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An Improved and Facile Synthesis of 2-Amino-1,1,3-tricyanopropene

Short Communication

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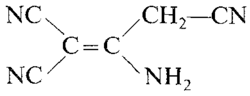
A simple method for the dimerization of malononitrile using alkali hydroxides in methanol or ethanol is described. Thereby 2-Amino-1,1,3-tricyanopropene, a keyintermediate for heterocyclic chemistry, is obtained in high yield.

Eine verbesserte und bequeme Synthese von 2-Amino-1,1,3-tricyan-propen (Kurze Mitteilung)

Eine einfache Dimerisierung von Malononitril unter Verwendung von Alkalihydroxid in Methanol und Ethanol wird beschrieben. Dabei entsteht in guter Ausbeute 2-Amino-1,1,3-tricyan-propen, ein wichtiges Ausgangsprodukt zur Synthese von Heterocyclen.

(Keywords: Malononitrile; Dimerization)

2-Amino-1,1,3-tricyanopropene ("Dimeric Malononitrile") (**1**) is an important key intermediate in synthetic organic chemistry, especially for the synthesis of various heterocyclic compounds like pyridines and pyrimidines[1,2].



1

As a multifunctional compound **1** is suitable for different conversions like condensations with carbonyl and heteroanalogous carbonyl functions, reactions under hydrolytic conditions or *Michael* additions. It has technical importance for the preparation of cyanoaminopyridines, which are used as coupling components for the synthesis of aza-dyes[3–5]. Condensations of **1** with aromatic nitroso compounds give useful textile coloring agents[6].

The preparation of **1** is based on dimerization of malononitrile. Several different reaction conditions using various catalysts are described in literature. As bases sodium sand in diethylether[7], sodium in absolute ethanol[8,9], aqueous alkali hydroxide with addition of copper sulfate[7] have been used, as acid dry hydrogen chloride in benzene[7,10]. Dimerization also takes place in the presence of nickel or palladium complexes[11,12]. The most convenient method so far has been dimerization using one half equivalent of sodium in absolute ethanol, which gives **1** in 83% yield.

It is possible, however, to avoid absolute ethanol and sodium methoxide by using alkali hydroxides in methanol or ethanol. When using half equivalents of sodium or potassium hydroxide in absolute ethanol, the corresponding alkali salts of **1** are precipitating after 30 min of heating to reflux. After dissolving the salts in water and acidifying, **1** is obtained in 80–87% yield. No loss of yield is observed when using 96% ethanol (using methanol the yield is slightly less). No considerable amount of **1** is obtained by simply using water under the same reaction conditions.

The advantage of this method, apart from the facile preparation method, is the usage of cheap solvents and cheap alkali hydroxides instead of hazardous methoxide. The yield is even higher than with the hitherto described methods.

Experimental

2-Amino-1,1,3-tricyanopropene (**1**)

To a cooled solution of 0.25 mol of alkali hydroxide in 100 ml of the corresponding alcohol, 33 g (0.5 mol) of malononitrile are added. The temperature is slowly raised under stirring to refluxing temperature. After 5–10 min the alkali salt of **1** precipitates. After 30 min of heating the mixture is cooled, the salt is filtered off, washed with cold alcohol and dried. After dissolving the salt in a small amount of water and acidifying with conc. hydrochloric acid to *pH* = 4, the separated product is filtered off and recrystallized from water to give colorless needles, m. p. 172 °C (Ref.[8]; m. p. 172–173 °C).

The yields when using different solvents are the following:

	ethanol abs.	ethanol 96%	methanol
NaOH	80%	79%	58%
KOH	87%	83%	60%

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