The Interaction of 1,1,2-Tricarbamoyl-2-cyanoethane with Crotonaldehyde

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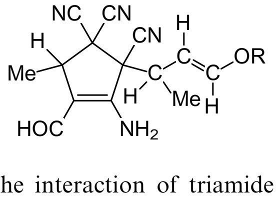
The interaction of 1,1,2-tricarbamoyl-2-cyanoethane with crotonaldehyde in water in the presence of a catalytic amount of triethylamine leads to 6-amino-7-carbamoyl-1-cyano-4-hydroxy-2-oxo-3-azobicyclo[3.2.1]oct-6-ene, the structure of which has been determined by X-ray crystallography.

Previously we showed that 1,1,2-tricarbamoyl-2-cyanoethane **1** is formed by reaction of 1,1,2,2-tetracyanoethane with pyruvic acid in the presence of water.[1] Proceeding with an investigation into the properties of compound **1**, we decided to use this in reactions with α,β-unsaturated aldehydes.

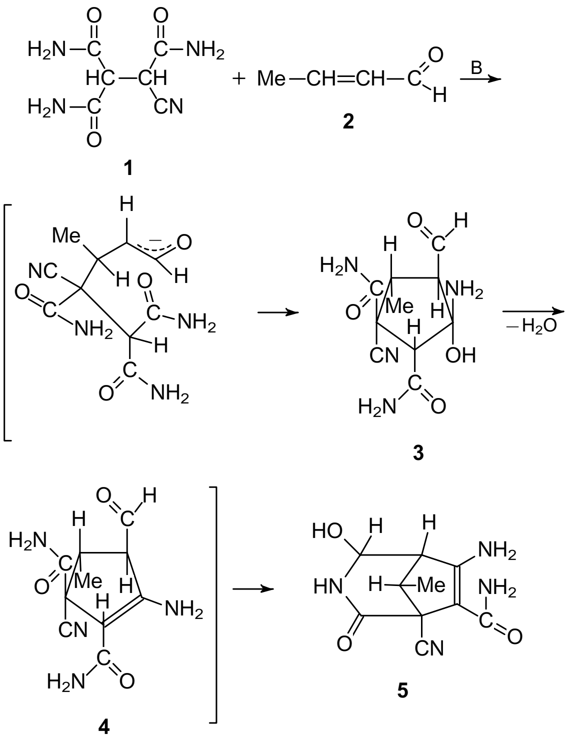
It is known that 1,1,2,2-tetracyanoethane reacts with crotonaldehyde in alcohols to give the corresponding vinyl esters.[2]



Our study of the interaction of triamide **1** with crotonaldehyde allowed us to determine that the reaction results in a compound the molecular weight of which indicates that the interaction occurred in 1:1 relative proportions. The reaction was carried out in water;† performing it in organic solvents (isopropyl alcohol, acetonitrile) led to the formation of tar in the reaction mixture.

According to an X-ray study of a monocrystal the resulting compound is 6-amino-7-carbamoyl-1-cyano-4-hydroxy-2-oxo-3-azabicyclo[3.2.1]oct-6-ene **5** (Scheme 1, Figure 1).‡

Based on the structure of **5** we suggest the following mechanism for the process. Under the action of a base, Michael addition of compound **1** to the double bond of



Scheme 1

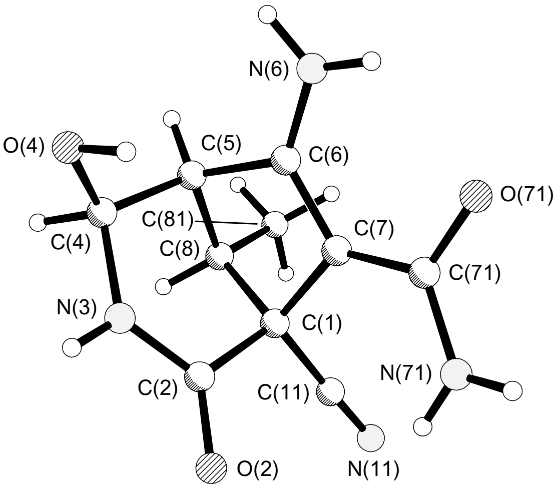


Figure 1 Molecular structure of **5** (bond lengths/Å): O(2)–C(2) 1.239(2), O(4)–C(4) 1.399(2), O(71)–C(71) 1.265(2), N(3)–C(2) 1.343(2), N(3)–C(4) 1.482(2), N(6)–C(6) 1.329(2), N(11)–C(11) 1.140(2), N(71)–C(71) 1.350(2), C(1)–C(11) 1.472(2), C(1)–C(2) 1.535(2), C(1)–C(7) 1.528(2), C(1)–C(8) 1.570(3), C(4)–C(5) 1.545(2), C(5)–C(6) 1.512(2), C(5)–C(8) 1.536(2), C(6)–C(7) 1.386(2), C(7)–C(71) 1.440(2), C(8)–C(81) 1.523(3).

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† *Preparation of compound* **5**. To a suspension of 0.5 g (2.7 mmol) of 1,1,2-tricarbamoyl-2-cyanoethane **1** in 5 ml of water was added 0.75 g (10.7 mmol) of crotonaldehyde **2**, then 0.084 g (0.83 mmol) of triethylamine was added to the stirred mixture. The mixture was stirred for 10 min at room temperature until dissolution of the starting compound **1** and the onset of precipitate formation. The reaction mixture was allowed to stand for 1 h and the resulting compound **5** was then filtered off, washed with water, recrystallized from water and air-dried to give 0.125 g (20%) of compound **5** with m.p. 191–192 °C. IR spectral data (vaseline oil, cm^{-1}): 3440, 3415, 3340, 3310, 3200 (ν_{OH}, ν_{NH}), 2255 ($\nu_{C=N}$), 1655, 1625, 1620 ($\nu_{C=O}$, σ_{NH}), 1575 ($\nu_{C=C}$). Mass spectral data, *m/z* (relative intensity, %): M^+ = 236(91) and the 10 most intensive peaks of fragment ions: 220(52), 219(95), 193(91), 191(95), 176(91), 175(91), 166(95), 165(100), 157(95), 118(96). Single crystals for an X-ray investigation having a satisfactory elemental analysis were grown from an acetonitrile–water mixture (1:1).

‡ *Crystal data for* **5**: $C_{10}H_{12}N_4O_3$, $M = 236.2$, monoclinic, space group $P2_1/c$, at −95 °C $a = 11.365(5)$, $b = 7.116(2)$, $c = 14.095(6)$ A, $\beta = 106.31(2)°$, $V = 1094.1(7)$ A , $Z = 4$, $d_c = 1.434$ g cm^{-3}. Unit cell parameters and reflection intensities were measured with an automated four-circle Siemens P3/PC diffractometer (178 K, λMoKα, graphite monochromator, θ/2θ-scan, θ ⩽ 52°). The structure was solved by a direct method and refined by a full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms located in the difference Fourier map were included in the isotropic approximation refinement with fixed isotropic thermal parameters $B_{iso} = 0.04$ Å^2. The final discrepancy factors are $R = 0.036$ and $R_w = 0.037$ for 2143 unique reflections with $I > 3\sigma(I)$. All calculations were carried out using SHELXTL PLUS programs. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC), see Notice to Authors, *Mendeleev Commun.*, 1995, Issue 1.

crotonaldehyde takes place followed by intramolecular cyclisation to cyclopentane **3**. Then, elimination of a water molecule from **3** leads to cyclopentene **4**, in which one more intramolecular cyclization proceeds *via* the interaction of a carbamoyl fragment with an aldehyde group located in the same plane. As a result of the last cyclization 6-amino-7-carbamoyl-1-cyano-4-hydroxy-8-methyl-2-oxo-3-aza-bicyclo-[3.2.1]oct-6-ene **5** is formed. It should be noted that of the two possible existing ways for the formation of enamines, the route *via* enaminoamide **4** (but not enaminoaldehyde as in ref. 2) is apparently taken; this is connected with the possibility of additional stabilization due to the intramolecular cyclization to bicycle **5**.

Compound **5** has three chiral centres at the C_1, C_4 and C_8 atoms. Crystal **5** represents a racemic mixture of *SSR*- and *RRS*-enantiomers.

The IR and mass spectral data completely agree with the structure suggested.

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