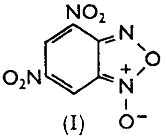
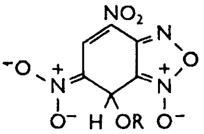
1006. *Two Explosive Compounds: The Potassium Salt of* 4,6-*Dinitrobenzofuroxan, and* 3,4-*Dimethyl*-4-(3,4-*dimethyl*-5-*isoxazolylazo*)*isoxazolin*-5-*one*

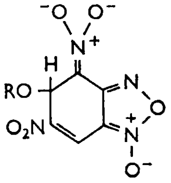
By A. J. Boulton and D. P. Clifford

The first title compound has been reinvestigated and found to be a Meisenheimer-type complex of hydroxide ion with the nitro-compound. Nitrous acid and 5-amino-3,4-dimethylisoxazole give the second compound named in the title.

In 1899 Drost[1] described the preparation of a series of salts of 4,6-dinitrobenzofuroxan (I) (called by him *m*-dinitro-*o*-dinitrosobenzene). The potassium salt, in particular, excited interest and has been evaluated as an explosive.[2] In Drost's Paper and in the subsequent literature these salts were formulated simply as the products of replacement of an aromatic proton by a metal. They are prepared from dinitrobenzofuroxan (I) by the action of mild aqueous alkali, and compound (I) is regenerated by dilute mineral acid.[1]


(I)


(II)


(III)

In order to determine the site of what appeared to be a remarkably stable carbanion, we treated the potassium salt with dilute deuterosulphuric acid. In the n.m.r. spectrum, compound (I) gives an AB quartet (τ_{A} 0·84, τ_{B} 1·10, $J_{\text{AB}} = 2$ c./sec. in dimethyl sulphoxide solution),[3] and, although the smallness of the separation of the signals reduces confidence in the assignment, it is likely, by analogy with other benzofuroxans,[3] that the low-field signal A arises from the proton at the 5-position, between the two nitro-groups, and the B signal from the 7-proton. Then, if salt formation involves metallation or carbanion formation at the 5-position, as suggested by Drost,[1] the deuterosulphuric acid treatment would introduce a deuterium atom at that site and the n.m.r. spectrum of the product would reveal a single peak, due to H_7.

Experimentally, it was found that no deuterium was incorporated into the product; the n.m.r. and infrared spectra were identical with those of the original dinitro-compound. This result eliminates Drost's formulation of the salt. The possibility that the anion might be of the form (II; R = H) or (III; R = H) was supported by the n.m.r. spectrum of the salt, which, in dimethyl sulphoxide, showed a single peak (τ 1·27), and an AB quartet (τ_{A} 3·74, OH; τ_{B} 4·06, CH; $J_{\text{AB}} = 7·5$ c./sec.). Recrystallisation from, or preparation of the salt in, deuterium oxide gave a product (II or III; R = D) in which the AB quartet had been replaced by a single peak at τ 4·10, leading to the assignments quoted above. A methoxy-analogue (II or III; R = Me) of the salt was prepared, using potassium methoxide or hydroxide in methanol, which gave peaks at τ 1·03, 3·98 (one proton), and 6·63 (three protons).* The methanol of crystallisation, suggested by the elemental analysis, did not show up clearly in a region very much complicated by solvent side-bands, but some spectra revealed a doublet at τ 6·75.

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* The proton on the methoxyl-bearingcarbon atom of the trinitrobenzene–sodium methoxide adduct absorbs at τ 3·86 (in dimethyl sulphoxide) (M. R. Crampton and V. Gold, *J.*, 1964, 4293).

[1] P. Drost, *Annalen*, 1899, **307**, 49.

[2] H. Rathsburg, *Z. angew. Chem.*, 1928, **41**, 1284.

[3] R. K. Harris, A. R. Katritzky, S. Øksne, A. S. Bailey, and W. G. Paterson, *J.*, 1963, 197.

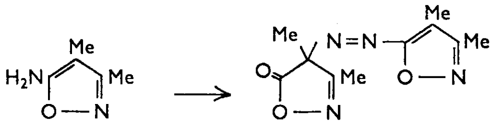
The infrared spectra also lent support to the proposed structures. The potassium salt, after careful drying *in vacuo*, showed a hydroxyl band at 3430 cm.$^{-1}$, while the deuterated salt had OD absorption at 2590 cm.$^{-1}$. The rest of their spectra were similar, and, although different in detail, were similar overall to the spectrum of 4,6-dinitrobenzofuroxan, with which the salts have many structural features in common.

Drost's analytical results are quoted for his structure with half a molecule of water of crystallisation. They are also in fair agreement with the figures required for 1 H_2O, equivalent to structure (II or III; R = H) for the anion, and his analysis of the silver salt is more satisfactorily explained on this basis.

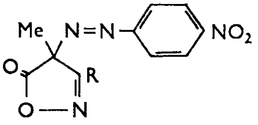
It is not possible to make a firm choice between structures (II) and (III) on the evidence available, but, as structure (II) seems to be more capable of spreading the negative charge, it may be considered the more likely.

The second compound was obtained as the product of an attempted diazotisation of 5-amino-3,4-dimethylisoxazole (IV). Addition of sodium nitrite solution to an aqueous acid solution of the amine led to the separation of a yellow tar, which solidified on standing. This tar was extracted into ether, and, after drying, the ether was removed on a steam-bath, whereupon the residue exploded with considerable violence. Experiments conducted on samples of the material obtained in another preparation, after purification, showed that it invariably decomposed with a sharp report if heated rapidly to 100°, but it appeared to be stable to percussion and friction.

Full combustion analysis data were not obtained for this compound, because of its explosive nature; however, spectra and a nitrogen analysis were in accord with structure (V). Thus, the n.m.r. spectrum showed resonances from four chemically distinct methyl groups (τ 7·67, 7·72, 7·85, and 8·08, in chloroform), and no evidence for any other proton. A carbonyl absorption at 1805 cm.$^{-1}$ (chloroform solution) is typical of 4*H*-isoxazolin-5-ones such as (V), and precludes position 2 as the site of attachment of the azo-grouping since 2*H*-isoxazolin-5-ones absorb at about 1740 cm.$^{-1}$ in chloroform solution.[4] The azo-grouping gives a band at 414 mμ (ε 170) in cyclohexane solution, which accounts for the yellow colour of the compound.



(IV) (V)



(VI)

Two analogues of compound (V) were prepared, for comparison. Diazotised *p*-nitroaniline gave yellow, apparently non-explosive, products with 5-amino-3,4-dimethylisoxazole and 4-methyl-3-phenylisoxazolin-5-one, to which spectral and analytical data allow the firm assignment of structures (VI; R = Me) and (VI; R = Ph), respectively.

EXPERIMENTAL

Potassium 4,6-*Dinitrobenzofuroxan Hydroxide Complex*.—This material was prepared according to Drost,[1] from 4,6-dinitrobenzofuroxan and aqueous potassium hydrogen carbonate. For the preparation of the deuteroxide analogue a small sample was recrystallised from heavy water, or heavy water was used in preparing the potassium hydrogen carbonate solution.

Potassium 4,6-*Dinitrobenzofuroxan Methoxide Complex*.—Potassium hydroxide (0·2 g.) in methanol (5 ml.) was added to 4,6-dinitrobenzofuroxan (0·4 g.) in methanol (20 ml.). The *complex* (0·35 g., 67%), which crystallised after a few minutes, was washed with a little methanol and dried *in vacuo*, giving fine red needles, m. p. 125° (decomp.) (Found: C, 29·5; H, 3·0; N, 16·8. $C_7H_5KN_4O_7,CH_3OH$ requires C, 29·3; H, 2·8; N, 17·1%).

3,4-*Dimethyl*-4-(3,4-*dimethyl*-5-*isoxazolylazo*)*isoxazolin*-5-*one* (V).—5-Amino-3,4-dimethylisoxazole (from hydroxylamine and 3-amino-2-methylcrotononitrile [5]) (0·5 g.), in sulphuric

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[4] A. J. Boulton and A. R. Katritzky, *Tetrahedron*, 1961, **12**, 41.

[5] E. Mohr, *J. prakt. Chem.*, 1914, [2], **90**, 196.

acid (2N; 30 ml.), was treated with sodium nitrite (0·32 g.) in water (10 ml.) at 0°. After 5 min. the partly solidified yellow tar which had separated was extracted into ether, the extract washed with water and dried ($MgSO_4$), and the ether removed under reduced pressure, without heating. Crystallisation of the residue from light petroleum containing a little diethyl ether gave the *azo-compound* (0·45 g., 85%) as yellow needles, m. p. 81—82° (Found: N, 23·6; $C_{10}H_{12}N_4O_3$ requires N, 23·7%), $\lambda_{max.}$ 298 (12,500), 414 mμ (ε 170); $\nu_{max.}$ ($CHCl_3$) 1805 (420), 1185 (75), 866 cm.$^{-1}$ (ε_A 200) (particularly characteristic of the 4*H*-isoxazolin-5-one system [4]).

3,4-*Dimethyl*-4-(4-*nitrophenylazo*)*isoxazolin*-5-*one* (VI; R = Me).—Diazotised *p*-nitroaniline (1·0 g.) in hydrochloric acid (4N; 30 ml.) was added to 5-amino-3,4-dimethylisoxazole (1·0 g.) in hydrochloric acid (4N; 20 ml.) at 0°. The *isoxazolinone* which separated was recrystallised from diethyl ether, giving yellow needles (1·05 g., 45%), m. p. 85° (Found: C, 50·4; H, 4·0; N, 21·35. $C_{11}H_{10}N_4O_4$ requires C, 50·4; H, 3·8; N, 21·4%), $\lambda_{max.}$ 281 (17,200), 416 mμ (ε 230); $\nu_{max.}$ 1790vs, 866s (isoxazolinone); 1522vs, 1345vs cm.$^{-1}$ (NO_2), were prominent in Nujol. N.m.r.: an AB system (apparently) with τ_A 1·50, τ_B 1·98, J_{AB} = 9 c./sec. from the *p*-nitrophenyl group (in dimethyl sulphoxide), and singlets at τ 7·85 and 8·05, from the methyl groups (in chloroform).

4-*Methyl*-4-(4-*nitrophenylazo*)-3-*phenylisoxazolin*-5-*one* (VI; R = Ph).—Diazotised *p*-nitroaniline (0·9 g.) in hydrochloric acid (4N; 27 ml.) was added to 4-methyl-3-phenylisoxazolin-5-one [6] (1·0 g.) in aqueous sodium hydroxide (1N; 120 ml.) at 0°. The *azo-isoxazolinone* separated and was recrystallised from ether, yellow needles (1·0 g., 54%), m. p. 88—89° (Found: N, 17·3. $C_{16}H_{12}N_4O_4$ requires N, 17·3%), $\lambda_{max.}$ 270 (23,100), 420 mμ (ε 270); $\nu_{max.}$ 1802vs, 862s (isoxazolinone), 1515vs, 1346vs cm.$^{-1}$ (NO_2) (Nujol). N.m.r.: an apparent AB system with τ_A 1·45, τ_B 1·92, J_{AB} = 9 c./sec. from the *p*-nitrophenyl group, and an unresolved multiplet, τ ~2·30, from the phenyl group (in dimethyl sulphoxide), and a singlet at τ 8·20, from the methyl group (in benzene).

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[6] A. Haller and E. Bauer, *Compt. rend.*, 1911, **152**, 1446.