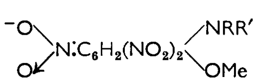
692. *Coloured Alkali Salts from* sym.-*Trinitrobenzene Derivatives. Part III.* Picramide Derivatives.*

By R. C. Farmer.

The coloured quinonoid nitronates obtained by the action of methoxide on picramide derivatives have been examined. Two alternative methods of preparation are given, proceeding by different routes. The coloured amino-compounds differ from the corresponding phenoxy-compounds, in that they lose their methoxy-groups on acidification and the amino- or anilino-group remains attached to the benzene ring. Trinitrophenylmethylnitramine was included as a nitramine. The splitting off of the methylnitramino-group was gradual and its separation was followed by sampling at intervals. A secondary reaction was found to occur, in which a nitro-group in the benzene ring was replaced by a methoxy-group, forming two isomeric compounds, 2-methoxy-4,6- and 4-methoxy-2,6-dinitrophenylmethylnitramine.

Picramide and its *N*-methyl and *N*-phenyl derivatives react with methoxide in the same manner as trinitrobenzene, forming coloured solutions; some solid salts have been obtained by Busch and Kögel.[1] It is now found that the coloured compounds can be obtained by two methods. Thus, the salt of an ion (I; R′ = H) can be made (1) by the action of methoxide on the aniline $(NO_2)_3C_6H_2{\cdot}NHR$, and (2) by the action of the amine $R{\cdot}NH_2$ on the anisole $(NO_2)_3C_6H_2{\cdot}OMe$.



(I)

The amino- or anilino-group is more firmly bound than the phenoxy-group, and whereas in the methoxy-phenoxy-quinonoid nitronates (Part II) the phenoxy-group was very readily split off and replaced by a methoxy-group, yielding trinitroanisole on acidification, the amino- or anilino-methoxy-compounds lose the methoxy-group on acidification and the amino- or anilino-group remains intact. It was not found possible to make coloured quinonoid nitronates containing two anilino-groups attached to the same carbon atom.

Trinitrophenylmethylnitramine (tetryl) was included as an example of a nitroamine. It reacted with methoxide forming a salt of the ion (I; R = NO_2, R′ = Me). This remained intact sufficiently long to enable it to be identified, but gradually lost the methylnitramino-group.

Tetryl reacted also with aqueous alkali, giving an intense red colour. On acidification immediately after mixing, pure tetryl was recovered, showing that the methylamino-group remained intact for a time, but decomposition slowly set in with formation of picric acid, etc.

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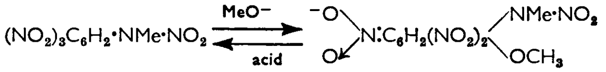
* Part II, preceding paper.

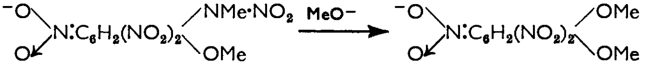
[1] Busch and Kögel, *Ber.*, 1910, **43**, 1549.

By-products of the Action of Methanolic Potash on Trinitrophenylmethylnitramine.—The yields of the methoxy-quinonoid compound fell considerably short of theory (60—65%). About 20% of a mixture of by-products was obtained. Two isomeric compounds were isolated and were identified as 2-methoxy-4,6- and 4-methoxy-2,6-dinitrophenylmethylnitroamine. This indicates that a nitro-group in the benzene nucleus was replaced by a methoxy-group. The action of methoxide on trinitrophenylmethylnitramine is thus as follows:

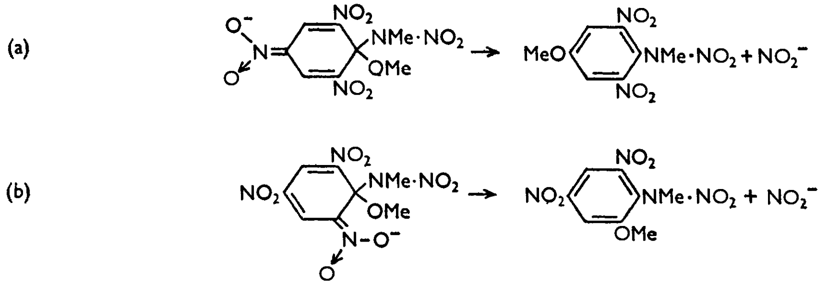
(1) Primary reaction. Formation of nitronic compound:



followed by gradual replacement of the methylnitramino-group by methoxy:

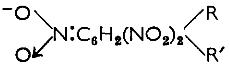


(2) Secondary reaction. Conversion of nitrone into methoxydinitrophenylmethylnitramines:



These have been previously synthesized by other methods, and their properties and reactions agree with the products obtained from tetryl in the present work. Their formation supports the generally accepted assumption that the coloured anions formed from trinitrobenzene derivatives are resonance hybrids intermediate between the two quinonoid forms.[2] The analogous replacement of a nitro-group by a methoxy-group was observed by Lobry de Bruyn [3] in the conversion of trinitrobenzene into dinitroanisole by sodium methoxide. This was confirmed in the present work. In this case two isomers are not possible, owing to the symmetry of the trinitrobenzene. In the case of trinitroanisole two isomers might be formed, but it was not found possible to obtain a product in which a nitro-group was substituted by a methoxy-group.

Experimental



(II)

Quinonoid Nitronates from Picramide Derivatives.—The following derivatives of the anion (II) have been examined. (i) R = NH_2, R′ = OMe. Picramide reacted with methanolic potash giving a deep red colour, and crystals of the quinonoid nitronate separated. The same product was obtained conversely from trinitroanisole and ammonia in methanol, followed by the addition of sufficient alkali to form the potassium salt (Found: K, 12·95. Calc. for $C_7H_7O_7N_4K$: K, 13·1%). Acidification regenerated picramide, m. p. 189°. No trinitroanisole was found.

(ii) R = NH_2, R′ = OEt. Analogous reactions of picramide with ethanolic potash, and of trinitrophenetole with ammonia plus alkali, gave red crystals which, on acidification, yielded picramide, m. p. 189°. No trinitrophenetole was formed.

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[2] Sidgwick, " The Organic Chemistry of Nitrogen," 1937, p. 260, Clarendon Press, Oxford.

[3] Lobry de Bruyn, *Rec. Trav. chim.*, 1890, **9**, 208.

(iii) R = NHMe, R′ = OMe. *N*-Methylpicramide gave a deep red colour with methanolic potash, but no solid separated. On acidification the methoxy-group split off and *N*-methylpicramide, m. p. 111°, was regenerated.

(iv) R = NHPh, R′ = OMe. 2,4,6-Trinitrodiphenylamine gave a deep red solution with methanolic potash, and 2,4,6-trinitroanisole reacted similarly with aniline and alkali. In each case, trinitrodiphenylamine was recovered on acidification, m. p. 176—177°.

(v) R = NHPh, R′ = OEt. Ethanolic potash reacted with 2,4,6-trinitrodiphenylamine, and conversely aniline reacted with trinitrophenetole, giving very dark crystals. In each case acidification gave trinitrodiphenylamine, m. p. and mixed m. p. 177°. No trinitrophenetole was detected.

(vi) R = *p*-$NH{\cdot}C_6H_4Me$, R′ = OMe. *N*-2,4,6-Trinitrophenyl-*p*-toluidine reacted with methoxide, and conversely 2,4,6-trinitroanisole reacted with *p*-toluidine, giving dark crystals. Each of the products gave *N*-trinitrophenyl-*p*-toluidine on acidification, m. p. 162°. In general, these nitronates are unstable to moisture.

(vii) R = R′ = NHPh. An attempt to prepare this compound by the action of aniline on trinitrodiphenylamine in presence of alkali was unsuccessful: no coloured compound was formed.

Trinitrophenylmethylnitramine (*Tetryl*).—Methanolic potash gave a deep red, clear solution. To ensure that no unchanged tetryl was present in the clear solution, the methanol was diluted to 50% with water, thus reducing the solubility of tetryl to about 1 in 4000. In the compound formed (I; R = NO_2, R′ = Me), the methylnitramino-group was more firmly attached than the methoxy-group. Addition of acid shortly after mixing regenerated tetryl almost quantitatively, m. p. and mixed m. p. 128°. Samples were taken at intervals and acidified; m. p.s of the products were as follows:

Time (min.) at 0—5°	1	3	7	19	44
M. p. to complete fusion	128°	126°	123°	115°	107°

The potassium salt, $KO_2N{:}C_6H_2(NO_2)_2(OMe)_2$ gradually separated. After long standing the acidified product from the solution was 2,4,6-trinitroanisole, m. p. 68°. Similar results were obtained with ether oxide. Acidification shortly after mixing gave pure tetryl (m. p. 128°); on long standing trinitrophenetole was obtained (m. p. 78·5°). Aqueous alkali reacted rapidly with tetryl, giving a clear, deep red solution. On acidification immediately after mixing, pure tetryl was regenerated. After some hours the methylnitramine group was decomposed by the alkali, forming acidic products (picric acid, etc.). When the alkali present was insufficient to neutralize the acids, some re-precipitation of the tetryl took place.

Aqueous ammonia reacted with tetryl, giving a deep red solution. Some picramide was formed (m. p. 190°).

By-products from Tetryl.—The yields of the dimethoxy-quinonoid nitronate depended on the alkali ratio and to a minor extent on the temperature and time of action. With 0·15 mol. of tetryl per l. at room temperature the yields were as follows:

Alkali ratio	0·67	1·00	1·18	2·00	2·51	5·0
Yield (%)	16	34	44	63	62	62

To account for the relatively low yields, the red sodium nitronate was converted into soluble picrate by dissolving it in water and allowing it to stand. A mixture of by-products remained insoluble. Under favourable conditions these amounted to 20%. They were practically colourless, showing absence of a quinonoid structure, and melted indefinitely at 85—120°. Nitrite was formed, indicating the loss of a nitro-group. The methylnitramino-group was still intact, as shown by the formation of nitric acid on addition of concentrated sulphuric acid,[9] and by the evolution of nitrous fumes on heating the dry compounds. Hence, a nitro-group in the benzene ring must have been split off. The compound was a dinitrobenzene derivative, as shown by the action of alkali in pyridine (purple colour) and by Janowski's test. Alcoholic alkali gave no colour in the cold (absence of trinitro-compound); a bright red colour was formed on warming, but disappeared on cooling. The compounds were insoluble in aqueous alkali (absence of phenols). Ferric chloride gave no colour.

The recorded observation of the conversion of trinitrobenzene into dinitroanisole by alcoholic alkali[3] was confirmed (yields 78—80%). By analogy with this, tetryl should give methoxydinitrophenylmethylnitroamine.

On separation, the by-products yielded two compounds, m. p. 117—118° and 124—125° respectively. Analysis showed them to be isomers of the composition $C_8H_8O_7N_4$ (Found, for former compound: C, 35·55; H, 3·1; N, 20·5; for latter compound: C, 35·5; H, 3·0; N, 20·4. Calc. for $C_8H_8O_7N_4$: C, 35·3; H, 3·0; N, 20·6%). The compound of m. p. 125° usually crystallised in prisms, but some thick hexagonal plates of the same m. p. were obtained. The compound of m. p. 118° crystallised in thin laminæ. That of m. p. 125° was identified as 4-methoxy-2,6-dinitrophenylmethylnitramine, which had been made by Rêverdin;[4] it agreed with the published work in (1) m. p. 125°, (2) formation of a bright red colour, turning pale orange, on addition of concentrated sulphuric acid, (3) Liebermann's reaction (intense blue), (4) conversion into 4-methoxy-*N*-methyl-2,6-dinitroaniline (m. p. 129°) on boiling with a pentyl alcohol solution of phenol containing a little sulphuric acid, as described by Pinnow.[5] This compound was reconverted into the methylnitramine, m. p. 125°, by nitric acid.

The compound of m. p. 118° had been synthesized by several methods and established as 2-methoxy-4,6-dinitrophenylmethylnitramine. As stated by Rêverdin,[6] it gave the Liebermann reaction, and with concentrated sulphuric acid gave a green solution fading slowly to dull brown. On heating with phenol and sulphuric acid in pentyl alcohol it gave 2-methoxy-*N*-methyl-4,6-dinitroaniline, m. p. 168°, in agreement with v. Romburgh.[7]

Tetryl, on similar treatment, gave *N*-methyltrinitrophenylaniline,[8] m. p. 111°, and this was reconverted into tetryl (m. p. and mixed m. p. 129·5°) by nitric acid.

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[4] Rêverdin, *J. prakt. Chem.*, 1911, **83**, 165; 1911, **84**, 555.
[5] Pinnow, *Ber.*, 1897, **30**, 838.
[6] Rêverdin, *J. prakt. Chem.*, 1910, **81**, 182.
[7] v. Romburgh, *Compt. rend.*, 1891, **113**, 506.
[8] v. Romburgh, *Rec. Trav. chim.*, 1886, **5**, 240.
[9] Thiele and Lachmann, *Annalen*, 1895, **288**, 269.