[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

SOME GAMMA-NITRO-BETA-FURYLBUTYROPHENONES[1]

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The addition of nitromethane and phenylnitromethane to α,β-unsaturated ketones such as benzalacetophenone has been studied extensively by Kohler and his pupils.[2] The work herein described is concerned with the preparation of certain γ-nitro-β-furylbutyrophenones, prepared by means of the addition of nitromethane and phenylnitromethane to furfuralacetophenone and furfural *p*-bromo-acetophenone.

Furfuralacetophenone has been prepared by Kostanecki and Podrajansky[3] and by Semmler and Ascher[4] but in each investigation the substance was obtained as an oil which apparently was not obtained in crystalline form. After considerable difficulty our oily product, prepared by condensation of furfural and acetophenone by means of 10% sodium hydroxide, was induced to crystallize. It formed long blunt yellow crystals which turned red on standing, and darkened rapidly in the sunlight. No difficulty was encountered in obtaining crystalline furfural-*p*-bromo-acetophenone. The latter substance also darkens on standing, but is much more stable than furfuralacetophenone.

The addition of nitromethane to the above-mentioned unsaturated ketones was carried out in a manner similar to that used in the case of benzalacetophenone. The furfural derivatives, however, are much more soluble in the reaction mixture than are the benzal derivatives, and consequently must be precipitated at the completion of the reaction by the addition of water. The use of a large excess of nitromethane was found necessary to give the best yields. Both products are very soluble in methyl and ethyl alcohols, ether and acetone, but sparingly soluble in petroleum ether.

The addition products of phenylnitromethane crystallize readily and were prepared with far less difficulty than the corresponding nitromethane addition products.

Experimental

Furfuralacetophenone.—A solution of 22 g. of stick sodium hydroxide in 196 cc. of water and 100 cc. of 95% ethyl alcohol were introduced into a beaker loosely covered

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[1] From a thesis submitted to the Graduate School of the University of Maryland by H. W. Gilbert in partial fulfilment of the requirements for the degree of Master of Science.

[2] Kohler and co-workers, THIS JOURNAL, **38,** 889 (1916); **41,** 1644, 1697 (1919); **44,** 624 (1922); **45,** 2144 (1923); **50,** 884 (1928).

[3] Kostanecki and Podrajansky, *Ber.*, **29,** 2248 (1896).

[4] Semmler and Ascher, *ibid.*, **42,** 2356 (1909).

with a disk of cardboard and provided with an efficient mechanical stirrer. Into the alkaline alcoholic solution was poured 52 g. of acetophenone, the stirrer was started and 42 g. of freshly distilled furfural was added slowly. Considerable heat was evolved at first and ice cooling was necessary to prevent the temperature from rising too high. After ten minutes the ice was replaced by water and the water-bath kept at 20–30° for three hours to complete the condensation. The water was then replaced by an ice and salt mixture, and after the temperature of the reaction mixture had become constant, a seed of furfuralacetophenone was added. Stirring was continued during the separation of the yellow granular condensation product. One-half hour was sufficient for crystallization. The crude product was sucked as dry as possible on a *cold* Büchner funnel and then dissolved in chloroform. After having been dried over sodium sulfate the chloroform was distilled off and the residue distilled *in vacuo.* Eighty grams of product was obtained. Furfuralacetophenone melts at 26°, and boils at 179° at 7 mm. pressure. Under 764 mm. pressure, the substance distils with considerable decomposition at 319°.

Furfural-*p*-bromo-acetophenone.—This substance was prepared as described above for furfuralacetophenone. The crude material boiled at 210–217° under 16–18 mm. pressure and melted at 79–80°. Recrystallization from hot ethyl alcohol yielded a product melting at 80–81°.

Anal. Calcd. for $C_{13}H_9O_2Br$: C, 56.3; H, 3.25. Found: C, 56.2, 56.2; H, 3.6, 3.5.

γ-Nitro-β-furylbutyrophenone.—To 35 g. of furfuralacetophenone in 50 cc. of dry methanol in a covered beaker provided with an efficient mechanical stirrer and heated in a beaker of boiling water was added rapidly a suspension of sodium nitromethane prepared by the addition of 40 g. of nitromethane to a well-cooled solution of 11 g. of sodium in 175 cc. of dry methanol. The container from which the suspension was added was rinsed with 100 cc. of dry methanol and the rinsings added to the reaction mixture. The latter was kept hot and stirred to insure the rapid course of the addition, which was marked by the disappearance of the solid. When all of the sodium nitromethane had disappeared, the mixture was cooled *immediately* in an ice and salt bath and acidified *very slowly* (over about forty-five minutes) with 60 cc. of glacial acetic acid. Stirring was continued for thirty minutes longer, the solution was then seeded with a crystal of the addition product and 150 cc. of water was added slowly to precipitate the nitro ketone. After thirty minutes the solid was filtered off, washed on the funnel with 500 cc. of water and three 50-cc. portions of 75% ethyl alcohol; 40 g. of a crude product, melting at 48°, was obtained. This was purified by dissolving it in the minimum quantity of 95% ethyl alcohol, adding 3 g. of norite and stirring the mixture for five hours. The charcoal was then filtered off and the product caused to crystallize by adding water. Thirty-five grams of material melting at 49.5–50° was obtained in this way.

Anal. Calcd. for $C_{14}H_{13}O_4N$: C, 64.85; H, 5.02. Found: C, 65.0, 64.9; H, 5.17, 5.20.

γ-Nitro-β-furyl-*p*-bromobutyrophenone.—This substance was prepared by the method described above for γ-nitro-β-furylbutyrophenone. For purification a charcoal treatment of a solution of the ketone in a mixture of one part acetone to nine parts of ethyl alcohol was used. The yield of purified material corresponded to 75% of that theoretically possible. The product melted from 72 to 73°.

Anal. Calcd. for $C_{14}H_{12}O_4NBr$: C, 49.7; H, 3.55. Found: C, 49.9, 49.8; H, 3.84, 3.78.

γ-Phenyl-γ-nitro-β-furylbutyrophenone.—19.8 grams of furfuralacetophenone was dissolved in 100 cc. of dry methanol in a round-bottomed flask fitted with a reflux condenser. To the solution was added 13.7 g. of phenylnitromethane dried over phosphorus pentoxide. The mixture was made alkaline by adding a solution of 0.5 g. of sodium in 10 cc. of dry methanol, then refluxed for three hours, and cooled in an ice and salt mixture with occasional shaking. The product which crystallized was sucked as dry as possible on a funnel and washed with 25 cc. of 95% ethyl alcohol which had been cooled on an ice and salt bath; 25 g. of a product melting from 90 to 105° was obtained. Recrystallization from alcohol yielded 18 g. of nitro ketone, melting at 153 to 153.5°.

Anal. Calcd. for $C_{20}H_{17}O_4N$: C, 71.7; H, 5.07. Found: C, 71.7, 71.8; H, 5.11, 5.20.

γ-Phenyl-γ-nitro-β-furyl-*p*-bromobutyrophenone.—This ketone was prepared as described for γ-phenyl-γ-nitro-β-furylbutyrophenone. A 29% yield of product melting at 87 to 88.5° was obtained.

Anal. Calcd. for $C_{20}H_{16}O_4NBr$: C, 58.0; H, 3.86. Found: C, 57.8, 57.8; H, 3.81, 3.75.

Summary

The addition products of nitromethane and phenylnitromethane to furfuralacetophenone and furfural-*p*-bromo-acetophenone are described.

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[Contribution from the Chemistry Laboratory of the University of Michigan]

THE REACTION BETWEEN THE BINARY SYSTEM MAGNESIUM + MAGNESIUM IODIDE AND AROMATIC ALDEHYDES

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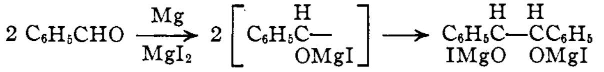
From the behavior of ketones, benzils and acids toward a mixture of magnesium and magnesium halide[1] it was inferred that the carbonyl group in aldehydes as well would be affected in a similar manner. Thus, benzaldehyde, the aldehyde which we have studied most in detail, should react as follows



$$2\,C_6H_5CHO \xrightarrow[MgI_2]{Mg} 2\left[\begin{matrix} H \\ C_6H_5C— \\ OMgI \end{matrix}\right] \longrightarrow \begin{matrix} H\quad H \\ C_6H_5C—CC_6H_5 \\ IMgO\quad OMgI \end{matrix} \qquad (1)$$

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It was found that the binary system reacts with benzaldehyde. Although, in reality, no hydrobenzoin to correspond to compound (I) is obtainable on the hydrolysis of the reaction mixture, there is nonetheless every reason to assume that the reaction indicated actually represents the first stage of the process. The disappearance of this intermediate product (I) is brought about by reactions subsequent to that given as the first step (Equation 1). We found, namely, that this hydrobenzoinate salt, which readily can be prepared directly from hydrobenzoin itself by treatment with methylmagnesium iodide, rapidly and completely reduces benzaldehyde to iodomagnesium benzylate (III), and thus becomes oxidized to iodomagnesium benzoinate (II).

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[1] Gomberg and Bachmann, This Journal, **49**, 236 (1927); **49**, 2584 (1927); **50**, 2762 (1928); Gomberg and Bailar, *ibid.*, **51**, 2229 (1929); Gomberg and Van Natta, *ibid.*, **51**, 2238 (1929); Bachmann and Shankland, *ibid.*, **51**, 306 (1929).