

## LETTERS TO THE EDITOR

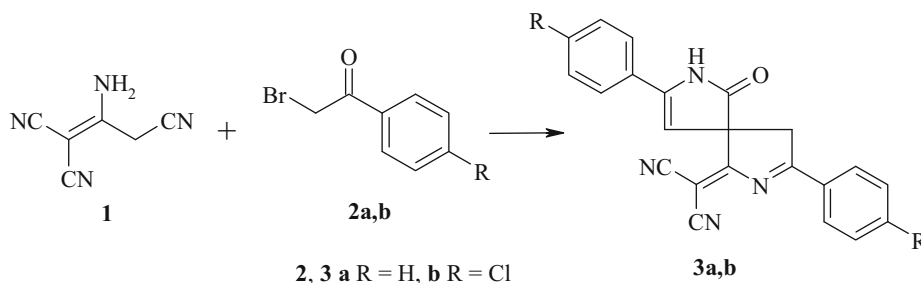
### UNEXPECTED SYNTHESIS OF 2-(3,8-DIARYL-6-OXO-2,7-DIAZASPIRO[4.4]NONA-2,8-DIEN-1-YLIDENE)MALONONITRILE, A NEW HETEROCYCLIC SYSTEM

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**Keywords:** 2-amino-1,1,3-tricyano-1-propene, 2-(3,8-diaryl-6-oxo-2,7-diazaspiro[4.4]nona-2,8-dien-1-ylidene)malononitrile, phenacyl bromides, alkylation.

2-Amino-1,1,3-tricyano-1-propene (**1**) obtained in the dimerization of malononitrile in an alkaline medium [1] is used in organic synthesis primarily as a CH-acid component in the preparation of functionalized pyridines [2–5].

We show here for the first time that the alkylation of tricyanopropene **1** using phenacyl bromides **2a** and **2b** in DMF in an alkaline medium gives previously unreported 2-(3,8-diaryl-6-oxo-2,7-diazaspiro[4.4]nona-2,8-dien-1-ylidene)malononitriles **3a** and **3b**.



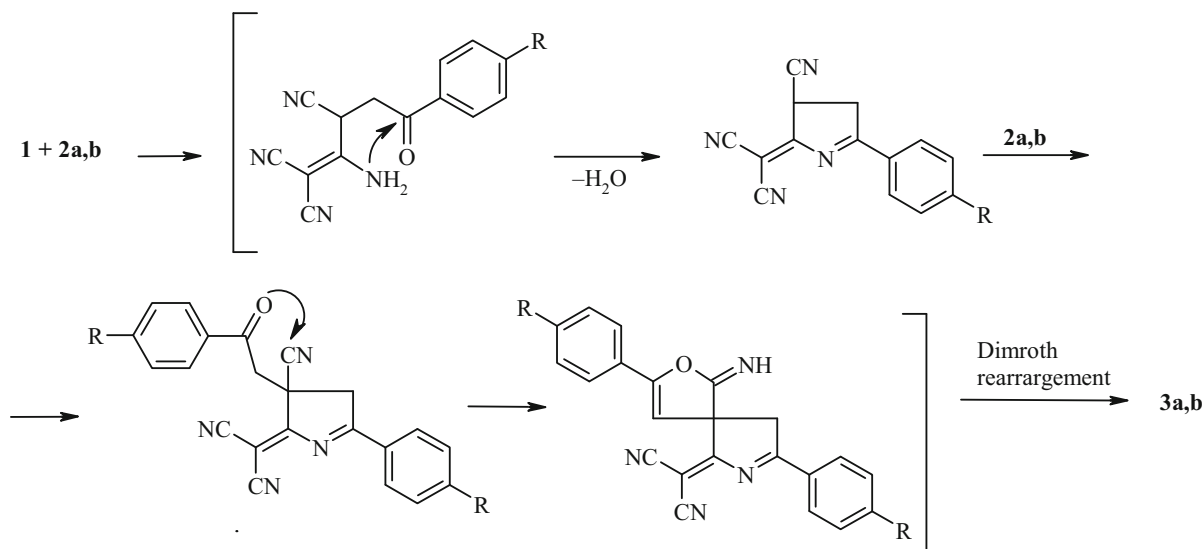
The mechanism of this reaction, the scope of its applicability, and the chemical and biological properties of malononitriles **3a** and **3b** are currently under study. The reaction mechanism presumably is as follows:

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The IR spectra were taken on a Perkin-Elmer FIR spectrum One spectrometer for KBr pellets. The  $^1\text{H}$  NMR spectra were taken on a Bruker DR-500 spectrometer at 500 MHz in  $\text{DMSO-d}_6$  with TMS as internal standard. The  $^{13}\text{C}$  NMR spectrum of malononitrile **3b** was taken on a Varian VXR-300 spectrometer at 75 MHz in  $\text{DMSO-d}_6$  with TMS as internal standard. The chemical ionization mass spectra were taken on a Crommass Hewlett-Packard 5890/5972 GC/MS at 70 eV using an HP-5 MS column in  $\text{CH}_2\text{Cl}_2$  solution. The reaction course and purity of the products were monitored by thin-layer chromatography on Silufol UV-254 plates using 3:5 acetone–hexane as the eluent with iodine vapor and UV light as the developer. The melting points were determined on a Koeffler block.

**2-(6-Oxo-3,8-diphenyl-2,7-diazaspiro[4.4]nona-2,8-dien-1-ylidene)malononitrile (3a).** 10% Aqueous KOH (11.2 ml, 20 mmol) and phenacyl bromide (**2a**) (4.0 g, 20 mmol) were added consecutively under stirring to a solution of malononitrile dimer **1** (1.32 g, 10 mmol) in DMF (20 ml), stirred for 2 h, and diluted by the addition of an equal volume of water. The precipitate formed was filtered off and washed with water, ethanol, and hexane to give 2.63 g (75%) compound **2a**; mp 244–246°C (acetic acid). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3332 (NH), 2228 ( $\text{C}\equiv\text{N}$ ), 1682 ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 4.95 (2H, s,  $\text{CH}_2$ ); 7.14 (1H, s, H-9); 7.37 (1H, t,  $J = 7.5$ , H Ph); 7.48 (2H, t,  $J = 7.5$ , H Ph); 7.63 (2H, t,  $J = 8.0$ , H Ph); 7.75 (3H, m, H Ph); 8.09 (2H, d,  $J = 7.0$ , H Ph); 12.62 (1H, br. s, NH). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 349  $[\text{M}-\text{H}]^+$  (100), 322  $[\text{M}-\text{H}-\text{HCN}]^+$  (18). Found, %: C 75.33; H 3.98; N 15.81.  $\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}$ . Calculated, %: C 75.42; H 4.03; N 15.99.

**2-[3,8-Di(4-chlorophenyl)-6-oxo-2,7-diazaspiro[4.4]nona-2,8-dien-1-ylidene]malononitrile (3b)** was obtained analogously to malononitrile **2a** using 4-chlorophenacyl bromide (**2b**) (4.66 g, 20 mmol). The yield of compound **3b** was 3.31 g (79%); mp 228–230°C (butanol). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3306 (NH), 2226 ( $\text{C}\equiv\text{N}$ ), 1692 ( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm ( $J$ , Hz): 4.96 (2H, s,  $\text{CH}_2$ ); 7.21 (1H, s, H-9); 7.58 (2H, d,  $J = 8.4$ , H Ar); 7.75 (2H, d,  $J = 8.5$ , H Ar); 7.81 (2H, d,  $J = 8.4$ , H Ar); 8.13 (2H, d, H Ar); 12.76 (1H, br. s, NH).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 31.67; 44.74; 94.67; 111.96; 113.49; 114.72; 126.20; 127.61; 129.25; 129.46; 129.66; 130.75; 133.28; 133.82; 134.63; 140.05; 192.73. Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 417  $[\text{M}-\text{H}]^+$  (100). Found, %: C 62.88; H 2.74; N 13.15.  $\text{C}_{22}\text{H}_{12}\text{Cl}_2\text{N}_4\text{O}$ . Calculated, %: C 63.02; H 2.88; N 13.36.

## REFERENCES

1. M. Mittelbach, *Monatsh. Chem.*, **116**, 689 (1985).
2. Yu. A. Sharanin, S. G. Krivokolysko, and V. D. Dyachenko, *Zh. Org. Khim.*, **30**, 581 (1994).
3. A. A. Fadda and H. M. Refat, *Monatsh. Chem.*, **130**, 1487 (1999).
4. A. M. M. El-Saghier, *Phosphorus, Sulfur, Silicon, Relat. Elem.*, **177**, 1213 (2002).
5. G. E. H. Elgemeie, N. Hanfy, H. Hopf, and P. G. Jones, *Acta Crystallogr.*, **C54**, 820 (1998).