: $\lambda_{max}^{CHCl_3}$ 5.78 μ; τ (CCl_4) 6.71 (1 H), 7.99 (3 H) and 8.92 (1 H, singlet superimposed on complex absorption).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.53; H, 9.89. Found: C, 72.11; H, 10.03.

A portion of collected *endo* acetate was saponified and a white solid obtained as with the *exo* acetate. The solid was acetylated and the product shown by capillary gc to yield only one peak, apart from that due to solvent, with a retention time corresponding to that of starting acetate.

Cyclopropanol Openings.—In a typical run 37 mg of *exo* acetate was saponified and the resulting white solid was dissolved in 0.2 ml of a *t*-butyl alcohol solution prepared by dissolving 20 mg of potassium in 0.5 ml. This solution was transferred to an nmr tube containing 20 mg of *p*-dichlorobenzene and the tube was partially immersed in a Dry Ice bath. The tube was evacuated and filled with nitrogen several times before being sealed under vacuum. It was then placed in an oil bath at 57° and thereafter removed periodically; the nmr spectrum of the solution was recorded. After 60 hr the tube was opened, the contents were poured into 10 ml of water, and the mixture was extracted with two 3-ml portions of pentane which were combined, washed with 1 ml of water, and dried over sodium sulfate. Solvent was almost completely removed by evaporation; the product was subjected to capillary gc which showed, apart from residual solvent and *p*-dichlorobenzene (12.4 min), only two major peaks at 10.3 and 11.2 min. These retention times corresponded to those of *trans*- and *cis*-dimethyl aldehyde, respectively, as shown by peak enhancements after separate addition of authentic *trans* and *cis* aldehydes and resubjection to capillary gc. Although preparative gc could not separate the two aldehydes, material corresponding to the peak for both was collected and shown to be aldehydic, λ_{max}^{film} 3.72 and 5.81 μ.

(18) General procedures: G. Tegner, *Acta Chem. Scand.*, **6**, 782 (1952); W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287 (1955); C. H. DePuy and L. R. Mahoney, *ibid.*, **86**, 2653 (1964).

Synthesis and Characterization of the *cis*- and *trans*-Trimethylsilylcyclohexanols[1]

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The syntheses of the *cis*- and *trans*-3- and -4-trimethylsilylcyclohexanols are described. Catalytic hydrogenation of the *m*- and *p*-trimethylsilylphenols yielded predominantly the 3-*trans* and 4-*cis* isomers, respectively. Oxidation of these trimethylsilylcyclohexanols, followed by lithium aluminum hydride reduction, yielded predominantly the 3-*cis* and 4-*trans* isomers. The isomers were purified by elution chromatography. Structure assignments were made on the basis of the nmr spectra and were substantiated, in the case of the 4-trimethylsilylcyclohexanols, by the rates of ethanolysis of their tosylates. On the basis of the relative rates of the ethanolysis, it is concluded that the trimethylsilyl group, like the *t*-butyl group, controls the stereochemistry of the cyclohexane ring.

In the course of our investigations in the area of the synthesis and the study of the biological activity of organosilicon compounds,[3] it was desired to separate and characterize the *cis*- and *trans*-trimethylsilylcyclohexanols. The similarity of the trimethylsilyl group to the *t*-butyl group is suggestive that these silylcyclohexanols could be used to elucidate the steric influence of the trimethylsilyl group. This report deals with the synthesis and identification of these isomers.

The synthetic path leading to the isomeric 4-trimethylsilylcyclohexanols is outlined in Chart I. The synthetic steps up to the silylphenol **4** were straightforward; the methods described by Speier[4] were followed without major variation. Good yields (72–95%) were obtained in each of these steps. Speier obtained a mixture of the *cis*- and *trans*-4-trimethylsilylcyclohexanols (**5**) by hydrogenation of **3** followed by hydrol-

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(4) J. L. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).