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Reduction of α,β-Unsaturated Nitrile to Saturated Nitrile with Sodium Borohydride

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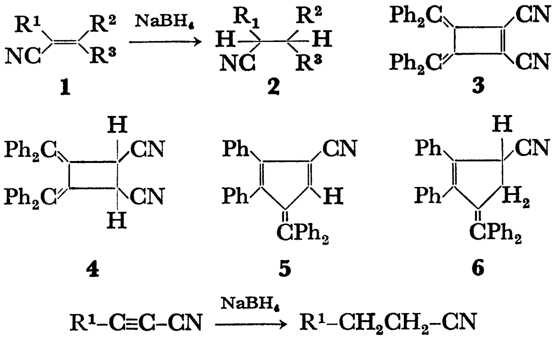
Synopsis. α,β-Unsaturated nitrile (**1**) was easily reduced to saturated nitrile (**2**) with sodium borohydride. Phenyl- (**7a**) and 2-phenanthryl-cyanoacetylene (**7b**) were also reduced with sodium borohydride to the saturated nitriles, **8a** and **8b**, respectively.

The reduction of α,β-unsaturated nitrile (**1**) to saturated nitrile (**2**) can be achieved in poor yield by photochemical,¹⁾ electrochemical,²⁾ and catalytic hydrogenation.³⁾ Profitt *et al.*⁴⁾ reported that magnesium in methanol is a good reagent for the reduction of **1** to **2**. On the other hand, we have found that sodium borohydride ($NaBH_4$) is effective for the reduction and that $NaBH_4$ is useful for the reduction of conjugated cyanoalkyne (**7**) to cyanoalkane (**8**).

Treatment of conjugated cyanoalkanes (**1a**—**h**) with $NaBH_4$ afforded the reduction products (**2a**—**c** and **2f**) in the yields summarized in Table 1. In the cases of **1e**, **1g**, and **1h**, however, the reduction of their double bonds was accompanied by the substitution with hydrogen of the nitro and methoxyl groups which had been bound to olefinic carbon. The substitution of nitro group with hydrogen is in contrast with the $NaBH_4$ reduction of nitroolefin to nitroalkane.⁶⁾ The cyclic cyanoalkenes, 1,2-dicyano-3,4-bis(diphenylmethylene)-1-cyclobutene (**3**) and 2-cyano-3,4,6,6-tetraphenylfulvene (**5**), were also easily reduced with $NaBH_4$ to their dihydro derivatives, **4** (85) and **6** (90%), respectively. On the contrary, the catalytic reduction of **3** on Raney-Ni afforded **4** only in 20% yield.



$$R^1\text{-C}\equiv\text{C-CN} \xrightarrow{NaBH_4} R^1\text{-CH}_2\text{CH}_2\text{-CN}$$

Scheme 1.

Since the $NaBH_4$ reduction product of **3** (**4**) was identical with the catalytic reduction product of **3**, **4** would have a *cis*-form, and the former reduction seems to proceed stereospecifically. Nevertheless, since the *rac*-form⁷⁾ of **2b** isomerized into the *meso*-form (**2b**) under the reduction conditions, it is not clear whether the steric course of the $NaBH_4$ reduction is stereospecific or not.

TABLE 1. YIELDS, MELTING POINTS AND NMR SPECTRAL DATA OF THE $NaBH_4$ REDUCTION PRODUCTS (**2**, **4**, **6**, AND **8**)

	Reactant			Product	Yield (%)	Mp (°C)	τ_{CH} (ppm)
	R^1	R^2	R^3				
1a	Ph	CN	H	**2a**⁵⁾	56	67— 68 (lit,⁵⁾ 67—68)	—
1b	Ph	CN	Ph	**2b**⁷⁾	92	235 (lit,⁷⁾ 238)	4.80 (s)
1c	Ph	H	Ph	**2c**⁸⁾	82	51— 52 (lit,⁸⁾ 52)	6.00 (1H, t, J=7 Hz) 6.90 (2H, d, J=7 Hz)
1d	Ph	Ph	H	**2c**	100	51— 52 (lit,⁸⁾ 52)	6.00 (1H, t, J=7 Hz) 6.90 (2H, d, J=7 Hz)
1e	Ph	NO_2	Ph	**2c**	92	51— 52 (lit,⁸⁾ 52)	6.00 (1H, t, J=7 Hz) 6.90 (2H, d, J=7 Hz)
1f	p-NO_2-C_6H_4-	H	Ph	**2f**	66	92— 93	5.75 (1H, t, J=7 Hz) 6.75 (2H, d, J=7 Hz)
1g	p-NO_2-C_6H_4-	NO_2	Ph	**2f**	92	92— 93	5.75 (1H, t, J=7 Hz) 6.75 (2H, d, J=7 Hz)
1h	p-NO_2-C_6H_4-	OMe	Ph	**2f**	75	92— 93	5.75 (1H, t, J=7 Hz) 6.75 (2H, d, J=7 Hz)
7a	Ph	—	—	**8a**⁸⁾	70ᵃ⁾	oil	—
7b	2-$C_{14}H_9$-	—	—	**8b**	78	118—120	6.95 (2H, t, J=6 Hz) 7.25 (2H, t, J=6 Hz)
3	—	—	—	**4**	85	231—232	5.63 (s)
5	—	—	—	**6**	90	196—198	4.65 (1H, t, J=6 Hz) 6.52 (2H, d, J=6 Hz)

a) The yield was calculated on the basis of the crude oil.

The $NaBH_4$ reduction was also useful for conjugated cyanoalkyne. The treatment of phenyl- (**7a**) and 2-phenanthrylcyanoacetylene (**7b**) with $NaBH_4$ afforded the tetrahydro derivatives, **8a** and **8b**, respectively (Table 1).

Experimental

All the melting points are uncorrected. The NMR spectra were measured in $CDCl_3$.

General Procedure of the $NaBH_4$ Reduction. To a stirred solution of conjugated cyanoalkene or cyanoalkyne (0.2 g) in 99% EtOH (20 ml) was added $NaBH_4$ by portions until gas evolution ceased (*ca.* 0.1 g) at room temperature. All the reactions were slightly exothermic and ceased within 1 h. The crude crystals formed by the decomposition of the reaction mixture with water were filtered and then recrystallized. When oily material was formed at the decomposition, it was taken up in ether. The ethereal solution was washed with water and dried over anhydrous Na_2SO_4. The crude crystals remaining after the evaporation of the solvent were recrystallized. O fthe reduction products, **2a—c** and **8a** were characterized by the comparison of their infrared spectra and/or melting points with those of authentic samples. All the new reduction products (**2f**, **4**, **6**, and **8b**) were characterized on the basis of their NMR spectra (Table 1) and elemental analyses. The analytical data are as follows:

2f) Found: C, 71.28; H, 3.97%. Calcd for $C_{15}H_{12}O_2N_2$: C, 71.41; H, 4.80%.

4) Found: C, 88.17; H, 5.02%. Calcd for $C_{32}H_{22}N_2$: C, 88.45; H, 5.10%.

6) Found: C, 90.58; H, 5.49%. Calcd for $C_{31}H_{23}N$: C, 90.92; H, 5.66%.

8b) Found: C, 88.21; H, 5.45%. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67%.

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