(1) The hydrogen of the methylene group of one molecule may add: (a) to the number 1 carbon atom or (b) to the 2 carbon of the second molecule. (2) The hydrogen of one of the methyl groups in the first molecule may add (a) to the number 1 carbon atom or (b) to the number 2 carbon atom of the second molecule. The predominance of the octene of formula V indicates that in the polymerization of isobutylene the reaction proceeds predominantly according to 2a, *i. e.*, the labile hydrogen for addition is in the methyl rather than in the methylene group, and the preferred direction of addition involves the addition of hydrogen to the more hydrogenated carbon atom. It should be noted that the presence of an octene of formula IV in the mixture does not necessarily indicate that addition took place according to scheme 1a since sulfuric acid would be expected to cause the rearrangement of an octene of formula V to one of formula IV.

Summary

Methyl neopentyl ketone, $(CH_3)_3CCH_2COCH_3$, and trimethylacetaldehyde were produced in the ratio of approximately 3.7 to 1 when di-isobutylene was ozonized and the ozonide hydrolyzed. This indicates that di-isobutylene contains two isomeric octylenes, *i. e.*, trimethyl-2,4,4-pentene-1,2 and trimethyl-2,4,4-pentene-2,3, with the former in considerable excess. It appears then that when isobutylene undergoes polymerization the labile hydrogen for addition is in the methyl rather than in the methylene group, and that the predominant direction of additions involves the addition of hydrogen to the more hydrogenated carbon atom.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

NITROFURFURAL AND NITROFURYLACRYLIC ACID

BY HENRY GILMAN AND GEORGE F. WRIGHT

RECEIVED MARCH 17, 1930 PUBLISHED JUNE 6, 1930

Introduction

In connection with the preparation of aminofurans and their diazo compounds, it was necessary to have a series of readily accessible nitrofurans and their derivatives. We turned to the nitration of furfural because this aldehyde is available in large quantities and at a low price. Apparently, the literature contains no description of the preparation of a nitrofurfural. However, attempts have been made to nitrate furfural.[1]

By means of the technique of Gilman and Wright[2] for introducing substituents in furfural, we have succeeded in preparing the first nitrofurfural. As might have been predicted, the nitro group markedly increases

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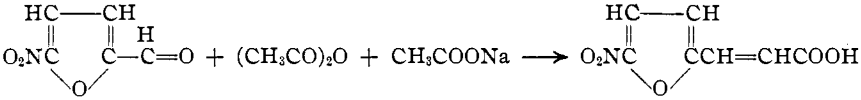
[1] Marquis, *Compt. rend.*, **135**, 505 (1902).

[2] Gilman and Wright, THIS JOURNAL, **52**, 1170 (1930).

the stability of the furan nucleus. The nitrofurfural has been characterized by a few selected derivatives. Among the reactions studied was a Perkin condensation leading to nitrofurylacrylic acid. The same nitrofurylacrylic acid was obtained by the nitration of furylacrylic acid and of its ethyl ester. However, the mechanism of the nitration of furfural diacetate is apparently unlike that of furylacrylic acid. In the latter case, it is unnecessary to close the furan ring with pyridine (see Experimental Part) inasmuch as the nitrofurylacrylic acid is precipitated directly in the nitrating mixture.[3]

The nitrofurfural was oxidized to the known nitrofuroic acid of Klinkhardt[4] and of Marquis.[5] If we provisionally accept the structure of nitrofuroic acid assigned by Hill and Palmer,[5] then our nitro group is in the 5-position,[6] and the following reaction illustrates the condensation leading to the 5-nitrofurylacrylic acid.



Experimental Part

Nitrofurfural Diacetate, $NO_2C_4H_2OCH(OCOCH_3)_2$.—The nitrating mixture was prepared by adding dropwise 43.7 g. (0.69 mole) of fuming nitric acid (sp. gr. 1.5) to 143 g. (1.4 moles) of acetic anhydride chilled to 0° and contained in a 500-cc. three-necked flask equipped with a mechanical stirrer, dropping funnel and thermometer. A solution of 49.5 g. (0.25 mole) of furfural diacetate[7] in 51 g. (0.5 mole) of acetic anhydride was added slowly to the nitrating mixture which was not allowed to rise above −5°. The time required for the addition was about thirty minutes. After allowing the reaction mixture to stir for three hours longer, it was poured into about one kilo of cracked ice. A sodium hydroxide solution (about 40%) was then added, with *vigorous* stirring, until precipitation of the oil was complete. The aqueous layer was then removed by decantation, and an almost equal volume of pyridine[8] was added very carefully and slowly, together with some cracked ice. Care must be exercised that the reaction starts after a few cc. of pyridine are added; otherwise the entire reaction mixture may be lost by violent ebullition. The mixture is diluted to 2 or 3 times its original volume by

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[3] A later paper will consider 1,4- and 1,6-addition reactions of furan types as a mechanism of nuclear substitution; see Gilman, Kirby and Kinney, THIS JOURNAL, **51**, 2252 (1929).

[4] Klinkhardt, *J. prakt. Chem.*, **25**, 41 (1882).

[5] Marquis, *Ann. chim. phys.*, [8] **4**, 196 (1905). See also Priebs, *Ber.*, **18**, 1363 (1885), and Hill and Palmer, *Am. Chem. J.*, **10**, 380 (1888).

[6] Marquis (Ref. 5) has assigned the nitro group in his nitrofuroic acid to either the 3- or the 4-position. We hope definitely to establish the position of the nitro group by a series of moderate and reliable reactions. In our bromination of furfural diacetate (Ref. 2), the bromine entered the 5-position.

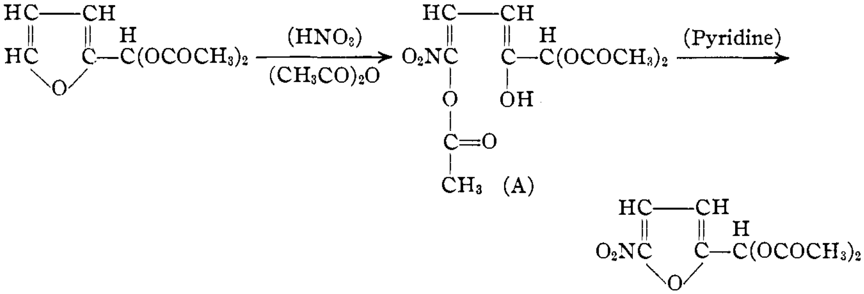
[7] The furfural diacetate was prepared in accordance with the directions of Gilman and Wright, *Iowa State College J. of Science*, **4**, 35 (1929). The yields reported in that article are rather modest. It has since been determined that the yields are in the range of 70%.

[8] The excess of pyridine appears to be essential.

means of iced water, and after standing until precipitation is complete (about one-half hour), the cold solution is filtered by suction, and washed free of pyridine by dilute acetic acid followed by a water washing. The crude nitrofurfural diacetate obtained in this manner weighs, when air-dried, 24.5 g. or 40% of the theoretical amount, and melts at 87°. It may be crystallized from hot alcohol and when purified it melts at 92.5°.

Anal. Calcd. for $C_9H_9O_7N$: C, 44.44; H, 3.73. Found: C, 44.85; H, 3.81.

Intermediate Ring Fission Compound.—It is possible to isolate the intermediate nitro compound prior to its closure by pyridine. If we assign to this intermediate a structure that conforms with that ascribed by Marquis[5] to the fission products of nitrofuran and nitrofuroic acid, the reaction with pyridine may be written



The heavy oil [Compound (A)] precipitated by addition of cracked ice to the reaction mixture, is extracted with ether, and after washing the ether solution with water and then chilling it, pyridine is added to neutralize the acids present.[9] The ether solution is then washed thoroughly with water, dried over sodium sulfate, filtered, and then concentrated by evaporation under reduced pressure until crystallization is complete. The product obtained by suction filtration weighs 31.6 g. (42% yield), melts 96–97°, and, when crystallized from a petroleum ether–benzene mixture, melts at 106–107°.

Anal. Calcd. for $C_{11}H_{13}O_9N$: C, 43.56; H, 4.32. Found: C, 43.03; H, 4.53.

When the intermediate compound (A) is dissolved in pyridine and then precipitated by dilution with water, it is converted quantitatively to the nitrofurfural diacetate melting at 92–93°. Inasmuch as this reaction is slightly endothermic, it is evidently necessary to maintain sufficient heat in the treatment of the precipitated oil in the original preparation of nitrofurfural diacetate to allow this ring closure by pyridine to take place.

Nitrofurfural, $NO_2C_4H_2OCHO$.—In an atmosphere of carbon dioxide, 24.3 g. (0.1 mole) of nitrofurfural diacetate was refluxed, with constant stirring, with a solution of 54 g. of concd. sulfuric acid in 108 g. of water for about fifteen minutes. The ether extract of the cooled hydrolysate was washed with water, dried over sodium sulfate, and then (after removing the ether) distilled at 128–132° (10 mm.). The yield was 10.95 g., or 77.8%. The nitrofurfural melted at 35–36° after crystallization from petroleum ether. It is colorless when pure and is somewhat soluble in water.

Anal. Calcd. for $C_5H_3O_4N$: C, 42.55; H, 2.14. Found: C, 42.64; H, 2.18.

Oxidation of 1.41 g. (0.01 mole) of the nitrofurfural by an equivalent quantity of sodium dichromate in sulfuric acid gave 0.64 g. or a 57% yield of crude nitrofuroic acid. This melted at 183° when crystallized from water and showed no depression in a mixed melting point determination with the acid prepared in accordance with the directions of

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[9] The point of neutralization may be determined by means of litmus paper and by noting the cessation of temperature rise during addition of the pyridine.

Marquis.[5] Marquis had previously shown that his nitrofuroic acid was identical with that of earlier investigators.[4,5]

It is interesting to note that the same nitrofuroic acid was obtained by us by oxidizing nitrofurfural diacetate with aqua regia.

Nitrofurfuraldoxime, $NO_2C_4H_2OCH{=}NOH$.—The oxime was prepared in a customary manner from hydroxylamine hydrochloride (10.4 g. or 0.15 mole), sodium hydroxide and 17.7 g. (0.073 mole) of nitrofurfural diacetate. Because of the sensitivity of the nitro group to alkali, the 6 g. (0.15 mole) of sodium hydroxide was added slowly, as a dilute solution, and with vigorous shaking. The yield of oxime melting at 121° was 8.0 g. or 70%. It is slightly sweet.[10]

The isomeric oxime is more readily prepared from nitrofurfural by a similar reaction. When crystallized from alcohol it melts at 153°. If the hydrochloride of the oxime melting at 121° is precipitated by sodium carbonate, it yields the higher-melting (153°) isomer.

Anal. Calcd. for $C_5H_4O_4N_2$: C, 38.46; H, 2.58. Found: C, 38.84; H, 2.72.

Nitrofurylacrylic Acid, $NO_2C_4H_2OCH{=}CHCO_2H$.—A mixture consisting of 14.1 g. (0.058 mole) of nitrofurfural diacetate, 40 g. (0.4 mole) of acetic anhydride, 20.0 g. (0.24 mole) of thrice fused sodium acetate[11] and a drop of pyridine was refluxed at 142° for eight hours with constant stirring. The reaction mixture was diluted with about 300 cc. of water, and sodium carbonate was added to neutrality. It was then heated to 90° with boneblack, filtered and acidified; the nitrofurylacrylic acid which separated melted at 229–230° and weighed 1.2 g. or 13% of the theoretical.[12] When crystallized from methyl alcohol, or preferably from furfural, it melted at 235–236°. It is of interest to observe that in this reaction the nitro-aldehyde diacetate and not the free aldehyde was used in the condensation. This points to the intermediate formation of a diacetate in the Perkin reaction.

In an experiment carried out under corresponding conditions, but starting with nitrofurfural (0.04 mole), the yield of nitrofurylacrylic acid was 27.4%.

The nitrofurylacrylic acid appears to be distinctly more stable than the corresponding unsubstituted furylacrylic acid. For example, it was apparently unaffected by chromic acid, which will oxidize furylacrylic acid.

Anal. Calcd. for $C_7H_5O_5N$: C, 45.90; H, 2.75. Found: C, 45.90; H, 2.83.

The same acid may be obtained in a 40% yield by nitrating 35 g. (0.25 mole) of furylacrylic acid dissolved in 51 g. (0.5 mole) of acetic anhydride with a nitrating mixture consisting of 87.5 g. (1.4 moles) of fuming nitric acid (sp. gr. 1.5) and 140 g. (1.4 moles) of acetic anhydride, prepared after the method described for the nitration of furfural diacetate. The mixture during nitration was kept at $-5°$, and toward the end of the reaction a precipitate separated. The yield of acid melting at 233° was 18.3 g., and attention should again be directed to the fact that this nitro acid precipitated directly from the reaction mixture and no pyridine was required to close the ring.

Ethyl Nitrofurylacrylate, $NO_2C_4H_2OCH{=}CHCO_2C_2H_5$.—The ethyl furylacrylate

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[10] See Gilman and Hewlett, *Iowa State College J. of Science*, **4**, 27 (1929), for a recent article on the correlation of sweet taste with constitution of some furan compounds; also, Gilman and Dickey, THIS JOURNAL, **52**, 2010 (1930) for a later related study.

[11] See Gilman, Brown, Wright and Hewlett, *Iowa State College J. of Science*, **4**, 355 (1930), for the helpful effect of several fusions of sodium acetate on the yield of furylacrylic acid.

[12] This low yield can probably be improved in larger-sized runs. Our chief object here was to prepare some of the acid in order to confirm that obtained by direct nitration of furylacrylic acid.

was prepared in accordance with the directions of Gilman, Brown and Jones[13] and 41.5 g. (0.25 mole) of it was nitrated after the procedure described for the nitration of furylacrylic acid. The mixture was stirred for three hours and during this time a yellow precipitate separated. When the temperature reached 0°, the reaction product was removed by filtration and washed several times with cold water. The yield of ethyl nitrofurylacrylate, melting at 123°, was 27 g. or 51%. When recrystallized from benzene, it melted at 125°.

Anal. Calcd. for $C_9H_9O_5N$: C, 51.18; H, 4.30. Found: C, 50.68; H, 4.43.

The ester is unusually stable, being quite resistant to thionyl chloride and phosphorus pentachloride. It may be hydrolyzed with 65% sulfuric acid by heating until solution is completed, to give the nitrofurylacrylic acid. The identity of this acid, like the other compounds described in this paper, was confirmed by a mixed melting-point determination, in this case with the acids obtained in the Perkin condensation and in the nitration of furylacrylic acid.

The authors gratefully acknowledge assistance from W. M. Selby for a part of the experimental work.

Summary

The first nitrofurfural has been prepared by the hydrolysis of nitrofurfural diacetate obtained by nitrating furfural diacetate. The mechanism of its formation is probably unlike that of nitrofurylacrylic acid and ethyl nitrofurylacrylate, which were obtained by direct nitration of furylacrylic acid and ethyl furylacrylate, respectively. The nitro group markedly increases the stability of the furan nucleus.

AMES, IOWA

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

THE SOLUBILITY OF ROTENONE. I. SOLUBILITY AND OPTICAL ROTATION IN CERTAIN ORGANIC SOLVENTS AT 20°

BY HOWARD A. JONES AND CHARLES M. SMITH

RECEIVED MARCH 18, 1930 PUBLISHED JUNE 6, 1930

Introduction

The root of *Derris elliptica* has long been used by the natives of the Malay Peninsula and the East Indies as a fish poison. One of the active insecticidal principles of this root is a white, crystalline material with a melting point of 163°. This material, now known as rotenone, crystallizes from alcohol in the form of six-sided plates apparently belonging to the orthorhombic system. The empirical formula $C_{23}H_{22}O_6$, now generally accepted, was first proposed by Takei and later substantiated by Butenandt. Much work has been done to determine its constitution but at present its structure is still unknown.

Rotenone is known to be practically insoluble in water, Gimlette stating its solubility to be of the order of one part in six million.[1] Numerous quali-

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[13] Gilman, Brown and Jones, *Iowa State College J. of Science*, **2**, 317 (1928).

[1] Gimlette, "Malay Poisons and Charm Cures," London, **1923**, 2d ed.