Syntheses with Unsaturated Nitriles; IV[1]. Synthesis of 4-Alkyl-2-amino-4-(substituted amino)-1,1,3-tricyano-1,3-butadienes via Selective Thermal Decomposition of Amino Adducts

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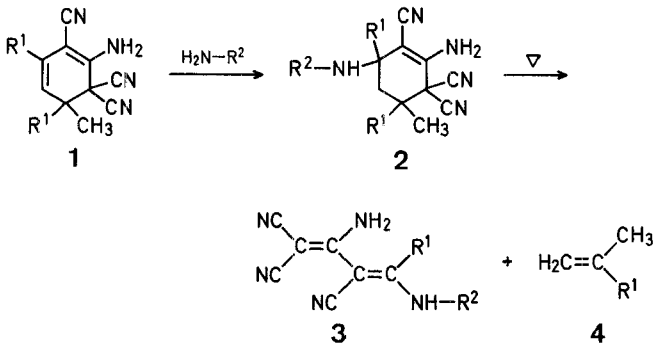
We have previously described a simple preparation of ylidenemalononitrile dimers[2] and selective transformation of their alkoxy adducts to monoketoesters[3]. As a continuation of our study on the applications of ylidenemalononitrile dimers in organic synthesis, we now report on the synthesis of a new type of 1,3-diene **3**.



The key step in this synthesis involves elaboration of the amino adducts **2** of ylidenemalononitrile dimers **1**. We have found that primary amines add smoothly to the dimers **1** in aqueous ethanol or dioxan solution, however, in some cases, addition of a more polar solvent i.e. dimethylformamide was required. The formation of amino adducts **2** takes place at room temperature and gives good yields.

Those adducts **(2a, b)** which possess two unsubstituted amino groups also react with phenyl isocyanate or phenyl isothiocyanate and we have found that only the amino group at the 5 position undergoes substitution forming *N,N'*-disubstituted derivatives of urea or thiourea **(2k, 2l)**, even with an excess of the isocyanate or isothiocyanate.

Adducts **2** may be considered as pseudo-adducts of Diels-Alder cycloaddition[4] and we have found that they undergo a retro-Diels-Alder process[5] under mild conditions. These reactions were carried out in a refluxing, non-polar solvent such as xylene or decalin, depending on the temperature required. All the dienes **3** are solids in contrast to the gaseous second component **4** of the decomposition reaction. This fact ensures that the reaction is clean and easy to perform and that the products can be isolated in satisfactory purity.

Analysis of the mass spectra of adducts **2** shows that the main fragmentation pattern is the retro-Diels-Alder process. In some cases we could not detect the molecular ions even when the temperatures of the inlet system and the ion source, and ionizing potential were decreased. In these spectra, the base ions correspond to the molecular ions of the main products of the thermal decomposition described above.

4-Amino-4,6-dialkyl-4-methyl-6-(substituted amino)-1,3,3-tricyanocyclohexenes 2; General Procedure:

A mixture of the dimer **1** (0.1 mol), solvent (10 ml; ethanol for **2a, c, e, g, h**; dioxan for **2f, i**; 2:1 dioxan/dimethylformamide for **2b, d**; dimethylformamide for **2j**), and concentrated aqueous ammonia (10 ml)

[12] P. D. Bartlett, L. H. Knox, *Org. Synth. Coll. Vol.* V, 196 (1973).

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Table 1. 4-Amino-4,6-dialkyl-6-(substituted amino)-1,3,3-tricyanocyclohexenes **2**

Product No.	R^1	R^2	Yield [%]	m.p. [°C]	Molecular formula[a] or Lit. m.p. [°C]	M.S. *m/e* (M^+)	^{1}H-N.M.R. (solvent) δ [ppm]
2a	CH_3	H	90	>300°	>300[6]	229	(DMF): 6.67 (s, 2H); 6.30 (s, 2H); 3.65 (s, 3H); 1.50 (s, 2H); 1.70 (s, 3H); 1.22 (s, 3H)
2b	C_2H_5	H	91	>300°	$C_{14}H_{19}N_5$ (257.3)	—	(DMF): 6.60 (s, 2H); 6.20 (s, 2H); 3.6 (m, 2H); 1.9–0.8 (m, 13H)
2c	CH_3	NH_2	95	>300°	$C_{12}H_{16}N_6$ (244.3)	244	insoluble
2d	C_2H_5	NH_2	89	>300°	$C_{14}H_{20}N_6$ (272.4)	—	[$(CD_3)_2CO$]: 2.95 (s, 3H); 2.42 (s, 2H); 1.6 (m, 6H); 1.25 (s, 3H); 0.95 (t, 6H)
2e	CH_3	CH_3	90	231°	$C_{13}H_{17}N_5$ (243.3)	243	[$(CD_3)_2CO$]: 3.07 (s, 3H); 2.87 (s, 3H); 1.72 (d, 2H); 1.57 (s, 3H); 1.20 (s, 6H)
2f	C_2H_5	CH_3	91	118°	$C_{15}H_{21}N_5$ (271.4)	—	(DMF): 6.47 (s, 2H); 4.35 (br s, 1H); 2.75 (s, 3H); 2.0–0.5 (m, 15H)
2g	CH_3	C_2H_5	86	132–134°	$C_{14}H_{19}N_5$ (257.3)	257	(DMF): 3.1 (br s, 3H); 1.9–1.4 (m, 5H); 1.3–0.8 (m, 11H)
2h	C_2H_5	C_2H_5	82	132°	$C_{16}H_{23}N_5$ (285.4)	285	(DMF): 8.00 (s, 1H); 6.82 (s, 2H); 4.17 (g, 2H); 2.0–0.8 (m, 18H)
2i	CH_3	C_6H_5—CH_2	66	143–144°	$C_{19}H_{21}N_5$ (319.4)	—	(DMSO): 7.25 (s, 5H); 6.9 (m, 1H); 6.60 (s, 2H); 4.2 (m, 2H); 1.42 (s, 3H); 1.02 (s, 6H)
2j	C_2H_5	C_6H_5—CH_2	64	260°	$C_{21}H_{25}N_5$ (347.4)	—	(DMSO): 7.17 (s, 5H); 5.55 (d, 1H); 2.35 (s, 2H); 1.17 (s, 3H); 0.9 (t, 6H)
2k	CH_3	C_6H_5—NH—CO	76	>300°	$C_{19}H_{20}N_6O$ (348.4)	—	[$(CD_3)_2CO$]: 7.8–7.0 (m, 5H); 6.50 (s, 1H); 3.57 (s, 1H); 2.92 (s, 2H); 1.85 (s, 2H); 1.67 (s, 3H); 1.27 (s, 6H)
2l	C_2H_5	C_6H_5—NH—CS	65	148–149°	$C_{21}H_{24}N_6S$ (392.4)	—	(DMSO): 11.95 (br s, 1H); 10.75 (br s, 1H); 7.8–7.0 (m, 7H); 3.57 (s, 2H); 1.8–0.8 (m, 13H)

[a] Satisfactory microanalyses obtained: C ±0.38, H ±0.47, N ±0.40.

Table 2. 4-Alkyl-2-amino-4-(substituted amino)-1,1,3-tricyano-1,3-butadienes **3**

Product No.	R^1	R^2	Yield [%]	m.p. [°C]	Molecular formula[a] or Lit. m.p. [°C]	M.S. *m/e* (M^+)	^{1}H-N.M.R. (DMSO/DSS) δ [ppm]
3a	CH_3	H	95	>300°	>300[6]	173	7.10 (s, 2H); 6.95 (s, 2H); 2.27 (s, 3H)
3b	C_2H_5	H	93	298–300°	$C_9H_9N_5$ (187.2)	187	7.25 (s, 2H); 7.07 (s, 2H); 2.60 (s, 2H); 1.22 (t, 3H)
3c	CH_3	NH_2	89	>300°	$C_8H_8N_6$ (188.2)	188	12.0 (br s, 1H); 7.15 (s, 2H); 5.67 (s, 2H); 2.50 (s, 3H)
3d	C_2H_5	NH_2	87	>300°	$C_9H_{10}N_6$ (202.2)	202	7.30 (s, 2H); 3.9 (br s, 3H); 2.85 (q, 2H); 1.30 (t, 3H)
3e	CH_3	CH_3	95	248–300°	$C_9H_9N_5$ (187.2)	187	7.30 (q, 1H); 6.96 (s, 2H); 2.90 (d, 3H); 2.42 (s, 3H)
3f	C_2H_5	CH_3	95	210–211°	$C_{10}H_{11}N_5$ (201.2)	201	7.35 (br s, 1H); 6.95 (s, 2H); 2.95 (d, 3H); 2.60 (s, 2H); 1.22 (t, 3H)
3g	CH_3	C_2H_5	92	228°	$C_{10}H_{11}N_5$ (201.2)	201	7.30 (t, 1H); 6.92 (s, 2H); 3.50 (s, 2H); 2.45 (s, 3H); 1.12 (t, 3H)
3h	C_2H_5	C_2H_5	90	132°	$C_{11}H_{13}N_5$ (215.2)	215	7.55 (s, 2H); 7.00 (s, 1H); 4.50 (q, 2H); 2.80 (s, 2H); 1.5–1.0 (m, 6H)
3i	CH_3	C_6H_5—CH_2	98	208°	$C_{15}H_{13}N_5$ (263.2)	263	7.92 (t, 1H); 7.30 (s, 5H); 7.02 (s, 2H); 4.60 (d, 2H); 2.35 (s, 3H)
3j	C_2H_5	C_6H_5—CH_2	94	285°	$C_{16}H_{15}N_5$ (277.3)	—	7.9 (br s, 5H); 7.15 (br s, 3H); 2.70 (s, 2H); 1.20 (t, 3H)

[a] Satisfactory microanalyses obtained: C ±0.37, H ±0.31, N ±0.36.

or 50% aqueous amine solution (10 ml) is stirred at room temperature for 2–3 h. The product is then filtered [for products **2f–j**, addition of water (20 ml) to the mother liquid is necessary to precipitate the adduct] and washed with cooled 70% aqueous ethanol (Table 1).

Reaction of 2a, b with Phenyl Isocyanate or Isothiocyanate:
The adduct **2a, b** (4 mmol), phenyl isothiocyanate or phenyl isocyanate (0.5 ml), and dioxan (10 ml) are boiled for 15 min. The mixture is then allowed to cool and water (20 ml) is added. The separated oil is treated with ethanol to give the crystalline product **2k, l** (Table 1).

4-Alkyl-2-amino-4-(substituted amino)-1,1,3-tricyano-1,3-butadienes 3; General Procedure:
A mixture of adduct **2** (2 mmol) and xylene (10 ml; for **2b, d, e, f, g, h, i, j)** or decalin (10 ml; for **2a, c)** is refluxed for 1 h. The mixture is then allowed to cool and the product is filtered off. In the case of **3b** and

3f, a few drops of hexane are added to precipitate the product. Samples for analysis are crystallized from 2:1 dimethylformamide/water.

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