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.[9] 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.[10]

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.*[11] 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.[12] 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.[9] 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[11] 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[9] (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 mixtures of ketones. Confirmation of the presence of bicyclo[3.2.1]octanone-3 was effected through the preparation of the known dibenzilidine derivative, m.p. 187.5–190° (lit.,[13] 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.,[11] b.p. 135°) was prepared by treatment of a mixture of *exo*- and *endo*-norbornylmethanol with phosphoric acid.[11] The mixed alcohols were prepared by catalytic reduction of "Cyclol," a commercially available mixture of 2-*exo*- and 2-*endo*-hydroxymethyl-5-norbornene.[14] 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.

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[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).

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

$$(CH_3)_2NCH_2CH_2Cl + Mg \longrightarrow (CH_3)_2NMgCl + C_2H_4$$

$$(CH_3)_2NCH_2CH_2Cl + (CH_3)_2NMgCl \longrightarrow (CH_3)_2NCH_2CH_2N(CH_3)_2 + MgCl_2$$

Therefore, it appears that the β-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,[2] Mason and Block,[5] and Goertner[3c] with β-haloalkoxides, and since no Grignard reaction product resulted when benzaldehyde was added in one of our experiments, it may be

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[1] Present address: Hoffmann-LaRoche. Inc., Nutley 10, N. J.

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

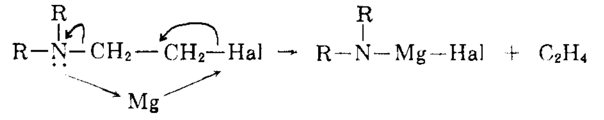
[3] (a) V. Grignard, *Compt. rend.*, **138**, 1048 (1904); (b) L. C. Swallen and C. E. Boord, *J. Am. Chem. Soc.*, **52**, 651 (1930); (c) Goertner, *ibid.*, **73**, 4400 (1951); (d) Dykstra, Lewis, and Boord, *ibid.*, **52**, 3396 (1930); (e) S. J. Cristol and L. E. Rademacher, *ibid.*, **81**, 1600 (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).

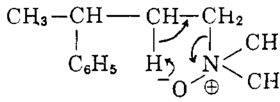
[5] J. P. Mason and H. W. Block, *J. Am. Chem. Soc.*, **62**, 1447 (1940).

[6] (a) K. Miescher, Rieben, and A. Marxer, U. S. Patent 2,211,664 (1946); (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 tetraethylpiperazinium dichloride with magnesium in tetrahydrofuran gave tetraethylethylenediamine in 70% yield. Experimental details are lacking however.

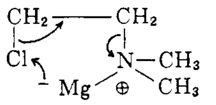
concluded that no Grignard reagent is actually formed. Instead a mechanism for this elimination is suggested whereby coördination of the metal with nitrogen occurs resulting in a displacement in the direction shown.



Further, we note the similarity between the elimination described here (I) and that observed in the Cope elimination of *N*-oxides (II),[7a,b] where retention of configuration was observed.



II



I

Experimental

All melting points are corrected.

I. **Preparation of 2-Dimethylaminoethyl Chloride.**—2-Dimethylaminoethyl chloride was isolated from its hydrochloride by addition of excess ice-cold sodium hydroxide to a cold concentrated solution of the amine hydrochloride covered with a layer of ether (in hood). The two phases were separated, the aqueous phase further extracted with ether, and the combined ether extracts dried over anhydrous sodium sulfate. Final drying was achieved by storage over calcium hydride. The free base was obtained by distillation at atmospheric pressure without a column. A fraction, b.p. 106–110°, was collected and stored over calcium hydride until used. In several 0.5-mole and 2-mole runs, yields of 54 to 67% of free 2-dimethylaminoethyl chloride were thus obtained. The yield is low because this amino chloride undergoes dimerization to form *N,N,N',N'*-tetramethylpiperazinium dichloride.[8]

II. **Reaction of 2-Dimethylaminoethyl Chloride (DAEC) and Magnesium.**—Two preliminary experiments were carried out. In the first, 0.15 g.-atom of magnesium was allowed to react with 0.05 mole of ethylene bromide in ether, followed by reaction with 0.1 mole of 2-dimethylaminoethyl chloride. A white precipitate formed which prevented further reaction. In the second, 1.75 g.-atoms of magnesium was found to react spontaneously with a portion of 1.34 moles of 2-dimethylaminoethyl chloride in 72 g. of tetrahydrofuran (THF), when the mixture was warmed to 55–60°. Additional portions of the 2-dimethylaminoethyl chloride and tetrahydrofuran were added. Evolution of a gas, took place, which decolorized bromine in chloroform. The gas was not absorbed by aqueous hydrochloric acid. Addition of 1.0 mole of benzaldehyde, and reflux, was followed by the usual Grignard work-up procedure. No benzaldehyde derivative was isolated, but 0.44 g.-atom of magnesium was recovered unchanged.

Further study was carried out in a conventional Grignard reactor, except that the condenser exit was connected in series with a Dry Ice trap, a safety flask to protect against pressure variations, and two bromine absorption flasks, respectively. The first bromine flask was immersed in an ice bath, and the second vented into the hood.

To 5.35 g. (0.22 g.-atom) of magnesium contained in the reaction flask was added portionwise one quarter to one half of 23.8 g. (0.22 mole) of dry 2-dimethylaminoethyl chloride (b.p. 108–110°) along with 10–15 ml. of pure dry tetrahydrofuran. Since the reaction did not commence on heating to 70°, additional 2-dimethylaminoethyl chloride was added portionwise until all was added. The reaction did not proceed. At this point 2–3 ml. of a reacting mixture of magnesium, tetrahydrofuran, and *ca.* 0.5 ml. of ethylene bromide was added. The reaction commenced vigorously with gas evolution and frothing. When the activity ceased, 8.2 g. (0.34 g.-atom) of magnesium turnings was added. This was followed by the dropwise addition of 36.1 g. (0.337 mole) of 2-dimethylaminoethyl chloride, along with the separate addition of 125 ml. of tetrahydrofuran. At the end of the exothermic stage the mixture was refluxed 40 min. further. It was then cooled and unchanged magnesium was removed by decantation of the supernatant liquid without exposure to the atmosphere. The recovered magnesium was washed with ether several times, dried, and weighed 4.46 g. (0.184 g.-atom). The Dry Ice trap was found to contain 12.4 g. of liquid which gave, when distilled through a 6-in. Vigreux column, 11.7 ml. of tetrahydrofuran, b.p. 64–67°, further identified by its infrared spectrum. A 2.7-ml. forerun was not investigated. The bromine from the absorption flasks was combined and distilled through a 6-in. Vigreux column. Isolated was 39.8 g. of ethylene bromide (0.212 mole), b.p. 127–131°, 55.3% based upon the magnesium consumed. It was identified by comparison of its infrared spectrum with that of an authentic sample of 1,2-ethylene dibromide. The residue of black tar remaining in the distillation flask weighed 10.0 g. and was not further investigated.

The tetrahydrofuran reaction mixture gave a negative Gilman-Grignard reagent test. It was hydrolyzed by addition of a solution of 100 g. of concd. hydrochloric acid in 500 ml. of water. This was followed by addition of a solution of 80 g. of sodium hydroxide in 160 ml. of water. During the hydrolysis and neutralization no gases were evolved which were soluble in ice-cold ether contained in an absorption flask. The aqueous alkaline hydrolysate was next extracted with four 150-ml. portions of ether. The combined extracts were dried over anhydrous potassium carbonate, and dry hydrogen chloride was passed in until no more precipitation occurred. The solid was removed by filtration and dried *in vacuo* over phosphorus pentoxide. It weighed 12.94 g. when dry and decomposed at 261–266°.

Anal.[9] Calcd. for $C_6H_{18}N_2Cl_2$: N, 14.82. Found: N, 14.43.

Recrystallization of 6.0 g. of this hydrochloride from methanol gave 3.6 g. of m.p. 295–296° dec.

Anal. Calcd. for $C_6H_{18}N_2Cl_2$: Cl, 37.49; N, 14.82. Found: Cl, 37.66; N, 14.69.

One gram of the hydrochloride was converted to the dipicrate, m.p. 258°. These facts identify the amine as *N,N,N',N'*-tetramethylethylenediamine.[10]

The alkaline hydrolysate remaining after extraction with ether was filtered and neutralized to pH 8. A solution of 30 g. of picric acid in 2 l. of water was added and the picrate obtained weighed 16.5 g. when dry and melted at 232–240°. Excess picric acid did not cause further precipitation. One gram of this material gave 0.87 g. of crystals, m.p. 253–254° dec., when recrystallized from water. Infrared spectra of all of the picrates prepared in this work were identical. Material recovered from earlier attempts to prepare a benzoate and urethane gave additional 2.08 g. of the dipicrate. The total of picrates and hydrochlorides thus isolated was 0.098 mole, 17.5%.

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(8) P. D. Bartlett, S. D. Ross, and C. G. Swain, *ibid.*, **69**, 2971 (1947).

(9) Analyses carried out by the Analytical Department of S. B. Penick & Co., Newark, N. J.

(10) Reported: *N,N,N',N'*-tetramethylethylenediamine dihydrochloride, dec. 300°, and dipicrate, dec. 252°; L. Knorr, *Ber.*, **37**, 3496 (1904).

Decarboxylation Studies. II. Preparation of Alkyl Phenyl Ketones[1,2]

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A recently published study[1] of the preparation of symmetrical, straight chain, aliphatic ketones has been extended to a study of the preparation of alkyl phenyl ketones by the thermal decarboxylation, in the liquid phase, of iron salts of mixtures of aliphatic and aromatic carboxylic acids. To the references recorded in the earlier publication[1] should be added the work of

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(1) Paper I of this series: R. Davis and H. P. Schultz, *J. Org. Chem.*, **27**, 854 (1962).

(2) Abstracted in part from the M.S. thesis of C. G., University of Miami, 1962.