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A Synthesis of 2-(2′-Hydroxyethyl)cyclopentanone by the Barton Reaction[*1]

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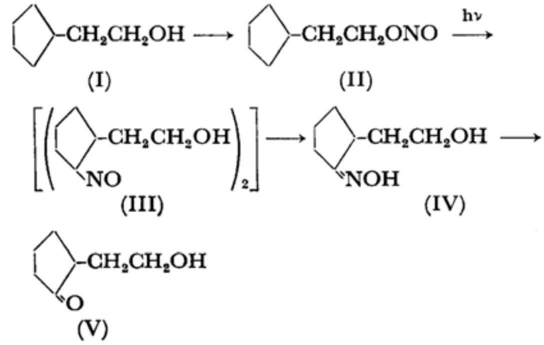
Previously, one of the present authors reported, during the course of his synthetic studies of aucubin,[1] the synthesis of 2-(2′-hydroxyethyl)cyclopentanone[*2] (V) as an intermediate in the syntheses of five-membered cyclic ketals.

In the present investigation, we attempted the synthesis of V from 2-cyclopentylethanol (I) by the Barton reaction[2] according to the following scheme:



2-(2′-Hydroxyethyl)cyclopentanone oxime (IV) was obtained from 2-cyclopentylethyl nitrite (II) in a 20% yield as a white crystal, which was identified by a comparison of its IR spectrum with that of an authentic sample. A mild hydrolysis of IV with dilute hydrochloric acid gave 2-(2′-hydroxyethyl)cyclopentanone (V), which was identified by a comparison of its IR spectrum with that of the previously-synthesized specimen.[1]

Experimental

2-Cyclopentylethanol (I).[3,4] This alcohol was prepared in an 82% yield by the lithium aluminum hydride reduction of cyclopentylacetic acid.[5] Bp 180—182°C, n_D^{20} 1.4552 (lit.[3] bp 179—181°C, n_D^{20} 1.4615).

2-Cyclopentylethyl Nitrite (II). Into a suspension of 5.0 g of I and 15.0 g of sodium nitrite in 30 m*l* of water, a mixture of 2 m*l* of water and 5 m*l* of concentrated sulfuric acid was vigorously stirred, drop by drop, over a period of about 2 hr while being cooled by an ice-salt mixture.

The acid solution was then added slowly, and the temperature was kept at ±1°C. After the addition had been completed, the reaction mixture was allowed to stand in the ice-salt bath until it separated into two layers; the liquid layers were then decanted from the sodium sulfate into a separatory funnel.

The aqueous layer was removed, and the 2-cyclopentylethyl nitrite layer was washed with a 1% aqueous sodium bicarbonate solution and then with water, dried over anhydrous sodium sulfate, and evaporated to yield 4.5 g (72%) of II as a light green liquid; bp 50—51°C/15 mmHg; n_D^{18} 1.4346. IR (neat): 2940, 2860, 1643, 1603, 790 cm^{-1}.

Photolysis of 2-Cyclopentylethyl Nitrite (II). A solution of 3.07 g of II in 450 m*l* of dry benzene was irradiated by means of a 100-W high-pressure mercury arc lamp (model HLV-B, manufactured by Taika Kôgyô Co.) placed in a water-cooled quartz immersion well. The solution was slightly agitated by means of a stream of nitrogen, and the reaction temperature was kept near 25°C by regulating the temperature of the cooling water.

After 3 hr the solvent was removed *in vacuo*, and the residue was refluxed in *n*-butyl alcohol for 5 hr.[*3] The solution was concentrated *in vacuo*, and the resulting viscous oil was chromatographed on a column of silica gel with ether. 2-(2′-Hydroxyethyl)cyclopentanone oxime (IV) was obtained as white crystals, which were then recrystallized from benzene. Yield, 0.625 g (20%); mp 80—82°C. This substance was found to be identical with the oxime of V which had previously been syn-

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1) H. Obara, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **82**, 62 (1961).

[*2] This compound was called 2-oxocyclopentylethanol in the previous report.[1]

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3) G. R. Yohe and R. Adams, *J. Am. Chem. Soc.*, **50**, 1505 (1928).

4) E. R. Shepard and J. F. Noth, *J. Org. Chem.*, **19**, 415 (1954); H. Pines, H. G. Rodenberg and V. N. Ipatieff, *J. Am. Chem. Soc.*, **76**, 771 (1954); V. N. Ipatieff, W. W. Thompson and H. Pines, *ibid.*, **73**, 555 (1951); W. Hückel and W. Gelmroth, *J. prakt. Chem.*, [2] **142**, 205 (1935).

5) E. E. Royals and A. N. Neal, *J. Org. Chem.*, **21**, 1448 (1956).

[*3] It is considered that this rearrangement product exists as a dimer (III), because the oxime (IV) was not identified in the irradiation products by TLC and appeared slowly after boiling with *n*-butyl alcohol.

thesized by a comparison of their IR spectra and by a mixed-melting-point determination.

Found: C, 58.74; H, 9.34; N, 9.86%. Calcd for $C_7H_{13}O_2N$: C, 58.72; H, 9.15; N, 9.78%.

2-(2′-Hydroxyethyl)cyclopentanone (V). A mixture of 110 mg of IV and 10 *ml* of 1N hydrochloric acid was stirred at 50°C for one hour. The solution was diluted about 1.5 times with water and extracted with methylene chloride. The methylene chloride solution was washed with a 10% aqueous sodium bicarbonate solution and water, dried over anhydrous sodium sulfate, and evaporated to yield 57 mg (58%) of a colorless liquid. The IR spectrum of this liquid was identical with that of the V which had previously been synthesized.[1] 2,4-Dinitrophenylhydrazone, mp 173—174°C (lit. 177—178°C,[1] 175°C[6]).

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6) H. Booth, F. E. King, K. G. Mason, J. Parrick and R. L. St. D. Whitehead, *J. Chem. Soc.*, **1959**, 1050.