mol) in boiling ethyl alcohol (100 ml) containing pyridine (5 ml) as base and then purified by distillation. All of the oximes are known.

**Nmr Spectra.**—Nmr spectra were determined at 60 MHz on a Varian A-60 spectrometer in $DCCl_3$ solutions (0.001 mol of oxime in 0.5 ml of $DCCl_3$) with TMS as internal reference. Tris(dipivalomethanato)europium(III) (Alfa Inorganics, Beverly, Mass.) (20 mg) was added to the above $DCCl_3$ solutions and spectra were recorded again.

**Beckmann Rearrangement of Methyl Isopropyl Ketoxime.**—To the oxime **6** (1.01 g, 0.01 mol) in 25 ml of dry ether, $PCl_5$ (3.12 g, 0.015 mol) was added in small quantities with stirring. After the addition, the mixture was stirred at room temperature for 30 min and poured into excess water. The water solution was extracted with chloroform. The chloroform extract was washed ($H_2O$) and dried ($MgSO_4$). Evaporation of chloroform gave 1 g (quantitative) of the mixture of *N*-isopropylacetamide and *N*-methylisobutyramide in the ratio of 86:14 [estimated from nmr ($CCl_4$) $\delta$ 1.87 (s, $COCH_3$ protons of *N*-isopropylacetamide[16]) and $\delta$ 2.70 (d, $J$ = 5 Hz, *N*-methyl protons of *N*-methylisobutyramide)[17]]. Nmr data for both amides are recorded.[16,17]

**Registry No.**—**1** (*E*), 10341-63-6; **1** (*Z*), 10341-59-0; **2** (*E*), 26306-10-5; **2** (*Z*), 26306-11-6; **3** (*E*), 30669-60-4; **3** (*Z*), 30669-61-5; **4** (*E*), 10341-61-4; **4** (*Z*), 10341-58-9; **5** (*E*), 10341-62-5; **5** (*Z*), 10341-60-3; **6** (*E*), 30669-66-0; **6** (*Z*), 30669-67-1; tris(dipivalomethanato)eurapium(III), 15522-71-1.

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## Bromohydrins of Methylenecyclobutane

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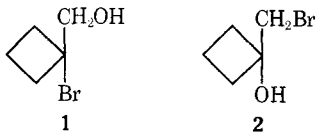
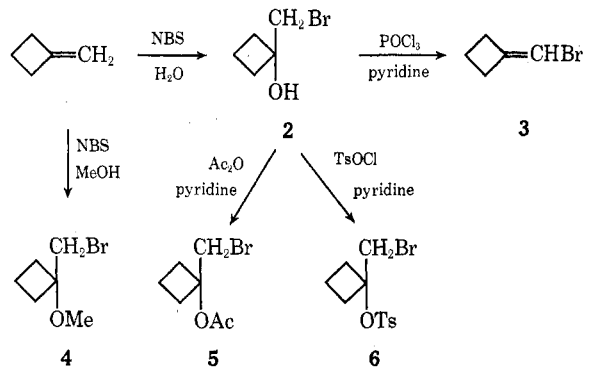
In connection with another investigation[1] we had need of 1-bromo-1-(hydroxymethyl)cyclobutane (**1**). This material had been reported[2] as essentially the only product formed in the treatment of methylenecyclobutane with hypobromous acid. We have repeated this work and have found that the major product is not **1** but its isomer, 1-(bromomethyl)cyclobutanol (**2**). An analogous misassignment of structure[2] in the case of the six-membered ring series has previously been noted.[3]



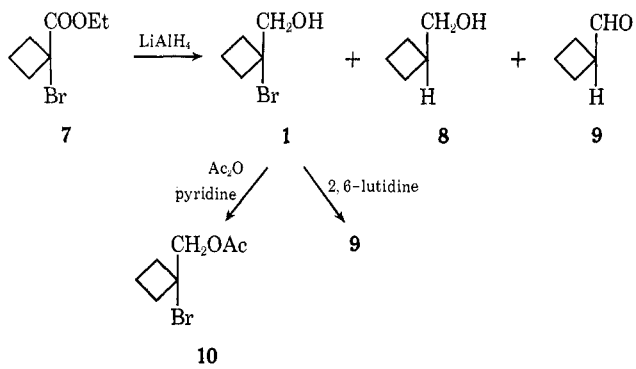

**1** **2**

The reaction of methylenecyclobutane with aqueous *N*-bromosuccinimide (NBS) proceeds rapidly at ice temperature. Distillation of the resultant product affords **2** in about 90% purity. A minor product, possibly **1**, is also formed but is quite unstable, eliminating hydrogen bromide to produce a carbonyl compound.

1-(Bromomethyl)cyclobutanol (**2**) forms an acetate and a tosylate, neither of which eliminated hydrogen bromide readily when treated with base. Dehydration of **2** occurred, however, to give bromomethylenecyclobutane (**3**). This latter transformation establishes the position of the bromine atom in **2**. Analogously, the reaction of methylenecyclobutane with NBS in anhydrous methanol afforded one major bromo ether, assigned structure **4**. This assignment is based upon the method of preparation of **4** (same conditions as for **2**) and a comparison of its nmr spectrum with that of **2** (see Experimental Section).




1-Bromo-1-(hydroxymethyl)cyclobutane (**1**)[4] was prepared by reduction of ethyl 1-bromocyclobutylcarboxylate (**7**). The conditions of the reduction are difficult to control so that unreduced bromo ester **7** is sometimes recovered along with a product of further reduction, cyclobutylmethanol (**8**), and small amounts of cyclobutanecarboxaldehyde (**9**). Bromohydrin **1**, purified by vapor phase chromatography, is clearly different from bromohydrin **2** in spectral properties. The former's structure is certain from its method of synthesis as well as by its facile loss of hydrogen bromide to give cyclobutanecarboxaldehyde (**9**).[4]




Further confirmation of the correct assignment of structure is obtained by a comparison of the nmr spectra of the bromohydrins and their respective acetates. The exocylic methylene group of **2** appears as a singlet at $\delta$ 3.63, while the acetate derived from it shows this same absorption at $\delta$ 3.93, corresponding to a downfield shift of $\delta$ 0.30 from the parent alcohol. On the other hand, in bromohydrin **1** the exocyclic methylene appears as a singlet at $\delta$ 3.84, and the acetate's corresponding absorption comes at $\delta$ 4.40, a downfield shift of $\delta$ 0.56 from the parent alcohol. The $\delta$ 0.56 value for the $\alpha$-acylation shift of **1** is in the proper range for a primary

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(2) J. G. Traynham and O. S. Pascual, *Tetrahedron*, **7**, 165 (1959).
(3) A. J. Sisti, *J. Org. Chem.*, **33**, 3953 (1968); C. Altona, H. J. Hageman, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **88**, 43 (1969).
(4) A. Burger, R. T. Standridge, N. E. Stjernstrom, and P. Marchini, *J. Med. Pharm. Chem.*, **4**, 517 (1961).

alcohol;[5] the β-acylation shift for **2**, as expected, is much smaller.

From these results and those of earlier workers with methylenecyclohexane,[3] it appears that the reaction of methylenecycloalkanes with hypobromous acid generates 1-(bromomethyl)cycloalkanols as the major products rather than 1-bromo-1(hydroxymethyl)cycloalkanes as originally reported.[2]

### Experimental Section

Boiling and melting points are uncorrected. Infrared spectra were recorded on a Perkin–Elmer Model 137 spectrophotometer. The nmr spectra were obtained with a Jeolco Model C-60H spectrometer using tetramethylsilane as an internal standard. Vapor phase chromatographic analyses were performed on a Varian Aerograph Model 90-P3 chromatograph. The following columns were used: 10 ft × 3/8 in., 3% SE-30 on 60–80 Chromosorb W and 10 ft × 1/4 in., 20% SE-30 on 60–80 Chromosorb W AW DMCS. Elementral analyses were performed by Chemalytics, Inc., Tempe, Ariz. and Galbraith Laboratories, Inc., Knoxville, Tenn.

**1-(Bromomethyl)cyclobutanol (2).**—In a 100-ml flask equipped with an overhead stirrer, reflux condenser, and stopper were placed 30 ml of water and 13 g (0.073 mol) of NBS. The mixture was cooled in an ice bath and with stirring 5.0 g (0.073 mol) of methylenecyclobutane (Aldrich Chemical Co., technical grade) was added through the open neck of the flask. The NBS disappeared rapidly, and after 10 min at ice temperature the solid was completely dissolved and an oily layer had formed at the bottom of the flask. Stirring was continued for 30 min, and then the bottom layer was separated and added to ether extracts of the water layer. The combined organic layers were then washed well with aqueous $NaHSO_3$ and dried ($MgSO_4$), and the ether was removed *in vacuo*. Distillation of the residue afforded 9.4 g (78%) of product, generally about 90% pure. Early, broad-boiling fractions were enriched in the minor product, but it could not be obtained pure without partial decomposition to a carbonyl compound. 1-(Bromomethyl)cyclobutanol (**2**) was obtained pure by careful distillation, bp 76–77° (10 mm) [lit.[1] bp 64–65° (10 mm)]. A vpc sample (3% SE-30, 110°) displayed ir (neat) 2.95, 7.02, 7.82, 8.10, 9.31 μ; nmr ($CDCl_3$) δ 1.4–2.5 (complex multiplets, 6 H, cyclobutyl $CH_2$), 3.25 (s, 1 H, OH), 3.63 (s, 2 H, $CH_2Br$).

The acetate **5** was prepared from 0.17 g (1.2 mmol) of bromohydrin and 1.02 g (10 mmol) of acetic anhydride (freshly distilled) in anhydrous pyridine at room temperature for 24 hr. The reaction mixture was extracted with ether, and the ether extracts were washed successively with dilute HCl to remove the pyridine and then with aqueous $NaHCO_3$ to remove the acids. After drying and removal of the ether, the acetate was flash distilled. An analytical sample (3% SE-30, 116°) displayed ir ($CCl_4$) 5.74, 7.98, 8.06, 8.19, 8.28 μ; nmr ($CDCl_3$) δ 2.10 (s, 3 H, $CH_3CO$), 1.4–2.6 (complex multiplets, 6 H, cyclobutyl $CH_2$), 3.93 (s, 2 H, $CH_2Br$).

*Anal.* Calcd for $C_7H_{11}BrO_2$: C, 40.60; H, 5.36; Br, 38.59. Found: C, 40.77; H, 5.36; Br, 38.61.

The tosylate **6** was prepared from 3.23 g (0.011 mol) of tosyl chloride and 1.65 g (0.010 mol) of bromohydrin in anhydrous pyridine initially at ice temperature. The reaction mixture was then warmed to room temperature and maintained there for 48 hr. Neutralization with HCl and ether extraction gave 2.23 g (73%) of a colorless solid, mp 60–63°. Crystallization from pentane afforded needles, mp 65–66°, ir (Nujol) 8.50 μ (S=O).

*Anal.* Calcd for $C_{12}H_{15}BrO_3S$: C, 45.15; H, 4.74. Found: C, 44.87; H, 4.62.

**Dehydration of 1-(Bromomethyl)cyclobutanol (2).**—To a solution of 1.0 g (0.006 mol) of bromohydrin **2** in anhydrous pyridine at ice temperature was added dropwise with stirring 0.92 g (0.006 mol) of phosphorus oxychloride. Stirring at ice temperature was continued for 8 hr. The mixture was poured into ice and extracted with *n*-hexane. The hexane extracts were neutralized with 2 *N* HCl, then washed with water, and dried, and the *n*-hexane was distilled. Flash distillation of the residue followed by vpc analysis (20% SE-30, 92°) showed the predominant product (0.63 g, 71%) to be bromomethylenecyclobutane (**3**) by comparison of its retention time and ir and nmr spectra with those of authentic material.[1]

**1-(Bromomethyl)-1-methoxycyclobutane (4).**—In 30 ml of absolute methanol cooled in an ice bath was suspended 13.0 g (0.073 mol) of NBS. To this was added 5.0 g (0.073 mol) of methylenecyclobutane, and the mixture was stirred at ice temperature for 30 min, then warmed slowly to room temperature over 2 hr. The mixture was poured into ice and extracted with ether. The ether extracts were washed with water and aqueous $NaHSO_3$ and then dried over $MgSO_4$, and the ether was removed. Distillation of the residue afforded 10.02 g (76%) of **4**, bp 77–80° (5 mm). A forerun of distillate contained mostly **4**, but was contaminated with a lower boiling component, which, by ir, could have been the isomeric bromo ether. An analytical sample (20% SE-30, 130°) of **4** displayed ir (neat) 7.82, 9.13 μ; nmr ($CDCl_3$) δ 1.4–2.4 (complex multiplets, 6 H, cyclobutyl $CH_2$), 3.22 (s, 3 H, $OCH_3$), 3.62 (s, 2 H, $CH_2Br$).

*Anal.* Calcd for $C_6H_{11}BrO$: C, 40.25; H, 6.19; Br, 44.63. Found: C, 40.10; H, 6.19; Br, 44.58.

**1-Bromo-1-(hydroxymethyl)cyclobutane (1).**[4]—A solution of lithium aluminum hydride (0.28 g, 0.007 mol) in 15 ml of anhydrous ether was added to a solution of ethyl 1-bromocyclobutanecarboxylate[6] (3.0 g, 0.015 mol) in 15 ml of anhydrous ether at 0°. After addition was complete, stirring was continued for 1 hr at 0°, then for 4 hr at room temperature. The mixture was decomposed with water and then with 20% $H_2SO_4$. The ether layer was decanted, and the residue was extracted with ether several times. The combined ether layers were dried over $MgSO_4$, and the ether was removed *in vacuo*. Distillation of the residue [bp 45–48° (8 mm)] afforded a mixture of recovered bromo ester **7**, cyclobutylmethanol (**8**), 1-bromo-1-(hydroxymethyl)-cyclobutane (**1**), and small amounts of cyclobutanecarboxaldehyde (**9**), the relative proportions of which varied from run to run. Compounds **7**, **8**, and **9** were identified by comparison of their retention times and ir spectra with those of authentic materials. A pure sample of bromohydrin **1** (20% SE-30, 127°) displayed ir (neat) 2.92, 9.0, 9.3–9.8 μ; nmr ($CDCl_3$) δ 2.91 (s, 1 H, OH), 1.8–2.9 (complex multiplets, 6 H, cyclobutyl $CH_2$), 3.84 (s, 2 H, $CH_2OH$); phenylurethane mp 64–65° (lit.[4] mp 69–70°).

The acetate **10** was prepared from 0.30 g (0.002 mol) of bromohydrin and 1.02 g (0.010 mol) of freshly distilled acetic anhydride in anhydrous pyridine kept at room temperature for 4 days. The reaction mixture was poured into water and extracted successively with aqueous $Na_2CO_3$ and dilute HCl. After the ether layer was dried and the ether removed, the residue was flash distilled, and the acetate was collected by vpc (20% SE-30, 129°), ir ($CCl_4$) 5.70, 8.25, 9.58, 9.70 μ; nmr ($CDCl_3$) δ 2.27 (s, 3 H, $CH_3CO$), 1.5–2.9 (complex multiplets, 6 H, cyclobutyl $CH_2$), 4.40 (s, 2 H, $CH_2OAc$).

*Anal.* Calcd for $C_7H_{11}BrO_2$: C, 40.60; H, 5.36; Br, 38.59. Found: C, 40.79; H, 5.29; Br, 38.90.

**Dehydrobromination of 1-Bromo-1-(hydroxymethyl)cyclobutane (1).**—The literature procedure was followed, substituting 2,6-lutidine for 5-ethyl-2-methylpyridine as the base. The cyclobutanecarboxaldehyde formed was identified by comparison of its retention time and ir spectrum with those of authentic material.[1]

**Registry No.**—**1**, 30896-87-8; **2**, 30800-70-5; **4**, 30800-71-6; **5**, 30800-72-7; **6**, 30953-07-2; **10**, 30800-73-8.

**Acknowledgment**—This work was supported by the Petroleum Research Fund, administered by the American Chemical Society.

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