Single Step Synthesis of 2,4-Dicyanonaphthylamines from Synthetic Equivalents of α-Cyanoalkynes

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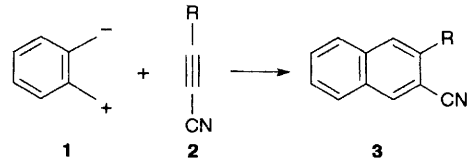
Nitrile thioethers R–CBr=C(SEt)CN **4** react like α-alkynenitriles with ambiphilic derivatives, as shown by a new synthesis of naphthylamines.

The simplest way of access to bicyclic compounds **3** seems to be the condensation of an α-alkynenitrile with a 1,4-dipole. To our knowledge this reaction has never been reported (Scheme 1). We now report the first carbocyclisation reaction in accordance with this principle, starting from bromoacrylonitriles **4**.[1] These compounds behave in fact like synthetic equivalents of α-alkynenitriles R–CBr=C(SEt)–CN ≡ R–C≡C–CN.

Naphthylamine **6**, for example, was readily obtained when dipole **5** was reacted with **4** (Scheme 2), using the following general procedure: the carbanion **5** generated from NaH (14 mmol) and 2-cyanophenylacetonitrile (or 2-cyano-5-methoxyphenylacetonitrile[2]) (15 mmol) in MeCN (15 cm^3) was



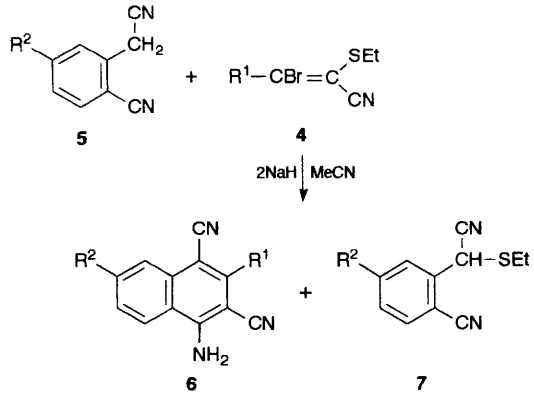
1 **2** **3**

Scheme 1

Table 1 Physical data for naphthylamines **6**[a]

	R[1]	R[2]	M.p/°C	Yield (%)	IR (Nujol): ν/cm^{-1} NH_2 (free)	IR (Nujol): ν/cm^{-1} C≡N
6a	Me	H	275–276	78	3452, 3362	2220
6b	Me	OMe	300–301	56	3447, 3374	2223, 2215
6c	Bu^n	H	161–163	73	3444, 3365	2221
6d[b]	Ph	H	357–360	86	3478, 3376	2228, 2218
6e	Ph	OMe	317–320	64	3470, 3363	2233, 2225
6f	*p*-ClC_6H_4	H	296–297	83	3478, 3376	2228, 2218
6g	*p*-$MeOC_6H_4$	H	273–275	79	3480, 3380	2230, 2225

[a] Satisfactory microanalytical and/or accurate mass measurements were obtained for all new compounds. [b] The reaction of freshly prepared phenylpropynenitrile, m.p. 38–39 °C (7 mmol), **5** (R^2 = H) (7.7 mmol) and NaH (7 mmol) under the same conditions gives **6d** in 80% yield.



Scheme 2

warmed to 45 °C, and acrylonitrile **4**† (7 mmol, in the same solvent) was added all at once. Stirring was pursued for 45 min to 45 °C, then the solution was refluxed for 45 min and the solvent was evaporated. The residue was stirred for 30 min with H_2O–Et_2O (Et_2O extracts completely by-product **7**) and the naphthylamine **6** filtered off and recrystallised (Table 1).

Isolation of the by-product **7** (characterised by unequivocal synthesis from 2-CN–C_6H_4–CH=O[3]) suggests to us the following mechanism with a sulphenium leaving group in the aromatisation step (Scheme 3).

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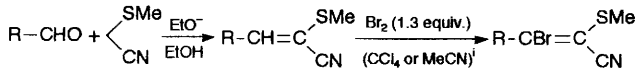
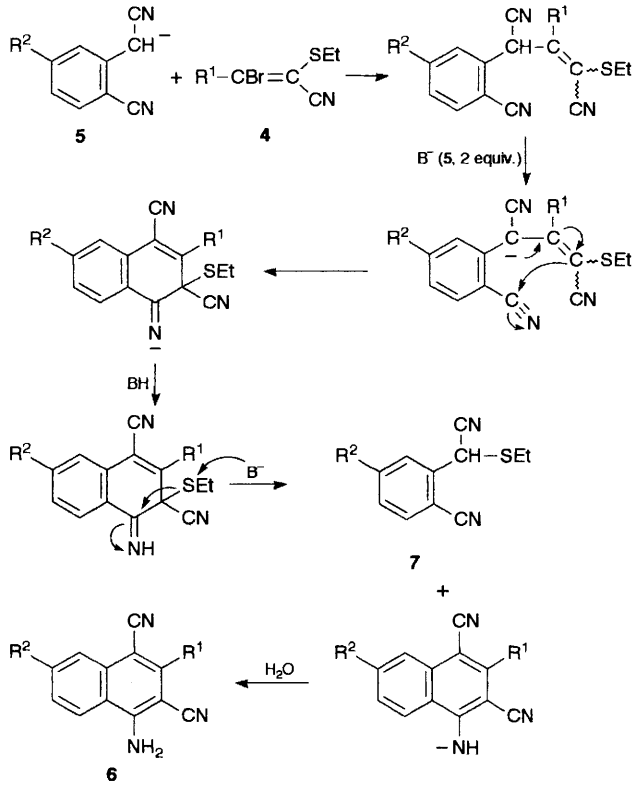
† The bromo-compounds **4** were prepared by the method in ref. 1.





Scheme 3

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