Anal. Calcd for $C_{17}H_{21}NO_4 \cdot C_6H_{13}NO_3S$: C, 57.25; H, 7.11; S, 6.65. Found: C, 57.2; H, 7.2; S, 6.3.

(±)-1α*H*,5α*H*-Tropane-2β,3β-diol 2-Benzoate 3-Acetate (11). Method A (from the 3-Acetate).—A solution of 0.80 g (4 mmol) of (±)-1α*H*,5α*H*-tropane-2β,3β-diol 3-acetate (**12**) in 5 ml of C_5H_5N was treated with 0.91 g (4 mmol) of benzoic anhydride at room temperature overnight. The usual work-up afforded 1.1 g of oily residue. Chromatography on four silica preparative plates using 50:47:3 Et_2O–pentane–*i*-$PrNH_2$ (R_f 0.36) followed by recrystallization from hexane gave 0.50 g of poorly formed crystals of 2-benzoate 3-acetate **11**, mp 91–95°. From wet ether, **11** formed a hydrate as beautiful, massive prisms which reverted to an oil when dried *in vacuo*. The air-dried prisms melted at 90–102° with bubbling and their nmr spectrum showed an excess of two hydrogens, presumably from H_2O. The mass spectrum gave a molecular ion peak at *m/e* 303 with abundant ions at *m/e* 244 (M^+ − OAc), 198 (M^+ − OBz), and 105 (OBz), and very intense peaks at *m/e* 17 (OH) and 18 (H_2O).

Anal. Calcd for $C_{17}H_{21}NO_4 \cdot H_2O$: C, 63.53; H, 7.22; N, 4.35. Found: C, 63.5; H, 7.3; N, 4.2.

Method B (from the 2-Benzoate).—A solution of 0.10 g (0.4 mmol) of (±)-1α*H*,5α*H*-tropane-2β,3β-diol 2-benzoate (**9**) in 5 ml of C_5H_5N and 2.5 ml of Ac_2O was heated on the steam bath for 2 hr. The usual work-up afforded 0.12 g of **11** as an oil that crystallized from hexane, mp 96–99°. A sample recrystallized from wet ether melted at 92–102° (bubbling). The nmr and ir spectral curves and the tlc R_f value were all identical with those of **11** prepared by method A. A mixture melting point was undepressed.

Method C (from the Diol).—A solution of 0.48 g (3.1 mmol) of diol **7** in 20 ml of C_5H_5N was treated with 0.72 g (3 mmol) of benzoic anhydride and the solution was heated on a steam bath for 2.5 hr. Ac_2O (4 ml) was added and the mixture was heated for 2 hr more. The usual work-up afforded 0.72 g of an oily residue. Tlc analysis (silica gel; Et_2O–pentane–*i*-$PrNH_2$ 50:47:3) showed a major spot with R_f 0.36 and a minor spot with R_f 0.21. Chromatography on four preparative plates using the same solvent system gave 0.50 g (54%) of the R_f 0.36 oil which crystallized as prisms from wet Et_2O. It was found to be identical with **11** by means of nmr, ir, mixture melting point, and tlc.

The band of R_f 0.21 material furnished 0.17 g of oil which crystallized from Et_2O and proved identical with the 2-acetate 3-benzoate **2** by the usual criteria.

When the experiment just described was repeated using $CHCl_3$ as the solvent instead of pyridine, tlc analysis of the product indicated that **2** was the major product.

Registry No.—**2**, 33780-46-0; **2** cyclohexanesulfamate, 33780-47-1; **3**, 33780-48-2; **4**, 33780-49-3; **5**, 33780-50-6; **6**, 33780-51-7; **7**, 33780-52-8; **8**, 33886-15-6; **8** cyclohexanesulfamate, 33886-16-7; **9**, 33872-63-8; **10**, 33780-53-9; **10** HCl, 33780-54-0; **11**, 33780-55-1; **12**, 33780-56-2; **13** HCl, 33780-57-3.

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A Simple Synthesis of 4-Hydroxycyclohexanone

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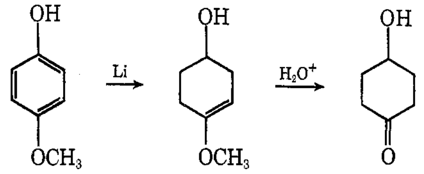
Recently in our laboratory we have found it desirable to prepare synthetically useful quantities of 4-hydroxycyclohexanone (**1**). We therefore had need of a simple high-yielding route to this compound. Jones and Sondheimer[2] developed a route, later modified by Trager,[3] which required the selective oxidation of a protected 1,4-cyclohexanediol. This multistep synthesis gave only a 25% yield based upon the starting diol and was not suited to our purpose.

Fried[4] has shown that phenols can be reduced under Birch conditions provided that high enough concentrations of Li in ammonia are used. The high concentrations of Li are required presumably because of the high potential barrier to formation of the dianion radical, which must come from the initially produced phenoxide anion.

When *p*-methoxyphenol (**2**) was subjected to reduction with lithium in ammonia (3.6 *M* Li), there was isolated after work-up the crude enol ether **3** which was directly hydrolyzed in 0.1 *N* HCl to afford **1** in 89% yield after distillation. The mole ratio of lithium to the phenol appears to be critical. When the mole ratio was reduced from 11:1 to 6:1 (both still 3.6 *M* in Li), considerable quantities of 1,4-cyclohexanedione are formed. This high-yielding simple route can be easily adapted to large scale reactions and renders this valuable synthetic intermediate (**1**) readily available.



2 **3** **1**

Experimental Section

4-Hydroxycyclohexanone (1).—Liquid ammonia (100 ml) after distillation through a KOH tower was collected with stirring in a thoroughly dry three-neck flask at −78°. The NH_3 inlet was replaced by a N_2 inlet and the remainder of the reaction was run under nitrogen. The reaction flask was allowed to warm to −50° and Li (2.5 g, 0.36 g-atom) was added all at once. After this, *p*-methoxyphenol (4.0 g, 32.2 mmol) in anhydrous ether (25 ml) was added to the ammonia solution over a period of 5 min. The reaction mixture was stirred at −50° for 45 min, absolute ethanol (1.9 ml, 32 mmol) was added, and stirring was continued for an additional 1 hr. Absolute ethanol (4 ml) was added at 30-min intervals until the blue color was discharged. A total of 25 ml of ethanol was used.

After the ammonia had been evaporated, saturated NH_4Cl (200 ml) was added to the residue, and the resulting brown solution was cooled in an ice bath. Concentrated HCl was added dropwise until the pH of the solution was approximately 1. This acidic solution was then heated to 50° for 1 hr to effect hydrolysis of the enol ether **3**. The cooled aqueous solution was extracted with $CHCl_3$ (8 × 50 ml), saturated with NaCl, and then reextracted. After drying and removal of solvent, 4.96 g of a brown oil was isolated. Distillation at 93° (0.3 mm) yielded 3.25 g (89%) of 4-hydroxycyclohexanone: M^+ 114; ir (neat) 5.95 (C=O), 2.98 μ (OH); nmr ($CDCl_3$–TMS) δ 4.16 (m, α to hydroxyl), 1.77–2.84 (m, ring CH_2 protons); 2,4-dinitrophenylhydrazone mp 152–153° (lit.[1] mp 150–151°).

Registry No.—**1**, 13482-22-9.

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[2] E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

[3] W. F. Trager, B. J. Nist, and A. C. Huitric, *J. Pharm. Sci.*, **56**, 698 (1967).

[4] J. Fried, N. A. Abraham, and T. S. Santhanakrishnan, *J. Amer. Chem. Soc.*, **89**, 1044 (1967).