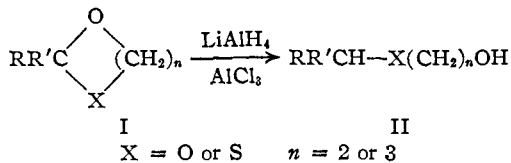


A NEW SYNTHESIS OF HYDROXYETHERS AND THIOETHERS

Sir:

In a previous communication¹ we described the reduction of acetals and ketals to ethers by means of lithium aluminum hydride-aluminum chloride. We now have extended this method to cyclic acetals and ketals and the corresponding hemithioacetals and hemithioketals. The cyclic oxygen derivatives (eq. X = O) are reduced to hydroxyethers. In the case of the sulfur derivatives (X =



S), the reductive cleavage involves largely, if not entirely, the carbon-oxygen bond, the carbon-sulfur-carbon bond being intact in the product. Thus this reduction constitutes a convenient method for synthesizing thioethers starting with aldehydes and ketones. The resulting thioethers contain a second functional group (hydroxyl) which is obviously capable of further chemical transformations.

Examples so far studied involve ethylene and trimethylene derivatives (eq., $n = 2$ or 3). Below are listed the aldehydes and ketones and the glycols or hydroxymercaptans from which the starting materials (I) were prepared and the yields in the reduction of I to the products II: cyclohexanone, ethylene glycol, 88%; cyclohexanone, trimethylene glycol, 89%; benzaldehyde, ethylene glycol, 89%; benzaldehyde, trimethylene glycol, 83%; cyclohexanone, mercaptoethanol, 91%; cyclohexanone, 3-mercapto-1-propanol, 91%; benzaldehyde, mercaptoethanol, 88%; benzaldehyde, 3-mercapto-1-propanol, 98%. All intermediates and products, where described in the literature, agreed in properties with those previously reported and, where new, had the correct carbon and hydrogen content. Moreover, the infrared spectra of all the reduction products were identical with those of authentic samples prepared (sometimes tediously) by the Williamson synthesis.

The method does not appear to be limited to hemithioketals of type I. For example, we have reduced 2-benzylthiotetrahydropyran, the addition product of dihydropyran and benzyl mercaptan, to 5-benzylthio-1-pentanol, $\text{HO}(\text{CH}_2)_5\text{SCH}_2\text{C}_6\text{H}_5$, in 58% yield.

The synthesis of 2-(cyclohexylthio)-ethanol is described as a typical example of the new method. In a 500-ml. three-necked flask equipped with a calcium chloride-protected reflux condenser, a sealed stirrer and a pressure-equalized addition funnel was placed 13.3 g. (0.1 mole) of aluminum chloride. The flask was cooled in an ice-bath for 0.5 hour and 100 ml. of sodium-dried ether was added slowly to dissolve the aluminum chloride, then 22.8 ml. (0.025 mole) of a 1.1M ethereal lithium aluminum hydride solution. After stirring for 0.5 hour, 7.9 g. (0.05 mole) of 1-oxa-4-

thiaspiro[4.5]decane² (cyclohexanone-mercaptoethanol hemithioacetal) dissolved in 100 ml. sodium-dried ether was added slowly to the cooled "mixed hydride" solution. Stirring was continued for 2 hours (temperature control at this stage is not essential). A total of 100 ml. of 10% sulfuric acid then was added to the cooled reaction mixture, dropwise at first. The layers were separated and the aqueous layer extracted with three 50-ml. portions of ether. The combined ether layers were dried, concentrated and the residue distilled to give 7.29 g. (91.1%) of 2-(cyclohexylthio)-ethanol, b.p. 84° (0.3 mm.), n_{D}^{25} 1.5128 (lit.³ b.p. 140° (18 mm.)) identical in infrared spectrum with a sample prepared from cyclohexyl mercaptan and ethylene oxide.

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ULTRAVIOLET LIGHT INDUCED TRANSFORMATION OF α -TROPOLONE¹

Sir:

Upon irradiation, colchicine (a methyl ether of a substituted α -tropolone)² and γ -tropolone methyl ether³ are transformed into valence tautomeric structures of the 3,2,0-bicycloheptadiene type. It has now been found that when α -tropolone is irradiated with ultraviolet light from a G. E. quartz mercury arc in aqueous solution, a 50% yield of a crude acid is obtained from which the pure 4-oxo-2-cyclopentene-1-acetic acid (I), m.p. 100.6–101.6°, $\epsilon_{\text{max}}^{218}$ 12,000, ν_{max} 1710 cm^{-1} ,⁴ can be obtained in 16% yield.

The spectral properties of I suggest the presence of either an unsubstituted cyclopentenone or an α,β -unsaturated acid chromophore. The former was shown to be present since I upon hydrogenation yielded a dihydro derivative (molecular distillation b.p. 100° (0.5 mm.), semicarbazone m.p. 203.0–203.4°) which in the infrared possessed bands at 1720 and 1740 cm^{-1} , characteristic of a carboxyl and a cyclopentanone group. The dihydro material upon Wolff-Kishner reduction yielded cyclopentaneacetic acid (*p*-bromophenacyl ester, m.p. 85.2–86.0°) which was identical with an authentic sample.

The carbonyl group of the dihydro derivative of the irradiation product was placed at C-3 on the cyclopentane nucleus by comparison with authentic samples of 2-oxo⁵ and 3-oxocyclopentane-1-acetic

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