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Abstract

Full Text

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ON THE ADDITION REACTION OF NITROALKANES TO BENZALACETONE

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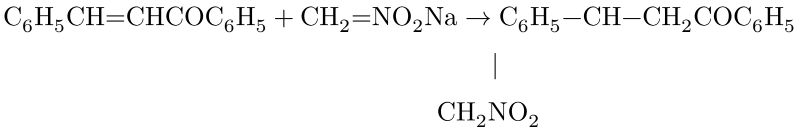
CHEMISTRY

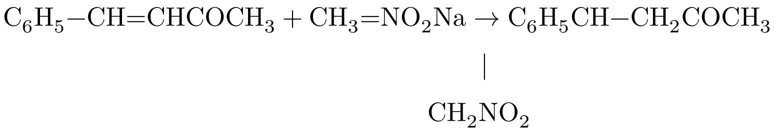
The first studies devoted to the addition reaction of nitroalkanes to α,β-unsaturated ketones date to 1916. Thus, Kohler (1) found that the sodium salt of nitromethane readily reacts with benzalacetophenone to form γ-nitro-β-phenylbutyrophenone:



$$\mathrm{C_6H_5CH{=}CHCOC_6H_5 + CH_2{=}NO_2Na \rightarrow C_6H_5{-}\underset{\displaystyle CH_2NO_2}{\underset{|}{CH}}{-}CH_2COC_6H_5}$$

This reaction takes place only in the presence of basic catalysts (sodium methylate, diethylamine, or piperidine). Free nitromethane does not react with benzalacetophenone.

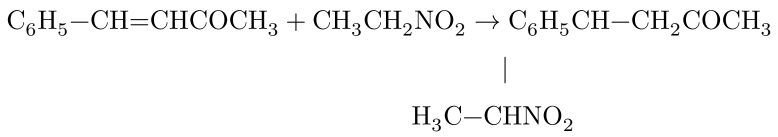
Later Kohler (2) added nitromethane to benzalacetone in the presence of sodium methylate:



$$\mathrm{C_6H_5{-}CH{=}CHCOCH_3 + CH_3{=}NO_2Na \rightarrow C_6H_5\underset{\displaystyle CH_2NO_2}{\underset{|}{CH}}{-}CH_2COCH_3}$$

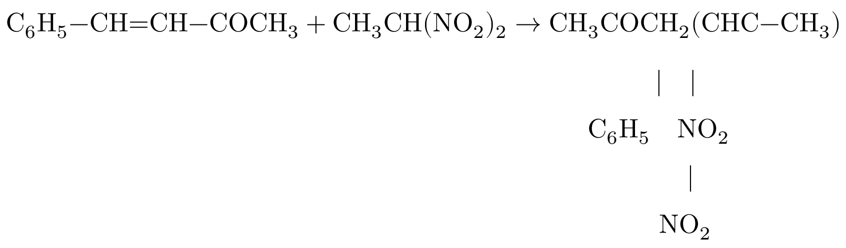
In 1947 Klötzel (2) described the addition of nitromethane and 1- and 2-nitropropanes to benzalacetone and other unsaturated ketones and showed the possibility of synthesizing in this way a series of substances that had previously been difficult to obtain. However, in the cited works the course of this reaction was not studied as a function of the number and position of nitro groups in the nitroalkanes. In the present work the addition reaction to benzalacetone of various mono- and polynitroalkanes has been studied as a function of the number of nitro groups and their position.

In the interaction of nitroethane with benzalacetone in the presence of a catalyst (an alcoholic solution of ethoxytrimethylphenylammonium), 2-nitro-3-phenylpentanone-5 was obtained in low yield:



$$C_6H_5{-}CH{=}CHCOCH_3 + CH_3CH_2NO_2 \rightarrow \underset{\underset{H_3C{-}CHNO_2}{|}}{C_6H_5CH}{-}CH_2COCH_3$$

1,1-Dinitroethane enters into the reaction considerably more readily and leads, in better yields, to the formation of 2,2-dinitro-3-phenylhexanone-5:



$$C_6H_5{-}CH{=}CH{-}COCH_3 + CH_3CH(NO_2)_2 \rightarrow CH_3COCH_2(\underset{\underset{C_6H_5}{|}}{CH}\underset{\underset{\underset{\underset{NO_2}{|}}{NO_2}}{|}}{C}{-}CH_3)$$

A considerably more acidic nitroalkane—trinitromethane—adds

to benzalacetone still more actively and, without catalysts, forms 1,1,1-trinitro-2-phenylpentan-4-one in good yields (80% of theory):

$$C_6H_5CH{=}CHCOCH_3 + CH(NO_2)_3 \rightarrow C_6H_5CH(\ C(NO_2)_3\ )CH_2COCH_3.$$

It is interesting to note that dinitromethane readily adds to benzalacetone in the presence of catalysts with formation of 1,1-dinitro-2-phenylpentan-4-one, without giving a product of addition of dinitromethane to two molecules of benzalacetone, as occurs in some other reactions of dinitromethane described in the literature (^{4}).

Experimental Part

Benzalacetone, obtained from benzaldehyde and acetone (^{5}), had the following constants: b.p. 129-130°/7 mm, m.p. 41.5-42°. Literature data for benzalacetone: b.p. 128-130°/13 mm, m.p. 37-38° (^{6}) and 41.5° (^{7}).

The addition reaction of nitroalkanes to benzalacetone was carried out in a four-necked flask equipped with a mechanical stirrer, dropping funnel, thermometer, and reflux condenser.

Addition of nitroethane. To a solution of 7.5 g (0.1 mole) of nitroethane in 25 ml of ethanol, 0.01 mole of an alcoholic solution of ethoxytrimethylphenylammonium was added, and then, with stirring, 14.6 g (0.1 mole) of benzalacetone was added. The mixture was then heated on a boiling water bath for 10–12 hours. The solvent was then distilled off, and the residue was distilled in vacuo.

Obtained: fraction I, 110–130°/3 mm (4.2 g);
fraction II, 130–140°/3 mm (2.2 g).

Fraction II is 2-nitro-3-phenylhexan-5-one, which on redistillation had b.p. 137°/3 mm.

Found, %:	C 65.59; 65.79;	H 6.96; 6.77;	N 6.48; 6.56
$C_{12}H_{15}NO_3$. Calculated, %:	C 65.10;	H 6.79;	N 6.34.

Addition of 1,1-dinitroethane. To a solution of 4.7 g (0.06 mole) of 1,1-dinitroethane in 20 ml of ethyl alcohol, 0.006 mole of ethoxytrimethylphenylammonium was added, and then, with stirring, 12.3 g of benzalacetone was added, after which the mixture was heated on a boiling water bath for 10 hours. On cooling the reaction mixture, white crystals separated, which were filtered off. Obtained 0.5 g of substance with m.p. 102–103°. 2,2-Dinitro-3-phenylhexan-5-one, after recrystallization from ethyl alcohol, had m.p. 103°.

Found, %:	C 54.07; 53.88;	H 5.46; 5.51;	N 10.31; 10.31
$C_{12}H_{14}O_5N_2$. Calculated, %:	C 54.2;	H 5.26;	N 10.5

A dinitrophenylhydrazone was obtained with m.p. 143°.

Addition of dinitromethane. To a solution of 10.6 g (0.1 mole) of dinitromethane in 30 ml of methanol, 0.01 mole of ethoxytrimethylphenylammonium in alcohol was added. Then 14.6 g of benzalacetone was added, after which the mixture was heated on a water bath for 2 hours. The reaction mass was then diluted with water and extracted with ether. The ethereal solution was dried over ignited Na_2SO_4. The residue after distillation of the ether in vacuo crystallized.

Obtained 15 g (60% of theory) of 1,1-dinitro-2-phenylpentan-4-one with m.p. 94° after recrystallization from alcohol.

Found, %:	C 52.73; 52	H 4.75;	N 11.28
$C_{11}H_{12}O_5N_2$. Calculated, %:	C 52.48;	H 4.77;	N 11.10

Addition of trinitromethane. To a solution of 15.1 g (0.1 mole) of trinitromethane in 45 ml of alcohol, 14.6 g (0.1 mole) of previously melted benzalacetone was added dropwise with stirring. The mixture was then heated at

70° on a water bath for 1.5 hr. (after 15-20 min. crystals began to precipitate from the solution). After cooling of the reaction mixture, the precipitated solid was filtered off and washed with alcohol. This gave 23.2 g (80% of theory) of 1,1,1-trinitro-2-phenylpentan-4-one—a white crystalline substance with m.p. 91° after recrystallization from alcohol.

Found, %:	C 43.16; H 3.75; N 14.09
$C_{11}H_{10}N_3O_7$. Calculated, %:	C 44.30; H 3.70; N 14.10

A dinitrophenylhydrazone with m.p. 160° was obtained.

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Note: Figure translations are in progress. See original paper for figures.

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