desired structure: δ 0.9 (t, 3, CH_3), 2.0 (m, 2, CH_2), 6.7 (m, 2, CH=CH), 7.1, and 7.7 ppm (2 m, 5, C_6H_5).

3-Ethyl-4-pentenophenone.—2-Pentenophenone (0.092 mol), dry tetrahydrofuran (150 ml), and cupric acetate monohydrate (1.0 g) were stirred together under a nitrogen atmosphere at −70°, and 150 ml of a 2 *M* solution of vinylmagnesium chloride in tetrahydrofuran[15] was added over a 2-hr period. The reaction mixture was warmed to room temperature, stirred for an additional 3 hr, and hydrolyzed with saturated ammonium chloride solution (250 ml). The phases were separated and the aqueous one was extracted with ether; the organic phases were combined and concentrated. Subsequent vacuum distillation gave material, bp 88° (0.03 mm), which was rich in aromatic ketone, according to its ir spectrum, but which was shown to contain several minor impurities by glpc analysis. Careful column chromatography (twice) on silica gel followed by vacuum distillation gave 4.86 g of material, $n^{23}D$ 1.5193, 99% pure (glpc). The nmr spectrum (neat) was consistent with the structure of 3-ethyl-4-pentenophenone: δ 0.9 (t, 3, CH_3), 1.4 (m, 2, CH_2), 2.8 (m, 3, CH_2—CH), 4.9 (m, 2, $=CH_2$), 5.7 (m, 1, CH=), 7.3 and 7.9 ppm (2 m, 5, C_6H_5). The ir spectrum showed strong absorptions at 1690 cm^{-1} (C=O) and at 915 and 980 cm^{-1} (terminal vinyl stretching).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.92; H, 8.58. Found: C, 82.94; H, 8.67.

The 2,4-dinitrophenylhydrazone of this ketone was prepared and recrystallized from ethanol–ethyl acetate to give fine red-orange needles, mp 148.5–150.5°.

Anal. Calcd for $C_{19}H_{20}N_4O_4$: C, 61.92; H, 5.47. Found: C, 61.75; H, 5.52.

3-Methyl-4-hexenophenone.—Acetophenone (240 g, 2.0 mol), cyclohexylamine (485 ml, 4.0 mol), and dry benzene (300 ml) were heated together in a flask fitted with a Dean–Stark tube for 100 hr, after which time 35 ml (97% of the theoretical amount) of water had been collected. Subsequent vacuum distillation gave 291 g (72.2%) of product, bp 125–135° (0.2 mm). Infrared analysis (strong absorption at 1640 cm^{-1}, C=N) showed this distillate to be the desired imine, uncontaminated by ketone.

Ethyl bromide (40 ml, 0.55 mol) was added dropwise to a stirred mixture of magnesium turnings (12.0 g, 0.50 g-atom) and dry tetrahydrofuran (160 ml) at room temperature over a 1-hr period. The resulting mixture was stirred overnight to complete the consumption of the magnesium.

The ethylmagnesium bromide solution was heated to gentle reflux, and the acetophenone cyclohexylimine (86.3 g, 0.43 mol) was added dropwise over a period of 45 min. The resulting reaction mixture was heated under reflux for 24 hr and then cooled to ambient temperature. 4-Chloro-2-pentene (44.0 g, 0.42 mol) was added dropwise, and the resulting mixture was heated to reflux for 2 hr, cooled to room temperature, and hydrolyzed with 10% hydrochloric acid (300 ml). The phases were separated and the aqueous one was extracted with ether; the combined organic phases were washed successively with 5% sodium bicarbonate and water, then dried over anhydrous calcium chloride, and concentrated in a rotary evaporator. Vacuum distillation followed by spinning-band fractionation gave 14.8 g (18.7%) of distillate, bp 80° (0.1 mm), $n^{26.5}D$ 1.5215, which was pure according to glpc analysis. The nmr spectrum (neat) was consistent with the structure of 3-methyl-4-hexenophenone: δ 1.0 (d, 3, CH—CH_3), 1.55 (d, 3, CH=CH—CH_3), 2.86 (m, 3, CH_2—CH), 5.5 (m, 2, CH=CH), 7.4 and 7.9 ppm (2 m, 5, C_6H_5). The ir spectrum showed strong absorptions at 1695 cm^{-1} (aromatic ketone) and 970 cm^{-1} (*trans* C=C), as well as the characteristic aromatic absorptions.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.92; H, 8.58. Found: C, 82.69; H, 8.61.

The 2,4-dinitrophenylhydrazone was prepared; recrystallization from ethanol–ethyl acetate gave red-orange prisms, mp 128–129.5°.

Anal. Calcd for $C_{19}H_{20}N_4O_4$: C, 61.92; H, 5.47. Found: C, 61.65; H, 5.46.

Thermal Rearrangements.—The thermolyses were carried out at 192 ± 0.5° and 217 ± 0.5° using refluxing decalin (*cis–trans* mixture) and naphthalene, respectively, as constant-temperature baths. Samples for rearrangement experiments consisted of 50-μl portions of 3-ethyl-4-pentenophenone sealed in Pyrex tubes at a pressure ≤2 μ after degassing by alternately freezing (in liquid nitrogen) and thawing repeatedly.

(15) H. Normant, *Advan. Org. Chem.*, **2**, 37 (1960).

Experiments on glpc analysis of mixtures of authentic 3-ethyl-4-pentenophenone and 3-methyl-4-hexenophenone using conventional, packed columns showed that partial but not base-line separation could be achieved. Using the optimum glpc conditions so determined for analysis, preliminary thermolyses of 3-ethyl-4-pentenophenone were carried out. These showed that rearrangement into 3-methyl-4-pentenophenone occurred cleanly at 192°, but that equilibration was incomplete even after 173 hr. On the other hand, heating at 217° produced equilibration in *ca.* 50 hr, but gave rise to an appreciable amount of side products.

Capillary glpc analyses[12,13] provided more quantitative rearrangement data. Authentic 3-ethyl-4-pentenophenone (99.2% pure) had a retention time of 40.8 min under the conditions chosen for the analyses. Authentic 3-methyl-4-hexenophenone was found to consist of two major components, one comprised 85.7% of the material, with a retention time of 41.6 min, and the other 10.3%, with a retention time of 37.2 min. On the basis of other data, it was presumed that the major component was the *trans* isomer and the minor one was the *cis* isomer of 3-methyl-4-hexenophenone.

The data obtained at 192 ± 0.5° and 217 ± 0.5° are presented in Table I.

Registry No.—**4b**, 21779-18-0; **4b** (2,4-dinitrophenylhydrazone), 21779-19-1; **8b**, *cis*, 21779-20-4; **8b**, *cis* (2,4-dinitrophenylhydrazone), 21779-21-5; **8b**, *trans*, 21779-22-6; **8b**, *trans* (2,4-dinitrophenylhydrazone), 21779-23-7.

Keto Tosylates. I. Monotosylation of *cis*-3-(2-Hydroxyethyl)cyclopentanol

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In connection with our study of the reactions of keto tosylates and enol tosylates, we have synthesized 3-(2-tosyloxyethyl)cyclopentanone (**5**) utilizing a route that depended upon the tosylation of a specific group of a diol (see Scheme I). According to this synthetic scheme, norcamphor (**1**) underwent a Baeyer–Villiger reaction to give *cis*-3-hydroxycyclopentylacetic acid lactone (**2**) in a yield of 25% after distillation using *m*-chloroperbenzoic acid as the oxidizing agent.[1] The lactone **2** was reduced with lithium aluminum hydride into give *cis*-3-(2-hydroxyethyl)cyclopentanol (**3**) in 94% yield after distillation.[2] The diol **3** could be converted into the primary monotosylate, *cis*-3-(2-tosyloxyethyl)-cyclopentanol (**4**), in 59% yield when a solution of *p*-toluenesulfonyl chloride in pyridine was added slowly to a cold solution of the diol **3** in pyridine. The last step, the oxidation of **4** to 3-(2-tosyloxyethyl)cyclopentanone (**5**), went smoothly in a yield of 89% according to the procedure of Nelson.[3]

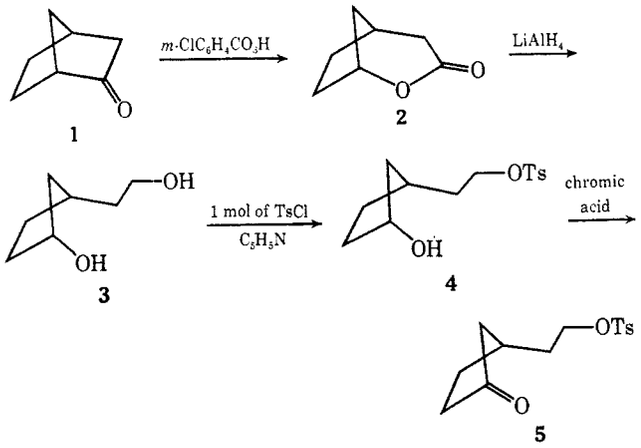
The success of the selective monotosylation of **3** to give **4** was found to depend critically upon the type of tosyl chloride addition. In contrast to previous mono-

(1) J. Meinwald and E. Frauenglass, *J. Amer. Chem. Soc.*, **82**, 5235 (1960). Meinwald reports a higher yield, but a cruder product, when using peracetic acid on norcamphor.

(2) A. Rassat and G. Ourisson [*Bull. Soc. Chim. Fr.*, 1133 (1959)] prepared **3** by this procedure, but they did not purify the product nor did they give a yield.

(3) N. A. Nelson and G. A. Mortimer, *J. Org. Chem.*, **22**, 1146 (1957).

SCHEME I



tosylations[4-7] in which a study was not made of the by-products, the present system was well suited for such a study owing to the easy separation of all products (see Experimental Section). The classical tosylation procedure of Tipson[8] (addition of solid tosyl chloride to an alcohol–pyridine solution) led to the desired monotosylate **4** and ditosylate **6** [*cis*-3-(2-hydroxyethyl)cyclopentanol di-*p*-toluenesulfonate ester], along with some recovered diol (see Scheme II). Under varying conditions of tosyl chloride addition, the amount of ditosylate **6** varied considerably (see Table I), with the best results occurring when a *solution* of reagent was added *slowly* to the alcohol–pyridine solution. No trace of the secondary monotosylate **7** was ever found[9] (see Experimental Section).

SCHEME II

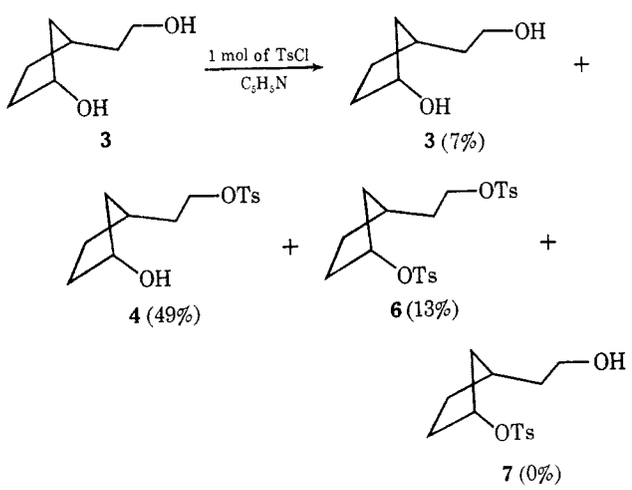


TABLE I

YIELDS OF 4 AND 6 FROM 3 UNDER VARYING REACTION CONDITIONS

Type of addition	Time for addition	Bath temp, °C	Yield, % 4	Yield, % 6
Crystals	10 min	0	49	13
Crystals	30 min	−5	46	8
Solution	5 min	0	32	6
Solution	30 min	−5	59	0

(4) E. A. Davidson, "Carbohydrate Chemistry," Holt, Rinehart, and Winston, Inc., London, 1967, p 216.

(5) F. Hardegger and R. M. Montavon, *Helv. Chim. Acta*, **29**, 1199 (1946).

(6) P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, **102**, 317 (1933).

(7) F. Cramer, H. O. Herbach, and H. Springman, *Chem. Ber.*, **92**, 384 (1959).

(8) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

Experimental Section

Melting points were determined by a Thomas–Hoover melting point apparatus. Gas chromatography analyses were performed on an F & M Model 700 gas chromatograph. Infrared spectra were recorded on a Perkin-Elmer 237 grating infrared pectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer, with tetramethylsilane as an internal reference unless otherwise designated.

***cis*-3-Hydroxycyclopentylacetic Acid Lactone (2).**—To a stirring solution of 2.24 g of norcamphor (Aldrich Chemical Co.), 3.6 ml of concentrated sulfuric acid, and 90 ml of glacial acetic acid cooled to 0° was added a solution of 4.13 g of *m*-chloroperbenzoic acid (Research Organic–Inorganic Chemical Co., Sun Valley, Calif., 87% minimum assay) in 24 ml of glacial acetic acid over a period of 30 min. After standing for 2 hr, the resulting mixture was worked up in the usual manner[1] and distilled to yield 0.65 g (25%) of **2**, bp 72–73° (0.8 mm). The distillate solidified spontaneously to give white flakes, mp 56–58° (lit.[1] mp 56–58°). The product was perfectly homogeneous by glpc analysis, using 10% Carbowax 20M on Chromosorb W (6 ft × 1/8 in.) and 10% UCW-98 on Chromosorb W (6 ft × 1/8 in.).

***cis*-3-(2-Hydroxyethyl)cyclopentanol (3).**—A mixture of 14.60 g of lactone **2**, 7.30 g of lithium aluminum hydride, and 600 ml of anhydrous ether was refluxed for 24 hr. After hydrolysis of the reaction mixture by the dropwise addition of 29 ml of water, the reaction mixture was filtered, concentrated under reduced pressure, and distilled to yield 14.14 g (94%) of a clear, viscous oil: bp 121–123° (0.25 mm); $n^{20}D$ 1.4844; ir (neat) 3315 cm^{-1} (OH); nmr (D_2O, using sodium 3-(trimethylsilyl)propanesulfonate as the internal standard) τ 6.48 (t, 2, J = 6 Hz, CH_2OH), 5.83 (m, 1, CHOH), 5.23 (s, 2, HOD from the exchange of the hydroxyl protons), and 7.7–9.0 (complex, 9).

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.76; H, 10.92.

The diol **3** was also characterized by its diacetate:[10] bp 127° (0.05 mm); $n^{20}D$ 1.4498; ir (neat) 1740 (C=O) and 1250 cm^{-1} (C—O); nmr (neat) τ 5.98 (t, 2, J = 6 Hz, CH_2OAc), 4.96 (m, 1, CHOAc), and 7.5–9.0 (complex, 15).

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.45. Found: C, 61.87; H, 8.26.

***cis*-3-(2-Tosyloxyethyl)cyclopentanol (4).**—To a stirring solution of 2.00 g of diol **3** in 19 ml of dry pyridine cooled to −5° was added dropwise over a period of 30 min a solution of 2.93 g of tosyl chloride in 9 ml of pyridine. After 41 hr of standing at 5°, the resulting mixture was poured over 200 ml of water and extracted with chloroform. The chloroform extract was dried with anhydrous magnesium sulfate and concentrated under reduced pressure to yield 2.59 g (59%) of a clear syrup (**4**) which would not crystallize: ir (neat) 3370 cm^{-1} (OH); nmr ($CHCl_3$) τ 5.99 (t, 2, J = 6 Hz, CH_2OTs), 5.9 (m, 1, CHOH), 6.55 (s, 1, OH), 2.23 (d, 2, J = 8 Hz, aromatic), 2.67 (d, 2, J = 8 Hz, aromatic), 7.63 (s, 3, CH_3), and 7.9–9.0 (complex, 9).

Anal. Calcd for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09; S, 11.28. Found: C, 59.18; H, 7.12; S, 11.11.

Unreacted diol could be recovered by saturating the aqueous phase with sodium chloride and extracting with ether. This procedure led to a 4% recovery of diol for the monotosylation procedure above.

Variations of the above procedure led to the formation of the ditosylate by-product (**6**). This by-product could be separated by filtering it from the reaction mixture immediately after the admixture with water and before the extraction with chloroform.

When the addition of the tosyl chloride solution was done over a period of 5 min, work-up of the reaction mixture after 2 hr gave a 32% yield of **4** and a 6% yield of **6**.

When Tipson's procedure[8] was used, in which tosyl chloride crystals were added over a period of 10 min, work-up of the

(9) The search for **7** was made by nmr analysis. From the chemical shifts of the α hydrogen in **3**, **4**, **5**, and **6**, it was concluded that the primary and secondary α hydrogens of **7** should have chemical shifts of *ca.* τ 6.5 and 5.2, respectively. No such pattern appeared in the nmr of crude **3**, **4**, and **6** isolated from the monotosylation procedures.

(10) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1964, p 247.

reaction mixture after 2.5 hr gave a 49% yield of **4**, a 13% yield of **6**, and a 7% yield of **3**.

When Tipson's procedure was used, in which tosyl chloride crystals were added over a period of 30 min, work-up of the reaction mixture after 2.5 hr gave a 46% yield of **4** and an 8% yield of **6**.

No trace of **7** was found in crude **3**, **4**, or **6** isolated in the above procedures.[9]

***cis*-3-(2-Hydroxyethyl)cyclopentanol Di-*p*-toluenesulfonate Ester (6).**—The reaction of the diol **3** with 2.2 mol of tosyl chloride according to the procedure of Tipson[8] gave crude ditosylate **6** in 87% yield, mp 82–84°. Recrystallization from hexane–ethyl acetate gave white needles: mp 89.1–90.0°; nmr ($CHCl_3$) τ 6.11 (t, 2, J = 6 Hz, CH_2OTs), 5.20 (m, 1, CHOTs), 2.25 (d, 4, J = 8 Hz, aromatic), 2.69 (d, 4, J = 8 Hz, aromatic), 7.59 (s, 6, CH_3), and 7.9–9.0 (complex, 9).

Anal. Calcd for $C_{21}H_{26}O_6S_2$: C, 57.51; H, 5.98; S, 14.62. Found: C, 57.42; H, 5.68; S, 14.39.

3-(2-Tosyloxyethyl)cyclopentanone (5).—A sample of 7.21 g of hydroxy tosylate **4** oxidized according to the procedure of Nelson[3] gave 6.34 g (89%) of a yellowish syrup which would not crystallize. Rapid elution through grade I neutral Woelm alumina with 90:10 benzene–ether gave a clear syrup: ir (neat) 1740 cm^{-1} (C=O); nmr ($CHCl_3$) τ 5.91 (t, 2, J = 6 Hz, CH_2OTs), 2.21 (d, 2, J = 8 Hz, aromatic), 2.65 (d, 2, J = 8 Hz, aromatic), 7.57 (s, 3, CH_3), and 7.5–8.9 (complex, 9).

Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43; S, 11.36. Found: C, 59.81; H, 6.21; S, 11.02.

Registry No.—**3**, 21298-09-9; **4**, 21298-10-2; **5**, 21298-62-4; **6**, 21298-11-3; **3** (diacetate), 21275-29-6.

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Stereoisomeric Geminal Dihalonorbornanes[1]

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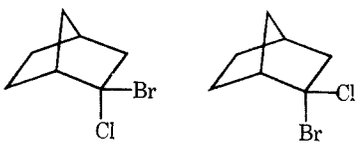
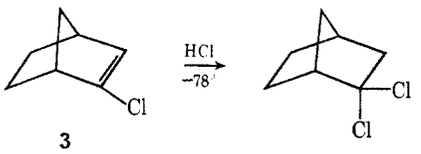
Although geminal halides constitute a rather common class of organic compounds, relatively little is known regarding the mechanisms by which they react. It was only very recently, for example, that hydrolysis of 2,2-dihalopropanes to 2-halopropenes was shown to proceed by the E1, rather than the E2, pathway.[2] Hydrolyses of benzal halides are also thought to proceed *via* initial ionization to α-halo carbonium ions, and some success has been achieved in correlating hydrolysis rates for this class of compound with the relative ability of the halogens to stabilize the carbonium ion to which they are bonded.[3] For example, the faster rate of hydrolysis of benzal chlorobromide relative to benzal dibromide suggests that chlorine is better able to stabilize a carbonium ion than is bromine.[3]

Almost nothing is known of the stereochemical course of reactions involving geminal dihalides, because almost all such compounds now known have both halogens the same, with the resulting symmetry precluding most stereochemical studies. Much information on the reactions and properties of this class of compounds could, however, be obtained by studies involving geminal halides with two *different* halogens bonded to the same carbon, provided that each halogen atom resides in a different, and known, stereochemical environment. For example, investigations involving the stereoisomeric 2-bromo-2-chloronorbornanes (**1** and **2**) could be correlated with an extensive body of literature already available concerning the reactivity of the norbornyl ring system. Isomeric pairs such as **1** and **2** would be a source of considerable information regarding stereochemical features of gas-phase,[4] base-promoted,[5] and solvolytic dehydrohalogenations,[2,6] and of other reactions such as the electrochemical reduction[7] and halogen–metal interchange reaction[8] (metalation) of geminal dihalides. We wish to report the synthesis of **1** and **2** by a route which appears to have some generality for the stereochemically controlled synthesis of isomeric geminal dihalides.



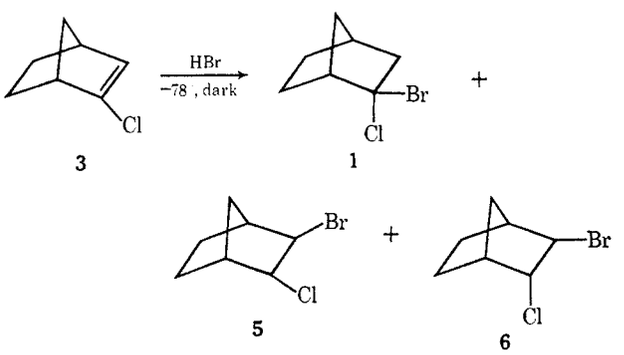
1 **2**

The hydrochlorination of 2-chloronorbornene (**3**) has been shown[9] to proceed rapidly, quantitatively, and regiospecifically[10] to 2,2-dichloronorbornane (**4**).



3 **4**

When **3** is allowed to react in the dark at −78° with liquid hydrogen bromide, there is obtained a mixture of adducts consisting of *exo*-2-bromo-*endo*-2-chloronorbornane (**1**) (95%), *endo*-2-chloro-*exo*-3-bromonorbornane (**5**) (4%), and a third isomer, tentatively assigned as *endo*-2-chloro-*endo*-3-bromonorbornane (**6**) (1%).



3 **1** **5** **6**

(1) Presented in part at the Second Middle Atlantic Regional Meeting of the American Chemical Society, New York, N. Y., Feb 1967.

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(3) A. Streitweiser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 102.

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(5) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *J. Amer. Chem. Soc.*, **88**, 4922 (1966).

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(8) (a) M. J. Goldstein and W. R. Dolbier, Jr., *ibid.*, **87**, 2293 (1965); (b) G. Köbrich, *Angew. Chem.*, **6**, 41 (1967).

(9) A. J. Fry and W. B. Farnham, *Tetrahedron Lett.*, 3345 (1968).

(10) A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).