reflux condenser and connected in series to a CO_2 collection apparatus; CO_2-free nitrogen was introduced through a soda-lime and $CaCl_2$ tube as a slow purging stream at the head of the reflux condenser. The CO_2 was caught in carbonate-free NaOH of sufficient concentration to exceed (in each trapping vial) the stoichiometric requirements anticipated from the sample. This carbonate solution was converted to barium carbonate by addition of $BaCl_2$, protected from the air with a serum cap, and alternatively washed and centrifuged until neutral; it was then washed twice with acetone, filtered, dried, weighed, and counted by the technique described.[43]

Estimation and Counting of Cyclic Ketones from Decarboxylation. The aqueous ethanolic HCl solution containing cyclic ketone after decarboxylation was extracted six times with benzene and the benzene solutions were combined, washed with saturated aqueous $NaHCO_3$, and distilled through a small vacuum-jacketed column. The last 0.5 mL of distillate was collected separately and further distilled in a small apparatus. The pot residue (0.1-0.2 g) was analyzed by GC (SE-30, 10 ft × $^1/_6$ in.) for cyclic ketone, in comparison with benzene solutions of authentic ketone. Extrapolations were made over no more than 10% of the concentration of ketone. Occasionally, analyses were interpolated between two standards differing by no more than 25% from the sample. Samples of 5 μL were injected.

If the concentration of ketone was too low in the concentrated distillate, the pot residue was distilled in a bulb-to-bulb unit, and distillate was analyzed. A portion of the distillate, after analysis, was weighed into a scintillation vial and counted, and the specific activity of the cyclic ketone was computed.

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Registry No. 7, 73789-73-8; **8**, 73789-74-9; **9**, 73789-75-0; **11a**, 73789-76-1; **11b**, 73789-77-2; **11c**, 30857-75-1; **12b**, 73789-78-3; **13b**, 73789-79-4; **13c**, 73789-80-7; **13d**, 73789-81-8; **13e**, 73789-82-9; **14a**, 73789-83-0; **15a**, 73789-84-1; polystyrene, 9003-53-6; ethyl hydrogen pimelate, 33018-91-6; 7-(*p*-cymyl) chloride, 2051-18-5; 7-(*p*-cymyl) methyl ether, 73789-85-2; 7-(*p*-cymyl) acetate, 59230-57-8; 7-(*p*-cymyl) alcohol, 536-60-7; cymyl bromide, 73789-86-3; 7-(*p*-cymyl) methyl sebacate, 73789-87-4; methyl hydrogen sebacate, 818-88-2; dibenzyl malonate, 15014-25-2; ethyl 5-bromovalerate, 14660-52-7; 5-bromovaleric acid, 2067-33-6; dibenzyl sodiomalonate, 65460-99-3; diethyl sodiomethylmalonate, 18424-77-6; 1-ethyl hydrogen 2-methylpimelate, 73789-88-5; 3-ethylglutaric acid, 620-36-0; methyl δ-bromovalerate, 14273-90-6; 7-methyl hydrogen 5-ethyl[1-^{14}C]pimelate, 73789-89-6; cumene, 98-82-8; [1-^{14}C]cyclohexanone, 13952-89-1.

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(43) Woeller, F. H. *Anal. Biochem.* **1961**, *2*, 508.

Potassium on Alumina as a Reagent for Reductive Decyanation of Alkylnitriles

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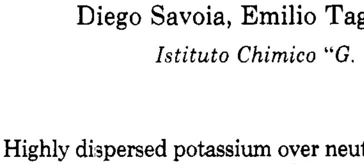
Highly dispersed potassium over neutral alumina (K/Al_2O_3), easily prepared by melting potassium over alumina in an inert atmosphere, is capable of effecting reductive cleavage of the cyano group in alkylnitriles in hexane at room temperature in 70-91% yield. This decyanation method is applied in the key step of a novel synthesis of (*Z*)-9-dodecen-1-yl acetate, the sex pheromone of *Paralobesia viteana*.

A very active area of research in organic chemistry involves the use of reagents supported on porous solids to effect synthetic transformations. Such reactions often occur under mild conditions with easy chemical operations. Recently alumina has been used as a support for different reagents to achieve highly selective organic reactions.[1] For example, alumina-supported metals have been used as hydrogenation catalysts.[2] More recently, a synthesis of nitriles[3] with cyanide ion impregnated over neutral alumina and a malonic ester synthesis[4] on basic alumina have been described.

We report that high-surface-area potassium on neutral alumina (K/Al_2O_3) in hexane is capable of effecting reductive cleavage of the cyano group in alkylnitriles (**1a-f**) to afford the corresponding alkanes (**2a-f**).[5]



1a-f **2a-f**

It is known that the same reduction[6] occurs when nitriles are treated with dissolved alkali metals in hexamethylphosphoric triamide in the presence of *tert*-butyl alcohol as a protic cosolvent[7] or with sodium in ammonia.[8] However, these methods suffer from the expensive or troublesome use of poisonous hexamethylphosphoric triamide or liquid ammonia.

The reagent K/Al_2O_3 is prepared by melting potassium over neutral alumina at 150 °C with vigorous stirring in an inert atmosphere. The alkylnitrile **1** in hexane is then added to this reagent at room temperature to obtain the corresponding decyanated product **2** in 70-91% yield.[9] As shown in Table I, the procedure is very efficient for the

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(1) (a) G. H. Posner, *Angew. Chem., Int. Ed. Engl.*, **17**, 487 (1978); (b) S. Quici and S. L. Regen, *J. Org. Chem.*, **44**, 3437 (1979).

(2) R. L. Augustine, "Catalytic Hydrogenation", Marcel Dekker, New York, 1965.

(3) S. L. Regen, S. Quici, and S. J. Liaw, *J. Org. Chem.*, **44**, 2029 (1979).

(4) G. Bram and T. Fillebeen-Khan, *J. Chem. Soc., Chem. Commun.*, 522 (1979).

(5) The hydrogen incorporated into the decyanated product may derive either from the hydroxyl groups of alumina or from the solvent.

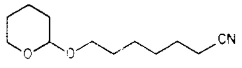
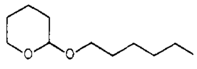
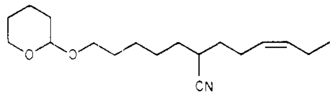
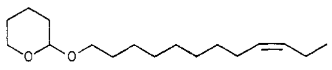
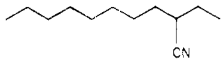
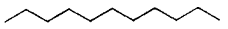
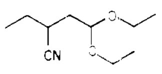
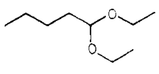
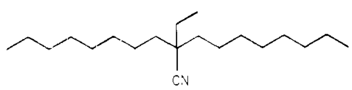
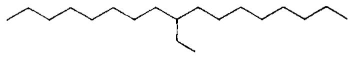
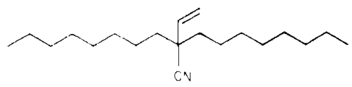
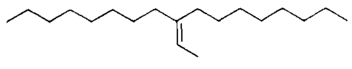
(6) An analogous reductive decyanation of alkylnitriles promoted by the $Fe(acac)_3$-sodium sand system has been described by E. E. van Tamelen, H. Rudler, and C. Bjorklund, *J. Am. Chem. Soc.*, **93**, 7113 (1971).

(7) (a) T. Cuvigny, M. Larcheveque, and H. Normant, *Bull. Soc. Chim. Fr.*, 1174 (1973); (b) M. Larcheveque and T. Cuvigny, *Tetrahedron Lett.*, 3851 (1975); (c) A. Debal, T. Cuvigny, and M. Larcheveque, *Synthesis*, 391 (1976).

(8) (a) C. Favre, M. H. A. Salem, and Z. Welvart, *Bull. Soc. Chim. Fr.*, 178 (1975); (b) J. A. Marshall, C. P. Hagan, and G. A. Flynn, *J. Org. Chem.*, **40**, 1162 (1975); (c) S. Yamada, K. Tomioka, and K. Koga, *Tetrahedron Lett.*, **61**, (1976); (d) J. A. Marshall and R. Bierenbaum, *J. Org. Chem.*, **42**, 3309 (1977).

(9) Al_2O_3 is not strictly necessary; however, by dispersing potassium over this support a higher surface area, and consequently an enhanced reactivity, is obtained. In two parallel experiments conducted with K/Al_2O_3 and K alone, first melted and then cooled with stirring, the conversion of **1a** to **2a** after 1 h under the same conditions is 95% and 60%, respectively. Moreover, quenching of the excess potassium in the second case is more hazardous.

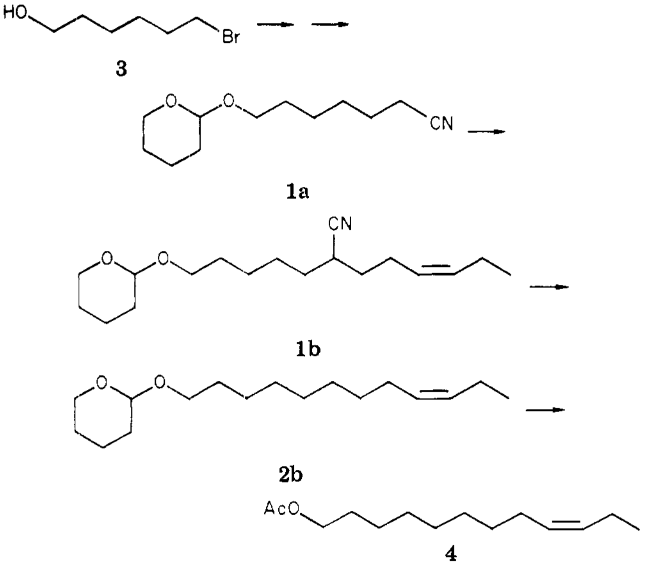
Table I. Reductive Cleavage of Nitriles

substrate	time, min	product	yield, %[a]
 **1a**	60	 **2a**	90
 **1b**	15	 **2b**	80
 **1c**	20	 **2c**	85
 **1d**	20	 **2d**	88
 **1e**	10	 **2e**	91
 **1f**	5	 **2f**	70

[a] Yield refers to pure isolated product.

reductive elimination of the cyano group from alkylnitriles.[10] A fivefold excess of potassium is required for the procedure. At least 20 min is required for the decyanation of secondary and tertiary nitriles, while primary alkylnitriles require ca. 60 min for good results. Cleavage of 2,2-dioctyl-3-butenenitrile **1f** does not afford 3-octyl-1-undecene but the corresponding 2-alkene **2f**. An analogous migration of the double bond was observed in the reductive cleavage of the C–S bond in allylic sulfones by means of potassium–graphite (C_8K) in ether.[11]

The reductive cleavage reaction was used to prepare the sex pheromone (**4**) of *Paralobesia viteana*[12] to demonstrate the usefulness of this method. For this purpose 6-bromo-1-hexanol (**3**), prepared from 1,6-hexandiol according to Butenandt,[13] is converted into **1a** through CN^- displacement under phase-transfer conditions,[14] followed by protection of the hydroxyl group as the THP derivative. Metalation of **1a** with lithium diisopropylamide and alkylation with (*Z*)-1-iodo-3-hexene affords **1b**. The elimination of the cyano group in **1b** is easily accomplished in hexane by means of potassium dispersed on alumina in 15 min. Finally, deprotection of the hydroxyl group in **2b** and acetylation are carried out in acetic acid and acetyl chloride at 120 °C for 1 h to give **4** in good yield.



In conclusion, this new reduction technique under aprotic conditions is quite general for alkylnitriles and allows a more convenient use of the activating cyano group in C–C bond formation reactions.

Experimental Section

^1H NMR spectra were recorded on a Perkin-Elmer R12B spectrometer (60 MHz) in tetrachloromethane. Chemical shifts are expressed as δ values, using tetramethylsilane as an internal standard. The infrared spectra (IR) were recorded on a Perkin-Elmer 710B instrument. Mass spectra were taken on a Varian MAT 111 (70 eV). Gas–liquid phase chromatography was performed on a Hewlett-Packard 5750B instrument, using 2 mm × 180 cm columns packed with 5% Carbowax 20M (poly(ethylene glycol)) on 90–100 mesh Anakrom ABS and 10% UC-W982 (silicon oil) on 80–100 mesh Chromosorb W. Thin-layer chromatography (TLC) was performed on silica gel sheets (IB2-F, Baker) with hexane as solvent. Hexane (Carlo Erba, mixture of isomers, bp 65–70 °C) was distilled and stored over sodium. Activated neutral alumina (Brockmann activity I, 70–230 mesh, ASTM) was purchased from Merck, and potassium from Carlo Erba (RPE, 99.5%). Boiling points are uncorrected.

Nitriles 1a–f. 7-[(Tetrahydro-2*H*-pyran-2-yl)oxy]heptanenitrile (1a). 1,6-Hexanediol was treated with 48% HBr at 100

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[10] We observed that in tetrahydrofuran solvent, acetonitrile and primary nitriles mainly undergo α-metalation, as shown by trapping the intermediate carbanions with an alkyl halide (unpublished results).

[11] D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Chem. Soc., Perkin Trans. 1*, 123 (1977).

[12] W. J. Roelofs, J. P. Tette, E. F. Taschenberg, and A. Comeau, *J. Insect Physiol.*, **17**, 2235 (1971).

[13] A. Butenandt, E. Hecker, M. Hopp, and W. Koch, *Justus Liebigs Ann. Chem.*, **658**, 39 (1962).

[14] C. M. Starks, *J. Am. Chem. Soc.*, **93**, 195 (1971).

°C under conditions of continuous extraction with refluxing 2,2,4-trimethylpentane to give after column chromatography 6-bromo-1-hexanol (**3**),[13] which was converted into the corresponding nitrile by treatment with 80% aqueous NaCN in *n*-decane under phase-transfer conditions using hexadecyltributylphosphonium bromide as catalyst at 100 °C.[14] After ether extraction of the aqueous phase and solvent evaporation, the crude oil was dissolved in tetrahydrofuran and stirred with a twofold excess of 3,4-dihydro-2*H*-pyran in the presence of a catalytic amount of dried Amberlyst H-15[15] to give **1a**: IR (film) 2240, 1130, 1110, 1070, 1030 cm^{-1}; NMR 4.45 (m, 1 H), 3.55 (m, 4 H), 2.3 (t, 2 H), 1.55 (m, 14 H).

2-[5-[(Tetrahydro-2*H*-pyran-2-yl)oxy]pentyl]-5(*Z*)-octenenitrile (1b). **1a** was metalated according to standard procedures[16] and alkylated with (*Z*)-1-iodo-3-hexene[17] to give **1b**: IR (film) 3020, 2240, 1140, 1120, 1080, 1030, 720 cm^{-1}; NMR 5.3 (m, 2 H), 4.45 (m, 1 H), 3.5 (m, 4 H), 2.1 (m, 5 H), 1.5 (m, 16 H), 0.95 (t, 3 H).

2-Ethyldecanenitrile (1c). Alkylation[16] of butanenitrile with 1-bromooctane afforded **1c**: IR (film) 2230 cm^{-1}; NMR 2.4 (m, 1 H), 1.3 (m, 16 H), 0.9 (m, 6 H).

2-Ethyl-4,4-diethoxybutanenitrile (1d). Alkylation[16] of butanenitrile with 1,1-diethoxy-2-bromoethane afforded **1d**: IR (film) 2230, 1120, 1050, 1010 cm^{-1}; NMR 4.65 (t, 1 H), 3.6 (m, 4 H), 2.55 (m, 1 H), 1.4–2.2 (m, 4 H), 1–1.3 (m, 9 H).

2-Ethyl-2-octyldecanenitrile (1e). Dialkylation[16] of butanenitrile with 1-bromooctane afforded (**1e**): IR (film) 2230 cm^{-1}; NMR 1.3 (m, 30 H), 0.9 (m, 9 H).

2,2-Dioctyl-3-butenenitrile (1f). Dialkylation of 2-butenenitrile[8d] gave the β,γ-unsaturated nitrile **1f**: IR (film) 2250, 990 cm^{-1}; NMR 5.35 (m, 3 H), 1.3 (m, 28 H), 0.9 (t, 6 H).

Preparation of Highly Dispersed Potassium on Alumina (K/Al_2O_3). Al_2O_3 (3.7 g) was placed in a 100-mL two-necked flask equipped with an argon inlet and a magnetic stirring bar and heated at 150 °C (external oil bath) for 15 min under a positive argon pressure. Then potassium (0.6 g, 15 mmol) was added in small pieces. After the potassium melted, heating was stopped and the mixture was vigorously stirred to obtain a homogeneous black powder of highly dispersed metal (14% K/Al_2O_3).[18] Potassium/alumina is oxygen and moisture sensitive and must be handled in an inert atmosphere.

Decyanation of 1f to 2f (General Procedure). To a slurry of 4.3 g of potassium/alumina in 15 mL of hexane was slowly added (3 min) a solution of 0.87 g of **1f** (3.0 mmol) in 10 mL of hexane under an inert argon atmosphere. After 5 min the excess potassium was decomposed with 0.5 mL of water and the white alumina was filtered and washed with ether. After evaporation of solvent, the residue was chromatographed (silica gel, hexane) to yield 0.56 g (70%) of **2f** that was 97% pure by GLC analysis: IR (film) 820, 720 cm^{-1}; NMR 5.1 (q, J = 7 Hz, 1 H), 1.95 (m, 4 H), 1.55 (d, J = 7 Hz, 3 H), 1.25 (24 H), 0.85 (t, 6 H); mass spectrum, *m/e* (M^+, 266).

2-(Hexyloxy)tetrahydro-2*H*-pyran (2a): bp 125 °C (15 torr); IR (film) 1130, 1110, 1070, 1030 cm^{-1}; NMR 4.6 (m, 1 H), 3.5 (m, 4 H), 1.4–1.8 (m, 14 H), 0.95 (t, 3 H); identical GLC retention time with a sample obtained by acid-catalyzed tetrahydropyranylation of 1-hexanol.

2-[(*Z*)-9-Dodecenyloxy]tetrahydro-2*H*-pyran (2b): IR (film) 3020, 1140, 1120, 1080, 1040 cm^{-1}; NMR 5.2 (m, 2 H), 4.45 (m, 1 H), 3.45 (m, 4 H), 1.95 (m, 4 H), 1.1–1.6 (m, 18 H), 0.9 (t, J = 7 Hz, 3 H); mass spectrum, *m/e* (M^+, 268).

Undecane (2c): bp 80 °C (15 torr); identical with an authentic sample (Merck).

1,1-Diethoxypentane (2d): bp 65 °C (15 torr); IR (film) 1180, 1140, 1020 cm^{-1}; NMR 4.4 (t, 1 H), 3.6 (m, 4 H), 1.5–1.2 (m, 6 H), 1.2 (t, 6 H), 0.9 (t, 3 H); identical GLC retention time with a sample obtained by acid-catalyzed acetalization of pentanal.

9-Ethylheptadecane (2e): bp 185 °C (15 torr); mass spectrum, *m/e* (M^+, 268).

(*Z*)-9-Dodecenyl Acetate (4) (Sex Pheromone of *Paralobesia viteana*). A solution of 0.54 g (2 mmol) of **2b** in 1.4 mL of acetic acid and 0.6 mL of acetyl chloride[19] was heated at 120 °C for 1 h in a sealed tube and then poured into 15 mL of saturated aqueous $NaHCO_3$ solution. The aqueous phase was extracted with ether and the concentrated organic phase was purified by column chromatography (silica gel, hexane–ether 98:2), affording 0.39 g (85%) of **4**: IR (film) 3010, 1740, 1240, 1030, 780 cm^{-1}; NMR 5.25 (m, 2 H), 3.9 (t, 2 H), 2.3–1.8 (m, 4 H), 1.95 (s, 3 H), 1.3 (m, 12 H), 1.05 (t, 3 H); mass spectrum, *m/e* (M^+, 226).

Registry No. 1a, 33803-59-7; **1b**, 73804-91-8; **1c**, 73804-92-9; **1d**, 73804-93-0; **1e**, 73804-94-1; **1f**, 73804-95-2; **2a**, 1927-63-5; **2b**, 50816-22-3; **2c**, 1120-21-4; **2d**, 3658-79-5; **2e**, 73804-96-3; **2f**, 73804-97-4; **3**, 4286-55-9; **4**, 16974-11-1; potassium, 7440-09-7; alumina, 1344-28-1; 1,6-hexanediol, 629-11-8; 3,4-dihydro-2*H*-pyran, 110-87-2; (*Z*)-1-iodo-3-hexene, 21676-03-9; butanenitrile, 109-74-0; 1-bromooctane, 111-83-1; 1,1-diethoxy-2-bromoethane, 2032-35-1; 2-butenenitrile, 4786-20-3.

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(15) A. Bongini, G. Cardillo, M. Orena, and S. Sandri, *Synthesis*, 618 (1979).

(16) (a) D. S. Watt, *Tetrahedron Lett.*, 707 (1974); (b) D. Savoia, C. Trombini, and A. Umani-Ronchi, *Tetrahedron Lett.* 653 (1977).

(17) (*Z*)-1-Iodo-3-hexene was obtained through I^- displacement of (*Z*)-1-tosyl-3-hexene in acetone, which was prepared from commercially available (*Z*)-3-hexenol (Aldrich, 97.3%) and tosyl chloride in pyridine.

(18) The X-ray diffraction pattern of K/Al_2O_3 was identical with that of Al_2O_3, with no observable diffractions due to the potassium.

(19) D. Warthen and M. Jacobson, *J. Med. Chem.*, 11, 1190 (1968).

Asymmetric Synthesis of Optically Active Trans Doubly Bridged Ethylene. (−)-(*R*)-D_2-Bicyclo[8.8.0]octadec-1(10)-ene

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Ultraviolet irradiation of the "cis" bicyclic α,β-unsaturated ketone **9** in diethyl $\mathrm{L_g}$-(+)-tartrate afforded a 1:7 mixture of *cis*-**9** and trans ketone **10** enriched in the (−)-enantiomer, whose Wolff–Kishner reduction yielded (−)-D_2-bicyclo[8.8.0]octadec-1(10)-ene (**3**; optical purity 0.5–1.0%) with the *R* configuration.

Our continuing interests in twisted gyrochiral[1] π-electron systems have led us to study the preparation, stereochemistry, and chiroptical properties of [*n*]-chochines (**1**,[2] see Chart I), [*m*][*n*]paracyclophanes (**2**),[3] and (−)-(*S*)-bicyclo[3.3.1]non-1-ene (**12**),[4] the first optically active

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(1) M. Nakazaki, K. Naemura, and S. Harita, *Bull. Chem. Soc. Jpn.*, 48, 1907 (1975).

(2) M. Nakazaki, K. Yamamoto, and S. Tanaka, *J. Chem. Soc., Chem. Commun.*, 433 (1972); M. Nakazaki, K. Yamamoto, S. Tanaka, and H. Kametani, *J. Org. Chem.*, 42, 287 (1977).