a means of characterization. All new compounds were characterized by elemental analyses within 0.5% of the calculated values.

Nmr spectra were determined on a Varian A-60 instrument at its operating temperature (*ca.* 35°) on samples of 5% w/v in the solvent indicated in Table I. They were referenced against internal chloroform (τ 2.73), tetramethylsilane (τ 10.0), or both. Reported spectra were determined at 500 cps full scale width.

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The Reduction of *gem*-Dibromocyclopropanes to Monobromocyclopropanes with Methylmagnesium Bromide

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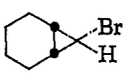
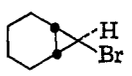
Methylmagnesium bromide in tetrahydrofuran solution reduces *gem*-dibromocyclopropanes to monobromocyclopropanes in good yields. Evidence is presented which suggests that this reaction occurs by a radical process with the hydrogen atom introduced into the product deriving from the solvent.

The conversion of the easily accessible *gem*-dibromocyclopropanes to monobromocyclopropanes has been a subject of some interest in recent years. Reagents which serve for this purpose include zinc dust in glacial acetic acid,[3] hydrogen (using a platinum catalyst in methanolic potassium hydroxide),[3] tri-*n*-butyltin hydride,[4] and the sodium salt of dimethyl sulfoxide (DMSO) in DMSO solution.[5] We report here that this reduction can be effected simply and in good yield by reaction of *gem*-dibromocyclopropanes with methylmagnesium bromide in tetrahydrofuran (THF) solution at room temperature.

Addition of 7,7-dibromobicyclo[4.1.0]heptane (henceforth 7,7-dibromonorcarane) to an equimolar quantity of methylmagnesium bromide in THF resulted in an exothermic reaction with precipitation of solid after a short induction period. Hydrolysis with saturated ammonium chloride gave an organic layer which was distilled to give a mixture of *cis*- and *trans*-7-bromonor-



cis-I



trans-I

carane (I) in 72.4% yield. Glpc analysis showed the *cis/trans* ratio to be 2.7. (In other experiments this ratio varied between this value and 2.2.) Similar reduction of 1,1-dibromo-2-*n*-amylcyclopropane was easily effected by this procedure, giving *trans*-1-bromo-2-*n*-amylcyclopropane (21%) and its *cis* isomer (54.2%). The monobromocyclopropanes thus produced were themselves unaffected by CH_3MgBr in THF at reflux.

Further work was concerned with a study of the mechanism of this apparently general reaction. In view of the known RMgX–R′X exchange reactions, which appear to be facilitated by THF solvent,[6] a mechanism involving exchange of CH_3MgBr with the *gem*-dibromocyclopropane to give II in the case of 7,7-

II

dibromonorcarane seemed a possibility that required consideration. Hydrolysis of II would then result in formation of the observed product. However, α-haloalkylmagnesium halides are, in general, not stable at room temperature,[7] and thus the survival of II until the hydrolysis step did not seem likely. That hydrolysis of II was not the reaction which produced product was shown by treatment of such a methylmagnesium bromide–7,7-dibromonorcarane reaction mixture with D_2O. The intervention of II as a *stable* intermediate in this reduction reaction would require formation in this case of 7-bromo-7-deuteronorcarane. However, the bromonorcarane obtained did not contain deuterium. Also, quenching of such a reaction mixture with trimethylchlorosilane gave only 7-bromonorcarane, not the trimethylsilyl derivative that might have been expected if II were a stable intermediate. Furthermore, nonhydrolytic work-up of such a CH_3MgBr + 7,7-dibromonorcarane reaction mixture gave 7-bromonorcarane.

Another possible mechanism, reduction of the dibromonorcarane directly by the Grignard reagent *via* a transition state such as III, was shown not to be operative by carrying out the reduction using CD_3MgI in THF. In this case also the 7-bromonorcarane isolated contained no deuterium.

III

Elimination of these possibilities leaves as possible alternatives (1) a route in which an α-bromocyclopropylmagnesium bromide such as II is only a transient intermediate which abstracts a hydrogen atom from a solvent molecule by a polar or a radical process, and (2) direct radical reduction of *gem*-dibromocyclopropanes by methylmagnesium bromide (eq 1 and 2), with the hydrogen atom introduced into the product being provided by the solvent as shown.

(1) Alfred P. Sloan Fellow, 1962–1966.

(2) Postdoctoral Research Associate, 1964–1966.

(3) K. Hofmann, S. F. Orchena, S. M. Sax, and G. A. Jeffrey, *J. Am. Chem. Soc.*, **81**, 992 (1959).

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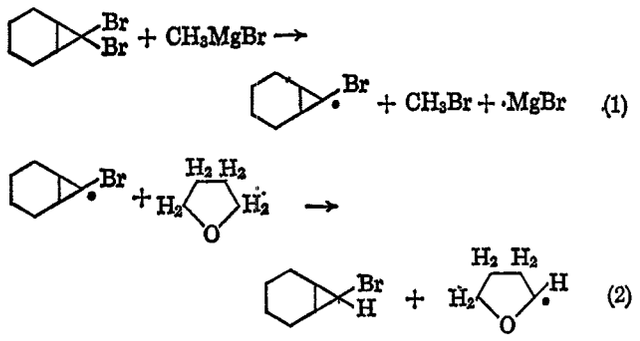

Radical reactions of Grignard reagents are known and usually observed in cases where the substrate which reacts with the Grignard reagent has a high electron affinity. Thus, to cite some recent examples, Maruyama[8] has reported on esr studies which demonstrated the appearance of a free radical of the ketyl type on interaction of arylmagnesium bromides with benzophenone and the formation of a radical, $C_6H_5N\ddot{O}\cdot$, when phenylmagnesium bromide reacted with nitrosobenzene. Russell and co-workers[9] have demonstrated the occurrence of electron transfer from *n*-butylmagnesium bromide to certain electron acceptors. It is known[4] that *gem*-dibromocyclopropanes are reduced very readily by tri-*n*-butyltin hydride, and such reactions have been shown[10] to be radical chain processes. The stereochemistry of the CH_3MgBr + 7,7-dibromonorcarane reaction provides some suggestion that a radical process may be involved. The 2.2–2.7 *cis/trans* 7-bromonorcarane ratios obtained in this study are to be compared with the 2.5 *cis/trans* ratio observed when 7,7-dibromonorcarane was reduced with tri-*n*-butyltin hydride.[4] In contrast, reduction of 7,7-dibromonorcarane with the sodium methylsulfinyl carbanion, a route which Gardner, *et al.*,[5] suggested almost certainly involves nucleophilic displacement on bromine to give a bromocyclopropyl carbanion which subsequently abstracts a proton from DMSO, gave a *cis/trans* ratio of 1/99. The close agreement between the stereochemical results of the tin hydride and CH_3MgBr reductions, however, does not demand the operation of a radical mechanism in the case of the Grignard reagent reduction, and a mechanism involving initial formation of an unstable α-bromocyclopropyl Grignard intermediate as a mixture of *cis* and *trans* isomers is not excluded.

In summary, the methylmagnesium bromide procedure for the partial reduction of *gem*-dibromocyclopropanes has considerable potential as a synthetic method. Most certainly, it is more practical than the tin hydride procedure. It is, however, lacking in stereospecificity, which is a drawback when it is compared with the NaDMSO method. The latter procedure appears to give only one isomer to the near exclusion of the other, a preparative virtue, provided one does not specifically require the other isomer.

Further investigation of this new reaction does not lie within the field of our present interests. A detailed study of its scope and of the organic functionality which is compatible with the reaction conditions, however, might prove to be worthwhile.

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It may be noted in conclusion that Moore and Ward[11] have found that the action of methyllithium on *gem*-dibromocyclopropanes produces allenes in excellent yield. With 7,7-dibromonorcarane these investigators obtained a number of products derivable from a bicyclo[4.1.0]heptylcarbene. Such products could not have been present in more than very minor yield in our reactions.

Experimental Section

General Comments.—All reactions were carried out under an atmosphere of prepurified nitrogen. Glpc analyses were carried out using an F&M Model 700 gas chromatograph (temperature range 40–210°, at 10°/sec, 45 psi of helium, 20% General Electric Co. SE-30 silicone gum on 80–100 mesh Chromosorb W). Infrared spectra were obtained using a Perkin-Elmer Model 337 infrared spectrophotometer, nmr spectra using a Varian Associates A-60 nmr spectrometer. Chemical shifts are given in parts per million downfield from tetramethylsilane. Combustion analyses were performed by Dr. S. M. Nagy, M.I.T. Microchemical Laboratory.

1,1-Dibromo-2-*n*-amylcyclopropane.—This compound was prepared from heptene-1 by the Doering–Hoffman procedure[12] in 52% yield, bp 121–123° (10 mm), $n^{25}D$ 1.4972.

Anal. Calcd for $C_8H_{14}Br_2$: C, 35.55; H, 5.18; Br, 59.25. Found: C, 35.85; H, 5.23; Br, 58.65.

Its infrared spectrum (pure liquid) showed bands at 3075 (w), 3010 (w), 2975 (vs), 2948 (vs), 2880 (s), 2868 (vs), 1476 (m), 1468 (m), 1449 (w), 1390 (w), 1350 (w), 1270 (w), 1230 (w), 1220 (w), 1118 (w), 1070 (m), 1045 (s), 1020 (w), 1009 (w), 971 (w), 928 (w), 903 (w), 882 (w), 837 (w), 800 (w), 730 (m), 683 (vs) cm^{-1}. 7,7-Dibromonorcarane, a known compound, was prepared using the same method.

Reaction of 7,7-Dibromonorcarane with Methylmagnesium Bromide in THF.—To a filtered solution of 0.05 mole of CH_3MgBr in 50 ml of THF in a 150 ml, three-necked flask, equipped with a mechanical stirrer, pressure-equalizing dropping funnel, and a condenser topped with a nitrogen inlet tube, was added with rapid stirring 12.7 g (0.05 mole) of 7,7-dibromonorcarane in 20 ml of THF. An exothermic reaction commenced about 20 min after the addition had been completed, and some white solid was formed. The reaction mixture was stirred at room temperature for 2 hr, then was hydrolyzed with saturated ammonium chloride solution. Hexane (40 ml) was added to the resulting mixture, and the separated organic layer was dried and fractionally distilled to give 6.3 g of 7-bromonorcarane (72.4% yield), bp 86–87° (24 mm), $n^{25}D$ 1.5142. Glpc analysis showed the presence of two components in 1:2.7 ratio in order of increasing retention time.

Anal. Calcd (mixed isomers) for $C_7H_{11}Br$: C, 48.02; H, 6.33; Br, 45.65. Found: C, 48.69; H, 6.30; Br, 45.07.

The compound with shorter retention time was identified as *trans*-7-bromonorcarane, $n^{25}D$ 1.5091 (lit.[4] $n^{25}D$ 1.5099). It had an nmr spectrum identical with that reported in the literature.[4] Its infrared spectrum (pure liquid) showed the following absorptions: 3050 (sh), 3028 (m), 2947 (vs), 2865 (vs), 1462 (m), 1410 (s), 1400 (w), 1362 (m), 1350 (m), 1260 (m), 1228 (vs), 1180 (w), 1148 (m), 1127 (w), 1080 (s), 1067 (s), 1012 (s), 968 (m), 957 (m), 926 (m), 907 (m), 902 (m), 845 (m), 830 (s), 783 (w), 762 (s), 725 (m), 685 (vs) cm^{-1}.

The other isomer was identified as *cis*-7-bromonorcarane, $n^{25}D$ 1.5179 (lit.[4] $n^{25}D$ 1.5182). It had an nmr spectrum identical with that reported for this isomer in the literature.[4] Its infrared spectrum (pure liquid) showed the following bands: 3051 (m), 3010 (s), 2950 (vs), 2940 (sh), 2880 (sh), 2870 (vs), 1472 (s), 1412 (vs), 1371 (m), 1350 (m), 1281 (s), 1260 (vs), 1223 (w), 1181 (w), 1160 (w), 1132 (m), 1093 (m), 1072 (w), 1015 (m), 969 (s), 958 (m), 929 (s), 904 (s), 825 (m), 809 (s), 758 (m), 725 (vs), 684 (w), 656 (s), 618 (vs) cm^{-1}.

A similar reaction carried out using 0.1 mole of CH_3MgBr in THF and 0.05 mole of 7,7-dibromonorcarane gave only 7-bromonorcarane (*cis/trans* ratio = 2.2) in 71% yield. A reaction (0.1 mole each of CH_3MgBr and 7,7-dibromonorcarane) was carried out as described above with the exception that the re-

(11) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

(12) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

action mixture was not hydrolyzed. Instead, the volatile materials were removed by a high vacuum trap-to-trap distillation and analyzed by glpc. A 78% yield (*cis/trans* ratio = 2.2) of 7-bromonorcarane was obtained. In still another such experiment carried out on a 0.05-mole scale the reaction mixture was quenched with D_2O. Trap-to-trap distillation at reduced pressure of the dried organic layer followed. The 7-bromonorcarane isomers (*cis/trans* ratio = 2.32) obtained in 73.3% yield were isolated by glpc. Their infrared spectra showed no bands attributable to C–D bonds, and analysis for deuterium content by the falling-drop method (J. Nemeth, Urbana, Ill.) showed that no deuterium had been incorporated. A similar reaction mixture was quenched with trimethylchlorosilane and hydrolyzed with saturated ammonium chloride. Distillation and glpc analysis of the organic layer showed the presence of only two components, *cis*- and *trans*-7-bromonorcarane (2.4:1 ratio) in 78% yield. No higher boiling organosilicon compounds could be detected.

Reaction of 7,7-Dibromonorcarane with CD_3MgI in THF.—The Grignard reagent was prepared from 0.036 mole of trideuteriomethyl iodide[13] in 25 ml of THF under argon. 7,7-Dibromonorcarane (0.036 mole) was added with vigorous stirring. The reaction mixture was stirred at room temperature (after the initial exotherm) for 2.5 hr and then was quenched with D_2O. The usual work-up procedure gave 7-bromonorcarane in 75% yield, $n^{25}D$ 1.5094, *cis/trans* ratio = 2.44. Infrared analysis showed no C–D bands, and analysis for deuterium by the falling-drop method demonstrated that no deuterium had been introduced.

Preparation of 1-Bromo-2-*n*-amylcyclopropane.—1,1-Dibromo-2-*n*-amylcyclopropane (13.5 g, 0.05 mole) was added slowly with stirring to 0.05 mole of CH_3MgBr in 30 ml of THF at room temperature under a nitrogen atmosphere. Some 15 min after completion of the addition, a vigorous, exothermic reaction occurred and solid was precipitated. The reaction mixture was stirred at room temperature for 2 hr, then was hydrolyzed with 10% hydrochloric acid. The dried organic layer was distilled *in vacuo* into a receiver at −78° and analyzed by glpc (isothermal, 20% SE-30 on Chromosorb W, at 172°, 15 psi of helium, *n*-dodecane external standard). The presence of 1-bromo-2-*n*-amylcyclopropane (75.3%) was demonstrated. The *cis/trans* ratio was 2.6. The combined isomers were analyzed.

Anal. Calcd for $C_8H_{15}Br$: C, 50.26; H, 7.85; Br, 41.88. Found: C, 50.42; H, 7.80; Br, 41.70.

trans-1-Bromo-2-*n*-amylcyclopropane, $n^{25}D$ 1.4579, had the shorter glpc retention time. Its nmr spectrum (CCl_4) showed a complex multiplet from 0.91 to 1.35 ppm and a quintet (J = 4.0 cps) centered at 2.5 ppm.

cis-1-Bromo-2-*n*-amylcyclopropane, $n^{25}D$ 1.4636, showed doublets at 0.98 and 1.4 ppm and a sextet (J = 7.5 cps) centered at 3.0 ppm.

Acknowledgments.—The authors are grateful to the National Science Foundation and to the Alfred P. Sloan Foundation for generous support of this work.

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Cyclic Aminimides

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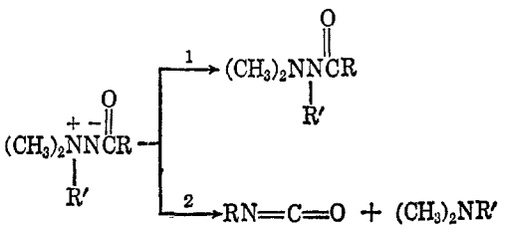
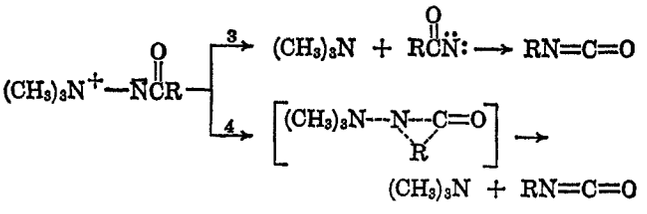
The preparation and reactions of cyclic aminimides of the type shown (A) are described. When R is benzyl a Wawzonek rearrangement takes place with the benzyl group migrating to the adjacent nitrogen atom. However, when R is methyl neither migration nor a Curtius N–N cleavage as observed in the acyclic case occurs. The possible implications of this result as applied to the mechanism of isocyanate formation is briefly discussed.

Recently aminimides which have their negative charge delocalized by means of an adjacent carbonyl group have been investigated and found to possess unusual chemical properties. Wawzonek and Yeakey[1] have found that compounds of this class, where R′ is benzyl or allyl, when heated undergo a Stevens-type rearrangement (1). Gibson and Murray,[2] on the other hand, have shown that when R′ is an alkyl group other than benzyl or allyl, N–N bond cleavage results to yield an isocyanate and tertiary amine (2), a result

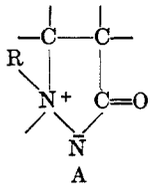


which has recently been confirmed by Wawzonek and Gueldner.[3] Isocyanate formation is of particular interest and can be assumed like the Curtius rearrangement to proceed by either a nitrene (3) or concerted pathway (4).

(1) S. Wawzonek and E. Yeakey, *J. Am. Chem. Soc.*, **82**, 5718 (1960).
(2) M. S. Gibson and A. W. Murray, *J. Chem. Soc.*, 880 (1965).
(3) S. Wawzonek and R. C. Gueldner, *J. Org. Chem.*, **30**, 3031 (1965).



A cyclic aminimide (structure A designated below)



would be expected to give similar rearrangements, a Wawzonek rearrangement if a benzylic substituent is present, and, if nitrene is an intermediate and R is methyl, a β-amino isocyanate. If on the other hand, nitrene is not an intermediate in isocyanate formation, it is doubtful that isocyanate would be formed in the cyclic case. A bicyclic transition state (i) would be required for a concerted mechanism which in all probability would possess a high energy of activation. To test these hypotheses, a cyclic aminimide (III) was