# Electrochemical and Metal–Ammonia Reduction of 1,4-Dihalonorbornanes[1]

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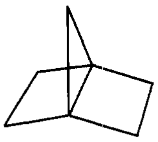
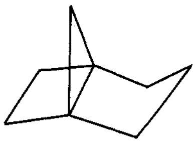
The electrochemical and metal–ammonia reductions of 1,4-dihalonorbornanes were examined as possible routes to the [2.2.1]propellane. The products were norbornane and 1,1′-binorbornane. In the metal–ammonia reductions, the amount of coupling product was found to be dependent on the concentration of the dihalide. It is suggested that local regions having a higher concentration of the dihalide may be responsible for the coupling.

The [2.2.1]propellane (**1**) is of particular interest in connection with the difference in thermal reactivity between the [3.2.1]propellane (**2**) and the [2.2.2]propellane (**3**). The low reactivity of **2** is readily understood since its cleavage to 1,3-dimethylenecyclohexane is orbital symmetry forbidden.[3,4] The high reactivity of **3** has been explained by involving an antibonding diradical intermediate which can open to 1,4-dimethylenecyclohexane in an orbital symmetry allowed reaction.[4,5,6] Alternately, this reactivity may simply be a reflection of the greater strain present in **3** (relative to **2**) which allows the cleavage to proceed via the symmetry forbidden pathway. A knowledge of the reactivity of **1** would serve to distinguish between these possibilities.


**1**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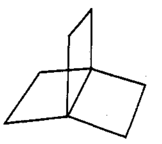
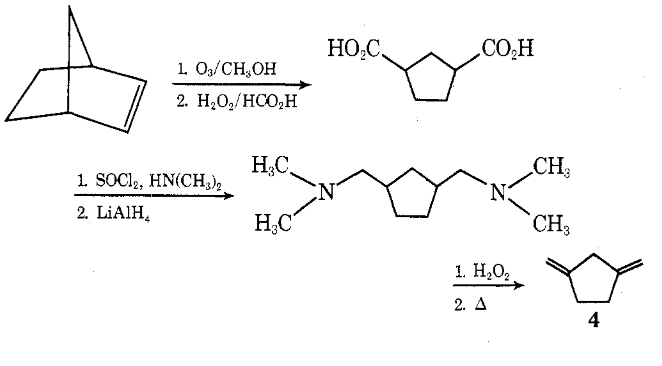

**3**

An organometallic derivative of the [2.2.1]propellane has been prepared[7] but neither the hydrocarbon nor any of its simple derivatives have, as yet, been reported. In view of the successful electrochemical ring closures of 1,5-dibromobicyclo[3.2.1]octane to **2**[8] and 1,4-dibromobicyclo[2.2.2]octane to **3**,[9] we have investigated the reduction of 1,4-dibromonorbornane. A suggestion that this approach might be fruitful is found in the work of Wilcox and Leung, who showed that 1,4-dichloronorbornane reacts with lithium to give the 1,4-dilithio derivative but no 4-chloro-1-norbornyllithium.[10]

The conversion of the readily obtained 1,4-dichloronorbornane[11] to the 1,4-dibromo derivative was effected using aluminum foil and a catalytic amount of bromine in methylene bromide.[12] The 1,4-diiodo derivative was prepared in a similar manner from the dichloride by reaction with aluminum foil and a catalytic amount of bromine in methylene iodide.[12] In anticipation of the need for a sample of the ring-opened isomer of **1** for comparison with products resulting from reduction of 1,4-dihalonorbornanes, an authentic sample of 1,3-dimethylenecyclopentane (**4**) was prepared according to Scheme I.

**Scheme I**



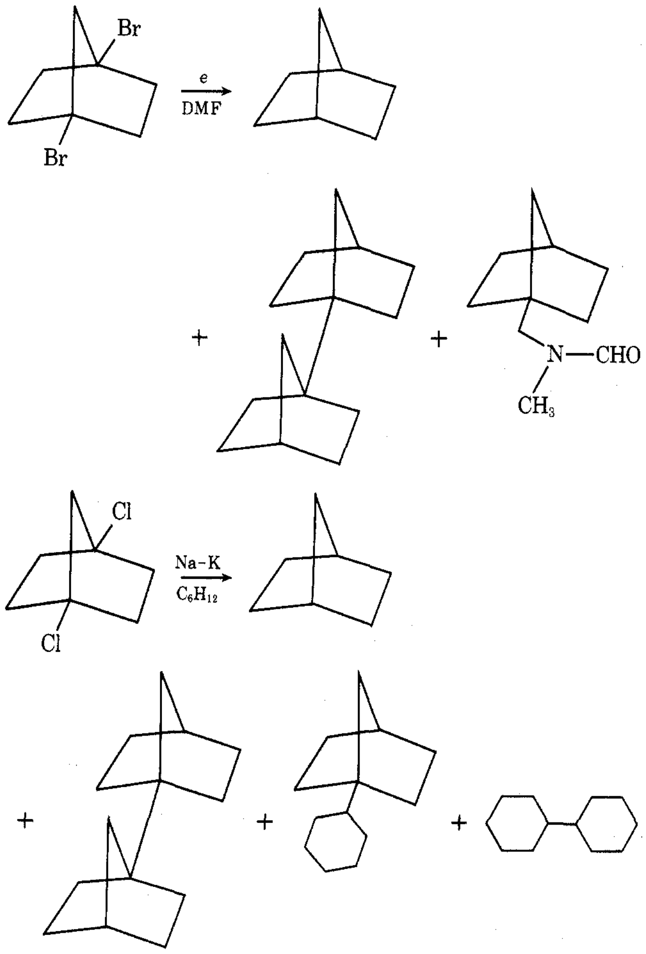
The electrochemical reduction of 1,4-dibromonorbornane was effected at a platinum electrode in dimethylformamide solution at −20 to −30 °C using tetraethylammonium bromide as the supporting electrolyte. The potential was maintained at −2.50 V vs. a mercury pool reference electrode.[13] The products of the reduction were norbornane, 1,1′-binorbornane, and a compound derived from the coupling of a norbornyl radical and dimethylformamide [tentatively assigned as *N*-methyl-*N*-(1-norbornylmethyl)formamide].[14] No 1,3-dimethylenecyclopentane was found, although a priori it could have formed either by thermal cleavage of **1** (if it had been produced) or via a Grob fragmentation[15] of the dibromide precursor. The possibility that **1** had been produced and had existed for a finite time in solution was investigated by repeating the electrolysis and saturating the catholyte with chlorine gas at −30 °C. The addition of chlorine across the C(1)–C(4) bond of any [2.2.1]propellane produced electrochemically is expected to be facile since both the [3.2.1]propellane and the [2.2.2]propellane readily add halogen across the central bond under analogous conditions.[3,5,9] Unfortunately, no 1,4-dichloronorbornane was detected in the product mixture.

The products resulting from the electrochemical reduction of 1,4-dibromonorbornane are similar to those formed when 1,4-dichloronorbornane is reduced with sodium–potassium alloy in cyclohexane; i.e., norbornane, 1,1′-binorbornane, and radical-coupling products[3] (Scheme II). The reactions themselves are analogous in than reduction is accomplished at a surface in both instances and the medium is, therefore, heterogeneous. It is perhaps somewhat surprising that the 1,4-dihalonorbornanes show no tendency to undergo Grob fragmentation under these conditions since the C–X bonds are locked in a conformation which should allow for facile fragmentation.[15] A rationale for the reluctance of 1,4-dihalonorobornanes to undergo Grob fragmentation has been advanced by Gleiter, Stohrer, and Hoffmann[4,16] in terms of the symmetry properties of the interacting orbitals. According to these authors, there is a symmetry imposed barrier to fragmentation of the intermediate in such reductions (be it the 1,4-diradical[4] or the 4-halo-1-anion[16]) due to the bonding nature of the interaction between the orbitals on C(1) and C(4) ("through-space coupling").[3,15]

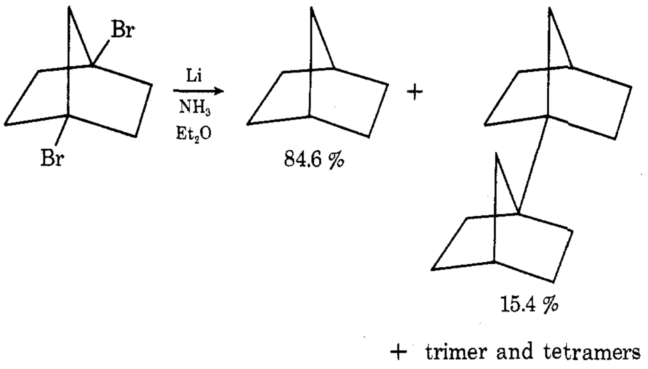
The formation of dimers and radical products in the reduction of 1,4-dihalonorbornanes at a surface may result from either free-radical coupling at the surface or from the formation of the [2.2.1]propellane followed by its rapid reaction with a norbornyl radical. It did not appear possible to distinguish between these possibilities and, therefore, we have attempted to effect the electron transfer under apparently homogeneous conditions.

The reduction of 1,4-dibromonorbornane with lithium in a mixture of ammonia and ether proceeded rapidly at −33 °C. The products of the reaction were norbornane (84.6%), 1,1′-binorbornane (15.4%), and traces of higher polymers (Scheme III). The reduction of the dichloro and diiodo derivatives as

Scheme II



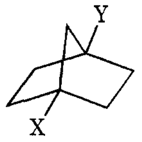
Scheme III



well as the 1-halonorbornanes also was studied giving the results summarized in Table I. Contrary to our initial expectations, the reduction of 1-bromo- and 1-iodonorbornanes produced significant amounts of 1,1′-binorbornane (3.9 and 4.3%, respectively).

If the reduction medium were truly homogeneous the formation of 1,1′-binorbornane could not reasonably be due to coupling of norbornyl radicals. The concentration of solvated electrons in the reaction medium was high since a large excess of lithium metal was used. Thus, any radicals formed from the initial electron transfer would be expected to add a second electron, at diffusion controlled rates,[17] to form the bridgehead anion. It should be noted that whereas the 1-norbornyl radical is relatively unstable,[18] the 1-norbornyl anion appears to possess unusual stability.[19,20]

**Table I. Products from the Lithium in Ammonia Reductions of Norbornyl Halides**



| Registry no. | Halide[a] | Norbornane, % | 1,1′-Binorbornane, % |
|---|---|---|---|
| 765-67-3 | X = Cl; Y = H | 100.0 | |
| 13474-70-9 | X = Br; Y = H | 96.1 | 3.9 |
| 930-80-3 | X = I; Y = H | 95.7 | 4.3 |
| 2941-51-7 | X = Y = Cl | 99.7 | 0.3 |
| 40950-22-9 | X = Y = Br[b] | 84.6 | 15.4 |
| 40950-21-8 | X = Y = I[b] | 80.8 | 19.2 |
| | X = Br; Y = H (inverse addition)[c] | 90.6 | 9.4 |
| | X = Br; Y = H (high dilution)[c] | 99.2 | 0.8 |

[a] Solutions were initially 0.50–0.54 M lithium in ammonia–ether and 0.050–0.054 M halide in ammonia–ether. The halide was 0.1–0.5 M in ether prior to addition to lithium in ammonia. [b] Trimers and tetramers were also detected. See Experimental Section. [c] See Experimental Section.

In order to test the radical-coupling hypothesis, two experiments were performed. In the first the lithium–ammonia solution was added to a solution of 1-bromonorbornane in a mixture of ammonia and ether (inverse addition). In this case the proportion of dimer increased from 3.9% to 9.4%. In the other experiment, 1-bromonorbornane was dissolved in a mixture of ammonia and ether and added slowly to a large volume of the lithium in ammonia–ether solution. In this experiment the proportion of dimer formed decreased markedly from 3.9% to 0.8%. Thus the formation of dimer and higher polymers is dependent on the concentration of norbornyl halide during the reduction.

Since it is unlikely that the concentration of radicals in the solution will be high enough to permit significant coupling, the observed concentration effect must have a more complex origin. One reasonable possibility is the formation of hydrophobic regions in the hydrogen-bonded medium, similar to the formation of micelles in water. As the concentration of halide is increased, the number of halide molecules in a given hydrophobic region would increase, permitting more facile radical coupling in the local environment.

Coupling of alkyl halides in metal–ammonia reductions has been observed previously,[21] as well as solvent effects[22] similar to those found in this investigation. The coupling has been proposed to proceed either via the coupling of radicals or by the formation of a carbanion which then effects an S$_N$2 displacement.[22] In the case of the bridgehead halides, the latter mechanism is not possible, and radical coupling is the only reasonable process. It appears that solvent effects on the coupling reaction may generally be explained by our hypotheses.

In any event, it is clear that the results of the electrochemical and metal–ammonia reduction of the 1,4-dihalonorbornanes do not provide evidence either for or against the formation of the [2.2.1]propellane as an intermediate in the reactions. Other types of experiments will be necessary to settle this question.

## Experimental Section

Melting points were determined on a Hoover-Thomas melting point apparatus and are uncorrected. Boiling points are uncorrected. Proton magnetic resonance spectra were recorded on a JEOL JNM-MH-100 spectrometer. Mass spectra were recorded on a Hitachi RMU-6 instrument. Preparative GLC was effected with an Aerograph A-90-P chromatograph equipped with 0.25-in. columns. Microanalyses were performed by Atlantic Microlab, Inc.

Literature procedures were followed in the preparation of 1-chloronorbornane,[23] 1-bromonorbornane,[24] 1-iodonorbornane,[20] and 1,4-dichloronorbornane.[11]

**1,4-Dibromonorbornane.** Following the general procedure of McKinley, Pincock, and Scott,[12] narrow strips of common aluminum foil (683.2 mg, 25.30 mmol) were placed in a 200-ml round-bottomed flask filled with a magnetic stirrer, immersion thermometer, and reflux condenser with drying tube. To this flask was added 240 ml of methylene bromide and 400 $\mu$l (7.8 mmol) of bromine. The mixture was heated on an oil bath at 80 °C for 1 h during which time the aluminum reacts to form a red-black suspension. The suspension was allowed to cool to room temperature and 2.00 g (12.12 mmol) of 1,4-dichloronorbornane[11] was added at once. The mixture was heated at 95–97 °C on a steam bath for 1 h. The contents of the flask were poured over 200 g of crushed ice and the organic layer washed successively with 100 ml of water, 100 ml of 10% aqueous sodium hydroxide, and 100 ml of brine. After drying ($MgSO_4$), the solvent was removed at reduced pressure to give a black, tarry residue which was sublimed at 55 °C (11–20 mm) to afford white needles, mp 73.5–74 °C (lit.[12] 73 °C) in yields of 68–81%: $^1H$ NMR ($CDCl_3$) $\delta$ 2.07 and 2.25 (AB pattern with further coupling, $J_{AB}$ = 8.0 Hz, 2 H), 2.36 (s, 2 H).

Anal. Calcd for $C_7H_{10}Br_2$: C, 33.1; H, 4.0; Br, 62.9. Found: C, 33.0; H, 4.0; Br, 63.1.

**1,4-Diiodonorbornane.** Following the general procedure described above,[12] a mixture of 683.2 mg (25.30 mmol) of aluminum foil, 50 ml of methylene iodide, and 254 $\mu$l (5.06 mmol) of bromine was heated at 60 °C for 1 h. After cooling to room temperature, 2.00 g (12.12 mmol) of 1,4-dichloronorbornane was added at once and the mixture was heated at 95–97 °C on a steam bath for 1 h. After the workup described above, sublimation of the tarry residue gave 70–74% of the diiodide: mp 102–103 °C (lit.[12] 101 °C); $^1H$ NMR ($CDCl_3$) $\delta$ 2.01 and 2.25 (AB pattern with further coupling, $J_{AB}$ = 8.0 Hz, 8 H), 2.40 (s, 2 H).

Anal. Calcd for $C_7H_{10}I_2$: C, 24.1; H, 2.9; I, 73.0. Found: C, 24.1; H, 2.9; I, 72.9.

***cis*-Cyclopentane-1,3-bis(*N*,*N*-dimethylcarboxamide).** *cis*-Cyclopentane-1,3-dicarboxylic acid[25] (75.8 g, 0.1 mol) was heated under gentle reflux with 70 g (0.59 mol) of thionyl chloride for 6 h. The excess thionyl chloride was removed under reduced pressure and the dark residue distilled to give 16.2 g (83%) of the acid chloride, bp 79–88 °C (0.35 mm), ir $\nu_{C=O}$ 1785 $cm^{-1}$.

This acid chloride (16.2 g, 83 mmol) was dissolved in 50 ml of anhydrous ether and added dropwise to a stirred solution of 50 g of dimethylamine in 200 ml of ether cooled to −20 °C. The mixture was allowed to warm to room temperature and stirred overnight. The precipitated amine hydrochloride was removed by filtration and washed with ether. The combined filtrate and washings were diluted with 50 ml of chloroform (controls had shown that the diamide was only slightly soluble in ether) and dried ($MgSO_4$). Evaporation of the solvent afforded 14.3 g (80%) of a semisolid mass containing both the cis and trans isomers of the product. The solid isomer was removed by filtration and sublimed at 80 °C (1 mm) to give 8.0 g of crystals, mp 79.8–82 °C. The liquid isomer was distilled [bath temperature 180 °C (0.2 mm)] to give a colorless oil: $^1H$ NMR solid isomer ($CDCl_3$) $\delta$ 1.7–2.2 (m, 4 H), 2.92 (s, 6 H), 3.10 (s, 6 H), 3.0–3.2 (m, 2 H); liquid isomer ($CDCl_3$) $\delta$ 1.7–2.2 (m, 4 H), 2.92 (s, 6 H), 3.12 (s, 6 H), 3.0–3.2 (m, 2 H).

Anal. Calcd for $C_{11}H_{20}N_2O_2$: C, 62.2; H, 9.5; N, 13.2. Found: C, 62.0; H, 9.6; N, 13.1.

**1,3-Bis(dimethylaminomethyl)cyclopentane.** A Soxhlet extractor was charged with 10.0 g (46.8 mmol) of the bisamide and the amide was slowly leached into a stirred, gently refluxing suspension of 2.81 g of lithium aluminum hydride in 350 ml of anhydrous ether over an 8-h period. The mixture was hydrolyzed by dropwise sequential addition of 2.8 ml of water, 2.8 ml of 15% aqueous sodium hydroxide, and 8.4 ml of water. The mixture was filtered, the filtrate concentrated, and the residue distilled to give 6.45 g (75%) of product, bp 80–81 °C (4.4 mm). An analytical sample was prepared by GLC on a 2.5-ft, 30% SE-30 on Chromosorb P (60–80 mesh) column at 105 °C: $^1H$ NMR ($CCl_4$) $\delta$ 0.8–1.8 (m, 8 H), 2.17 (s, 12 H).

Anal. Calcd for $C_{11}H_{24}N_2$: C, 71.7; H, 13.1; N, 15.2. Found: C, 71.4; H, 13.2; N, 15.2.

**1,3-Dimethylenecyclopentane.** A solution of 6.00 g (32.55 mmol) of 1,3-bis(dimethylaminomethyl)cyclopentane in 18 ml of 30% hydrogen peroxide was stirred at room temperature for 40 h. Excess hydrogen peroxide was decomposed by adding 50 mg of platinum black and stirring for an additional 6 h. The mixture was filtered and concentrated at 0.2–1.0 mm (temperature <40 °C) to afford a viscous oil. A small amount (ca. 20 mg) of hydroquinone was added to the oil and the mixture was heated on an oil bath maintained at 180–190 °C (130–150 mm). The pyrolysate was collected in a dry ice cooled trap. Following the pyrolysis, 5 ml of pentane was added to the trap and the pentane-immiscible portion was discarded. The organic layer was washed successively with 2 ml of water, two 2-ml portions of 5% aqueous hydrochloric acid, 2 ml of water, and 2 ml of brine. The pentane solution was cooled to −77 °C and decanted from the ice. This dry solution was concentrated at atmospheric pressure and the residue distilled to give 2.01 g (92.5%) of the diene: bp 102 °C; ir (neat) 3050 (s), 1655 (s), and 870 $cm^{-1}$ (s); $^1H$ NMR ($CCl_4$) $\delta$ 2.42 (apparent singlet, 4 H), 3.01 (broad s, 2 H), 4.88 (nearly equivalent $=CH_2$, 4 H).

Anal. Calcd for $C_7H_{10}$: C, 89.3; H, 10.7. Found: C, 89.4; H, 10.6.

**Electrochemical Reduction of 1,4-Dibromonorbornane.** The electrolysis cell was constructed from a 700-ml beaker fitted with a magnetic stirrer, cooling bath, and a four-hole rubber stopper to accommodate the anode, cathode, reference electrode, and nitrogen inlet-outlet tube. The cathode (purchased from the Arthur H. Thomas Co.) consisted of a reinforced platinum gauze cylinder (45 mesh, 2 in. high by 1 in. diameter) with a connecting platinum wire. The anode consisted of a coiled platinum wire dipping into background electrolyte and separated from the cathodic cell by means of a salt bridge prepared from methyl cellulose and electrolyte solution as described by Dryhurst and Elving.[26] The potential was controlled relative to a mercury pool reference electrode by means of a Wenking 61 RS potentiostat.

The electrolysis cell was charged with 500 ml of 0.1 M tetraethylammonium bromide in dry dimethylformamide[27] and 635 mg (2.5 mmol) of 1,4-dibromonorbornane was added. A constant stream of nitrogen was passed through the stirred solution and the cell was maintained at −20 to −30 °C throughout the electrolysis. A potential of −2.50 V vs. a mercury pool was maintained (current 100–140 mA) for 7–8 h. The catholyte was diluted with an equal volume of cold, saturated aqueous sodium chloride and extracted with two 250-ml portions of pentane–ether. The organic extract was washed with water, dried ($MgSO_4$), and concentrated. GLC analysis of the residue on a 10 ft, 30% SE-30 on Anakrom M (60–80 mesh) column at 119 °C indicated that no 1,3-dimethylenecyclopentane had been produced. Three products were detected in addition to short retention time components derived from reduction of dimethylformamide and the supporting electrolyte. The shortest retention time product was identified as norbornane by coinjection with an authentic sample. The longest retention time product was collected and sublimed at 80 °C (20 mm) to give a solid, mp 109–111 °C, having a mass spectrum identical with that of 1,1′-binorbornane[28] (lit.[29] mp 111–112.5 °C). The intermediate retention time product was not isolated in sufficient quantity to permit unambiguous characterization. On the basis of its spectral properties the compound appears to have been derived from DMF and a norbornyl radical.[30]

In a separate experiment, the electrolysis was run as described above and the catholyte saturated with chlorine gas at −30 °C. After standing at −30 °C overnight the dimethylformamide solution was worked up. GLC analysis revealed the presence of the products described above. No 1,4-dichloronorbornane was detected.

**Lithium in Ammonia Reduction of Norbornyl Halides.** Experiments were conducted such that the initial concentrations would be 0.50–0.54 M lithium in ammonia–ether and 0.050–0.054 M halide in ammonia–ether. Typically, 2 mmol of the halide in dry diethyl ether (0.1–0.5 M solutions) was added to a rapidly stirred solution of 20 mmol of lithium in twice distilled ammonia[31] cooled to −78 °C. The cooling bath was removed and the mixture was stirred at reflux for 1 h. Reductions were quenched by cautious addition of solid ammonium chloride to discharge the characteristic blue color. The ammonia was allowed to evaporate and the ethereal solution was washed successively with water, 5% aqueous hydrochloric acid, and brine. The solution was dried ($MgSO_4$) and analyzed by gas chromatography on a Perkin-Elmer Model 900 chromatograph equipped with flame ionization detector and interfaced with a Hewlett-Packard 3370A integrator. Product yields were determined on a 10 ft, 30% SE-30 on Anakrom $\mu$ (60–80 mesh) column with linear temperature programming from an initial temperature of 80 °C for 8 min to 210 °C at a rate of 6.5 °C/min. Area ratios were corrected to mole ratios with the response factors determined for norbornane and 1,1′-binorbornane under identical conditions. Results are given in Table I.

The solutions resulting from reduction of 1,4-dibromo- and 1,4-diiodonorbornane were concentrated to dryness and subjected to sublimation to remove norbornane and 1,1′-binorbornane. Analysis of the residues by mass spectroscopy revealed parent peaks (*m/e* 378 and 284) and fragmentation patterns expected for the trimer [1-(1-norbornyl)-4-(1-norbornyl)norbornane] and the tetramer[4,4′-di-(1-norbornyl)-1,1′-binorbornane].

**Lithium in Ammonia Reduction of 1-Bromonorbornane with Inverse Addition.** A solution of 134.8 mg (19.5 mmol) of lithium metal in 60 ml of twice-distilled ammonia[31] was added dropwise to a rapidly stirred solution of 351.1 mg (2.00 mmol) of 1-bromonorbornane in 50 ml of doubly-distilled ammonia and 10 ml of dry diethyl ether. The characteristic blue color of lithium in ammonia was immediately discharged upon addition to the halide solution. Following the addition, excess lithium was destroyed with solid ammonium chloride as described above. GLC analysis of the ethereal residue revealed 90.6% norbornane and 9.4% 1,1′-binorbornane.

**Lithium in Ammonia Reduction of 1-Bromonorbornane at High Dilution.** A solution of 500 mg (2.86 mmol) of 1-bromonorbornane in 50 ml of dry diethyl ether was diluted with 150 ml of twice-distilled ammonia[31] and added dropwise to a rapidly stirred solution of 250 ml (35.7 mmol) of lithium in a mixture consisting of 500 ml of twice-distilled ammonia[31] and 100 ml of dry diethyl ether at reflux. Following the addition, the reaction mixture was allowed to stir for 1 h at reflux and was then quenched with solid ammonium chloride as described above. GLC analysis of the ethereal residue revealed 99.2% norbornane and 0.8% 1,1′-binorbornane.

**Registry No.**—4, 59219-48-6; *cis*-cyclopentane-1,3-dicarboxylic acid, 876-05-1; *cis*-cyclopentane-1,3-dicarboxylic acid chloride, 59219-49-7; *cis*-cyclopentane-1,3-bis(*N,N*-dimethylcarboxamide), 59219-50-0; *trans*-cyclopentane-1,3-bis(*N,N*-dimethylcarboxamide), 59219-51-1; 1,3-bis(dimethylamino)cyclopentane, 59219-52-2; *N*-methyl-*N*-(1-norbornylmethyl)formamide, 59219-53-3; lithium, 7439-93-2; ammonia, 7664-41-7.

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(1) This investigation was supported by a grant from the National Science Foundation.
(2) To whom correspondence should be addressed.
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(28) We thank Dr. K. Shen for providing us with a sample of 1,1′-binorbornane.
(29) R. A. Alden, J. Kraut, and T. G. Traylor, *J. Am. Chem. Soc.*, **90**, 74 (1968).
(30) This product is tentatively assigned the structure depicted in Scheme II [*N*-methyl-*N*-(1-norbornylmethyl)formamide)] on the basis of the following spectral properties: MS *m/e* 167 ($M^+$), 138 ($M^+ - CHO$), 95 (base), 72 ($M^+$ − norbornyl); ir ($CCl_4$) 2840 (m), 1630 $cm^{-1}$ (s); $^1H$ NMR ($CCl_4$) $\delta$ 1.3–2.05 (m, 10), 2.1–2.3 (m, 1), 3.06 (s, 5 H).
(31) Ammonia was first distilled from the tank into a flask containing lithium metal and then from the lithium metal into the reaction vessel.

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# Displacement of an Alkyl Group from Quaternary Ammonium Chlorides by Certain Neutral Nucleophiles

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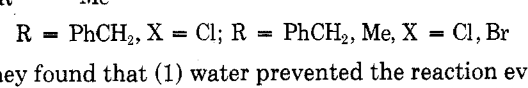
Heating $(Me_3SiO)_3Si(CH_2)_3Cl$ with excess trimethylamine caused almost quantitative yields of $(Me_3SiO)_3Si(CH_2)_3NMe_2$ and $Me_4N^+Cl^-$. Some conditions influencing the yields of products from alkyl chlorides and tertiary amines were studied. One alkyl group can be displaced from quaternary salts easily at 100 °C in nonpolar media by neutral nucleophiles with the following approximate order of reactivity: $NH_3 \leq RSH < HOAc < RNH_2 < R_2NH < R_3N$.

Recently we heated 3-[tris(trimethylsiloxy)silyl]propyl chloride (I) with an excess of trimethylamine expecting to obtain 3-[tris(trimethylsiloxy)silyl]propyltrimethylammonium chloride (III),[1] but obtained instead 3-[tris(trimethylsiloxy)silyl]propyldimethylamine (II) and tetramethylammonium chloride in almost quantitative yield. Dr. C. L. Frye of this laboratory suggested that these products might be an example of a type IV, $S_N2$ reaction, the first example of which was described by Hughes and Whittingham[2] in 1960:

$$Ph_2MeNMe^+ + Me_3N \rightarrow Me_3NMe^+ + Ph_2MeN$$

This type of reaction had been predicted in 1935[3] and many examples have been found since 1960 in which an alkyl group is transferred to an uncharged nucleophile from an onium ion, including ions such as sulfonium, oxonium, or halonium ions.

Hutchinson and Tarbell[4] in 1969 showed that the reaction for ammonium ions was reversible and they studied the equilibrium



$R = PhCH_2, X = Cl; R = PhCH_2, Me, X = Cl, Br$

They found that (1) water prevented the reaction even at 140 °C; (2) bromides reacted faster than chlorides; (3) equilibria were reached most rapidly in nonpolar solvents; (4) a