financial support and Dr. E. A. Hill, University of Wisconsin—Milwaukee, for obtaining the 100-MHz nmr spectra for us.

Registry No.—**1**, 4393-06-0; **5**, 93-55-0; **6**, 40600-05-3; **7**, 40600-06-4; **8**, 17180-39-1; **9**, 40132-63-6; **10**, 40132-64-7; **11**, 40587-41-5; **12**, 22665-13-0; **13**, 6051-52-1; **14**, 495-40-9; **15**, 4518-65-4.

Conversion of 1,3-Dihalopropanes to Propanes and/or Cyclopropanes on Treatment with Different Reducing Agents[1]

MELVIN S. NEWMAN,* G. S. COHEN,[2] ROBERT F. CUNICO,[3] AND L. W. DAUERNHEIM[4]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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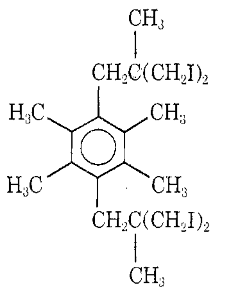
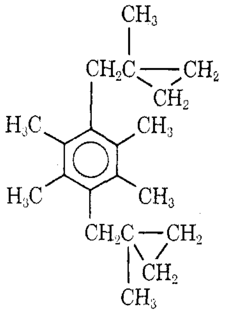
Treatment of 2-benzyl-2-methyl-1,3-diiodopropane (**3a**) with lithium aluminum hydride in ether or chromous sulfate in dimethylformamide yields mainly 1-benzyl-1-methylcyclopropane (**5**), whereas, when tri-*n*-butyltin hydride is used, solvent-dependent mixtures of **5** and neopentylbenzene (**6**) result. When 2-benzyl-2-methyl-1,3-dibromopropane (**3b**) is treated with $LiAlH_4$, solvent-dependent mixtures of **5** and **6** are formed. When 2-benzyl-1,3-dihalopropanes are treated with $LiAlH_4$, mixtures rich in isobutylbenzene, **8**, are obtained.

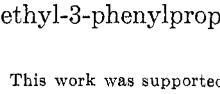
The cyclization of **1** to **2** on treatment with lithium aluminum hydride, W-2 Raney nickel, and sodium in liquid ammonia has been reported.[5] A similar reduction of 1,3-diiodocyclobutane to bicyclobutane by $LiAlH_4$ has been observed.[6] Because of continuing interest in this type of reaction, further studies on the reduction of 1,3-dihalides with a variety of reducing agents have been made. As substrates 2-benzyl-2-methyl-1,3-dihalopropanes **3a–c** and 2-benzyl-1,3-dihalopropanes **4a–c** were chosen.



1



2



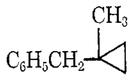
$C_6H_5CH_2C(CH_3)(CH_2X)_2$

3a, X = I
b, X = Br
c, X = Cl

$C_6H_5CH_2CH(CH_2X)_2$

4a, X = I
b, X = Br
c, X = Cl

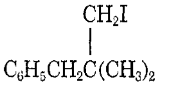
Reductions with Lithium Aluminum Hydride.—Reduction of **3a** with $LiAlH_4$[7] in refluxing ether, tetrahydrofuran (THF), and dioxane yielded mixtures of 1-benzyl-1-methylcyclopropane (**5**) (about 95%) and neopentylbenzene (**6**) (about 5%). When pure 2,2-dimethyl-3-phenylpropyl iodide (**7**) was reduced similarly only **6** was formed. Thus, **5** is formed directly from **3a**. Competitive reduction of **3a** and **7** showed that **3a** is reduced slightly faster[4] than **7**. These results indicate that two competitive processes are involved, one leading directly to the formation of **5** and the second to **7** which is then further reduced to **6**.



5

$C_6H_5CH_2C(CH_3)_3$

6



$C_6H_5CH_2C(CH_3)_2CH_2I$

7

In contrast to the behavior of **3a**, reduction of the dibromide **3b** with $LiAlH_4$ in THF yielded mixtures of **5** and **6** in a ratio of about 5:95, respectively. In dioxane the ratio was about 30:70. Reduction of the dichloride **3c** proved too slow in ether or THF to be considered as a synthetic route to hydrocarbons. In refluxing dioxane reduction occurred slowly to yield about 18% of **5** and 62% of **6**.

In order to compare the behavior of less hindered 1,3-dihalides with that of **3a–c** the reduction of the corresponding halides **4a–c** was studied. In all cases, isobutylbenzene (**8**) was the main product. With the iodide **4a** small amounts of benzylcyclopropane (**9**) were produced but with **4b** only **8** was detected.

The above results are summarized in Table I.

Reductions with Other Reducing Agents.—The behavior of **3a** on treatment with a variety of reducing agents is summarized in Table I. The most discriminating reagent with regard to cyclopropane formation is chromous sulfate,[8] a reagent used earlier to effect dehalogenation of vicinal dihalides.[9] The reductions with Raney nickel and sodium in ammonia were not studied in detail because they did not seem to offer promising synthetic routes to **5** or **6**.

The reaction of **3a** with tri-*n*-butyltin hydride (TBTH)[10] was studied not only because cyclopropane formation seemed predominant but also because reduction of halides with TBTH undoubtedly involves free-radical chain processes[10] in contrast to $LiAlH_4$ reductions, which are assumed to proceed by hydride

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[1] This work was supported in part by Grant 12445 from the National Science Foundation.

[2] Summer NSFURP Fellow, 1967.

[3] Postdoctoral Research Associate, The Ohio State University, 1966–1968.

[4] Taken in part from the Ph.D. thesis of L. W. Dauernheim, The Ohio State University, 1969. Details of the reduction experiments are given.

[5] M. S. Newman, J. R. LeBlanc, H. A. Karnes, and G. Axelrod, *J. Amer. Chem. Soc.*, **86**, 868 (1964).

[6] W. von E. Doering and J. F. Cobuin, Jr., *Tetrahedron Lett.*, 991 (1965).

[7] Unless otherwise stated a ratio of 2 mol of $LiAlH_4$ to 1 mol of halide was used.

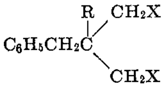
[8] J. K. Kochi and D. M. Singleton, *J. Org. Chem.*, **33**, 1027 (1968).

[9] W. C. Kray, Jr., and C. E. Castro, *J. Amer. Chem. Soc.*, **86**, 4603 (1964).

[10] H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).

TABLE I

REDUCTION OF 2-BENZYL-1,3-DIHALOPROPANES[a]

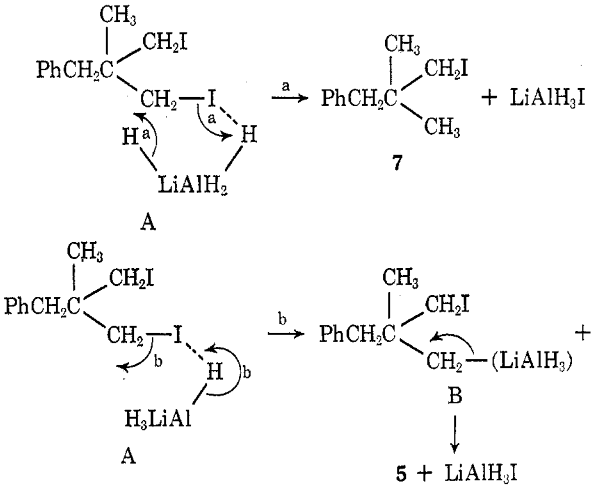
	Reducing agent, solvent	**6**	**5**
3a, R = CH_3; X = I	$LiAlH_4$, ether[b]	3	97
	W-2 Ni	67	33
	Na, NH_3	20	80
	$CrSO_4$, DMF	0	100
	$(C_4H_9)_3SnH$, benzene	6	94[c]
	$(C_4H_9)_3SnH$, ether	14	86[d]
	$(C_4H_9)_3SnH$, cyclohexane	56	44[e]
3b, R = CH_3; X = Br	$LiAlH_4$, THF	95	5
	$LiAlH_4$, dioxane[f]	68	30
3c, R = CH_3; X = Cl	$LiAlH_4$, ether[g]	UD[h]	UD[h]
	$LiAlH_4$, THF[i]	4	4[j]
	$LiAlH_4$, dioxane	62	18[k]
		8	**9**
4a, R = H; X = I	$LiAlH_4$, ether	70	30
	$LiAlH_4$, THF[l]	96	4
4b, R = H; X = Br	$LiAlH_4$, THF[l]	D[m]	UD[h]
4c, R = H; X = Cl	$LiAlH_4$, THF[n]	D[m]	UD[h]
X = OMs	$LiAlH_4$, THF (6)	D[m]	UD[h]

[a] In general 0.02 mol of $LiAlH_4$ was used for 0.01 mol of dihalide. [b] Refluxed for 20 hr. Similar results were obtained after 6 hr at reflux in THF and dioxane. [c] Hydrogen (60% based on cyclopropane formed) obtained. [d] Hydrogen, 80% as for *c*. [e] Hydrogen, 70% as for *c*. [f] 1:1 ratio of $LiAlH_4$ to halide, 24 hr at reflux. [g] 25 hr. [h] UD = undetected by glpc. [i] 82 hr. [j] In addition, 52% of 2-benzyl-2-methyl-1-chloropropane and 40% of **3c** were shown to be present by glpc. [k] In addition 20% of 2-benzyl-2-methyl-1-chloropropane was present. [l] At reflux, 5 hr. [m] Detected by glpc. [n] At reflux, 26 hr.

ion (or complexed hydride) intermediates.[11-13] Interestingly, the proportions of **5** and **6** formed from **3a** with TBTH proved sensitive to solvent. The reaction in benzene and in ether gives mainly **5**, whereas in cyclohexane the formation of **6** predominates (see Table I).

Mechanism ($LiAlH_4$).—Because of the difficulty of designing crucial experiments, little can be said with certainty about the mechanism of the $LiAlH_4$ reductions. We do not believe that the formation of **6** occurs by two SN2 displacements of halide ion, a type of reaction generally assumed to occur in reductions of halides and other functions because of the studies reported.[11,12] Rather, we suggest that the diiodide **3a** first interacts with $LiAlH_4$ by association of an iodine atom with hydrogen to form the complex A. Two paths are available for further reaction of A: in path a, an intramolecular rearrangement leads to **7** and $LiAlH_3I$ (reduction of **7** by a path similar to path a leads to the formation of **6**); in path b, a different intramolecular decomposition leads to formation of a molecule of hydrogen iodide (which reacts further with $LiAlH_4$ to form hydrogen[14,15] and $LiAlH_3I$) and a new intermediate, B, which rapidly cyclizes with loss of I^- to yield **5**. Alternately, an anion (formed by removal of the $LiAlH_3^+$ ion) cyclizes with expulsion of an iodide ion. These reactions are outlined in Scheme I.

SCHEME I

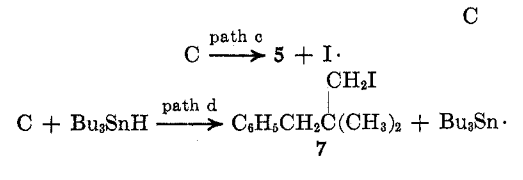


We prefer the above explanations largely because of the steric factors involved which should militate against SN2 type reactions. The initial interaction of **3a** with $LiAlH_4$ by hydrogen–iodine attraction would not be expected to be sterically hindered and subsequent reactions (paths a and b) are intramolecular and hence less slowed by steric factors than intermolecular reactions. In addition, the formations of **5**, **6**, and **7** are all accompanied by a release of strain.

The differences in behavior of the halides **3a**, **3b**, and **3c** can be interpreted in terms of the differences in size of the atoms, coordination tendencies, and strengths of bonds. However, we do not feel that the experimental results justify detailed comment. The preference of **3b** to yield **6** rather than **5** is rationalized by assuming that reaction by path a is preferred over reaction by path b. In the case of the reduction of the halides **4a**, **4b**, and **4c**, the incursion of SN2-type reactions[11,12] becomes more likely because of the decreased steric factors. Hence, the greater proportions of reduction to isobutylbenzene may be attributed to SN2 reduction rather than reaction by path a.

Mechanism (TBTH).—The formation of the cyclopropane **5** from **3a** seems best explained as shown in Scheme II. We prefer to view the formation of **5** from

SCHEME II



$$Bu_3Sn\cdot + \underset{\mathbf{3a}}{C_6H_5CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}(CH_2I)_2} \longrightarrow Bu_3SnI + \underset{\mathbf{C}}{C_6H_5CH_2\underset{\underset{\displaystyle CH_2I}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_2\cdot}$$

$$C \xrightarrow{\text{path c}} \mathbf{5} + I\cdot$$

$$C + Bu_3SnH \xrightarrow{\text{path d}} \underset{\mathbf{7}}{C_6H_5CH_2\overset{\overset{\displaystyle CH_2I}{|}}{C}(CH_3)_2} + Bu_3Sn\cdot$$

the radical C by expulsion of an iodine atom (path c) rather than to assume a reaction between C and another

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[11] L. W. Trevoy and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 1675 (1949).

[12] E. L. Eliel, *ibid.*, **71**, 3970 (1949).

[13] However, it is noteworthy that a small amount of a mixture of *dl*- and *meso*-2,3-diphenylbutane was obtained on reduction of α-chloroethylbenzene with $LiAlH_4$.[12] Hence, a free-radical path might be involved to some extent.

[14] The gas formed was assumed to be hydrogen. In the reductions with TBTH, we thank Professor Sheldon Shore for the determination of hydrogen by gas density measurement.

[15] See R. J. Strunk, P. M. D. Giacomo, K. Aso, and H. G. Kuivila, *J. Amer. Chem. Soc.*, **92**, 2849 (1970), for an analogous reaction with vicinal dibromides.

radical to produce a 1,3-diradical which cyclizes[16] to **5**. The formation of cycloalkanes from diiodides has been noted and discussed.[17-19] In the cases studied unsaturated dihaloalkanes were involved, whereas in **3a** in *gem*-dialkyl effect is present[20] and may be responsible for the much higher yield of cyclopropane.

The fact that neopentylbenzene (**6**) is formed shows that the radical C can abstract a hydrogen atom from another species (probably TBTH or solvent) to yield the monoiodo compound **7** (path d). The latter is then converted to **5** by a conventional free radical path.[10] The sensitivity to solvent of the relative rates by paths c and d is remarkable and may indicate that TBTH in cyclohexane is a better donor of H· to C than it is in benzene or ether. This view seems preferable to an alternate one which would require C to collapse to **5** and I· less readily in cyclohexane than in benzene or ether.

Experimental Section

Gas-liquid phase chromatography (glpc) was carried out using a 5 ft × 0.125 in. stainless steel column of 5% SE-30 on 60–80 mesh Chromosorb W. An Aerograph Hi-Fi with glass-lined injection port and flame ionization detector was employed. Analyses of reduction mixtures were determined at an initial column temperature of 90°, followed by maximum programming of the oven temperature to 200° one minute after elution of **5** and **6**. Yield determinations were obtained from glc data by disk integration and corrected for detector response variations. Bromomesitylene, unreactive under the conditions employed for reduction and analyses, was used as an internal standard. Infrared data was obtained on a Perkin-Elmer Infracord. Nmr spectra were obtained with a Varian A-60 spectrometer in carbon tetrachloride or deuteriochloroform solutions containing tetramethylsilane as internal standard. All proton integration value were consistent with the structures assigned. All microanalyses were by the Galbraith Laboratories, Knoxville, Tenn.

2-Benzyl-2-methyl-1,3-propanediol Bismethanesulfonate.—To an ice-cooled solution of 132 g of 2-benzyl-2-methyl-1,3-propanediol, mp 68–70°, prepared in 86% yield essentially as described[21] by reduction of diethyl benzylmethylmalonate[22] with $LiAlH_4$ in THF, in 320 g of pyridine and 500 ml of benzene was added 450 g of methanesulfonyl chloride dropwise to maintain the temperature at 10° or below. After 6 hr the solution was held at room temperature for 42 hr and then poured into 1 l. of cold water. After a conventional work-up, including a Darco G-60 (charcoal) treatment of the crude yellow oil in absolute ethanol, there was obtained 218 g (86%) of colorless, needlelike crystals of the bismethanesulfonate, mp 48–50°. A recrystallized sample (ethanol) melted at 49–50°.

Anal. Calcd for $C_{13}H_{20}O_6S_2$: C, 47.1; H, 6.2. Found: C, 47.0; H, 6.2.

2-Benzyl-2-methyl-1,3-diiodopropane (**3a**[23] ‡).—A mixture of 36.0 g of the above bismethanesulfonate, 170 g of potassium iodide, and 300 ml of freshly distilled 2-ethoxyethanol was stirred at reflux for 10.5 hr. After a conventional work-up, the crude diiodide was rapidly distilled at low pressure to yield a brown liquid. Two low-temperature crystallizations from 60-ml portions of absolute alcohol followed by vacuum drying at 0–10° for 20 hr yielded 29.0 g (68%) of **3a** as a light yellow, powdery solid, mp 22.0–22.5° (98% pure by glpc). A glass liner was needed at the injection part. This diiodide did not discolor further if kept sealed in a refrigerator.

Anal. Calcd for $C_{11}H_{14}I_2$: C, 33.0; H, 3.5. Found: C, 33.3; H, 3.7.

2-Benzyl-2-methyl-1,3-dibromopropane (**3b** ‡).—A stirred mixture of 60.0 g of dimesylate, 102 g of dry lithium bromide, and 400 ml of freshly distilled 2-ethoxyethanol was held at reflux for 46 hr. After a conventional work-up, fractional distillation through a 170 × 19 mm Vigreux column afforded 46.0 g (87%) of colorless **3b**, bp 115–120° (0.7 mm). Crystallization from absolute ethanol at −78° followed by distillation yielded 37 g (70%) of colorless pure **3b**, bp 94–95° (0.1 mm), mp 29–30°.

Anal. Calcd for $C_{11}H_{14}Br_2$: C, 43.2; H, 4.6. Found: C, 43.5; H, 4.4.

2-Benzyl-2-methyl-1,3-dichloropropane (**3c** ‡).—A stirred mixture of 80 g of bismethanesulfonate, 80 g of lithium chloride, and 500 ml of 2-ethoxyethanol was held at reflux for 52 hr and worked up as usual. On fractionation 47.0 g (90%) of **3c**, bp 100-104° at 0.25 mm, was obtained. Glpc analysis showed this to be 99% pure.

Anal. Calcd for $C_{11}H_{14}Cl_2$: C, 60.8; H, 6.5. Found: C, 60.6; H, 6.5.

2-Benzyl-1,3-propanediol Bismethanesulfonate.—Treatment of diethyl benzylmalonate with $LiAlH_4$ essentially as described above yielded colorless crystals of 2-benzyl-1,3-propanediol,[24] mp 66.5–69.0°, in 66% yield. Mesylation as described above afforded the bismethanesulfonate as colorless crystals, mp 84.0–86.5°, in 97% yield in the best run.

Anal. Calcd for $C_{12}H_{18}O_6S_2$: C, 44.8; H, 5.6. Found: C, 45.0; H, 5.4.

2-Benzyl-1,3-diiodopropane (**4a**).—A stirred mixture of 25.0 g of bismethanesulfonate, 70 g of potassium iodide, and 200 ml of 2-ethoxyethanol was held at reflux for 8 hr. After a conventional work-up there was obtained 29.5 g (91%) of brown liquid, **4a**, bp 140–150° (3 mm). Low-temperature crystallization and drying as described above for **3a** afforded 18.0 g of pale yellow solid, **4a**, mp 39.0–43.5°.

Anal. Calcd for $C_{10}H_{12}I_2$: C, 31.1; H, 3.1. Found: C, 31.1; H, 3.3.

2-Benzyl-2-methyl-1-iodopropane (**7**).[25]—A stirred mixture of 14.4 g (0.10 mol) of isobutyl 2-methylpropanoate, 6.0 g of a 50% sodium hydride dispersion in mineral oil (0.12 mol of NaH), and 12.7 g (0.10 mol) of benzyl chloride was heated at 100° under nitrogen for 2 hr. Dioxane (50 ml) was then added to the thick slurry, and the reaction mixture was refluxed for an additional 2 hr. After hydrolysis and work-up, distillation afforded 10.4 g (44%) of isobutyl 2,2-dimethyl-3-phenylpropanate, bp 135–137° (9 mm). Reduction with $LiAlH_4$ yielded 6.4 g (90%) of 2,2-dimethyl-3-phenyl-1-propanol,[25] bp 68° (0.2 mm). Mesylation of this alcohol followed by reaction with potassium iodide essentially as described above gave 64% of **7**, bp 68–70° (0.1 mm).

Anal. Calcd for $C_{11}H_{15}I$: I, 46.3. Found: I 46.6.

W-2-Raney Nickel Reduction of 3a.—A mixture of 10.4 g of W-2 Raney nickel,[26] 0.5 g of **3a**, and 40 ml of absolute ethanol was refluxed under nitrogen. Aliquots taken 0.5 hr later and subsequently all showed a 2:1 distribution of **6** to **5**. No **3a** or **7** was in evidence after 0.5 hr; the glpc-determined yield of products after 4 hr was 88%.

Sodium in Ammonia Reduction of 3a.—Sodium was introduced piecemeal into a rapidly stirred solution of 1.0 g of **3a** in 30 ml of liquid ammonia and 20 ml of dry tetrahydrofuran until the persistence of a dark blue color. After 10 min, the reaction mixture was quenched with ammonium chloride. Glpc analysis indicated a 20:80 ratio of **6** to **5**.

Chromous Sulfate Reduction of 3a.—A mixture of 1.0 g (2.5 mmol) of **3a**, 50 ml of a chromous sulfate–zinc sulfate solution 0.7 *N* in Cr(II),[27] and 60 ml of dimethylformamide was stirred under nitrogen for 92 hr at 25°. After work-up, glpc analysis showed only the presence of **5**.

Tri-*n*-butyltin Hydride Reduction of 3a.—The following procedure was used with all solvents employed. A dry, steamed-out, one-neck flask was equipped with stirring bar and addition

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[16] K. V. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971, p 81 ff.

[17] W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

[18] J. F. Garst and J. T. Barbas, *J. Amer. Chem. Soc.*, **91**, 3385 (1969).

[19] R. F. Drury and L. Kaplan, *J. Amer. Chem. Soc.*, **94**, 3982 (1972).

[20] For a discussion of the *gem*-dialkyl effect see M. S. Newman and R. E. Dickson, *J. Amer. Chem. Soc.*, **92**, 6880 (1970), and references cited therein.

[21] G. Ferrari and C. Casagrande, *Farmaco, Ed. Sci.*, **18**, 780 (1963).

[22] D. F. DeTar and C. Weis, *J. Amer. Chem. Soc.*, **79**, 3045 (1957).

[23] All compounds marked with ‡ gave nmr and *m/e* consistent with the formulas proposed. We thank Mr. R. Weisenberger for the mass spectra.

[24] R. Mozingo and K. Folkers, *J. Amer. Chem. Soc.*, **70**, 227 (1948).

[25] The procedure used here is similar to that of P. Warrick, Jr., and W. Saunders, Jr., *J. Amer. Chem. Soc.*, **84**, 4095 (1962).

[26] E. C. Horning, Ed., "Organic Syntheses," Collect. Vol. 3, Wiley, New York, N. Y., 1955, p 181.

[27] C. E. Castro, *J. Amer. Chem. Soc.*, **83**, 3262 (1961).

funnel. After a solution of 0.50 g (1.3 mmol) of **3a** in 2 ml of the appropriate solvent was introduced to the flask, the addition funnel was charged with a solution of 0.75 g (2.6 mmol) of TBTH in 4 ml of the same solvent. Immediately after attaching the gas-measuring line (water displacement and dibutyl phthalate in a leveling buret were both used), the hydride solution was added at once to **3a**. Gas evolution began after a short (about 1 min) induction period; after correction to standard conditions, comparison was made with the amount of gas expected on the basis of the actual yield of **5** obtained (Table I). This evolved gas was shown to be hydrogen by gas-density measurements.[14] A control reaction in which the evolved gas was passed through a sodium hydroxide solution of known strength showed that no significant amount of acidic material was lost from the reaction.

Glpc analyses were performed by withdrawing aliquots and quenching with one-fourth their volume of methyl iodide. Bromomesitylene was then added as internal standard. Besides consuming excess hydride, methyl iodide inhibited the thermal (wall-catalyzed) cyclization of **3a** upon contact with the hot injection part of the gas chromatograph. Combined yields of **6** and **5** were typically in the 95–100% range by glpc, with **6**:**5** ratios as reported in Table I.

In a large-scale run, 21.9 g (75.3 mmol) of TBTH was added at once to 15.0 g (37.5 mmol) of **3a** in 120 ml of dry benzene. After gas evolution was complete, solvent was removed and distillation afforded 4.9 g (90%) of material, bp 80–84° (14 mm), which glpc analysis indicated to be a 5:95 mixture of **6** and **5**. 1-Benzyl-1-methylcyclopropane (**5**) had nmr ($CDCl_3$) δ 7.22 (s, PhH), 2.58 (s, $PhCH_2$), 0.80 (s, CH_3), and 0.38 (m, CH_2CH_2). A near-infrared spectrum of **3a** (Applied Physics Corp., Cary Model 14, 0.500 *M* **3a** in CCl_4) displayed an absorption maximum at 1.642 μ with a molar absorptivity (*A*) of 0.33 per cyclopropyl methylene group.[28]

Measurement of Hydrogen Evolution from $LiAlH_4$ Treatment of 3a.—A flask and Claisen head assembly was fitted with a septum seal, stirring bar, and gas line to a leveling buret containing di-*n*-butyl phthalate. After 2 ml of a $LiAlH_4$ in ether solution (2.5 mequiv $LiAlH_4$/ml), the hydride was diluted with 20 ml more ether, and after the system had stabilized, 1.20 g (3.00 mmol) of **3a** was introduced by syringe through the septum. Slow but steady gas evolution began immediately, leading to a total of 65.3 ml of gas (corrected to STP) over a 15-hr period (further standing led to a 5-ml *decrease* of volume over a 2-day period). Assuming that of **3a** is converted to products in a typical ratio of 3:97 (**6**:**5**), this represents a quantitative yield of gas based on the amount of **5** formed.

Registry No.—**3** (X = OMs), 40548-53-6; **3** (X = OH), 2109-99-1; **3a**, 40548-52-5; **3b**, 40548-55-8; **3c**, 40548-56-9; **4** (X = OMs), 40548-57-0; **4** (X = OH), 2612-30-8; **4a**, 40548-59-2; **4b**, 35694-75-8; **4c**, 40548-61-6; **5**, 30836-86-3; **6**, 1007-26-7; **7**, 40548-64-9; **8**, 538-93-2; **9**, 1667-00-1; $LiAlH_4$, 16853-85-3; TBTH, 688-73-3; methanesulfonyl chloride, 124-63-0; potassium iodide, 7681-11-0; lithium bromide, 7550-35-8; lithium chloride, 7447-41-8; isobutyl 2-methylpropanoate, 97-85-8; isobutyl 2,2-dimethyl-3-phenylpropanate, 40548-66-1; 2,2-dimethyl-3-phenyl-1-propanol, 13351-61-6.

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[28] Compare λ_{max} = 1.638 μ and *A* = 0.324 for the known 1-benzylcyclopropane; P. G. Gassman and F. V. Zalar, *J. Org. Chem.*, **31**, 166 (1966).

Intermediates in the Reaction of Grignard Reagents with Nitromethane

STANLEY WAWZONEK* AND JAMES VERN KEMPF[1]

Department of Chemistry, The University of Iowa, Iowa City, Iowa 52242

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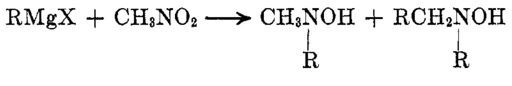
The reaction of *n*-butylmagnesium bromide with nitromethane formed *N*-*n*-butyl-*N*-methylhydroxylamine, *N*-*n*-pentyl-*N*-methylhydroxylamine, octane, and *n*-butyl alcohol. The same reaction in the presence of styrene gave a small amount of 2-butyl-5-phenylisoxazolidine. These results point to a complex between nitromethane and *n*-butylmagnesium bromide and to 2-butylnitrone as intermediates in the formation of the hydroxylamines isolated.

The actual mechanism for the formation of hydroxylamines from Grignard reagents and nitromethane is not known.[2] Semiquantitative studies of



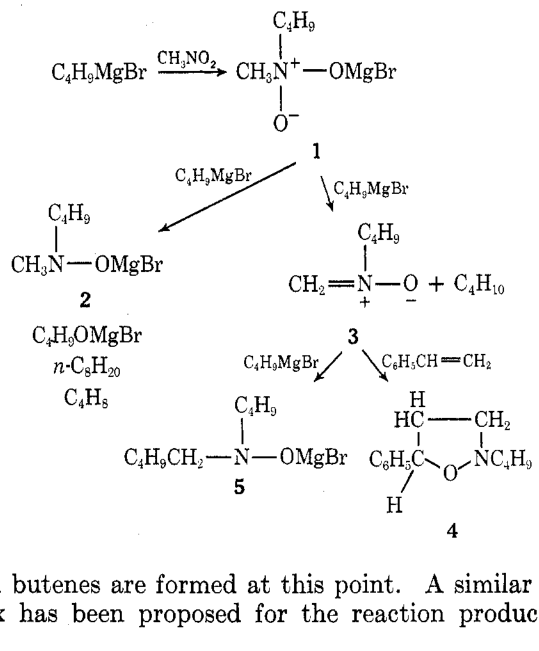
$$RMgX + CH_3NO_2 \longrightarrow \underset{\displaystyle R}{CH_3\overset{|}{N}OH} + \underset{\displaystyle R}{RCH_2\overset{|}{N}OH}$$

the reaction of ethylmagnesium bromide and *n*-butylmagnesium bromide with nitromethane carried out in the present work gave results which point to certain intermediates in this reaction.

The reaction with ethylmagnesium bromide was used to follow the influence of the concentration of the Grignard reagent upon the ratio of the hydroxylamines produced. The hydroxylamines were converted into the *O*-trimethylsilyl derivatives and analyzed by vpc. The results are shown in Figure 1.

The reaction using *n*-butylmagnesium bromide with nitromethane gave information about the gases evolved and the neutral products formed. The amounts of butane and butenes generated with the addition of successive amounts of Grignard reagent are shown in Figures 2 and 3. This reaction also produced *n*-octane and *n*-butyl alcohol.

These results point to the following steps in the formation of the hydroxylamines. The addition of 1 mol of *n*-butylmagnesium bromide to nitromethane forms mainly the complex **1** since very little butane and butenes are formed at this point. A similar complex has been proposed for the reaction product be-



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[1] Abstracted in part from the Ph.D. Thesis of J. V. K., 1973.

[2] S. Wawzonek and J. V. Kempf, *Org. Prep. Proced. Int.*, **4**, 135 (1972).