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LETTERS TO THE EDITOR

Synthesis of Substituted Cyclobutane and Aniline Derivatives by Condensation of Aliphatic Aldehydes with Malonodinitrile

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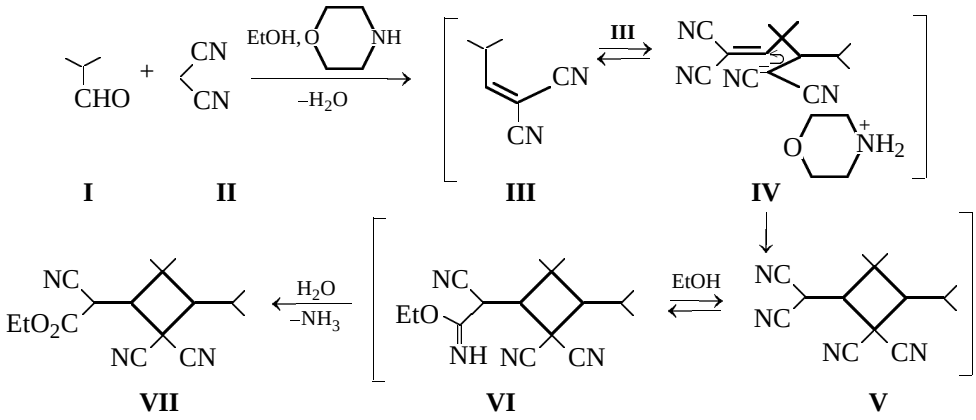
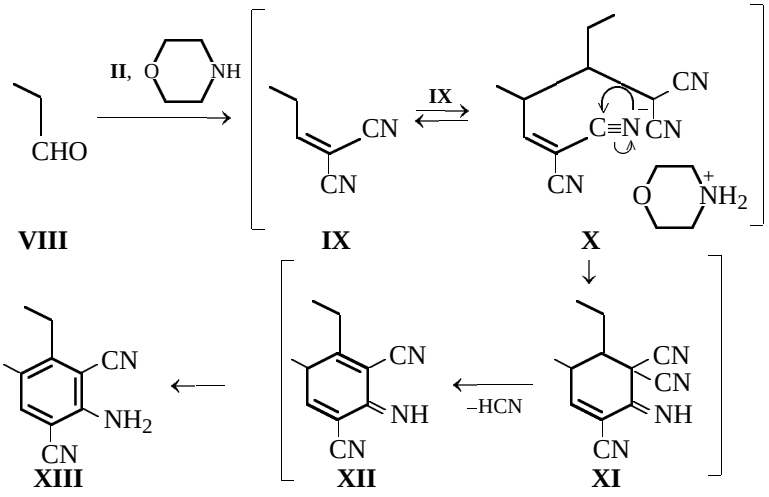
Condensation of aliphatic carbonyl compounds with malonodinitrile yields unstable alkenes which dimerize to form mainly linear products and cyclohexadienes [1–3].

In this work we found new unusual products of such reaction. Condensation of isobutyraldehyde **I** with malonodinitrile **II** in ethanol at 20°C yields substituted cyclobutane **VII** via intermediates **III**–**VI**:



Condensation of malonodinitrile **II** with propionaldehyde **VIII** under the same conditions yields previously unknown substituted aniline **XIII**, presumably via intermediates **IX**–**XII**. The pathways of condensation of other aliphatic aldehydes with malonodinitrile and cyanoacetic acid ester are under investigation.



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The structures of **VII** and **XIII** were proved by single crystal X-ray diffraction; the results will be published later.

4-Isopropyl-3,3-dimethyl-2-[(cyanoethoxycarbonyl)methyl]-1,1-dicyanocyclobutane VII. Yield 77%, mp 118–119°C (from EtOH). IR spectrum, ν, cm^{-1}: 1718 (C=O), 2255 sh (C≡N)]. ^1H NMR spectrum, δ, ppm: 0.92 d and 1.03 d (3H each, 2Me, ^3J 6.84 Hz), 1.06 s (3H, Me), 1.27 s (3H, Me), 1.39 t (3H, C*H*$_3$CH$_2$O, ^3J 6.14 Hz), 2.03 m [1H, C*H*Me$_2$], 2.43 d (1H, C^{4}H, ^3J 6.80 Hz), 3.39 d (1H, C^{2}H, ^3J 7.22 Hz), 4.30 m (3H, CH$_2$ and C$^{1'}$H). Found, %: C 66.72; H 7.25; N 14.54. $C_{16}H_{21}N_3O_2$. Calculated, %: C 66.88; H 7.37; N 14.62.

4-Methyl-2,6-dicyano-3-ethylaniline XIII. Yield 67%, mp 122–123°C (from EtOH), fluoresces under UV irradiation. IR spectrum, ν, cm^{-1}: 1643 [ν(NH$_2$)], 2210, 2222 [ν(C≡N)], 3275, 3360, 3451 [ν(NH$_2$)]. ^1H NMR spectrum, δ, ppm: 1.16 t (3H, C*H*$_3$CH$_2$), 2.17 s (3H, Me), 2.73 q (2H, CH$_2$, ^3J 7.62 Hz), 6.09 br.s (2H, NH$_2$), 7.38 s (1H, C^{5}H). Mass spectrum, *m/z* (I_{rel}, %): 186 (15) $[M + 1]^+$, 185 (100) $[M]^+$, 184 (23) $[M - 1]^+$, 170 (86), 156 (44), 143 (15), 129 (8), 116 (23), 102 (9), 89 (13), 77 (12), 63 (8), 51 (13), 39 (14). Found, %: C 71.18; H 6.08; N 22.74. $C_{11}H_{11}N_3$. Calculated, %: C 71.33; H 5.99; N 22.68.

The IR spectra were recorded on an IKS-40 spectrophotometer (mulls in mineral oil). The ^1H NMR spectra of **VII** and **XIII** were taken on Varian Mercury-400 (400.397 MHz) and Bruker DR-500 (500.13 MHz) spectrometers, respectively, in DMSO-d_6 with TMS as internal reference. The mass spectrum of **XIII** was taken on a Kratos MS-890 device (70 eV) with direct sample inlet.

REFERENCES

1. Freeman, F., *Chem. Rev.*, 1969, vol. 69, no. 5, p. 591.
2. Freeman, F., *Chem. Rev.*, 1980, vol. 80, no. 4, p. 329.
3. Sharanin, Yu.A., Promonenkov, V.K., and Litvinov, V.P., *Malononitril* (Malononitrile), Ser.: *Organicheskaya khimiya* (Organic Chemistry), Moscow: VINITI, 1991, vol. 20, part 1.