Single-stage synthesis of 3-amino-1,2-dicyano-4,6-diazabicyclo[3,2,1]oct-2-en-7-ones from β,β,γ,γ-tetracyanoalkanones

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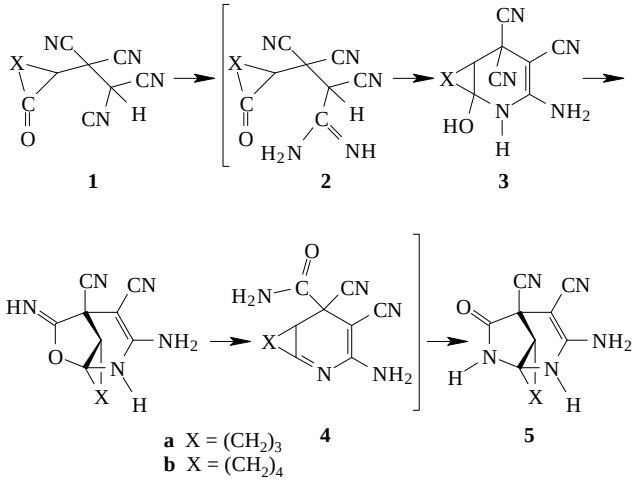
The interaction of β,β,γ,γ-tetracyanoalkanones with aqueous ammonia leads to 3-amino-1,2-dicyano-4,6-diazabicyclo[3,2,1]oct-2-en-7-ones; their structure has been established by X-ray crystallography.

We have found that when β,β,γ,γ-tetracyanoalkanones **1**[1] are mixed with aqueous ammonia at room temperature 3-amino-1,2-dicyano-4,6-diazabicyclo[3,2,1]oct-2-en-7-ones **5** are formed.† We suppose that the reaction begins with addition of ammonia to one of the terminal cyano groups, as in the case of interaction of ketones **1** with acids.[2–4] Then, in intermediate **2**, the interaction of an amino group with a carbonyl group proceeds. In tetrahydropyridine **3** hydrolysis of an axial cyano group possibly occurs. This internal molecular process proceeds *via* formation of cyclic iminoether and its further decyclization to amide **4**. The addition of a carbamoyl fragment from the C=N bond in intermediate **4** leads to bicycles **5** (Figure 1). Their structure has been determined by X-ray research on monocrystal **5b** (Tables 1 and 2).‡



1 **2** **3**

a X = $(CH_2)_3$ **4** **5**
b X = $(CH_2)_4$

† *Synthetic procedure*: 0.01 mol of β,β,γ,γ-tetracyanoalkanone **1a**,**b** was mixed with 10 ml of propan-2-ol and 10 ml (10–20%) of aqueous ammonia. The mixture was kept at room temperature during 24 h. The precipitate was filtered off, washed with propan-2-ol and recrystallized from propan-2-ol.

For **5a**: yield 78%, mp 126–127 °C, IR (vaseline oil, cm^{-1}): 3440–3160 (ν_{NH}), 1690 (δ_{NH}), 2270, 2190 ($\nu_{C\equiv N}$), 1720 ($\nu_{C=O}$), 1630 ($\nu_{C=C}$).

For **5b**: yield 90%, mp 273–274 °C, IR (vaseline oil, cm^{-1}): 3480–3120 (ν_{NH}), 1640 (δ_{NH}), 2285, 2135 ($\nu_{C\equiv N}$), 1720 ($\nu_{C=O}$), 1590 ($\nu_{C=C}$).

‡ *Crystal data for* **5b**: $C_{12}H_{13}N_5O$, M = 243.26, crystals are triclinic, at 20 °C a = 7.150(1), b = 8.035(1), c = 12.096(2) Å, α = 93.45(1), β = 104.71(1), γ = 113.74(1)°, V = 604.8(2) $Å^3$, d_{calc} = 1.336 g cm^{-3}, Z = 2. The space group is $P\bar{1}$. The cell parameters and intensity of 2337 independent reflections were measured on a four-circle automatic diffractometer Siemens P3/PC (λMoKα, graphite monochromator, $\theta/2\theta$-scanning to θ = 25°). The terminal discrepancy factors are $R_1(F)$ = 0.033, w$R_2(F^2)$ = 0.088. The whole calculation was carried out according to the program SHELXTL PLUS. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, 1997, Issue 1. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/17.

Concentration of the aqueous ammonia solution does not influence the process.

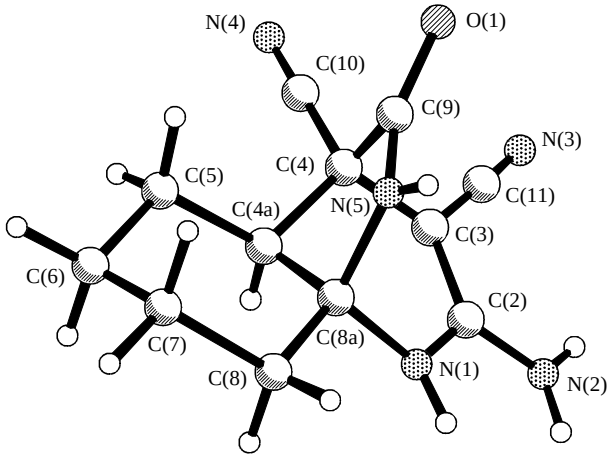


Figure 1 Molecular structure of **5b**.

Table 1 Bond lengths/Å for **5b**.

O(1)–C(9)	1.2224(14)	C(3)–C(4)	1.523(2)
N(1)–C(2)	1.361(2)	C(4)–C(10)	1.466(2)
N(1)–C(8a)	1.452(2)	C(4)–C(4a)	1.541(2)
N(2)–C(2)	1.340(2)	C(4)–C(9)	1.550(2)
N(3)–C(11)	1.148(2)	C(4a)–C(5)	1.525(2)
N(4)–C(10)	1.135(2)	C(4a)–C(8a)	1.546(2)
N(5)–C(9)	1.3434(14)	C(5)–C(6)	1.525(2)
N(5)–C(8a)	1.4700(14)	C(6)–C(7)	1.525(2)
C(2)–C(3)	1.391(2)	C(7)–C(8)	1.517(2)
C(3)–C(11)	1.401(2)	C(8)–C(8a)	1.517(2)

Table 2 Bond angles/° for **5b**.

C(2)–N(1)–C(8a)	120.13(9)	C(4)–C(4a)–C(8a)	97.30(8)
C(9)–N(5)–C(8a)	112.78(9)	C(6)–C(5)–C(4a)	112.07(11)
N(2)–C(2)–N(1)	116.97(11)	C(5)–C(6)–C(7)	111.96(11)
N(2)–C(2)–C(3)	123.71(11)	C(8)–C(7)–C(6)	110.60(12)
N(1)–C(2)–C(3)	119.31(11)	C(8a)–C(8)–C(7)	111.88(10)
C(2)–C(3)–C(11)	120.67(11)	N(1)–C(8a)–N(5)	110.52(9)
C(2)–C(3)–C(4)	117.81(10)	N(1)–C(8a)–C(8)	110.35(9)
C(11)–C(3)–C(4)	120.65(10)	N(5)–C(8a)–C(8)	112.43(10)
C(10)–C(4)–C(3)	113.00(10)	N(1)–C(8a)–C(4a)	107.91(9)
C(10)–C(4)–C(4a)	114.49(10)	N(5)–C(8a)–C(4a)	100.32(8)
C(3)–C(4)–C(4a)	110.23(9)	C(8)–C(8a)–C(4a)	114.87(10)
C(10)–C(4)–C(9)	112.32(9)	O(1)–C(9)–N(5)	128.39(10)
C(3)–C(4)–C(9)	104.55(9)	O(1)–C(9)–C(4)	126.52(10)
C(4a)–C(4)–C(9)	101.22(9)	N(5)–C(9)–C(4)	104.98(9)
C(5)–C(4a)–C(4)	113.65(10)	N(4)–C(10)–C(4)	179.3(2)
C(5)–C(4a)–C(8a)	112.51(10)	N(3)–C(11)–C(3)	179.1(2)

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