

5-10% of retained water the films were heated at 160° for one hour immediately before spectral analysis. Determinations showed that during the time it took to measure the spectra no appreciable absorption of moisture occurred.

Instrument.—The spectral measurements¹¹ were made on a Perkin-Elmer infrared spectrometer Model 12-A using a 40-cycle chopper, a Strong nickel-strip bolometer, an a. c. amplifier and a Brown Instrument Company potentiometer. The data were obtained on a point-to-point basis, the points being taken from 5 to 10 cm.⁻¹ apart at frequencies up to 1900 cm.⁻¹ and at larger intervals at higher frequencies.

(11) We are indebted to Mr. Dwight Merrill for some of the spectral measurements.

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A Convenient Synthesis of Octahydropyrrocoline and 2-(γ -Hydroxypropyl)-piperidine

BY V. BOBKELHEIDE AND S. ROTHCHILD¹

It has been found that octahydropyrrocoline, which has previously been prepared in poor yield by procedures involving three or more steps,² can be obtained readily in excellent yield by the direct hydrogenation of 2-(γ -hydroxypropyl)-pyridine³ at 200° and 2500 lb. pressure with Raney nickel catalyst.

When the reduction was carried out at 125° instead of 200°, the product was not octahydropyrrocoline but rather 2-(γ -hydroxypropyl)-piperidine. The yield of 2-(γ -hydroxypropyl)-piperidine is practically quantitative and this is undoubtedly the best method for its preparation.⁴ At temperatures intermediate between 125 and 200° the reduction gave mixtures of octahydropyrrocoline and 2-(γ -hydroxypropyl)-piperidine. Although it is probable that 2-(γ -hydroxypropyl)-piperidine is an intermediate in the formation of octahydropyrrocoline, 2-(γ -hydroxypropyl)-piperidine is not readily affected by heat and can be distilled repeatedly without change.

Experimental⁵

Octahydropyrrocoline.—A mixture of freshly distilled 2-(γ -hydroxypropyl)-pyridine (9.0 g., 0.066 mole), Raney nickel (2 g.), and absolute alcohol (10 cc.) was heated at 200° with shaking under an initial pressure of 2540 p. s. i. of hydrogen. At the end of one hour the drop in hydrogen pressure corresponded to that calculated. After removal of the catalyst by filtration, the oily product was distilled yielding 6.4 g. (78%) of a colorless oil; b. p. 71-72° at 32 mm.; n_{20}^{D} 1.4702.

For purposes of identification, there were prepared the

(1) Aided by a Grant from the National Foundation for Infantile Paralysis.

(2) (a) Loeffler and Kaim, *Ber.*, **42**, 94 (1909); Loeffler and Flugel *ibid.*, **42**, 3423 (1909), and Tullock and McElvain, *THIS JOURNAL*, **61**, 961 (1939); (b) Clemo and Ramage, *J. Chem. Soc.*, 2969 (1932); (c) Wibaut and Beets, *Rec. trav. chim.*, **60**, 905 (1940); (d) Diels and Alder, *Ann.*, **498**, 16 (1932).

(3) 2-(γ -Hydroxypropyl)-pyridine is available from Reilly Tar and Chemical Co., Indianapolis, Indiana.

(4) Previous methods for preparing 2-(γ -hydroxypropyl)-piperidine are given in ref. (2a).

(5) Analysis by Mrs. G. L. Sauvage. All melting points are corrected.

following derivatives: picrate, m. p. 228-9° (lit.,² m. p. 226°, 231-232°); gold chloride double salt, m. p. 188-192° (lit.,² m. p. 191-193°).

The methiodide of octahydropyrrocoline was formed in benzene and proved to be unstable in the presence of air. The amorphous solid, obtained from benzene, decomposed at 280-283° and was analyzed directly without further purification.

Anal. Calcd. for C₉H₁₃NI: C, 40.46; H, 6.79. Found: C, 40.00; H, 7.10.

2-(γ -Hydroxypropyl)-piperidine.—A mixture of freshly distilled 2-(γ -hydroxypropyl)-pyridine (14.0 g., 0.102 mole), Raney nickel (2 g.), and absolute alcohol (4 cc.) was heated at 125° with shaking under an initial pressure of 2500 p. s. i. of hydrogen. At the end of four hours the pressure drop corresponded to that calculated. After removal of the catalyst and solvent, the product was distilled yielding 12.5 g. (85%) of a colorless oil; b. p. 101-102° at 3 mm.; n_{20}^{D} 1.4882.

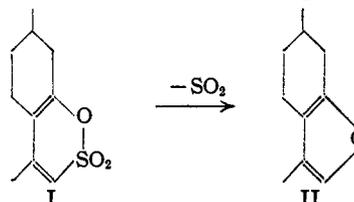
For identification there was prepared the hydrochloride, m. p. 128-129° (lit.,^{2b} m. p. 127-128°), and the mercuric chloride complex, m. p. 180-182° (lit.,^{2a} m. p. 182-183°).

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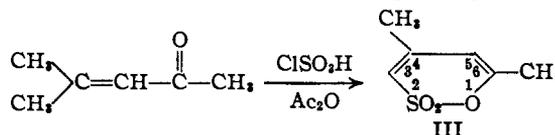
The Sulfonation of Mesityl Oxide

BY RICHARD H. EASTMAN AND DON GALLUP¹

In seeking a convenient method for the synthesis of alkylated furans we have sought to extend to simple α,β -unsaturated ketones and aldehydes the observation of Treibs² that pulegone on treatment in acetic anhydride at ice temperature with concentrated sulfuric acid yields cyclopulegenol-sulfonic ester (I) from which menthofuran (II) is obtained in excellent yield on pyrolysis with zinc oxide at atmospheric pressure.



We have attempted the sulfonation under varied conditions of concentration and temperature, using both sulfuric acid and chlorosulfonic acid, of crotonaldehyde, cyclohexylidencyclohexanone, 3,4-dimethylhexene-3-on-2 and mesityl oxide. A clean-cut reaction was obtained only in the case of the sulfonation of mesityl oxide which on sulfonation with chlorosulfonic acid in acetic anhydride gave the cyclic sulfonic ester III in good yield. Pyrolysis of the cyclic sulfonic ester of mesityl oxide (III) at atmospheric pressure,



(1) The work reported here is taken from a thesis presented by Don Gallup to Stanford University in partial fulfillment of the requirements for the degree of Master of Science.

(2) W. Treibs, *Ber.*, **70B**, 85 (1937).

under reduced pressure and in an atmosphere of nitrogen did not effect the transformation analogous to I→II, but led rather to intractable tars.

Bromination of III with one mole of bromine resulted in a substitution product, formulated tentatively as the 5-bromo derivative of III. Treatment of III with an excess of bromine led to an unstable compound $C_6H_7O_3SBr_3$, formulated tentatively as the 5-bromo-3,4-dibromide of III.

Experimental

Mesityl Oxide Cyclic Sulfonic Ester (III).—Mesityl oxide (19.6 g.) was added to 41 g. acetic anhydride and the mixture was cooled to 0°. Chlorosulfonic acid (22.3 g.) was added dropwise while the temperature was kept at 0° with an ice-salt-bath. The mixture was stirred for one-half hour after the addition of the acid was complete, and then placed in the cold-room overnight. The reaction mixture was decomposed by pouring it into an equal volume of ice-water with vigorous stirring. The light-yellow precipitate which formed was separated and purified by crystallization from methanol to yield 13 g. (41%) of stout, colorless prisms of m. p. 65–67°.

Anal. Calcd. for $C_9H_8O_3S$: C, 45.0; H, 5.03. Found: C, 45.1; H, 5.19.

After several weeks a sample of the compound suddenly decomposed with violence, the production of sulfur dioxide and a black tar.

Bromination of the Cyclic Sulfonic Ester of Mesityl Oxide.—A 5.0-g. sample of the ester (III) was dissolved in carbon tetrachloride (25 ml.) and bromine was added dropwise during ten minutes until the decolorization of it became slow. A precipitate formed rapidly and hydrogen bromide was evolved. A slight excess of bromine was removed with sodium thiosulfate solution and the solvent was removed by distillation. The crude product was crystallized from alcohol to give 3.0 g. of white, crystalline material of m. p. 75–76° (mixed with III, m. p. 46–47°).

Anal. Calcd. for $C_9H_7O_3SBr$: C, 30.1; H, 2.95. Found: C, 30.4; H, 3.36.

The substance is a powerful skin irritant and is formulated as the 5-bromo derivative of the cyclic sulfonic ester of mesityl oxide (III).

A 5.0-g. sample of the cyclic sulfonic ester (III) was dissolved in 25 ml. of carbon tetrachloride and 10 g. of bromine was added rapidly. The mixture was allowed to stand for a day and the precipitate that formed was separated and washed thoroughly with methanol-water (1:1). The white crystalline product turned dark near its melting point and then melted with decomposition at 156–60°.

Anal. Calcd. for $C_9H_7O_3SBr_2$: C, 18.2; H, 1.88. Found: C, 18.3; H, 1.77.

This substance is formulated as the 5-bromo-3,4-dibromide of the cyclic sulfonic ester (III).

(3) Melting points are not corrected.

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The Reaction of *t*-Butylmagnesium Chloride with Ethyl Oxalate

By G. F. HENNION AND CHARLES F. RALEY

In connection with another problem we have recently had occasion to re-examine the reaction of *t*-butylmagnesium chloride with ethyl oxalate.¹ Our observations are not entirely in accord with

(1) Egorov², *J. Russ. Phys.-Chem. Soc.*, **41**, 1454 (1909); *Chem. Zentr.*, **81**, 1003 (1910).

the previous report which states that the reaction gives a mixture of products containing *t*-butylglycolic acid, ethyl *t*-butylglycolate, α -ethoxy- β,β -dimethylbutyric acid and smaller amounts of substances thought to be *t*-butyl neopentyl ketone and *sym*-di-*t*-butylglycol. *t*-Butylglycolic acid and its ethyl ester were obtained in the present study but the other products could not be found; instead, several other compounds were isolated.

We have carried out the reaction in three ways: addition of ethyl oxalate to the Grignard reagent (1:4); addition of the Grignard reagent to the ester (2:1); and simultaneous reaction of magnesium (2.5), *t*-butyl chloride (2.0), and ethyl oxalate (1.0). In each case there was considerable evolution of gas, evidently isobutylene, and after working up the products in the usual way complex mixtures were encountered. In view of the latter fact the reaction seems to have little preparative value.

Experimental

A. Direct Addition.—When 0.385 mole of ethyl oxalate was added dropwise to 1.54 moles of *t*-butylmagnesium chloride in anhydrous ether (previously filtered through glass wool), 0.7 mole of isobutylene was recovered by absorption in sulfuric acid. After hydrolysis of the reaction mixture with ice and hydrochloric acid in the usual way, extraction of the ether layer with sodium bicarbonate solution removed 18 g. of impure *t*-butylglycolic acid. The neutral components, after removal of the ether, were saponified and thus yielded an additional 10 g. of the acid. It was best purified by vacuum distillation (b. p. 110–117° at 4 mm.), followed by crystallization from water; m. p. 85–86°. Smaller amounts of other products were formed also; of these only hexamethylethane and diisobutylene were recognized.

B. Reverse Addition.—In this experiment, when 1.35 moles of filtered Grignard reagent was added to 0.676 mole of ester, the only acidic substance recovered was 2.5 g. of impure oxalic acid. There was obtained by distillation of the ether layer after hydrolysis, etc., 27 g. of ethyl *t*-butylglycolate and 30 g. of a substance whose analysis corresponds to $C_{12}H_{24}O_2$. There was good evidence that the latter compound is the previously unknown ethyl di-*t*-butylglycolate, $(t-C_4H_9)_2C(OH)COOC_2H_5$. In addition to these two compounds there was 26 g. of higher boiling material.

C. Barbier Reaction.—When this method was employed with 2.5 gram atoms of magnesium, 2.0 moles of *t*-butyl chloride and 1.0 mole of ethyl oxalate (the latter mixed and added slowly to the magnesium under ether), hydrolysis and removal of the ether left 137 g. of pale yellow oil. Distillation *in vacuo* through a helix-packed column yielded 38 g. of impure ethyl *t*-butylglycolate and 40 g. of ethyl di-*t*-butylglycolate. The remainder of the product was distilled at 2.5–3.0 mm. without the column and appeared to decompose somewhat in the process. The distillate (39 g.) deposited a crystalline solid; after removal and crystallization from aqueous alcohol it melted at 113–113.5°. The analytical data corresponded with the formula $C_{14}H_{28}O_2$. Despite the oxygen content this substance gave none of the tests specific for alcohols, carbonyl compounds, etc. It was tentatively decided that the compound is di-*t*-butylpivaloylcarbinol, $(t-C_4H_9)_2C(OH)COC(CH_3)_2$. Decomposition by strong heating and the failure to respond to functional group reactions are consistent with this structure.

The physical properties and the analytical data for purified samples of the various products are summarized below.

***t*-Butylglycolic acid:** b. p. 118° at 9 mm.; m. p. 85–86°. Calcd. for $C_6H_{12}O_3$: C, 54.52; H, 9.15; neutral equiv.,