

slightly, and then concentrated on a steam bath under water-pump vacuum. The residual oil was cooled, taken up in 50 ml. of distilled water, and the solution added dropwise during 10 min., with mechanical stirring, to a solution of 8.6 g. (0.025 mole) of sodium tetraphenylboron in 100 ml. of distilled water. The mixture was stirred for 10 min. after the addition was complete. The precipitated solid was filtered, washed with distilled water, and air-dried to give 11.3 g. (93.2%) of white solid product. Upon gradual heating, the solid turned, with effervescence, to a cloudy oil from 150 to 154°, gradually resolidified from 155 to 165°, and then melted to a yellow oil from 173–190°.

*Anal.* Calcd. for  $C_{35}H_{35}BN_2O_3$ : C, 77.5; H, 6.46; N, 5.13. Found: C, 77.7; H, 6.4; N, 4.7.

Recrystallization from 200 ml. of ethyl acetate gave 8.17 g. (67.6%) of pale yellow crystals, m.p. 158–160° dec. On further heating, it resolidified and melted again from 171–179°. Found: C, 77.7; H, 6.5.

One gram of the product was heated to 165° for 5 min., cooled, and recrystallized from dimethylformamide-acetonitrile to give 0.7 g. of white needles, m.p. 175–181°. The infrared spectrum of this material was identical with that of an authentic sample of pyridinium tetraphenylboride (made by mixing pyridine hydrochloride with sodium tetraphenylboron in water). A mixture melting point showed no depression.

*Anal.* Calcd. for  $C_{25}H_{25}BN_2O_3$ : C, 87.2; H, 6.52; N, 3.51. Found: C, 85.9; H, 6.6; N, 4.5.

**1-(3,5-Dioxo-6-oxa-4-azatetracosyl)pyridinium Bromide. A.**—A solution of 10.0 g. (0.0223 mole) of octadecyl  $\beta$ -bromopropionylcarbamate<sup>3</sup> and 100 ml. of dried pyridine was refluxed for 15 hr., cooled, and the precipitated solid filtered, sucked dry, and recrystallized twice from 100-ml. portions of dioxane to give 7.3 g. (62%) of white crystals, m.p. 130–131°.

*Anal.* Calcd. for  $C_{27}H_{47}BrN_2O_3$ : C, 61.5; H, 8.90; Br, 15.2; N, 5.31. Found: C, 61.3; H, 9.2; Br, 15.2; N, 5.2.

**B.** A solution of 9.6 g. (0.021 mole) of octadecyl  $\beta$ -bromopropionylcarbamate,<sup>3</sup> 1.7 g. (0.021 mole) of pyridine, and 50 ml. of acetonitrile was treated as in A to give 8.2 g. (74%) of product, m.p. 131–132°. The same product was obtained in 62% yield by refluxing octadecyl acrylylcarbamate with one equivalent of pyridine hydrobromide in acetonitrile for 15 hr.

**2-Carbamoylethylpyridinium Bromide.**—In experiment A the use of pyridine, which had not been dried, gave a 76% yield of colorless crystals, m.p. 198–200°, not improved by recrystallization from ethanol.

*Anal.* Calcd. for  $C_8H_{11}BrN_2O$ : C, 41.6; H, 4.76; Br, 34.7; N, 12.1. Found: C, 42.1; H, 4.9; Br, 34.3; N, 11.7.

The same product was obtained in 84% yield by similar treatment of cholesteryl 3- $\beta$ -bromopropionylcarbamate.<sup>3</sup> Concentration of the filtrate and recrystallization of the gummy residue from ethanol gave a 68% recovery of cholesterol, identified by m.m.p. and infrared spectrum.

**1-(3,5-Dioxo-6-oxa-4-azatetracosyl)triphenylphosphonium Bromide.**—Substitution of triphenylphosphine for pyridine in procedure B gave, after two recrystallizations from ethyl acetate, 9.3 g. (60%) of colorless crystals, m.p. 99–102°.

*Anal.* Calcd. for  $C_{40}H_{55}BrN_2O_3P$ : C, 67.6; H, 8.03; Br, 11.3; N, 1.97; P, 4.36. Found: C, 66.9; H, 8.3; Br, 11.5; N, 1.8; P, 4.1.

**1-(3,5-Dioxo-6-oxa-4-azatetracosyl)tri-*n*-butylphosphonium Bromide.**—Substitution of tri-*n*-butylphosphine for pyridine in procedure B gave 6.1 g. (42%) of colorless needles, m.p. 88.5–89.5°.

*Anal.* Calcd. for  $C_{34}H_{59}BrN_2O_3P$ : C, 63.0; H, 10.6; Br, 12.3; N, 2.15; P, 4.76. Found: C, 62.7; H, 10.4; Br, 12.6; N, 2.3; P, 4.6.

**II. Eliminations. Octadecyl Acrylylcarbamate.**—A solution of 6.44 g. (0.0143 mole) of octadecyl  $\beta$ -bromopropionylcarbamate,<sup>3</sup> 1.45 g. (0.0143 mole) of triethylamine and 65 ml. of acetonitrile was refluxed overnight, filtered while hot, and the filtrate was allowed to cool to room temperature. The solid was filtered, washed with acetonitrile, and air-dried to give 4.38 g. (83.6%) of white crystals, m.p. 88–89°.

*Anal.* Calcd. for  $C_{22}H_{41}NO_3$ : C, 72.0; H, 11.2; N, 3.82. Found: C, 71.8; H, 11.4; N, 3.5.

The acetonitrile filtrate was concentrated on a steam bath under water-pump vacuum to give 2.48 g. (95.3%) of triethylamine hydrobromide.

*Anal.* Calcd. for  $C_6H_{15}BrN$ : C, 39.6; H, 8.80; Br, 44.0; N, 7.70. Found: C, 39.7; H, 8.7; Br, 44.0; N, 7.8.

Similar treatment of 10.0 g. (0.0223 mole) portions of octadecyl  $\beta$ -bromopropionylcarbamate with 4.1 g. (0.022 mole) of tri-*n*-butylamine and with 2.52 g. (0.0223 mole) of *N*-ethylpiperidine gave octadecyl acrylylcarbamate in 92% and 85% yields, respectively. When 2.50 g. (0.0223 mole) of 1,4-diazabicyclo[2.2.2]octane was used, 1.8 g. (42%) of the amine monohydrobromide, purified by boiling in dioxane and recrystallizing from ethanol, was obtained. It decomposed upon heating, starting at 270°.

*Anal.* Calcd. for  $C_6H_{13}BrN_2$ : C, 37.3; H, 6.74; Br, 41.3; N, 14.5. Found: C, 37.4; H, 6.9; Br, 40.0; N, 14.5.

Use of 1.26 g. (0.0112 mole) of 1,4-diazabicyclo[2.2.2]octane gave 1.7 g. (56%) of the amine dihydrobromide, m.p. 290–300° dec., after two recrystallizations from dimethylformamide.

*Anal.* Calcd. for  $C_6H_{14}Br_2N_2$ : C, 26.3; H, 5.11; Br, 58.4; N, 10.2. Found: C, 27.9; H, 5.3; Br, 56.2; N, 10.4.

**Cholesteryl 3-Acrylylcarbamate.**—Similar treatment of cholesteryl 3- $\beta$ -bromopropionylcarbamate with one equivalent of tri-*n*-butylamine gave a 79% yield of colorless powder, m.p. 200–202°, not improved by recrystallization from dimethylformamide.

*Anal.* Calcd. for  $C_{31}H_{49}NO_3$ : C, 77.0; H, 10.1; N, 2.9. Found: C, 77.4; H, 10.3; N, 2.9.

**Ethyl Acrylylcarbamate.**—Similar treatment of ethyl  $\beta$ -bromopropionylcarbamate with one equivalent of triethylamine gave a 75% yield of triethylamine hydrobromide. Work-up of the filtrate gave, after recrystallization from 1:1 benzene-ligroin (b.p. 66–75°), a 79% yield of colorless crystals, m.p. 80–82°.

*Anal.* Calcd. for  $C_6H_9NO_3$ : C, 50.3; H, 6.30; N, 9.78. Found: C, 50.6; H, 6.4; N, 9.8.

**Acknowledgment.**—The authors are grateful to Dr. D. L. Fields, of these laboratories, for helpful discussions during the course of this work, and to Mrs. M. L. Klein and Miss E. M. Kekwick for preparing some of the starting materials.

## Ring Enlargement Reactions of Bicyclo[2.2.1]-heptane Derivatives

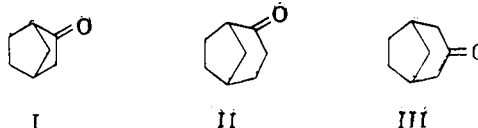
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Utilization of bicyclo[2.2.1]heptane derivatives as precursors for the synthesis of bicyclo[3.2.1]octane derivatives is of interest owing to the availability of the former and the lack of general syntheses of the latter. Two potential ring expansion reactions of norbornyl derivatives have been investigated in this study, namely, the reaction of diazomethane with norcamphor(I) and solvolysis of 2-*exo*- and *endo*-hydroxymethylnorbornyl tosylates (IV).

Reaction of equimolar quantities of norcamphor (I) and diazomethane led to a complex mixture which contained five major components. Three of them were shown by gas chromatography to be norcamphor, bicyclo[3.2.1]octanone-2 (II), and bicyclo[3.2.1]octanone-3 (III). The last two peaks were very likely

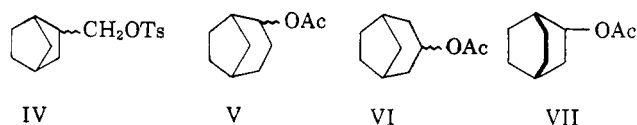


(1) Abstracted in part from the B. S. thesis of R. J. T., Rutgers, 1962.

nine-carbon ketones, the result of further reaction of diazomethane with the eight-carbon ketones.

The ratio of II to III, 1:1.6, indicated that migration of the methine carbon was slightly favored over migration of the methylene carbon, in contrast to the recent results of House, Grubbs, and Gannon.<sup>2</sup> It was necessary to investigate the possibility that this ratio should probably be corrected since further reaction of the two ketones with diazomethane would probably proceed at different rates. In a second experiment, only 5% of the theoretical amount of diazomethane was allowed to react with norcamphor. Under these conditions, the ratio of II to III was 2 to 1 in good agreement with the ratio (2:1) of propyl to isopropyl migration aptitudes that can be calculated from the data of House and co-workers.<sup>2</sup> The interesting conclusion that can be drawn from these results is that the 2-ketone must react faster than the 3-ketone with the second mole of diazomethane.

The second part of this study was concerned with the acetolyses of the *exo*- and *endo*-norbornylmethyl tosylates corresponding to IV. Unfortunately, product analyses could not be carried out directly; it was necessary to convert the acetate esters<sup>3</sup> into the correspond-

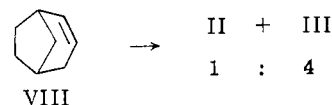


ing ketones. In both cases, the major product was the 2-ketone, the result of methylene migration.

These results are surprising both from an electronic point of view and a steric point of view. Electronically, one would expect<sup>4</sup> the more highly substituted carbon to migrate in preference to the methylene carbon. Sterically, one might apply the arguments advanced to explain anomalous Baeyer-Villiger reactions.<sup>5</sup> That is to say, migration of methylene in the *exo*-tosylate must proceed *via* a transition state which resembles a boat-form of a cyclohexane ring, whereas migration of the methine carbon would proceed *via* a transition state which resembles a chair form. Thus, both the electronic factor and the steric factor favor methine migration with the *exo*-tosylate. With the *endo*-tosylate, the chair-boat situation is reversed and the steric argument favors methylene migration and the electronic effects favor methine migration. Although the *exo*-tosylate does lead to a higher 3-ketone/2-ketone ratio than that obtained from the *endo*-tosylate, 1:14 *vs.* 1:70, it is

likely that some more subtle conformational effect is controlling these migrations.

The reference sample of bicyclo[3.2.1]octanone-3 used in this study was prepared by a new route. Bicyclo[3.2.1]octene-2 (VIII) was subjected to the elegant hydroboration-oxidation procedure of Brown and Garg<sup>6</sup> to give a 70% yield of a 1:4 mixture of II and III.



The n.m.r. spectrum of VIII was surprisingly complex. The olefinic protons form an AB system with  $J = 9.5$  c.p.s. Each of the high field peaks were further split into seven peaks with separations of 1 to 2 c.p.s. The low field multiplet was also split several times and a  $J$  of 6.5 c.p.s. could be extracted for one of the couplings.

#### Experimental<sup>7</sup>

**Reaction of Norcamphor with Diazomethane.**—A mixture of 13 g. (0.058 mole) of *N*-nitroso-*N*-methyl-*p*-toluenesulfonamide, 5.5 g. (0.050 mole) of norcamphor, 15 ml. of 95% ethanol and 1 ml. of water was cooled to 2° and treated dropwise with a solution of 1.5 g. of potassium hydroxide in 10 ml. of 50% aqueous ethanol. The temperature was kept between 10 and 15° during the addition time (15 min.). Stirring was continued for 45 more minutes after which time the solution was made acidic with 2 *N* hydrochloric acid. Ten grams of potassium hydroxide was then added with enough ethanol to make the solution homogeneous. After heating at reflux for 3 hr. most of the ethanol was distilled under vacuum and the residue was extracted with petroleum ether (30–60°). After drying and evaporation of the extracts there was obtained 4.4 g. of a semisolid mass.

The product was analyzed on an 8-ft. Carbowax 20M (20%) column at 190°. Five main peaks were observed. The peak with the shortest retention time corresponded to norcamphor; the next two peaks (in the ratio 1.6 to 1) were III and II in that order. The last two peaks were not identified. The first three components were also identified on a 6-ft. Craig polyester (20%) column at 143°.

The experiment was repeated with only 5% of the theoretical amount of diazomethane. There was obtained 4.6 g. of product in which the ratio of III to II was 1 to 2. The amount of by-products was reduced. The yields of 8-carbon ketones were small in both cases.

**Solvolyses of 2-*exo*- and 2-*endo*-Hydroxymethylnorbornane *p*-Toluenesulfonates.**—The two esters were prepared by the procedures published by Berson, *et al.*<sup>8</sup> The *exo*-tosylate was an oil (lit.,<sup>8</sup> m.p. 41–42°); and the *endo*-tosylate was a solid m.p. 41.5–43.5° (lit.,<sup>8</sup> m.p. 44–45°). The homogeneity of the tosylates was checked by their infrared spectra as well as by gas chromatography of the intermediate norbornenyl methanols from which they were derived.

Solvolyses were carried out at 120° for 30 hr. in 30 ml. of glacial acetic acid containing 4.9 g. (0.0175 mole) of tosylate, 2.9 g. of sodium acetate and 1.3 g. of acetic anhydride.

The reaction mixtures were diluted with water and extracted with pentane. After washing with sodium bicarbonate solution the extracts were dried and evaporated to give 2.2 g. of product from the *endo*-tosylate and 2.5 g. from the *exo*-tosylate. The mixed acetates could not be resolved on the following gas chromatography columns: Carbowax 20M (150°), Craig polyester (177°), and silicone SE-30 (130°). The acetates were then con-

(2) H. O. House, E. J. Grubbs, and W. F. Gannon, *J. Am. Chem. Soc.*, **82**, 4099 (1960).

(3) J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **84**, 682 (1962) reported that solvolysis of the *endo*-brosylate corresponding to IV gave mainly a mixture of acetates V and virtually no VI or VII. P. Nedenskov, H. Heide, and N. Clauson-Kaas, *Acta Chem. Scand.*, **16**, 246 (1962) reported that solvolysis of a mixture of tosylates corresponding to IV led to an 88% yield of products corresponding to V.

(4) For an elegant study of the migrational aptitude of alkyl groups to a cationic center see M. Stiles and R. P. Mayer, *J. Am. Chem. Soc.*, **81**, 1497 (1959). Unpublished results of S. Winstein, R. P. Magee, and K. Nelson quoted by J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959) also support the sequence 3° > 2° > 1°.

(5) M. F. Murray, B. A. Johnson, R. R. Pederson, and A. C. Ott, *ibid.*, **78**, 981 (1956); J. Meinwald and E. Frauenglass, *ibid.*, **82**, 5235 (1960).

(6) H. C. Brown and C. P. Garg, *ibid.*, **83**, 2951 (1961).

(7) The n.m.r. spectrum was determined on a Varian Model A-60 spectrometer using tetramethylsilane as internal standard. Melting points are corrected. Relative g.l.c. peak areas were used to calculate product ratios.

(8) J. A. Berson, J. S. Walla, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Am. Chem. Soc.*, **83**, 3996 (1961).

verted to alcohols by reduction in ether with lithium aluminum hydride. The ethereal solutions were analyzed on the Craig (120°) and Carbowax (157°) columns. Although complete resolution of the products was not achieved, the major product from the *endo*-tosylate was *endo*-bicyclo[3.2.1]octanol-2 (*vide infra*). The products from the *exo*-tosylate appeared to be approximately equal amounts of *exo*- and *endo*-bicyclo[3.2.1]octanol-2. Small amounts of olefins were present in both samples.

The ether solutions were then oxidized using the new procedure of Brown and Garg.<sup>9</sup> After 2 hr. at room temperature with 5 ml. of dichromate solution, there was obtained 0.6 g. (80%) of ketones from 1.0 g. of acetates (both series). The ratios of 2-ketone to 3-ketone were determined on an 8-ft. Carbowax column at 180°; the ratios were 70:1 (*endo*) and 14:1 (*exo*). Although bicyclo[2.2.2]octanone could not be resolved under these conditions, it was concluded from analysis of these ketones on a 6-ft. Craig column at 142° that essentially none of this material was present.

2-*exo*- and *endo*-Bicyclo[3.2.1]octanols (mixed) and bicyclo[3.2.1]octanone-2 were prepared according to the procedure from norbornylmethyl amine given by Walborsky and co-workers.<sup>10</sup>

Bicyclo[2.2.2]octanone-2 was prepared in admixture with bicyclo[3.2.1]octanone-2. Bicyclo[3.2.1]octene-2 (*vide infra*) was treated with sulfuric acid and acetic acid according to directions given by Alder, *et al.*<sup>11</sup> A ternary mixture of acetates is obtained which contains the esters of *cis*- and *trans*-bicyclo[3.2.1]octanol-2 and bicyclo[2.2.2]octanol-2.<sup>12</sup> The acetates were reduced to the alcohols with lithium aluminum hydride in ether. The two ketones were prepared by oxidation by the procedure of Brown and Garg.<sup>9</sup> From 8 g. of alcohols there was obtained 5 g. of ketones which contained bicyclo[3.2.1]octanone-2 and bicyclo[2.2.2]octanone in a ratio of 2.5 to 1. The two were separated by gas chromatography on the Carbowax column. The infrared spectrum of the former was essentially the same as the spectrum of this material prepared above.

**Hydroboration-Oxidation of Bicyclo[3.2.1]octene-2.**—To a solution of 3.85 g. (0.036 mole) of olefin VIII<sup>13</sup> in 40 ml. of dry ether was added 1.10 g. (0.029 mole) of sodium borohydride and about 10 mg. of zinc chloride. A solution of 1.5 ml. (*ca.* 0.012 mole) of boron trifluoride-etherate in 5 ml. of ether was added over 5 min. The slurry was stirred for 2 hr. at room temperature after which time the excess borohydride was decomposed with 4 ml. of water. Sodium dichromate solution<sup>9</sup> (45 ml.) was added and the two-phase system was stirred over night. After separation of the layers and further extraction with ether, there was obtained 3.1 g. (70%) of a semisolid mixture of ketones. Confirmation of the presence of bicyclo[3.2.1]octanone-3 was effected through the preparation of the known dibenzilidene derivative, m.p. 187.5–190° (lit.,<sup>13</sup> m.p. 187°).

The gas chromatogram showed two main peaks in a ratio of 4 to 1. The smaller one had a retention time identical with that of bicyclo[3.2.1]octanone-2 on both Carbowax and Craig columns.

Bicyclo[3.2.1]octene-2, b.p. 124° (lit.,<sup>11</sup> b.p. 135°) was prepared by treatment of a mixture of *exo*- and *endo*-norbornylmethanol with phosphoric acid.<sup>11</sup> The mixed alcohols were prepared by catalytic reduction of "Cyclol," a commercially available mixture of 2-*exo*- and 2-*endo*-hydroxymethyl-5-norbornene.<sup>14</sup> The n.m.r. spectrum (neat) showed olefinic proton absorption at –354 and –322 c.p.s. with  $J = 9.5$  c.p.s. A further coupling of 6.5 c.p.s. could be extracted from the multiplet at –354 c.p.s. Each peak of the –322 system was split into at least seven peaks. The aliphatic protons appeared as a complex multiplet between –110 and –137 c.p.s.

**Acknowledgment.**—The authors wish to thank the National Science Foundation for funds toward the purchase of the spectrometer.

(9) H. C. Brown and C. Garg, *J. Am. Chem. Soc.* **83**, 2952 (1961).

(10) A. A. Youssef, M. E. Baum, and H. M. Walborsky, *ibid.*, **81**, 4709 (1959).

(11) K. Alder, H. Krieger, and H. Weiss, *Ber.*, **88**, 144 (1955).

(12) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1397 (1961).

(13) K. Alder and R. Reubke, *Ber.*, **91**, 1525 (1958).

(14) We are indebted to the Interchemical Corp., New York, N. Y., for generous quantities of this material.

## Reaction of 2-Dimethylaminoethyl Chloride with Magnesium

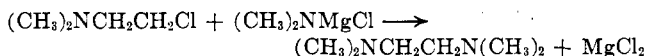
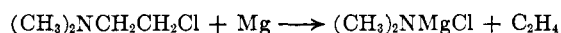
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Reactions of  $\beta$ -halogen ethers, amines, and sulfides with metals were reviewed briefly by Amstutz.<sup>2</sup> He attempted to show that the elimination reaction, which resulted in the formation of ethylene, was general for  $\beta$ -halogen ethers, amines, and sulfides. Although much data is available on reaction of  $\beta$ -haloalkoxy compounds,<sup>3</sup> less is reported on reaction of  $\beta$ -halo sulfides with metals. However, such reaction has been realized with  $\beta$ -bromoethyl phenyl sulfide<sup>2</sup> and mustard.<sup>4</sup> Confirmation of the lack of reactivity of 2-haloamines is given by Mason and Block<sup>5</sup> who found that *N*- $\beta$ -chloroethylmorpholine did not react with magnesium, by Amstutz<sup>2</sup> who verified their work, and by Miescher, Rieben, and Marxer<sup>6a,b</sup> who state that 2-diethylaminoethyl chloride does not react with magnesium under the usual conditions.

We have found that 2-dimethylaminoethyl chloride does indeed react with magnesium in ether and in tetrahydrofuran. Ethylene is eliminated and *N,N,N',N'*-tetramethylethylenediamine is formed as a result of the interaction of *N*-chloromagnesiumdimethylamine and 2-dimethylaminoethyl chloride. The yield of ethylene, isolated as ethylene bromide, was 55.3% (based on magnesium consumed) and the amount of the tetramethylethylenediamine was 17.5%. The low yield of the isolated nitrogenous derivative is indicative of the further reaction of the eliminated species. The reaction can be summarized as shown.



Therefore, it appears that the  $\beta$ -halogen elimination reaction with magnesium is indeed general for ethers, amines, and sulfides, and perhaps with other elements of groups V and VI. Since a negative Gilman test for the Grignard reagent was obtained in this reaction, in agreement with the experience of Amstutz,<sup>2</sup> Mason and Block,<sup>5</sup> and Goertner<sup>3c</sup> with  $\beta$ -haloalkoxides, and since no Grignard reaction product resulted when benzaldehyde was added in one of our experiments, it may be

(1) Present address: Hoffmann-LaRoche, Inc., Nutley 10, N. J.

(2) E. D. Amstutz, *J. Org. Chem.*, **9**, 310 (1944).

(3) (a) V. Grignard, *Compt. rend.*, **138**, 1048 (1904); (b) L. C. Swallen and C. E. Boord, *J. Am. Chem. Soc.*, **52**, 651 (1930); (c) Goertner, *ibid.*, **73**, 4400 (1951); (d) Dykstra, Lewis, and Boord, *ibid.*, **52**, 3396 (1930); (e) S. J. Cristol and L. E. Rademacher, *ibid.*, **81**, 1600 (1959); (f) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112 (1959); (g) H. O. House and R. S. Ro, *J. Am. Chem. Soc.*, **80**, 182 (1958).

(4) Kretov, *J. Russ. Phys. Chem. Soc.*, **61**, 2345 (1929); *Chem. Abstr.*, **24**, 3750 (1930).

(5) J. P. Mason and H. W. Block, *J. Am. Chem. Soc.*, **62**, 1447 (1940).

(6) (a) K. Miescher, Rieben, and A. Marxer, U. S. Patent 2,211,664 (1948); (b) Since submission of this manuscript, the work of J. Sadet and M. P. Rumpf, *Compt. rend.*, **254**, 3105 (1962), has come to our attention. They failed to obtain reaction of magnesium and diethylaminoethyl chloride, but claimed that prolonged heating of tetraethylpiperazine dichloride with magnesium in tetrahydrofuran gave tetraethylethylenediamine in 70% yield. Experimental details are lacking however.