this reaction involves first the formation of the radicals **2a** and **2b**, respectively, from **1a** and **1b**. Before radicals **2a** and **2b** interconvert to any appreciable extent, they react with the second mole of sodium naphthalenide to produce the respective carbanions **3a** and **3b**. The rate of electron transfer between the naphthalene radical anion and free radicals is virtually diffusion controlled, since the reaction of optically active cyclopropyl bromides affords the respective cyclopropane with net retention.[8] In addition, radicals **2a** and **2b** might be expected to be stabilized by bridged structures involving the neighboring bromine and thus be prevented from interconverting by bond rotation.[9]

Finally, the lower stereospecificity in the case of the *erythro*-dibromide **1a** *vs.* the threo isomer **1b** arises from a methyl–ethyl repulsion in carbanion **3a** *vs.* a methyl–methyl repulsion in carbanion **3b**. Consequently, for **3a** bond rotation competes more effectivity with trans ejection of the bromine than for **3b**.

Experimental Section

Sodium naphthalenide was prepared according to the procedure of Scott[10] by dissolving 23 g (1.0 g-atom) of clean sodium metal in 1000 ml of dimethoxyethane (freshly distilled from the benzophenone ketyl radical) containing 134 g (1.0 mol) of naphthalene. The dark green solution was standardized by removing 2.0 ml of the stock solution by means of a calibrated syringe and quenching with 1.0 ml of methanol. The pale yellow solution was titrated with 0.100 *N* hydrochloric acid using methyl red as indicator.

***erythro*-2,3-Dibromo-3-methylpentane (1a)** was obtained in 34% yield (79.9% isomeric purity by glpc), bp 74° (12 mm), $n^{20}\mathrm{D}$ 1.5126 [lit.[11] 79.5° (16 mm)], using the method of van Risseghem,[11] starting with 5.02 g (0.0597 mol) of (*Z*)-3-methyl-2-pentene [Columbia Organic, bp 67.5° (758 mm), $n^{20}\mathrm{D}$ 1.4021] and 9.6 g (0.060 mol) of bromine.

***threo*-2,3-Dibromo-3-methylpentane (1b)** was obtained in 36% yield (78.6% isomeric purity by glpc), bp 75° (14 mm), $n^{20}\mathrm{D}$ 1.5121 [lit.[11] 75° (15 mm)], using the method of van Risseghem,[11] starting with 5.02 g (0.0597 mol) of (*E*)-3-methyl-2-pentene [Columbia Organic, bp 70° (758 mm), $n^{20}\mathrm{D}$ 1.4050] and 9.6 g (0.060 mol) of bromine.

General Method of Dehalogenation.—A 5-ml vial, capped with a rubber septum and supplied with a spinbar, was charged under a nitrogen atmosphere with 1.0 ml of a 2 *M* solution of the dibromide in DME (freshly distilled from the benzophenone ketyl radical). While stirring magnetically, a stoichiometric (2 mol of naphthalenide per mole of dibromide) amount of the standardized sodium naphthalenide solution was added through the rubber septum by means of a syringe. The colorless reaction mixture was stirred for 60 sec, quenched with 0.5 ml of methanol, and centrifuged to remove the sodium bromide precipitate. The supernatant liquid was submitted to glpc analysis. The results are summarized in Table I.

Registry No.—**1a**, 32675-17-5; **1b**, 32675-18-6; sodium naphthalenide, 12521-84-5.

Acknowledgments.—Financial aid by the Petroleum Research Fund, the National Science Foundation, and the Sloan Foundation is gratefully appreciated.

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Marked Differences between the Sodium–Ammonia and Calcium–Ammonia Reduction of Nitriles

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The reduction of nitriles with the alkali metals has been reported under a variety of conditions.[1–11] Normally the product isolated is the corresponding amine or the hydrocarbon resulting from reductive decyanation, a reductive fission process.[12] Recently, Arapakos, *et al.*, using sodium–ammonia or lithium–ethylamine solutions, found that tertiary nitriles give exclusive reductive decyanation products, whereas primary and secondary nitriles give both the expected amine as well as decyanation products.[10,11] In particular, dodecyl cyanide was reduced to dodecane (35%) and tridecylamine (65%).[11]

While working on another problem it became necessary to learn the fate of various aliphatic nitriles in the presence of calcium–ammonia solutions. For a direct comparison to the results reported for the alkali metal–ammonia or amine reductions,[10,11] dodecyl cyanide was chosen for the initial studies with calcium–ammonia solutions. In the presence of this reducing medium, dodecyl cyanide gave trace amounts of dodecane. Tridecylamine was the major product, accompanied by small amounts of 1-dodecyl-1-aminotridecane. Because of the marked difference in the amount of reductive decyanation found using calcium–ammonia solutions in comparison to the results reported using sodium–ammonia or lithium–ethylamine solutions,[10,11] other nitriles were reduced by addition of the nitrile to a heterogeneous solution of isooctane, calcium, and ammonia to see if this observation was a general phenomenon.

The results are shown in Table I. For convenience, the more volatile amines were isolated as derivatives from the isooctane solutions after removal of ammonia and represent the minimum amount of amine actually produced. No effort was made to measure the hydrocarbons or HCN produced by reductive fission due to the solvent used, the method of work-up and the *pyrophoric nature* of the calcium residues.

The alkali metal–ammonia or amine reductions of primary, secondary, and tertiary nitriles give increasing quantities of decyanation products (hydrocarbon

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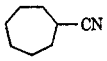
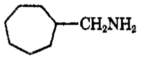
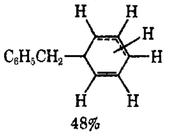
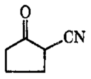
TABLE I

REDUCTION OF NITRILES WITH CALCIUM–AMMONIA SOLUTIONS

Nitrile	Product	Yield, %
$CH_3CH_2CH_2CN$	$CH_3CH_2CH_2CH_2NH_2$[a]	31–46
$(CH_3)_2CHCN$	$(CH_3)_2CHCH_2NH_2$[a]	32–43.5
$(CH_3)_3CCN$	$(CH_3)_3CCH_2NH_2$[b]	42.0
$CH_3CH_2CH_2CH_2CN$	$CH_3CH_2CH_2CH_2CH_2NH_2$[a]	40–65
		63
$(C_6H_5)_2CHCN$	$(C_6H_5)_2CH_2$ 52% +  48%	100.0[c]
$(C_6H_5)_2CHCN$ (Na^0)	$(C_6H_5)_2CH_2$	100.0[c]
$NC(CH_2)_4CN$		39

[a] Isolated from isooctane as *n*-phenylthiourea derivative. [b] Isolated from isooctane as benzamide derivative. [c] Based on consumed starting material.

or olefin) and decreasing quantities of amine in the order listed.[10,11] In contrast to these results, the calcium–ammonia system reduced primary, secondary, and tertiary nitriles to give modest, synthetically useful amounts of the expected amine product and little decyanation based on the result obtained with dodecylcyanide. Under the same reaction conditions employed with calcium, a heterogeneous solution of sodium–ammonia in isooctane reduced diphenylacetonitrile to diphenylmethane in accord with earlier reports.[10,11] However, the calcium–ammonia system gave nearly equal amounts of diphenylmethane and further reduction products of diphenylmethane as a result of partial reduction of the aromatic nuclei. A dinitrile, adiponitrile, reacted with calcium–ammonia solutions to give 2-cyanocyclopentanone after a hydrolytic work-up.

The results obtained employing calcium–ammonia solutions are similar to those reported for reductions of nitriles with sodium and alcohol solutions[3,8,9] or sodium–ammonia solutions containing an alcohol.[4] In all cases, the blue metal–ammonia solutions could be effectively "titrated" with the nitrile, the blue color being instantly discharged. Calcium amide, the byproduct of reduction, is produced rapidly. The isolation of 2-cyanocyclopentanone as the major hydrolysis product from adiponitrile attests to this fact as it is the expected hydrolysis product from the well-known base-catalyzed cyclization of adiponitrile.[13] The intermediate imine apparently tautomerizes rapidly in the basic medium to the enamine and is not reduced further.[13]

$$2Ca + 12NH_3 + RCN \longrightarrow RCH_2NH_2 + 8NH_3 + 2Ca(NH_2)_2$$

In metal–ammonia reductions, the solvated electron is considered to be the reducing specie.[12] However, the differences between the alkali metal–ammonia (or amine) solutions and calcium–ammonia solutions in the reduction of nitriles have also been observed in similar metal–ammonia reductions of monothioketals,[14] monothioacetals,[14] 1,3-dithiolanes,[15] and 1,3-dithianes.[15] This suggests that factors, such as the coordinating ability of the substrate toward the metal, or the degree of aggregation of the metal, may be of importance.

All derivatives prepared were found to be identical (nmr, ir, melting point) with authentic samples synthesized from commercially available amines.

Experimental Section

General Procedure for Nitrile Reduction.—Calcium (8.0 g, 0.2 mol) was charged to a dry, nitrogen-purged reactor. Ammonia (100 ml) was added slowly with adequate cooling to control the highly exothermic reaction. Isooctane (Phillips ASTM grade, redistilled from 4A molecular sieves, under N_2, 200 ml) was added slowly to the reactor. The rapidly stirred blue mixture was cooled to −50°. Nitrile (0.1 mol) was added rapidly dropwise. The blue color could be essentially titrated with the nitrile. The cooling bath was removed and the gray slurry was allowed to come to room temperature, venting the ammonia. Isooctane (300 ml) was added in portions (100 ml) during this time. In a nitrogen-filled drybox the reaction mixture was gravity filtered. The appropriate derivatizing agent (0.1 mol) was added to the filtrate. Usually the amine derivative rapidly precipitated, was filtered and recrystallized from an appropriate solvent.

Note. The calcium residue should be placed under a nonprotic solvent in the drybox and destroyed by the careful and slow addition of isopropyl alcohol to the slurry in a well-vented hood (HCN is liberated in some cases). In air, the semidry calcium residue is pyrophoric if not treated in the above manner.

Reduction of Cycloheptylnitrile.—Cycloheptylnitrile (12.3 g, 0.1 mol) was reduced as described above. After removal of ammonia, dilute HCl (20%, 400 ml) was added slowly with cooling (−10 to −20°). The water layer was extracted with 100 ml of ether. The aqueous layer was made strongly basic with 50% sodium hydroxide and extracted with ether (five 100-ml portions). The ethereal extract was washed with 100 ml of a saturated aqueous solution of sodium chloride, dried (Na_2SO_4), concentrated, and distilled, giving 8.0 g (63%) of cycloheptylmethylamine, bp 101° (35 mm). The *n*-phenylthiourea derivative was prepared, mp 125.5–127°.

Anal. Calcd for $C_{15}H_{22}N_2S$: C, 68.66; H, 8.45; N, 10.68. Found: C, 68.50; H, 8.38; N, 10.64.

Reduction of Adiponitrile.—Adiponitrile (10.8 g, 0.1 mol), calcium (4.0 g, 0.1 mol), and 500 ml of isooctane were placed in a reactor equipped with a high-speed stirrer and cooled to −35 to −40°. Approximately 100 ml of ammonia was added as rapidly as possible. The heterogeneous solution turned blue and then white; 20 ml of *tert*-butyl alcohol was added; and stirring was continued for 20 min. The ammonia was weathered off. Product was obtained by acidifying (10% diluent HCl), extraction of water layer ($CHCl_3$), concentration of organic layers, and vacuum distillation to give 4.39 g of 2-cyanocyclopentanone (39%), bp 67–69° (<1 mm) [lit.[16] bp 125–130° (4 mm)], semicarbazone mp 195–197° (lit. mp 192–195°).

Reduction of Dodecyl Cyanide.—Dodecyl cyanide (32.1 g, 0.15 mol) was reduced with calcium (0.15 mol) in 300 ml of ammonia. Isooctane (1000 ml) was added and the ammonia was weathered off. Water (0.2 mol) was added. The hydrocarbon layer was concentrated and distilled. Dodecane was isolated by glc and identified by mass spectroscopy, identical in all respects with the published spectrum. Tridecylamine had bp 80° (1.5 mm), mass spectrum parent mass 199.229989 (calcd, 199.229959). The benzoyl derivative was made, mp 69.5–70.5° (lit. mp 71.0°). The ir and nmr spectra were in agreement with the structure. Acetic anhydride was added to the distillation residue. Recrystallization from ethanol gave the acetamide of 1-dodecyl-1-aminotridecane, mp 105.5–106.0°. *Anal.* Calcd for $C_{27}H_{55}NO$: C, 79.14; H, 13.53; N, 3.42. Found: C, 79.16; H, 13.49; N, 3.46. Ir (KBr) 3.05 (NH), 3.42, 3.50 (CH_3–, CH_2–), 6.09 (NHC=O), 7.31 (CH_3CO), 13.82 μ (–CH_2–); nmr ($CDCl_3$) δ 0.87 (t, 6, CH_3–), 1.26 (s, 40, –CH_2–), 1.97 (s, 3, CH_3CO), 3.93 (broad signal, 1, CHN), 5.15 (m, 1, NH); mass spectrum A.E.I. MS-9 (70 eV) *m/e* (rel intensity)

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M^+ 409.428630 (1.4) (calcd, 409.428344), 366 (1), 240 (100), 198 (81); m* (409 → 240) 140.83; m* (240 → 198) 163.65.

Registry No.—Sodium, 7440-23-5; calcium, 7440-70-2; ammonia, 7664-41-7; cycloheptylnitrile, 32730-85-1; cycloheptylmethylamine, 4448-77-5, 32730-87-3 (*N*-phenylthiourea derivative); adiponitrile, 111-69-3; dodecyl cyanide, 629-60-7; tridecylamine, 2869-34-3; acetamide of 1-amino-1-dodecyltridecane, 32730-89-5.

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A New Synthesis of Unsymmetrical Azo Compounds[1]

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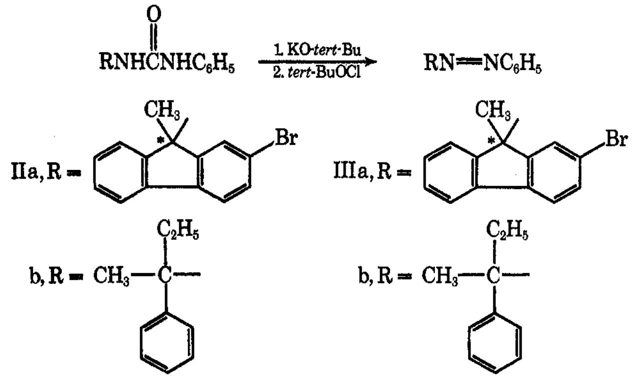
The relative rates of bond breaking of the two carbon–nitrogen bonds in the thermal decomposition of unsymmetrical azo compounds has been investigated recently.[2] This and other studies have resulted in the modification of old and development of new synthetic procedures for the preparation of the requisite unsymmetrical azo compounds.[3]

In connection with our studies, we required an azo compound of the general formula I in which the tertiary carbon is optically active. Since none of the existing methods for the preparation of unsymmetrical azo compounds could be modified to give a compound of type I, we explored new routes to this structure.[4]

$$\mathrm{RN{=}NAr}$$
$$\mathrm{I},\ \mathrm{R} = tert\text{-alkyl}$$

The treatment of unsymmetrical ureas (IIa,b) with potassium *tert*-butoxide in *tert*-butyl alcohol followed by the addition of *tert*-butyl hypochlorite at room temperature for 15 min produced azo compounds IIIa,b in approximately 20% yield. The ureas are readily obtained by the reaction of phenyl isocyanate with a *tert*-alkylamine. In addition, IIIa was produced optically active by beginning with resolved 2-bromo-9-methyl-9-aminofluorene, which was prepared from 2-bromofluorenone.



This method resembles the sequence which Greene[5] reported in the synthesis of diaziridones. However, it is not known if a diaziridone is an intermediate in this reaction.

Experimental Section[6]

2-Bromofluorenone.—2-Bromofluorene was oxidized according to the procedure of Ross and coworkers[7] to give 2-bromofluorenone in 73% yield, mp 144–146° (lit.[7] mp 146–148°), after recrystallization from ethanol.

2-Bromo-9-methylfluoren-9-ol.—To 22 g of 2-bromofluorenone in 700 ml of dry benzene was added 100 ml of CH_3MgBr (Aldrich, 2.2 *M*) over 20 min. The solution was stirred at room temperature for 1 hr and poured into 1 *N* H_2SO_4. The benzene layer was separated and the acid extracted with benzene. The benzene was dried ($MgSO_4$) and evaporated and the residue crystallized from chloroform-petroleum ether (bp 30–60°) to give 15.7 g (67%) of product, mp 143.5–144.5° (lit.[8] mp 148–149°).

2-Bromo-9-methyl-9-azidofluorene.—2-Bromo-9-methylfluoren-9-ol was converted to the azide according to the procedure of Coombs[9] in 85% yield and used as the oil without further purification: nmr spectrum (CCl_4) δ 1.67 (s, CH_3) and 7.1–7.8 (m, aromatics).

2-Bromo-9-methyl-9-aminofluorene.—To 9 g of $LiAlH_4$ (Ventron) in 225 ml of dry ether cooled in an ice bath was added with stirring 51.4 g of 2-bromo-9-methyl-9-azidofluorene at a rate which maintained vigorous refluxing. After addition was complete the reaction mixture was stirred at room temperature for 30 min. The excess $LiAlH_4$ was decomposed by the *slow* addition of 39 ml of 20% NaOH to the cooled reaction mixture. The white granular precipitate was filtered and the ether evaporated (frothing!) to give 42 g (89%) of a very viscous nearly colorless oil: nmr spectrum (CCl_4) δ 1.55 (s, CH_3), 7.1–7.8 (m, 7 aromatic H's), 1.41 (s, broad, NH_2).

Resolution of 2-Bromo-9-methyl-9-aminofluorene.—The amine (27.4 g) in 350 ml of ethyl ether was added to 12.5 g of *d*-10-camphorsulfonic acid in 50 ml of ethyl alcohol. The solution was allowed to stand at room temperature for 2 hr and at 16° for 1 hr and filtered to give 12.1 g of the camphorsulfonate salt. The amine from this salt was used to prepare the (+) azo compound. The filtrate was evaporated and the amine liberated. To 19.4 g of this amine was added 10.6 g of *d*-tartaric acid in 350 ml of ethanol. This was allowed to stand at 25° overnight and yielded 11.9 g of the tartrate salt. The amine liberated from this salt was used to prepare the (−) azo compound. In order to ascertain the rotation of the respective amines, they were each converted to the urea with phenyl isocyanate as described below and the rotations measured. The urea from the camphor-

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

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[4] Since this method was developed Porter, *et al.*,[2] have reported a synthetic sequence which also leads to this type of compound and involves the unsymmetrical sulfamide.

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