REACTIONS OF N_2O_4 WITH ORGANIC COMPOUNDS

VIII*. TRINITROMETHYL DERIVATIVES OF PYRIDINE AND THIOPHENE

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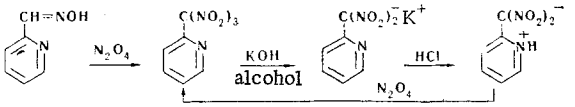
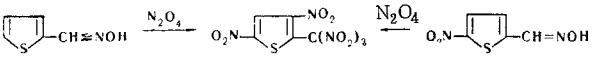
The previously described method for the one-step synthesis of aryltrinitromethanes from araldoximes may be utilized for the preparation of trinitromethyl derivatives of pyridine and thiophene. In the latter case, in addition to the conversion of the oxime group into the trinitromethyl group, nitration of the thiophene ring also occurs.

A single-stage synthesis of aryltrinitromethanes from araldoximes has been described previously [2]. This paper shows that heterocyclic trinitromethyl derivatives may also be obtained by this method. Thus, α-formylpyridine oxime on treatment with N_2O_4 gives a 65% yield of α-trinitromethylpyridine. Like other aryltrinitromethanes [3], trinitromethylpyridine on treatment with hot alcoholic alkali is converted into the potassium salt of dinitromethylpyridine. On acidification, dinitromethylpyridine, which exists as an internal salt [4], is obtained, and this α-dinitromethylpyridine reacts with N_2O_4 to give a 68% yield of α-trinitromethylpyridine.



Examination of the reaction of N_2O_4 with aldoximes of the thiophene series shows that, in addition to conversion of the oxime group into trinitromethyl, nitration of the thiophene ring also occurs. Thus, the reaction of N_2O_4 with α-thiophenealdoxime gives a pentanitromethylthiophene in 1.6% yield. The same compound is obtained by reaction of N_2O_4 with 5-nitro-2-thiophenealdoxime (50% yield).



The positions of the nitro groups were established by conversion of 2,4-dinitro-5-trinitromethylthiophene into the known [5] 2,4-dinitrothiophene-5-carboxylic acid.

EXPERIMENTAL

α-Trinitromethylpyridine. To a solution of 20 g (0.16 mole) of α-formylpyridine oxime [6] (mp 110-112° C) in 1 liter of dry acetonitrile, cooled to 3° C, there was added dropwise with stirring 45 g (0.49 mole) of N_2O_4. An additional 180 g (1.95 mole) of N_2O_4 was added all at once, and the mixture was heated quickly to 55° C. The mixture was evaporated at room temperature until it separated into an aqueous acid layer and an oil; the oil crystallized on standing. The α-trinitromethylpyridine (I) was filtered off, washed with water, and dried in air giving 24.2 g (64.6%), mp 70-72° C (from methanol). Found, %: C 31.46, 31.81;

* For part VII, see [1].

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H 1.48, 1.79; N 24.60; 24.36. Calculated for $C_6H_4N_4O_6$, %: C 31.59; H 1.77; N 24.56. The IR spectrum (1625, 1600, 1582, 1300 and 808 cm^{-1}) showed the presence of the trinitromethyl group [7]. α-Trinitromethylpyridine is a colorless crystalline solid, insoluble in the cold in caustic alkalies, but readily soluble in H_2SO_4, alcohol, dichloroethane, and chloroform, and sparingly soluble in petroleum ether.

Reaction of α-Trinitromethylpyridine (I) with Alcoholic Alkali. To a solution of 3.5 g (0.015 mole) of I in 10 ml of alcohol was added a solution of 2 g (0.036 mole) of KOH in 20 ml of alcohol. The reaction mixture was heated to boiling, and the precipitate which separated was filtered off, washed with a small amount of water, and dried in air to give 1.5 g (43%) of the salt II. Recrystallization of this from water gave 0.7 g of coarse, bright-yellow crystals of the potassium salt II, mp 214-215° C (vigorous decomposition). Found, %: K 17.52, 17.50. Calculated for $C_6H_4N_3O_4K$, %: K 17.67. To an aqueous solution of 0.5 g (0.0022 mole) of the salt II was added dropwise 5% HCl until the solution no longer became turbid. The oil which first separated soon crystallized, and the α-dinitromethylpyridine (III) was filtered off, washed with water, and dried in air to give 0.25 g (62%), mp 115-115.5° C (decomp, from water). α-Dinitromethylpyridine is a yellow crystalline solid, sparingly soluble in organic solvents but readily soluble in aqueous caustic alkalies and the carbonates and bicarbonates of the alkali metals.

Reaction of N_2O_4 with α-Dinitromethylpyridine (III). To a solution of 0.5 g (0.0027 mole) of III in 70 ml of dry acetonitrile was added 5 ml (0.054 mole) of N_2O_4, and the reaction mixture heated to 70° C. The α-trinitromethylpyridine was isolated as in the reaction of N_2O_4 with α-formylpyridine oxime, to give 0.4 g (68%) of α-trinitromethylpyridine. A mixed mp with an authentic sample gave no depression.

Reaction of N_2O_4 with 5-Nitrothiophenealdoxime. 2-Thiophenealdehyde was obtained by the Vilsmeier formylation of thiophene [8]. It was nitrated with HNO_3 in acetic anhydride to give 5-nitro-2-thiophenealdehyde diacetate, which, on hydrolysis, gave 5-nitro-2-thiophenealdehyde [9-11]. The oxime of these aldehydes were prepared in the usual way.

To a solution of 2 g (0.012 mole) of 5-nitrothiophenealdoxime (mp 156° C) [12] in 50 ml of dry acetonitrile cooled to -5° C, was added a solution of 15 g (0.163 mole) of N_2O_4 in 20 ml of dry acetonitrile. The first half of the oxide mixture was added dropwise, and the second half quickly. The reaction mixture was then heated rapidly to 60° C. After evaporation, the residue of 2,4-dinitro-5-trinitromethylthiophene (IV) was drained and then washed with a mixture of hexane and chloroform to give 1.9 g (50%) of product, mp 84-85° C (decomp, from a chloroform–hexane mixture). Found, %: C 18.62, 18.74; H 0.63, 0.64; N 21.56, 21.56; S 9.91, 10.17. Calculated for $C_5HN_5O_{10}S$, %: C 18.58; H 0.31; N 21.67; S 9.92. The IR spectrum (1640, 1600, 1537, 1347, 1297, and 803 cm^{-1}) indicated the presence of the trinitromethyl group [7].

On boiling with concentrated HNO_3, IV was converted in 34% yield into 2,4-dinitro-5-thiophenecarboxylic acid, mp 135-136° C (from water) [4]. Found, %: C 27.58, 27.38; H 0.88, 0.98; N 15.06, 14.87. Calculated for $C_5H_2N_2O_6S$, %: C 27.54; H 0.92; N 14.70.

Reaction of N_2O_4 with 2-Thiophenealdoxime. A 3-g (0.0024 mole) quantity of 2-thiophenealdoxime (mp 142° C [13]) was reacted with N_2O_4 as described in the preceding experiments, giving 0.11 g (1.6%) of 2,4-dinitro-5-trinitromethylthiophene. A mixed mp with material obtained as described above gave no depression.

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