The interaction of 2,5-diphenyl-3,3,4,4-tetracyanopyrrolidine with vinyl ketones

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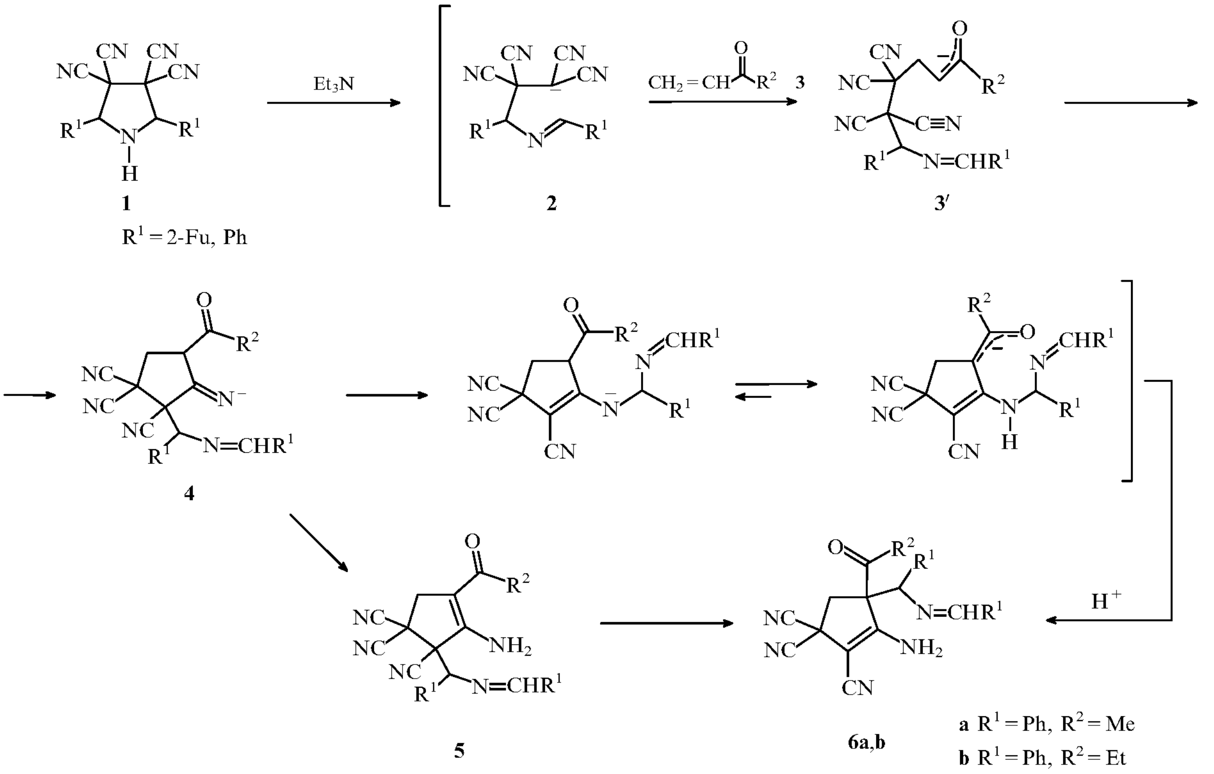
In the presence of an equimolar amount of triethylamine, 2,5-diphenyl-3,3,4,4-tetracyanopyrrolidine 1 reacts with vinyl ketones 3 to give 1-amino-5-acyl-2,3,3-tricyano-5-[phenyl(benzylidenamino)methyl]cyclopent-1-enes 6; the structure of molecule 6b has been determined by an X-ray study of the monocrystal.

The ring-chain isomerization of tetracyanopyrrolidines **1** determines different pathways for interactions between primary alcohols and amines.[1–3] This allowed us to suggest the use of an anionic linear centre in Michael addition reactions.

Alkyl vinyl ketones **3** were chosen as objects of the present investigation. From their interaction in isopropyl alcohol, 1-amino-5-acyl-2,3,3-tricyano-5-[phenyl(benzylidenamino)methyl]cyclopent-1-enes **6a,b**[†] were isolated. The structure of compound **6b** (Figure 1) was determined by an X-ray study of the monocrystal.[‡] The structure of **6a** has been established by IR and ^{13}C NMR spectral data.[†]



[†] *Preparation of compounds* **5**, **6a,b**. After addition of 0.01 mol triethylamine to a suspension of 0.01 mol of compound **1** in 20 ml of isopropyl alcohol, 0.015 mol of alkyl vinyl ketone **3** was added quickly. The reaction mixture was stirred for 5 min at room temperature until dissolution of pyrrolidine **1**, then the reaction mixture was kept standing for 30–40 min. If a precipitate did not deposit, the reaction mixture was acidified with 0.02 mol glacial acetic acid. The resulting precipitate was collected by filtration, washed with isopropyl alcohol, recrystallized from isopropyl alcohol–acetonitrile (2:1) and air-dried to give **6a,b**. Compound, yield (%), mp/°C, IR spectral data (vaseline oil, ν/cm^{-1}): **6a**, 27, 138–140 (decomp.), 3420, 3340, 3270 (νNH$_2$) 2260, 2210 (νC$\equiv$N), 1675 (νC=N), 1630, 1625 (δNH$_2$, νC=N); **6b**, 31, 145–147 (decomp.), 3410, 3330, 3260, 3220 (νNH$_2$), 2260, 2210 (νC$\equiv$N), 1680 (νC=O), 1640, 1625 (δNH$_2$, νC=N). ^{13}C NMR spectral data for **6a** (DMSO, 75 MHz): 164.21 (C-1), 70.09 (C-2), 37.16 (C-3), 37.04 (C-4), 68.21 (C-5), 114.90, 115.80 (C$\equiv$N), 202.05 (C=0), 27.6 (CH$_3$), 71.19 (CH), 164.01 (CH=N), 127.74–135.21 (2C$_6$H$_5$); **5**, 31, 120–121, 3380, 3265 (νNH$_2$), 2260 (νC$\equiv$N), 1650 (νC=0), 1640 (δNH$_2$). ^{13}C NMR spectral data for **5** (DMSO, 75 MHz): 152.3 (C-1), 100.82 (C-2), 37.51 (C-3), 38.67 (C-4), 58.34 (C-5), 194,24 (C=O), 64,06 (CH–N=), 153.34 (CH=N), 114.06, 112.92, 111.53 (C–N). Single crystals for X-ray investigation were grown from acetonitrile and had satisfactory elemental analysis.

[‡] *Crystal data for* **6b**: C$_{25}$H$_{21}$N$_5$O, triclinic, space group $P\bar{1}$, at 163 K, $a = 9.001(4)$, $b = 10.501(4)$, $c = 13.449(5)$ A, $D_c = 1.212$ g cm^{-3}, $Z = 2$, $V = 1116.8(7)$ A^3, $F(000) = 428$. 4171 independent reflections were measured with a Siemens P3/PC automated diffractometer (163 K, λMo Kα, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leqslant 52°$). The structure was determined by a direct method and refined by a full-matrix least-squares technique with an anisotropic approximation for non-hydrogen atoms (isotropic for H atoms). The refinement converged at $R = 0.044$, $R_W = 0.043$ for 3068 reflections with $F^2 \geqslant 3\sigma$. Atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre, see Notice to Authors, *Mendeleev Commun.*, 1996, issue 1. Any request to the CCDC for supplementary data should quote the full literature citation and the reference number 1135/4.

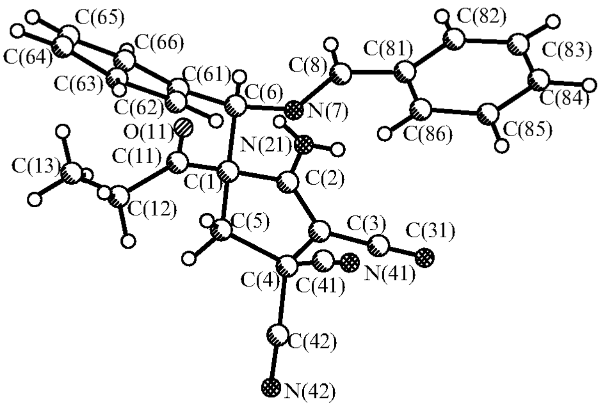


Figure 1 Molecular structure of **6b**.

Based on the structure of compound **6b** the following path can be suggested for the reaction. The reaction begins as a 1,4-addition of the linear form **2**, formed by the interaction of an equimolar amount of base with compound **1**, to vinyl ketone **3**. After intramolecular cyclization of intermediate **3′** into **4** the formation of compounds **6a**,**b** presumably proceeds as follows: either *via* two consecutive Claisen rearrangements[2,3] or [3,3] sigmatropic rearrangament directly on the carbon atom derived from cyclopentene **5**. Depending on the kind of substitution in the starting compound **1** the reaction can finish at the stage of formation of **5** without any rearrangements. For example, on interaction of 2,5-difuryl-3,3,4,4-tetracyanopyrrolidine with methyl vinyl ketone **2** under the same conditions compound **5** is formed. This result and the fact that the yields of compounds **5** and **6a**,**b** are comparable, suggests that cyclopentenes **6a**,**b** are formed by an intramolecular rearrangement.

Financial support by the State Committee of the Russian Federation on higher education [Scientific and Technical Program ‘Fine organic synthesis’ (grant no. FT-22) headed by Academician N. S. Zefirov] is gratefuly acknowledged.

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Received: Moscow, 6th October 1995
Cambridge, 15th February 1996; Com. 5/06682D