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Studies on Furan Compounds. III. A New Synthesis of Furyl Ketones

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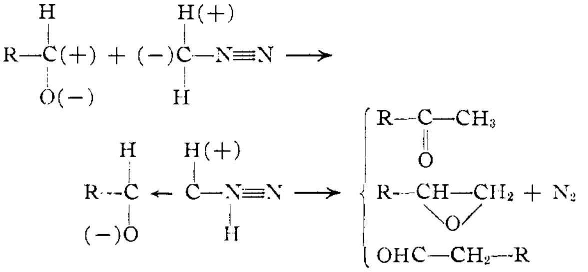
For continuation of our studies on furan compounds[1] we needed ketone derivatives as starting materials. Though several furyl ketones are described, most of them are difficult to prepare, and the yields are unsatisfactory. Since the aldehyde derivatives are the most easily accessible of the furan compounds, it appeared desirable to employ them as starting materials for the synthesis of ketones. As is known, aldehydes can react with diazomethane in three ways. Depending on the nature of the attached substituents, they give rise to ketones, ethylene oxides or aldehydes, respectively, according to the following scheme.[2]



We did not find any information in the literature on the behavior of furfural and its simple derivatives toward diazoalkyls; however, it seemed probable, on the basis of analogy, that these compounds or at least their simplest representative, furfural, should be similar to benzaldehyde in this respect,[3] *i.e.*, would give rise to ketones.

On the basis of this consideration we made use of furfural, 5-methylfurfural and 5-hydroxymethylfurfural together with diazomethane and diazoethane for our experiments. In all cases the expected ketones were obtained in good yields. The ketones, 2-acetofuran, 2-propiofuran, 5-methyl-2-propiofuran and 5-hydroxymethyl-2-acetofuran, were identified and characterized by their semicarbazones and oximes. One of them, 5-methyl-2-propiofuran, had not been described hitherto in the literature.

The reactions of the above-mentioned furylaldehydes took place with diazoethane particularly smoothly, yielding uniform products. Diazomethane reacted much more slowly than diazoethane and, owing to side reactions, the resulting ketones were not quite pure. 5-Methylfurfural remained unchanged even after three weeks of standing with ethereal diazomethane solution.

Experimental

General Procedure.—In order to carry out the experiments the aldehydes were kept in dry ether solution, free of alcohols, in the presence of 1.5 equivalents of diazoalkyl at room temperature until the aldehyde reaction had become negative or the nitrogen evolution ceased (two to fourteen days). The ketones which formed were then separated by distillation. With diazoethane initial cooling was necessary.

Nitrosomethylcarbamide, used as the diazomethane source, was prepared according to Arndt,[4] and nitrosoethylcarbamide, for producing diazoethane, in a similar manner.

2-Acetofuran.[5]—This ketone was prepared from furfural and diazomethane: time of reaction, until the aniline acetate test became almost negative (about 12 days); yield, 70–75%; b. p., 169–173°, m. p. of the semicarbazone,[6] 148°. Though the ketone was sufficiently pure for further reactions it did not crystallize at 0°.

2-Propiofuran[7] was prepared from furfural and diazoethane: time of reaction, two to three days; yield nearly quantitative; b. p. 182–183°, m. p. 28–30°; m. p. of the semicarbazone,[7] 189°.

5-Methyl-2-propiofuran.—Prepared from 5-methylfurfural[8] and diazoethane; time of reaction, until a sample did not give a violet coloration with α-naphthol and concentrated sulfuric acid (two to three days); colorless liquid, b. p. 94–96° (14 mm.); yield almost quantitative.

Semicarbazone.—The mixture of an alcohol solution of the ketone with a concentrated water solution of semicarbazide hydrochloride and potassium acetate was left overnight at room temperature. The precipitate which formed was then recrystallized from dilute alcohol; m. p., 162–164°.

Anal. Calcd. for $C_9H_{13}O_2N_3$: C, 55.47; H, 6.71; N, 21.53. Found: C, 55.03; H, 7.11; N, 21.13.

Oxime.—A mixture of 1.5 g. of ketone, 1 g. of hydroxylamine hydrochloride and 1 g. of sodium acetate was boiled on a water-bath for four hours. After addition of water the precipitated oil soon became solid, m. p. 110°.

Anal. Calcd. for $C_8H_{11}O_2N$: C, 62.73; H, 7.23; N, 9.14. Found: C, 62.57; H, 7.34; N, 9.26.

5-Hydroxymethyl-2-acetofuran.[9]—Prepared from 5-hydroxymethylfurfural[10] and diazomethane; time of reaction, until a sample did not give a red coloration with alcoholic pyrocatechol and concentrated sulfuric acid (about 14 days); b. p., 130° (3 mm.); yield 40%.

Semicarbazone.—This derivative was prepared like 5-methyl-2-propionylfuran semicarbazone and recrystallized from dilute alcohol; m. p. 194°.

Anal. Calcd. for $C_8H_{11}O_3N_3$: C, 48.71; H, 5.62; N, 21.31. Found: C, 49.00; H, 5.71; N, 21.40.

Summary

Several furyl ketones have been synthesized, furyl aldehydes and diazoalkyls being used as starting materials.

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[1] Vargha, Ramonczai and Bite, THIS JOURNAL, **70**, 371 (1948); Vargha, Ramonczai and Báthory, *ibid.*, **71**, 2652 (1949).

[2] Arndt, *Ber.*, **61**, 1118 (1928); **62**, 44 (1929).

[3] Schlotterbeck, *ibid.*, **40**, 479 (1907).

[4] Arndt, *Z. angew. Chem.*, **43**, 444 (1930); **46**, 47 (1933); *Ber.*, **73**, 607 (1940).

[5] Sandolin, *Ber.*, **33**, 492, 1176 (1900); Torrey and Zanetti, THIS JOURNAL, **44**, 391 (1910); Hartough and Kosak, *ibid.*, **69**, 1013 (1947).

[6] Bouveault, *Bull. soc. chim.*, [3] **25**, 440 (1901).

[7] Asahina and Murayama, *Chem. Centr.*, **90**, IV, 1196 (1919); Borsche, Leditschke and Lange, *Ber.*, **71**, 961 (1938); Mexim, *Bull. soc. chim. Rom.*, **12**, 33 (1930).

[8] Rinkes, *Rec. trav. chim.*, [4] **52**, 14, 337 (1933).

[9] Chute, Orchard and Wright, *J. Org. Chem.*, **6**, 157 (1941).

[10] Haworth and Jones, *J. Chem. Soc.*, 667 (1944).