Reaction of 1,4-Diiodobutane. Employing the above procedure, we stirred 3.1 g (10 mmol) of 1,4-diiodobutane for 3 h in the presence of 1.2 g (10 mmol) of $NOBF_4$ in acetonitrile. The combined CH_2Cl_2 extracts were washed with saturated $NaHSO_3$ solution, and upon solvent removal 2.08 g (85%) of a yellow-orange oil was obtained: ^1H NMR ($CDCl_3$) δ 1.2-2.3 (m, 7), 3.0-3.6 (m, 4), 7.0 (1); ^{13}C NMR (relative to $CDCl_3$ at 77 ppm) δ 6.4, 22.9, 30.0, 30.4, 38.2, 170.6 (C=O) ppm; IR (neat) 3290, 2960, 1645, 1540 cm^{-1}.

The structure was confirmed by reduction with powdered zinc (1.1 g) in acetic acid (10 mL) for 1 h at 95 °C. Extraction with CH_2Cl_2 (3 × 10 mL) and washing with saturated $NaHCO_3$ afforded 1.0 g (46%) of 1-butylacetamide upon solvent removal.[14]

Acknowledgment. Support of this work by the National Science Foundation (Grant No. CHE 76 21992) and the National Institutes of Health (Grant No. ES 00761-07) is gratefully acknowledged. R.D.B. would also like to thank Professor J.-M. Lehn for his generous hospitality during his sabbatical leave at the University of Strasbourg where this manuscript was written.

Registry No. 1-Adamantyl iodide, 768-93-4; 1-adamantyl bromide, 768-90-1; 1-adamantyl chloride, 935-56-8; 1-adamantyl methyl ether, 6221-74-5; *tert*-butyl bromide, 558-17-8; *exo*-2-norbornyl bromide, 2534-77-2; *exo*-2-norbornyl chloride, 765-91-3; *exo*-2-norbornyl methyl ether, 10395-53-6; *endo*-2-norbornyl chloride, 2999-06-6; *endo*-2-norbornyl methyl ether, 10395-55-8; isopropyl bromide, 75-26-3; cyclohexyl chloride, 542-18-7; 2-butyl iodide, 513-48-4; 1-butyl iodide, 542-69-8; 4-iodobutyl iodide, 628-21-7; benzyl bromide, 100-39-0; 2-octyl bromide, 557-35-7; 1-adamantylacetamide, 880-52-4; *tert*-butylacetamide, 762-84-5; *exo*-2-norbornylacetamide, 28607-02-5; 2-norbornanone, 497-38-1; isopropylacetamide, 1118-69-0; cyclohexylacetamide, 1124-53-4; 2-butylacetamide, 1189-05-5; 1-butylacetamide, 1119-49-9; 4-iodobutylacetamide, 71988-86-8; benzylacetamide, 588-46-5; 2-octylacetamide, 23602-00-8; 3-octylacetamide, 23602-01-9; 2-octanone, 111-13-7; $NOBF_4$, 14635-75-7.

(14) **Note Added in Proof**: A recent paper disclosed a similar method for the conversion of alkyl halides into amides with $NOPF_6$. Olah, G. A.; Balaram, G.; Subhash, C. N. *Synthesis* **1979**, 274.

Reduction of α,β-Unsaturated Nitriles with a Copper Hydride Complex

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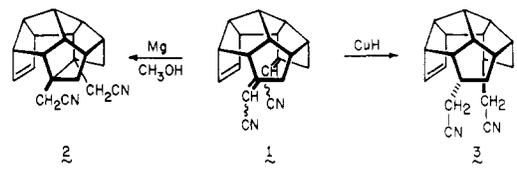
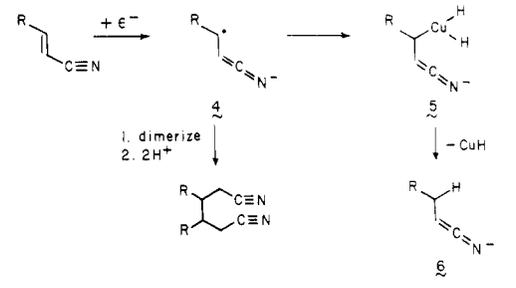
The reduction of conjugated nitriles to their saturated counterparts has long been a vexatious synthetic problem because of oft-encountered overreduction to the amine,[2] hydrodimerization,[3] decyanation,[4] and/or polymerization.[5] Recently, Profitt, Watt, and Corey published results achieved with magnesium metal in methanol.[6] Not only did reductions performed with this reagent proceed readily and in high yield but compatibility with a variety of other functional groups was also demonstrated. Accordingly, when the need arose in these laboratories to reduce the pair of conjugated double bonds in hexaquinane **1** regioselectively, we sought to take advantage of this recent development. However, magnesium in methanol proved versatile in transforming **1** uniquely into the unwanted transannular product **2**. This finding caused us to search for alternative methodology with which to achieve the desired conversion to **3**. Herein we describe our general success with the copper hydride reagent prepared from cuprous bromide, Vitride, and *sec*-butyl alcohol in the solvent tetrahydrofuran.[7]



2 1 3

Table I presents the results obtained with a variety of α,β-unsaturated nitriles which were prepared from the corresponding ketones by the Wadsworth-Emmons procedure[8] or purchased commercially. By means of a similar procedure, **3** was isolated in 70% yield.

The differing behavior of **1** under the two sets of conditions is particularly significant when considering the mechanisms of these complementary reactions. The dissolving action of elemental magnesium is thought to result in electron transfer with formation of a transient radical anion of type **4**. The characteristic[9] dimerization and



6

protonation of this species ensues. A parallel mechanism has been invoked for reduction with copper hydride species.[7,10,11] The absence of detectable transannular bonding in this instance probably has its origins in the rapid conversion of **4** to a covalently bonded copper species exemplified by **5** or perhaps in the direct production of such an intermediate. The copper atom presumably serves to retard hydrodimerization while making possible the delivery of **6** by reductive elimination of CuH or hydrogen abstraction from the medium.

Whatever the actual situation, it would appear that the copper hydride species described herein constitutes a useful reagent for the reduction of conjugated nitriles. Certainly, its reactivity is greater than that of sodium borohydride in refluxing isopropyl alcohol which has been reported not to reduce 2-butenenitrile,[12] as well as that of sodium cyanoborohydride which appears to require the presence of two activating groups at C_1.[13]

Experimental Section

General Reduction Procedure. To 1.86 g (13.0 mmol) of cuprous bromide in anhydrous tetrahydrofuran (10 mL) cooled

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(10) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59.
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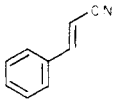
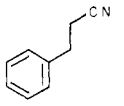
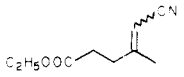
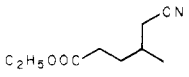
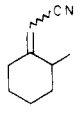
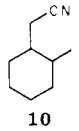
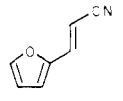
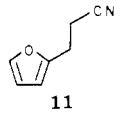
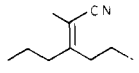
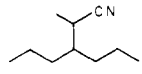
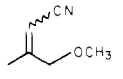
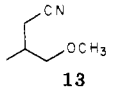
Table I. Reductions with Copper Hydride Complex[a]

substrate	product	yield, %
	 7	99
	 8	32
	 9	70
	 10	92
	 11	51
	 12	83
	 13	29

[a] See Experimental Section for details.

to 0 °C under a nitrogen atmosphere was added 7.4 mL (26.0 mmol) of Vitride[12] (3.5 M solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene). The resulting dark solution was stirred at 0 °C for 30 min and brought to −78 °C. 2-Butanol (2.3 mL, 26.0 mmol) was cautiously introduced via syringe, followed by a solution of the ene nitrile (1.3 mmol) in dry tetrahydrofuran (5 mL). After 2 h at this temperature, the reaction mixture was maintained at room temperature for a minimum of 4 h before being treated with saturated ammonium chloride solution (6 mL). The product was extracted into dichloromethane and the organic phase was dried, filtered, and evaporated. Silica gel chromatographic purification of the residue (elution with ether–hexane, 1:1) afforded the dihydro product in the yields (nonoptimized) cited in Table I.

As concerns characterization, **7** is a commercially available commodity,[14] whereas **8** and **10** were previously reported by Profitt, Watt, and Corey.[6] The furan derivative **11** has also been described earlier.[15]

For **9**: ν_{max} (neat) 2930, 2210, 1460, 1430 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.18 (m, 2 H), 0.89 (br s, 4 H), 0.60–0.20 (m, 5 H); *m/e* calcd 109.0891, obsd 109.0895.

For **12**: ν_{max} (neat) 2960, 2870, 2220, 1455, 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50–1.10 (m, 13 H), 0.90 (m, 6 H); *m/e* calcd 153.1517, obsd 153.1522.

For **13**: ^{1}H NMR ($CDCl_3$) δ 3.35 (s, 3 H), 3.5–3.2 (m, 1 H), 2.40 (d, J = 5 Hz, 2 H), 1.08 (d, J = 6.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 75.6, 59.1, 31.1, 21.4, 16.3 ppm (nitrile carbon shift not recorded); *m/e* calcd 113.0841, obsd 113.0844.

Acknowledgment. This investigation was made possible by a grant from the National Institutes of Health (AI-11490).

Registry No. **3**, 72017-14-2; **7**, 645-59-0; **8**, 52162-21-7; **9**, 72017-15-3; **10**, 53154-06-6; **11**, 21446-61-7; **12**, 72017-16-4; **13**, 21589-41-3; (*E*)-3-phenyl-2-propenenitrile, 1885-38-7; ethyl 4-(cyanomethylene)pentanoic acid, 72017-17-5; 3-cyclopropyl-2-butenenitrile, 822-95-7; (2-methylcyclohexylidene)acetonitrile, 53153-81-4; (*E*)-3-(2-furanyl)-2-propenenitrile, 6125-63-9; 2-methyl-3-propyl-2-hexenenitrile, 72017-18-6; 4-methoxy-3-methyl-2-butenenitrile, 72017-19-7.

(14) Available from the Aldrich Chemical Co.
(15) Sorm, F.; Brandejs, J. *Collect. Czech. Chem. Commun.* **1947**, *12*, 444.

Reactions of Dianions with Nitriles. A New Pyridine Synthesis

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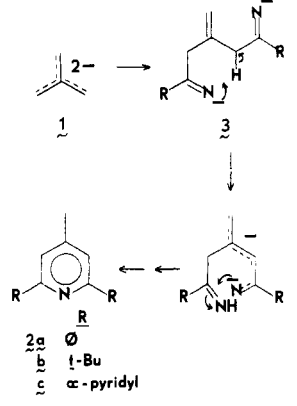
The 2-methyleneallyl dianion (**1**) has previously been reacted with many electrophiles[1] but not with nitriles. When we added dianion **1** in THF–pentane to 2 equiv of benzonitrile at −78 °C and warmed the mixture to 25 °C, 2,6-diphenyl-4-methylpyridine[2] (**2a**) was formed in 85% yield. Similar reactions with trimethylacetonitrile and



α-cyanopyridine gave 2,6-di-*tert*-butyl-4-methylpyridine[3] (**2b**, 30%) and 2,6-di-(2-pyridyl)-4-methylpyridine (**2c**, 18%), respectively; the former is a sterically hindered base, and the latter is an excellent tridentate ligand.[4] With acetonitrile (and probably other nitriles with α-hydrogens), however, no product of this type was detected, presumably due to rapid proton abstraction by the dianion. Other nitriles which gave no product of this type (perhaps due to rapid electron transfer[5]) were 2-cyanophenanthroline and 2,6-dicyanopyridine.

A possible mechanism for the formation of pyridines **2** is shown; a key step is intramolecular proton transfer in **3** via a six-membered-ring transition state. This mecha-

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(3) A. G. Anderson and P. J. Stang, *J. Org. Chem.*, **41**, 3034 (1976).
(4) **2c** is a new compound, but its coordinating properties should closely resemble those of the well-known but not readily available compound lacking the methyl group (F. A. Cotton and G. Wilkenson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, 1972, p 723). Indeed, oxidation and decarboxylation of **2c** might provide a competitive route to the latter.
(5) S. L. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967); H. O. House, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **36**, 2361 (1971).

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