Studies of Meso-ionic Compounds. XV[1]*. The Preparation of ψ-3,5-Dihydro-3-methyl-5-keto-1-oxa-2,3,4-triazole*

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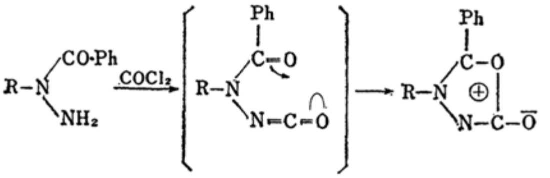
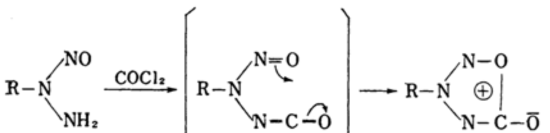
In a previous paper[2], we reported that ψ-oxadiazole (II) was prepared by the action of acyl chloride upon *N*-substituted N-benzoylhydrazine (Ia). The formation of the ψ-oxadiazole ring presumably involves the bond formation between two unsaturated groups of the intermediate acyl isocyanate (Ib). Thus, it could be expected that replacement of the acyl group of I with a nitroso group gives a new type of meso-ionic compound (IV) having an iso-electronic structure with II.



Ia Ib II

Fig. 1



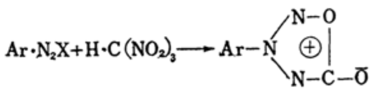
IIIa IIIb IV

R=CH_3

Fig. 2

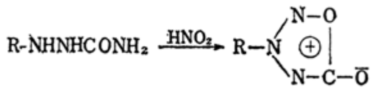
In the present paper, we report the preparation of compound IV by the action of carbonyl chloride upon *N*-nitroso-*N*-methylhydrazine (IIIa), which is readily accessible.

On the other hand, a few analogues of compound IV have already been obtained by routes different from that described above; Ponzio[3] prepared 3-aryl derivatives (V) by treating nitroform with diazonium salts, and recently Boyer and Canter[4] reported that 1-(2-methylcyclohexyl)- or 1-menthyl-semicarbazides and nitrous acid give the corresponding 3-alkyl derivatives (VI). The latter reaction apparently proceeds through the intermediate nitroso isocyanate (IIIb; R=2-methylcyclohexyl or menthyl), and therefore the formation mechanisms of IV and VI are perhaps essentially the same.



V

Fig. 3



VI

R=2-Methylcyclohexyl, menthyl

Fig. 4

In the present experiment, *N*-nitroso-*N*-methylhydrazine (IIIa) was subjected to the action of carbonyl chloride in chloroform in the presence of potassium carbonate to give colorless needles, m. p. 11°C, giving a negative test with the Liebermann nitroso reaction. The product can be distilled at 101∼101.5°C (3 mmHg) and is unreactive towards hot absolute ethanol, as has been reported by Ponzio and Boyer and Canter. Elemental analysis indicated the product to be the expected meso-ionic compound, ψ-3,5-dihydro-3-methyl-5-keto-1-oxa-2,3,4-triazole** (IV), whose structure was also supported by the infrared spectrum described below. The disappearance of the N–H stretching bands at 3315 and 3220 cm^{-1} observed for the precursor (IIIa) and the lack of a characteristic band for isocyanate in the infrared spectrum of ψ-oxatriazole IV suggest the formation of the meso-ionic ring. The strong absorption band at 1780 cm^{-1} in the spectrum of IV is indicative of the carbonyl group and

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[1] Part XIV of this series; K. Kishimoto and M. Ohta, This Bulletin, **34**, 1402 (1961).

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[2] M. Hashimoto and M. Ohta, This Bulletin, **34**, 668 (1961).

[3] G. Ponzio, *Gazz. chim. ital.*, **63**, 471 (1933); *Chem. Abstr.*, **28**, 748 (1934).

[4] J. H. Boyer and F. C. Canter, *J. Am. Chem. Soc.*, **77**, 1280 (1955).

** Designated following the systematic nomenclature suggested by W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, **1949**, 311.

is in close agreement with Boyer and Canter's observation ($1790\ cm^{-1}$)[4] and the carbonyl band of ψ-oxadiazole II ($1755\ cm^{-1}$)[2] having an iso-electronic structure with IV.

Experimental

***N*-Nitroso-*N*-methylhydrazine (IIIa).**—The compound was prepared by Thiele's method[5].

ψ-3, 5-Dihydro-3-methyl-5-keto-1-oxa-2, 3, 4-triazole (IV).—To a solution of IIIa (2 g.) in chloroform (200 ml.) was added finely powdered, anhydrous potassium carbonate (20 g.), and then a violent stream of carbonyl chloride was vigorously stirred in at $-7\sim-8$°C for 10 min. After the mixture had been kept standing at room temperature for 2 days, the precipitates were filtered off, the filtrate was concentrated and the residue was rectified to give 1.8 g. of IV, b. p. $104\sim106$°C/4 mmHg. Redistillation of IV yielded a fraction boiling at $101\sim101.5$°C/3 mmHg, m. p. 11°C, in the form of colorless needles, giving a negative test with the Liebermann nitroso reaction.

Found: C, 24.00; H, 3.00; N, 40.01. Calcd. for $C_2H_3O_2N_4$: C, 23.77; H, 2.99; N, 41.58%.

A solution of IV in absolute ethanol was refluxed for 3 hr. and evaporated under reduced pressure to give colorless needles, m. p. 11°C, giving a negative test with the Liebermann nitroso reaction.

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[5] J. Thiele, *Ann.*, 376, 244 (1910).