[Contribution from the Chemical Laboratory of Iowa State College]

NITROFURFURYL ALCOHOL

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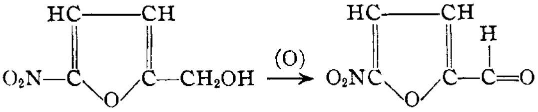
Introduction

In continuation of studies on direct substitutions of the furan nucleus, a first nitrofurfuryl alcohol has been prepared. The synthesis has been effected by the nitration of furfuryl acetate, followed by hydrolysis of the nitro ester to the nitro alcohol. The nitrofurfuryl alcohol can be oxidized to the recently prepared nitrofurfural.[1]



The nitro group in nitrofurfural has been placed provisionally[2] in the 5 position. It is highly significant that the aldehydic group and the alcoholic (acetate) group orient to the same position. Very probably the mode of substitution in both cases is that described earlier, namely, a 1,4-addition to a conjugated system.[3] Again,[1] the nitro group has a marked stabilizing effect on the furan nucleus.

Experimental Part

Nitration of Furfuryl Acetate.—To 286 g. of acetic anhydride, kept at a temperature below −5°, is added dropwise 87.4 g. (1.38 moles) of fuming nitric acid (sp. gr. 1.51). Then 70 g. (0.5 mole) of furfuryl acetate[4] dissolved in 102 g. of acetic anhydride is added, with stirring and at −20°, to the nitrating mixture.[5] When addition is complete the reaction is stirred for one hour at −20°, and then poured upon cracked ice. Sodium hydroxide solution, together with ice to maintain the low temperature, is added with vigorous stirring until the solution is exactly neutral. The oil which separates is drawn off and the solution extracted once with about 700 cc. of ether. The combined oil and ether extract is treated with about 200 cc. of pyridine; after a few hours the ether is evaporated, and the residue diluted with water and chilled. Thereupon, the oil which separates becomes solid, and gives 55 g., a 59.5% yield, of nitrofurfuryl acetate melting at 40°. Crystallization from an alcohol–water solution gives pure white crystals melting at 47°.

Anal. Calcd. for $C_7H_7O_5N$: N, 7.57. Found: N, 7.46.

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[1] Gilman and Wright, This Journal, **52**, 2550, 4165 (1930).

[2] The definite position of this and other substituents is being determined by a miscellany of methods including an absolute method of orientation, concerning which reference might be made to a recent study by Gilman and Wright, *Iowa State College J. of Sci.*, **5**, 85 (1931).

[3] Gilman and Wright, This Journal, **52**, 3349 (1930).

[4] Prepared in accordance with the procedure described in "Organic Syntheses," **1927**, Vol. VII, p. 44.

[5] The temperature was maintained by chilling with a solid carbon dioxide–furfural mixture.

The direct nitration of the so-called water-insoluble form of furfuryl alcohol proceeds smoothly, but decomposition sets in on subsequent treatment with pyridine.[1] Apparently nitrofurfuryl nitrate is among the products which are being investigated.

Hydrolysis of Nitrofurfuryl Acetate.—Eighteen and one-half g. (0.1 mole) of nitrofurfuryl acetate is refluxed for twenty minutes with 200 cc. of 5% sulfuric acid. The solution is chilled and filtered by suction to remove 0.2 g. of an as yet unidentified compound[6] melting at 73°. The filtrate is extracted thrice with 50-cc. portions of ether and the combined ether extracts are dried over sodium sulfate. The residue, after removal of the ether, is distilled under reduced pressure (157°, 8 mm.), to give a yellow oil which solidified overnight to the nitrofurfuryl alcohol melting at 32°. The yield is 9–10 g. or 49–55%.

Anal. Calcd. for $C_5H_5O_4N$: C, 41.95; H, 3.52. Found: C, 41.96; H, 3.76.

Oxidation of Nitrofurfuryl Alcohol.—The nitrofurfuryl alcohol was oxidized by heating for two days at 40–50° with a mixture of manganese dioxide and 50% sulfuric acid. The ether extract from this oxidation gave nitrofurfural melting at 36°. This showed no depression in a mixed melting point determination with an authentic specimen.[1]

The authors are grateful to R. R. Burtner for assistance in this study. He has shown that furfuryl chloride and furfuryl methyl ether also undergo ready substitution, the chloromethyl and alkoxymethyl groups orienting like the acetate group.

Summary

The first nitrofurfuryl alcohol has been prepared by the hydrolysis of nitrofurfuryl acetate, which was obtained by the direct nitration of furfuryl acetate. The nitro group markedly stabilizes the furan nucleus.

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THE IDENTIFICATION OF PHENOLS AS THE ESTERS OF 3,5-DINITROBENZOIC ACID

By Max Phillips and George L. Keenan

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In connection with an investigation on the chemistry of lignin which one of the authors has been conducting, an occasion arose requiring the identification of the phenols produced when lignin is subjected to destructive distillation or is distilled with zinc dust in an atmosphere of hydrogen. Attempts were made to prepare the usual derivatives of phenols such as the benzoyl derivatives, the phenyl, diphenyl and α-naphthyl urethans, and the *p*-nitrobenzyl ethers, but all these were found to be liquid at room temperature and therefore unsuitable for the purpose of identification. It was found, however, that 3,5-dinitrobenzoyl chloride condensed with the phenols under investigation and yielded products which could be

[6] The same compound has been isolated in small quantities from the direct nitration of water-insoluble furfuryl alcohol in acetic anhydride.