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Abstract

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SYNTHESIS OF γ-TRINITROMETHYL KETONES

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A study of the Michael addition of nitroform at the site of the triple bond to various acetylene derivatives was undertaken with the aim of synthesizing substances in which the double bond, through the mechanism of π–σ conjugation, would be activated by the electrophilic trinitromethyl group.

However, in attempting to carry out this reaction with vinylacetylene (I) and butyne-2-diol-1,4 (II), we unexpectedly found that the products obtained did not possess the expected properties: they did not show the presence of double bonds or hydroxyl groups (product II), but all contained a carbonyl group. The studies of N. I. Nazarov concerning the transformations of acetylene derivatives into vinyl ketones came to our aid ([1,2]).

Indeed, under our conditions (divalent mercury ion, presence of moisture), the starting alkynes (I, II), first as a result of hydration and isomerization, were converted into vinyl ketones, which then immediately added nitroform and formed γ-trinitromethyl ketones (I, II). The transformations studied open up a convenient route for the synthesis of γ-trinitromethyl ketones, excluding the special preparation of vinyl ketones.

$$\begin{array}{ccc} \mathrm{CH_2{=}CHC{\equiv}CH} \quad (I') & & \mathrm{HOCH_2C{\equiv}CCH_2OH} \quad (II') \\ & \downarrow \mathrm{Hg^{2+}(H_2O)} & \\ \left| \begin{array}{c} {}^{+\delta}\mathrm{CH_2{=}CH{-}C{-}R} \\ \| \\ \mathrm{O} \end{array} \right|^{-\delta} & & \mathrm{R:\ -CH_3,\ CH_2OH} \\ & \downarrow \mathrm{HC(NO_2)_3} & \\ \mathrm{(O_2N)_3CH_2CH_2CCH_3} \quad (I) & & \mathrm{(O_2N)_3CCH_2CH_2CCH_2OH} \quad (II) \\ \| & & \| \\ \mathrm{O} & & \mathrm{O} \end{array}$$

For its implementation, compounds containing the vinylacetylene grouping may be used, or substances in which, during the course of the reaction, a vinyl ketone residue is formed.

Experimental Part

5,5,5-Trinitropentan-2-one (I). In ether. Freshly prepared, still moist mercuric oxide, obtained by the action of caustic potash on an aqueous solution of 0.5 g of mercuric nitrate, is added to 7.2 g of nitroform in 30 ml of ether. Into the solution at 0° over the course of an hour, 5 g of gaseous vinylacetylene is passed. The reaction mixture is then kept for 24 hours at room temperature until the acidic reaction to Congo red disappears in a test sample; the ether is then evaporated, and the residue is distilled with steam. Yield of crude product (m.p. 34-36°), 4.6 g. 5,5,5-Trinitropentan-2-one (I), m.p. 43-43.5° (from 70% aqueous methanol), colorless leaflets, readily soluble–

soluble in methanol, benzene, acetone. Yield 4.24 g, 40% (calculated on nitroform).

$C_5H_7N_3O_7$.	Found, %:	C 27.65, 27.48;	H 3.45, 3.74;	N 19.47, 19.61
	Calculated, %:	C 27.19;	H 3.19;	N 19.04

In water. To 5 g of nitroform in 30 ml of water is added an aqueous suspension of mercuric oxide, well washed by decantation, prepared by the action of caustic potash on a solution of 0.5 g of mercuric nitrate. The solution is saturated for 1.5 hr at room temperature with 3.8 g of gaseous vinylacetylene. On the next day the reaction mixture is distilled with steam. Product I has m.p. 42° (from aqueous 70% methanol). Yield 2.3 g, 31% of theory.

Reaction of methyl vinyl ketone with nitroform. To an ice-cooled solution of 4.5 g (0.03 mole) of nitroform in 30 ml of ether, at a temperature not above 10°, is added a solution of 2.3 g (0.033 mole) of methyl vinyl ketone in 20 ml of ether. After evaporation of the solvent, a colorless product with m.p. 41–42° is isolated; a mixed sample with product I gave no depression. Yield 6.3 g, 95%.

5,5,5-Trinitropentanol-1-one-2 (II). To a solution of 3 g (0.02 mole) of nitroform in 5 ml of water is added 0.2 g of mercuric sulfate (or nitrate). Then at 0° and with mechanical stirring, over the course of three hours, a solution of 2 g (0.023 mole) of butyne-2-diol-1,4 in 5 ml of water is added. After 1–2 hr from the start of the addition of butynediol, separation of a crystalline precipitate of the reaction product gradually begins. The reaction mixture is stirred for another three hours at the same temperature and left overnight at 0°. The product obtained is filtered off, washed with water until the acid reaction on Congo paper disappears, and dried at 65–70°. Yield 3.2–3.4 g, 68–72% of theory.

5,5,5-Trinitropentanol-1-one-2 (II), m.p. 80° (20% aqueous ethanol or chloroform)–colorless thin needles, readily soluble in alcohol, acetone, ethyl acetate, acetic acid, insoluble in petroleum ether, moderately soluble in chloroform.

$C_5H_7O_7N_3$.	Found, %:	N 17.59, 17.51
	Calculated, %:	N 17.72

2,4-Dinitrophenylhydrazone of 5,5,5-trinitropentanol-1-one-2 (III). An aqueous-alcoholic solution of sulfuric-acid 2,4-dinitrophenylhydrazine is gradually added, with cooling, to an alcoholic solution of 5,5,5-trinitropentanol-1-one-2. The precipitate that separates is filtered off and thoroughly washed on the filter from traces of acid. 2,4-Dinitrophenylhydrazone of 5,5,5-trinitropentanol-1-one-2, decomp. 161°, on slow heating (from ethanol, then an ethanol–ethyl acetate mixture)—a crystalline product, readily soluble in acetone and ethyl acetate, sparingly soluble in alcohol.

$C_{11}H_{11}O_{11}N_7$.	Found, %:	N 23.67, 23.57
	Calculated, %:	N 23.50

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CITED LITERATURE

1. N. I. Nazarov, *Izv. AN SSSR, OKhN*, **1940**, 223, 453, 545; **1941**, 314.

2. N. I. Nazarov, N. V. Torgov, *Izv. AN SSSR, OKhN*, **1947**, 495.

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