

SHORT
COMMUNICATIONS

Decomposition
of 5-Amino-1,8,8-trimethyl-3-dicyanomethylene-
2-azabicyclo[2.2.2]oct-5-ene-4,6-dicarbonitrile
at Treatment with Hydrogen Sulfide

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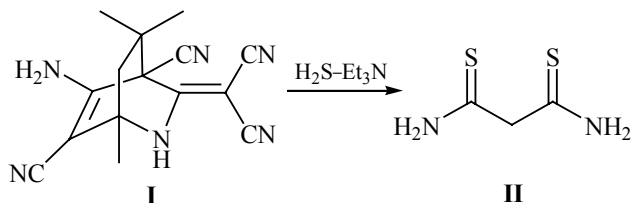
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5-Amino-1,8,8-trimethyl-3-dicyanomethylene-2-azabicyclo[2.2.2]oct-5-ene-4,6-dicarbonitrile (**I**) we formerly synthesized by the reaction of malononitrile with mesityl oxide [1]. Compound **I** formed also in the condensation of malononitrile with acetone in the presence of bases [2] or of mixture $\text{KF-Al}_2\text{O}_3$ [3]. Its boiling in xylene results in decomposition into a mixture of 4-amino-6-methyl-3,5-dicyano-2-dicyanomethylenepyridine and isobutylene [3]. The other reactions of compound **I** are unknown.

It was demonstrated for the first time that the reaction of 5-amino-1,8,8-trimethyl-3-dicyanomethylene-2-azabicyclo[2.2.2]oct-5-ene-4,6-dicarbonitrile (**I**) with hydrogen sulfide in pyridine at 20°C in the presence of triethylamine afforded the malonic acid dithioamide (**II**). The mechanism of decomposition of bicyclic compound **I** and its reactions with the other nucleophilic reagents are under investigation.



Malonic acid dithioamide (II). To a dispersion of 2.8 g (10 mmol) of compound **I** in 20 ml of pyridine was added 1.4 ml (10 mmol) of triethylamine, and a moderate flow of hydrogen sulfide was bubbled for 2 h. Afterwards

the mixture was maintained in a refrigerator for 24 h. The formed precipitate was filtered off, washed with ethanol and hexane. Yield 0.3 g (46%), yellow powder, mp 188–190°C (212°C [4]). ¹H NMR spectrum, δ, ppm: 3.79 s (2H, CN₂), 9.32 br.s (2H, NH₂), 9.62 br.s (2H, NH₂). ¹³C NMR spectrum was analogous to previously described [5].

¹N NMR spectrum was registered on a spectrometer Varian Mercury-400 (400.397 MHz) from solution in DMSO-*d*₆ with TMS as internal reference. The melting point was measured on a Köffler heating block. The reaction progress was monitored by TLC on Silufol UV-254 plates, eluent acetone–hexane, 3:5, development in iodine vapor and under UV irradiation.

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