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Transamination reactions of 1,1-diamino-2,2-dinitroethene (FOX-7)

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Treatment of 1,1-diamino-2,2-dinitroethene (FOX-7) with a variety of amines and hydrazine, results in at least one, and in some cases both, of the amino groups being replaced to give *N*-substituted and *N,N′*-disubstituted 1,1-diamino-2,2-dinitroethenes.

Keywords. 1,1-diamino-2,2-dinitroethene, FOX-7, transamination

1,1-Diamino-2,2-dinitroethene, also known as FOX-7, has generated considerable interest in recent years as an explosive with relatively high performance and low sensitivity to both friction and impact.[1] However, it is also of interest as an example of a 'push-pull' alkene of the nitroenamine type,[2] and it is its chemical behaviour as a member of this group of compounds that we report here. One of the typical reactions of nitroenamines is their facility to undergo transamination reactions,[3,4] via an addition–elimination mechanism. We have found that when 1,1-diamino-2,2-dinitroethene is treated with a variety of amines (predominantly primary amines), and related nucleophiles, at least one, and in some cases both, of the amino groups are replaced to give *N*-substituted and *N,N′*-disubstituted 1,1-diamino-2,2-dinitroethenes:

$$(H_2N)_2C{=}C(NO_2)_2 + RNH_2 \rightarrow RNH(H_2N)C{=}C(NO_2)_2 \rightarrow (RNH)_2C{=}C(NO_2)_2$$

The reactions have been studied both spectroscopically (^1H and/or ^{13}C NMR spectroscopy) and preparatively. In most cases, the progress of the substitution reaction may be followed by the disappearance of NMR signals of the starting materials (^1H and ^{13}C for the amine, ^{13}C only for 1,1-diamino-2,2-dinitroethene), and the appearance of NMR signals of the product(s). The amines/nucleophiles chosen for study were 3-aminopentane, 1-aminobutane, 2-aminoethanol, 3-aminopropan-1-ol, benzylamine, diethylamine, 1,2-diaminoethane, 1,3-diaminopropane, hydrazine and guanidine.

Reaction of 1,1-diamino-2,2-dinitroethene with 3-aminopentane was a clean reaction and gave 1-amino-1-(pent-3-ylamino)-2,2-dinitroethene in almost quantitative yield after 3 days at 90°C in *N*-methylpyrrolidin-2-one (NMP). There was no evidence for further substitution. Reaction with the less sterically hindered 1-aminobutane was faster, and gave clear evidence for double substitution, but the individual substitution products could not be isolated. Likewise, both 2-aminoethanol and 3-aminopropan-1-ol gave mixtures of mono- and bis-substitution.

The di-amines 1,2-diaminoethane and 1,3-diaminopropane, both gave cyclic products (2-dinitromethylidene-1,3-diazacycloalkanes, **1** and **2** respectively) resulting from double substitution by both amine groups in the nucleophile. When, however, the reaction with 1,2-diaminoethane was conducted in neat di-amine, the product (25%) was 1′,3′-diazacyclopent-2′-ylidene-2*H*-imidazole (**3**).

The reaction between 1,1-diamino-2,2-dinitroethene and hydrazine gave 1-amino-1-hydrazino-2,2-dinitroethene (**7**). With an excess of hydrazine, the water-soluble, hydrazinium salt of the conjugate base of **7** was isolated.

The reaction between 1,1-diamino-2,2-dinitroethene and guanidine did not lead to a substitution product, but instead gave the guanidinium salt of the conjugate base of 1,1-diamino-2,2-dinitroethene.

Caution: 1,1-Diamino-2,2-dinitroethene and the various derivatives described below are potentially explosive and should be treated with appropriate precautions *e.g.* use small amounts and protective shielding and avoid friction, impact and vigorous heating.

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References: 7

Formulae: 9

Table 1 Transamination of 1,1-diamino-2,2-dinitroethene

Scheme 1 Formation of **3**

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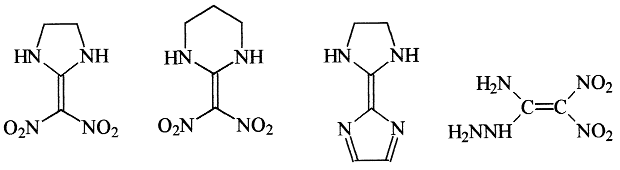

1 **2** **3** **7**

Formulae

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