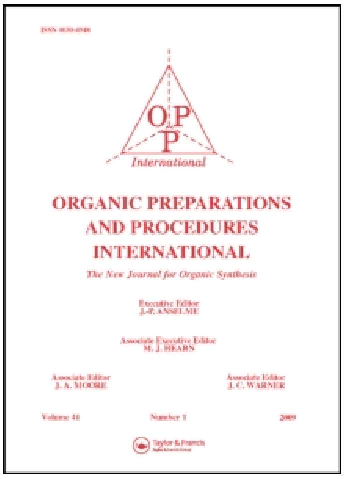

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A SIMPLE SYNTHESIS OF ALICYCLIC *Trans*-GLYCOLS VIA HYDROBORATION OF SILYL ENOL ETHERS

Hiromichi Kono[a]; Yoichiro Nagai[b]
[a] Sagami Chemical Research Center, Sagamihara, Japan [b] Department of Chemistry, Gunma University, Kiryu, Gunma, Japan

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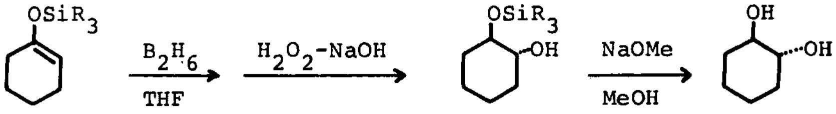
A SIMPLE SYNTHESIS OF ALICYCLIC Trans-GLYCOLS VIA HYDROBORATION OF SILYL ENOL ETHERS

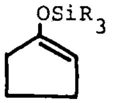
Hiromichi KONO
Sagami Chemical Research Center
4-4-1 Nishi-Onuma, Sagamihara 229, Japan.
and Yoichiro NAGAI
Department of Chemistry
Gunma University, Kiryu, Gunma 376, Japan.

The hydroboration-oxidation of substituted cycloalkenes has been extensively investigated[1] as a method for the selective preparation of trans-alicyclic glycols. Recently, the preparation of 1,2-diols from two silyl enol ethers by hydroboration-oxidation has been reported briefly by Klein, Levene and Dunkelblum[2]. At about the same time we started to study the hydroboration of several silyl enol ethers and now report our own results of this convenient synthetic procedure for trans-glycols from several silyl enol ethers (Table 1).

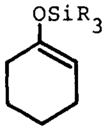


Thus, a 1-silyloxycycloalkene was converted to 2-silyloxycycloalkanol by hydroboration-oxidation in high yield and treatment of the resulting 2-silyloxyalkanol with methanol in the presence of a small amount of sodium methoxide gave a high yield of the corresponding <u>trans</u>-glycol.

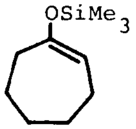
Table 1.



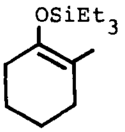
R= Me; I-a
Et; IV-a



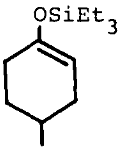
R= Me; II-a
Et; V-a



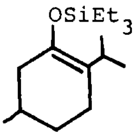
III-a



VI-a



VII-a



VIII-a

From the silyl enol ethers, I-a∼VII-a, the corresponding 2-silyloxycycloalkanols were obtained (I-b∼VII-b in Table 2). Glpc analysis of VII-b indicated it to be a 3:2 mixture of two isomers. The hydroboration of VIII-a gave a complex mixture and the corresponding silyloxycycloalkanol could not be isolated.

Treatment of the reaction mixture, obtained by the hydroboration-oxidation of a silyl enol ether, with methanol in the presence of a small amount of sodium methoxide afforded the corresponding <u>trans</u>-glycols(I-c, II-c, III-c and VIII-c in Table 3). The pure samples of IV-b, V-b, VI-b and VII-b were converted to the corresponding <u>trans</u>-diols in quantitative yield (glpc) by the same method as above. Isolation of these diols was achieved by preparative glpc. VII-c was a mixture of two isomers in the ratio of 61:39 (glpc).

EXPERIMENTAL

Materials.– 1-Trimethylsilyloxycycloalkenes(I-a∼III-a) were prepared by House's method[3] and 1-triethylsilyloxycycloalkenes (IV-a∼VIII-a) were obtained by the condensation of the cyclic ketones and triethylsilane according to the method[4] which was reported recently from our laboratory. New compounds used in this study were:

1-Trimethylsilyloxycycloheptene(III-a), bp. 54°(2.5 mmHg); n_D^{20} 1.4516. *Anal*. Calcd.: C, 65.15; H. 10.93. Found: C, 65.54; H, 10.64.

1-Triethylsilyloxy-2-methylcyclohexene(VI-a), bp. 84.5-85.5°(2.5 mmHg). *Anal*. Calcd.: C, 68.95; H, 11.57. Found: C, 69.13; H, 11.32.

1-Triethylsilyloxy-4-methylcyclohexene(VII-a), bp. 76-78 (1 mmHg). *Anal*. Calcd.: C, 68.95; H, 11.57. Found: C, 68.62; H, 11.23.

3-Triethylsilyloxy-p-menth-3-ene(VIII-a), bp. 92°(0.5 mmHg); n_D^{23} 1.4645. *Anal*. Calcd.: C, 71.57; H, 12.01. Found: C, 71.54; H, 11.73.

Hydroboration-Oxidation of silyl enol ether.– The general procedure used is illustrated by the reaction of 1-trimethylsilyloxycyclohexene. In a 100 ml three-necked flask fitted with a dropping funnel, a thermometer, a reflux condenser and magnetic stirring bar were placed diborane (10 mmoles)[5] and

Table 2. Yield and Physical Properties of 2-Silyloxycycloalkanol

2-Silyloxyalkanol	bp °C (mmHg)	n_D^{20}	Yield[a] (%)	Elemental Analysis % Calcd. (Found) C	H
2-Trimethylsilyloxycyclopentanol(I-b)	58-9 (2.7)	1.4442	90[b]	55.12 (55.25)	10.41 (10.37)
2-Trimethylsilyloxycyclohexanol(II-b)	52 (0.3)	1.4497	95	57.39 (57.13)	10.70 (10.41)
2-Trimethylsilyloxycycloheptanol(III-b)	47 (0.2)	1.4587	92[b]	59.35 (59.78)	10.95 (10.85)
2-Triethylsilyloxycyclopentanol(IV-b)	93-5 (1.2)	1.4593	93[b]	61.05 (60.85)	11.18 (10.88)
2-Triethylsilyloxycyclohexanol(V-b)	86-7 (0.5)	1.4581[d]	94	62.55 (62.37)	11.37 (11.24)
2-Triethylsilyloxy-1-methylcyclohexanol(VI-b)	78-9 (0.2)	1.4602[e]	92	63.88 (63.68)	11.55 (11.38)
2-Triethylsilyloxy-5-methylcyclohexanol(VII-b)	86-7 (0.45)	1.4580[f]	98	63.88 (63.99)	11.55 (11.34)

[a] Glpc yield based on silyl enol ether. [b] A part of product was converted to the glycol on the condition of oxidation with alkaline hydrogen peroxide. [c] A mixture of two isomers (3:2). [d] At 27°. [e] At 25°. [f] At 23°.

10 ml of tetrahydrofuran. To this stirred mixture was added dropwise a solution of 1-trimethylsilyloxycyclohexene (3.4 g, 20 mmoles) in 5 ml of THF at 4°. The reaction mixture was stirred at room temperature for 30 min., then treated with 2.2 ml of 3N aqueous sodium hydroxide (6.6 mmoles) and 2.1 ml of 30% hydrogen peroxide (20 mmoles) below 20°. The reaction mixture was stirred for an additional hour at room temperature and analyzed by glpc (10% QF-1, 2.9 m, 130°). At this stage glpc analysis indicated a 95% yield of 2-trimethylsilyloxycyclohexanol. The mixture was extracted with ether (50 ml×3),

and the extract was washed with brine, dried over $MgSO_4$, filtered, concentrated on a rotary evaporator and distilled under reduced pressure to give 3.32 g (88%) of trimethylsilyloxycyclohexanol as a colorless liquid, bp. 52/0.3 mmHg; n_D^{20} 1.4497. The yields and physical properties of all silyloxycycloalkanols obtained are summarized in Table 2.

Methanolysis of 2-trialkylsilyloxycycloalkanol.– The procedure described for the methanolysis of 2-trimethylsilyloxycyclohexanol is representative. The reaction mixture obtained by the hydroboration-oxidation of 1-trimethylsilyloxycyclohexene (3.41 g, 20 mmoles) was saturated with NaCl. The organic layer which separated was dried over $MgSO_4$ and filtered.

Table 3. Yield of Alicyclic Glycol

1-Silyloxy-cycloalkene	Alicyclic Glycol	mp(lit) °C	Yield (%)
I-a	trans-Cyclopentane-1,2-diol(I-c)	49(50)[6]	94[a]
II-a	trans-Cyclohexane-1,2-diol(II-c)	104(104)[7]	95[a]
III-a	trans-Cycloheptane-1,2-diol(III-c)	62-3(64-5)[8]	88[a]
VI-a	trans-1-Methylcyclohexane-1,2-diol(VI-c)	81-3(84)[7,c]	98[b]
VII-a	trans-4-Methylcyclohexane-1,2-diol(VII-c)	oil[c,d]	97[b]
VIII-a	trans-p-Menthane-3,4-diol(VIII-c)	oil[c]	51[a]

a. Isolated yield based on silyl enol ether. b. Glpc yield based on 2-silyloxyalkanol. c. Pure product was isolated by column chromatography and preparative gas chromatography, and characterized by ir, nmr and elemental analysis. d. A mixture of two isomers (61:39).

The filtrate was concentrated on a rotary evaporator and treated with 100 mg of sodium methoxide in 10 ml of methanol for 2 hrs at room temperature. The reaction was exothermic. Evaporation of volatile materials under vacuum and crystallization from benzene gave 2.23 g (96%) of trans-1,2-cyclohexanediol as white crystals, mp. 104°. All alicyclic glycols obtained in this study are listed in Table 3.

REFERENCES

1. (a) J. Klein and E. Dunkelblum, Tetrahedron, 24, 5701(1968); (b) H. C. Brown and R. M. Gallivan, Jr., J. Am. Chem. Soc., 90, 2906(1968); (c) A. Hassner, R. E. Barnett, P. Catsoulacos and S. H. Wilen, ibid., 91, 2632(1969); (d) A. Suzuki, K. Ohmori and M. Itoh, Tetrahedron, 25, 3707(1969); (e) H. C. Brown and R. L. Sharp, J. Am. Chem. Soc., 90, 2915(1968); (f) H. C. Brown and E. F. Knights, ibid., 90, 4439 (1968); (g) D. J. Pasto and J. Hickman, ibid., 90, 4445(1968).
2. J. Klein, R. Levene and E. Dunkelblum, Tetrahedron Lett., 2845(1972).
3. H. O. House, L. J. Czuba, M. Gall and H. D. Olmstead, J. Org. Chem., 34, 2324(1969).
4. Y. Nagai, K. Uetake, T. Yoshikawa and H. Matsumoto, J. Synth. Org. Chem. Japan, 31, 759(1973).
5. G. Zweifel, K. Nagase and H. C. Brown, J. Am. Chem. Soc., 84, 183 (1962).
6. L. N. Owen and P. N. Smith, J. C. S., 4026(1952).
7. H. Adkins and A. K. Roebuck, J. Am. Chem. Soc., 70, 4041(1948).
8. L. N. Owen and G. S. Sahara, J. C. S., 2582(1953).

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