[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

CYCLOPROPANE HYDROCARBONS FROM *gamma*-BROMOETHERS[1]

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The synthesis of olefins by the de-alkoxybromination of *beta*-bromoethers with zinc in aqueous ethanol is a well known and highly developed reaction (1). Adaptation of the method to the preparation of cyclopropane hydrocarbons by the de-alkoxybromination from *gamma*-bromoethers has barely been tried.

Wolkoff and Menschutkin (2) treated 1-ethoxy-3-bromopropane (ethyl γ-bromopropyl ether) with zinc dust in 96% alcohol, and upon warming the reaction mixture to 60–70° obtained an "almost theoretical yield" of propylene. Paul (3) treated 1-phenoxy-3-iodopropane with magnesium in dry butyl ether and obtained an "*abondant degagement*" (copious evolution) of cyclopropane. He also attempted to prepare cyclopropane from 1-ethoxy-3-chloropropane by this method, but obtained none; reaction conditions were not specified. Hammonet (4) prepared Grignard reagents from many of the higher bromoethers, but made no attempt to convert them into the corresponding hydrocarbons.

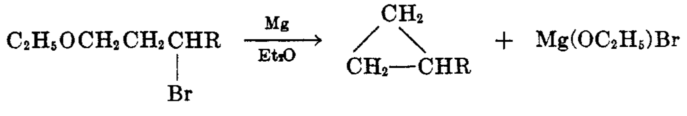
It may be said that, in general, far less work has been reported on methods of synthesis for mono-alkylcyclopropanes than for polyalkylcyclopropanes. In the course of the present research we have developed what appears to be a general method for the preparation of mono-alkylcyclopropanes by the de-alkoxybromination of γ-bromoethers with magnesium; the scheme of synthesis starts with the commercially available 3-ethoxypropionaldehyde (see equations I–III). It was also found that cyclopropane, itself, and polyalkylcyclopropanes can be prepared in three steps (equations IV–VI) from appropriate homologs of trimethylene glycol.

In the preparation of the mono-alkylcyclopropanes, 3-ethoxypropionaldehyde was condensed with a Grignard reagent to produce a γ-hydroxyether, from which the corresponding γ-bromoether was prepared by reaction with phosphorus tribromide.

I $C_2H_5OCH_2CH_2CHO + RMgX \rightarrow C_2H_5OCH_2CH_2CH(OH)R$

II $3C_2H_5OCH_2CH_2CH(OH)R + PBr_3 \rightarrow 3C_2H_5OCH_2CH_2CH(Br)R$

III



$$C_2H_5OCH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HR \xrightarrow[Et_2O]{Mg} \overset{CH_2}{\diagup\diagdown}\!\!\!\!\!\underset{CH_2—CHR}{} + Mg(OC_2H_5)Br$$

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TABLE I

CYCLOPROPANE HYDROCARBONS FROM 3-ETHOXYPROPIONALDEHYDE *via* γ-BROMO-ETHERS

Step I		Step II	Step III	
Grignard reagent	Yield of hydroxyether,[a] %	Yield of bromo-ether,[b] %	Cyclopropane	Yield,[c] %
Ethyl	51	57	Ethyl	51
n-Propyl	56	46	*n*-Propyl	28
n-Butyl	65	50	*n*-Butyl	23
Phenyl	69	65	Phenyl[d]	5

[a] From 3-ethoxypropionaldehyde
[d] From hydroxyether
[c] From bromoether
[d] Not fully characterized

The cyclopropane hydrocarbons (Table I) were produced by treating the bromoethers with magnesium in ether to form the Grignard reagents, raising the temperature of the reaction mixtures to 100–140° by adding toluene or xylene to the prepared Grignard reagents, and then distilling off the ether. The cyclopropane hydrocarbons were isolated by fractionation of the distillate, which was composed of ether, toluene or xylene, and the cyclopropane hydrocarbon.

In all cases the cyclopropane hydrocarbons, as redistilled, had constant boiling points and refractive indices and occurred with no close-boiling impurities. This method has an advantage over cyclization by the Gustavson debromination of 1,3-dibromides, in that olefinic hydrocarbons, which are sometimes difficult to remove, are not and cannot (by the nature of the reaction) be produced as impurities here. If some dehydrohalogenation takes place in step 3, an olefinic ether (which can be readily separated by distillation) is formed instead of an olefin isomeric with the desired alkylcyclopropane. The yield of hydrocarbon appears to be inversely proportional to the size of the side chain. The presence of larger amounts of high-boiling material, probably Wurtz-type products, in the residues from the distillations of the higher homologs suggests that the yields of the higher molecular weight cyclopropanes could be increased if the ring closure reactions were done at higher dilution.

The ethyl- and *n*-propyl-cyclopropanes were identified on the basis of their infrared spectra and on comparison of their physical properties with reliable literature values. The identity of the *n*-butylcyclopropane was established by an independent synthesis of the hydrocarbon and comparison of the physical properties and spectra of the two samples. In the second synthesis, 3-hydroxy-1-heptene, produced by condensation of acrolein with butylmagnesium chloride, was converted to the corresponding bromide by treatment with phosphorus tribromide. Hydrogen bromide was then added to the bromo-olefin in the presence of benzoyl peroxide to produce 1,3-dibromoheptane, which on debromination by zinc in aqueous ethanol gave *n*-butylcyclopropane.

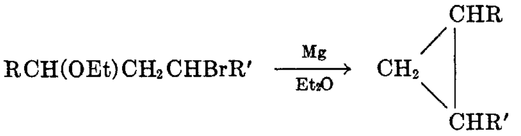
The attempt to prepare phenylcyclopropane was disappointing as the yield was very small. The product was not fully characterized, but its infrared spectrum was consistent with that which would be expected for phenylcyclopropane by consideration of the spectra of isopropylbenzene and of some mono-alkylcyclopropanes. When 3-bromo-3-phenylpropyl ethyl ether was treated with zinc in alcohol, no material boiling in the range of phenylcyclopropane was noted, but a small amount of a liquid which had physical properties approximating those estimated for 3-phenylpropyl ethyl ether was obtained.

Cyclopropane and 1,2-dimethylcyclopropane were prepared from 1-ethoxy-3-bromopropane and 2-ethoxy-4-bromopentane in 52 and 49% yield, respectively, by the same ring closure procedure as used for the mono-alkylcyclopropanes. The *cis* and *trans* isomers of the 1,2-dimethylcyclopropane were formed in almost equal amounts. The 1-ethoxy-3-bromopropane was prepared by the reaction of the mono-ethyl ether of trimethylene glycol with phosphorus tribromide, and the 2-ethoxy-4-bromopentane was prepared in a similar manner from 2-ethoxy-4-hydroxypentane made by etherifying the commercially available 2,4-pentanediol (see equations IV–VI). The cycloparaffins were identified by comparison of their physical properties and spectra with those of known authentic samples.

IV $$\mathrm{RCHOHCH_2CHOHR'} \xrightarrow[\mathrm{EtBr}]{\mathrm{Na}} \mathrm{RCH(OEt)CH_2CHOHR'}$$

V $$\mathrm{RCH(OEt)CH_2CHOHR'} \xrightarrow{\mathrm{PBr_3}} \mathrm{RCH(OEt)CH_2CHBrR'}$$

VI



Attempts were made to prepare cyclopropane from 1-ethoxy-3-bromopropane by treatment with zinc in 90% aqueous *n*-propanol, in 85% aqueous ethanol, and in molten acetamide; in each case the only product found was ethyl *n*-propyl ether.

An attempt to produce cyclobutane from 1-ethoxy-4-bromobutane was unsuccessful, the chief product isolated being ethyl *n*-butyl ether.

EXPERIMENTAL

3-Ethoxypropionaldehyde. This chemical, obtained as a concentrate from Carbide and Carbon Chemicals Co., was vacuum-distilled in a column rated at about 15 plates at atmospheric pressure, and that portion boiling at 57 to 63°/40 mm. (n_D^{20} 1.4049 to 1.4077) was taken as suitably pure for use.

1-Ethoxy-3-hydroxypentane. In a 5-liter, 3-neck flask fitted with a motor-driven stirrer, reflux condenser, and addition funnel, 5 moles of ethylmagnesium bromide was prepared in about 800 ml. of ether, by use of conventional techniques. To this solution of Grignard reagent, freshly distilled 3-ethoxypropionaldehyde mixed with an equal volume of ether was added slowly, while the temperature of the reaction mixture was maintained near 0°. After about 3.4 moles of the aldehyde had been added, the mixture became extremely viscous, so hydrolysis was carried out at once with dilute hydrochloric acid. (The thickening, which was found to be mitigated by addition of benzene but not by addition of more ether, was not pronounced when other Grignard reagents were used). The ether solution of product and three ether washings of the aqueous layer were combined, stripped of ether, and distilled under reduced pressure on a column rated at about 15 plates at atmospheric pressure. There was obtained 273 g. (51% yield from 3-ethoxypropionaldehyde) of nearly constant-boiling 1-ethoxy-3-hydroxypentane, a middle fraction of which had the following properties: b.p. 94°/35 mm.; n_D^{20} 1.4224; d_4^{20} 0.8918.

1-Ethoxy-3-bromopentane. 1-Ethoxy-3-hydroxypentane (205 g., 1.55 moles) was placed in a 500-ml., 3-neck flask, fitted with a stirrer, addition funnel, a gas outlet tube and a thermometer, and was surrounded by Dry Ice. When the temperature of the stirred alcohol reached −20°, 138 g. (0.51 mole) of PBr_3 was added at a rate permitting temperature to be held between −20 and −10°; then the mixture was maintained at Dry Ice temperature for 12–18 hours, after which it was allowed to stand at room temperature for five days. The reaction product was poured into and stirred with water and cracked ice. The crude bromide was separated, washed with 5% sodium carbonate solution, dried over sodium sulfate, and fractionally distilled. The yield of nearly constant-boiling bromide was 173 g. or 57%, and a middle fraction had the following properties: b.p., 99°/57 mm., n_D^{20} 1.4489, d_4^{20} 1.1841.

Ethylcyclopropane. Magnesium (21 g., 0.87 g.-atom) and enough dry tetrahydrofuran to cover it were placed in a 1-liter, 3-neck flask, fitted with a mercury sealed stirrer, addition funnel, and a reflux condenser connected by glass tubing to a receiver immersed in a Dry Ice-acetone bath. (Tetrahydrofuran was used in place of ethyl ether, b.p. 34.6°, which would be very difficult to separate from ethylcyclopropane, b.p. 36.0°). A few ml. of 1-ethoxy-3-bromopentane and about 0.2 g. of iodine were added. Once the Grignard reaction had started (warming was necessary) the remainder of the bromo-ether (170 g. or 0.87 mole, in all), diluted with an equal volume of tetrahydrofuran, was added dropwise to the stirred, refluxing reaction mixture. Then 250 ml. of dry (reagent grade) xylene was added and refluxing was continued for an hour, at which time only about 4 g. of material had collected in the Dry Ice-cooled trap. A take-off condenser was substituted for the reflux condenser, and all the material boiling up to 135° was distilled out of the reaction flask, after which the semisolid white residue gave a negative Michler's ketone test for Grignard reagent. The distillate was redistilled at about 20-plate efficiency, and the lowest-boiling component was 32 g. (51% yield) of ethylcyclopropane [b.p. 35.95–35.98° (760 mm.), n_D^{20} 1.3783, d_4^{20} 0.6843, lit. (5) b.p. 35.94°, n_D^{20} 1.3786, d_4^{20} 0.6839]. An infrared absorption spectrogram of this hydrocarbon was obtained and was virtually identical with that reported previously (5).

The residue from the Grignard reaction was hydrolyzed by stirring with dilute hydrochloric acid, and the top layer was separated and distilled along with the tailings from the distillation described above. The only product obtained was 13 g. of crude ethyl *n*-amyl ether (6) (b.p. 113–122°, n_D^{20} 1.4122–1.4266), apparently containing some xylene.

1-Ethoxy-3-hydroxyhexane. 3-Ethoxypropionaldehyde (3.92 moles) was condensed with *n*-propylmagnesium bromide by the same general procedure as was used for preparing 1-ethoxy-3-hydroxypentane, and 321 g. (a 56% yield) of 1-ethoxy-3-hydroxyhexane was obtained after distillation. A center fraction had the following physical properties: b.p. 95.5°/26 mm.; n_D^{20} 1.4253; d_4^{20} 0.8840.

1-Ethoxy-3-bromohexane. This bromide was produced from 320 g. of 1-ethoxy-3-hydroxyhexane and 216 g. of phosphorus tribromide by the same procedure used in the preparation of 1-ethoxy-3-bromopentane. There was obtained 208 g. (a 46% yield) of 1-ethoxy-3-bromohexane (b.p. 87°/19 mm.; n_D^{20} 1.4508; d_4^{20} 1.1602).

Anal. Calc'd for $C_8H_{17}BrO$: C, 45.92; H, 8.33; Br, 38.19.
Found: C, 46.42; H, 8.17; Br, 37.47.

n-Propylcyclopropane. This hydrocarbon was obtained from 1-ethoxy-3-bromohexane by the procedure described for the preparation of ethylcyclopropane, except that ether was used in place of tetrahydrofuran, and dry toluene was substituted for xylene. All the material boiling up to 111° was distilled from the reaction flask, and this distillate was refractionated on a column at about 35-plate efficiency. From 208 g. of the bromo-ether, there was obtained 24.3 g. (28% yield) of *n*-propylcyclopropane: b.p. 69.15°/760 mm., n_D^{20} 1.3930, d_4^{20} 0.7112 (lit. 7): b.p. 69–70°, n_D^{20} 1.3926). An infrared absorption spectrogram of this material was obtained and showed the expected features.

1-Ethoxy-3-hydroxyheptane. This compound was made by the same general procedure described for the preparation of 1-ethoxy-3-hydroxypentane. From reaction of 4.5 moles of *n*-butylmagnesium chloride and 433 g. (4.2 moles) of 3-ethoxypropionaldehyde there was obtained 430 g. (65% yield) of distilled 1-ethoxy-3-hydroxyheptane (b.p. 108–110°/19 mm.; n_D^{20} 1.4290–4298). A center fraction had the following properties: b.p. 92°/8 mm.; n_D^{20} 1.4294; d_4^{20} 0.8789.

1-Ethoxy-3-bromoheptane. Reaction of 1-ethoxy-3-hydroxyheptane with phosphorus tribromide in the manner described previously, produced a 50% yield of 1-ethoxy-3-bromoheptane (b.p. 102°/10 mm.; n_D^{20} 1.4537; d_4^{20} 1.1422).

Anal. Calc'd for $C_9H_{19}Br$: C, 48.4; H, 8.6; Br, 35.8.

Found: C, 48.18; H, 8.34; Br, 36.38.

n-Butylcyclopropane. This hydrocarbon was prepared by the procedure described for the synthesis of ethylcyclopropane. From 207 g. (0.97 mole) of 1-ethoxy-3-bromoheptane there was obtained 22 g. (0.22 mole) of *n*-butylcyclopropane. The product, after careful distillation, still contained a small amount of the xylene solvent as indicated by a gradual increase in the refractive index of consecutive fractions (n_D^{20} 1.4047–1.4053). The aromatic was removed by percolating the hydrocarbon through a tube of silica gel maintained at 10–15°; physical properties determined on the purified *n*-butylcyclopropane were: b.p. 99.50°/760 mm., m.p. −124.7°, d_4^{20} 0.7285, n_D^{20} 1.4042. Although the material crystallized well and a satisfactory melting curve was obtained, it was not possible to produce a meaningful freezing point curve because of excessive supercooling.

The infrared absorption spectrogram of this product showed the 9.8–9.9 μ band characteristic of the cyclopropane ring (9). Its identity was also verified by an independent synthesis of *n*-butylcyclopropane and comparison of the spectra of the two samples.

1,3-Dibromoheptane. 3-Hydroxy-1-heptene (b.p. 81°/50 mm., d_4^{20} 0.8361, n_D^{20} 1.4337) was prepared in 59% yield from acrolein and butylmagnesium chloride by conventional Grignard techniques. Treatment of the unsaturated alcohol with phosphorus tribromide in pyridine at −20° gave a 71% yield of 3-bromo-1-heptene (b.p. 63–75°/24 mm.; n_D^{20} 1.4585–1.4734). Young (8) reported that the product from this reaction was a mixture composed of 47% 1-bromoheptene-2 and 53% of 3-bromoheptene-1 and gave the following physical properties: 1-bromoheptene-2, b.p. 32°/3 mm., n_D^{20} 1.4740; 3-bromoheptene-1, b.p. 23–25°/3 mm., n_D^{20} 1.4555–1.4585. Two moles of the bromo-olefin containing 15 g. of benzoyl peroxide was saturated with gaseous hydrogen bromide and the resulting bromide was poured into cold water. The crude dibromide was separated, washed with 5% solution of sodium carbonate and a 15% solution of sodium thiosulfate, and was dried over sodium sulfate. Distillation under reduced pressure gave 394 g. (83% yield) of 1,3-dibromoheptane, along with 25 g. of recovered starting material. A center fraction of the dibromide had the following physical properties: b.p. 104°/12 mm.; n_D^{20} 1.4995; d_4^{20} 1.5152.

n-Butylcyclopropane (alternate synthesis). 1,3-Dibromoheptane (394 g., 1.52 moles) was treated with 3 g.-atoms of powdered zinc in 75% ethanol at reflux temperature by the classical procedure (10). The hydrocarbon that formed was distilled from the reaction flask as an azeotrope (b.p. 69°), and was washed thoroughly and then dried. The yield of crude *n*-butylcyclopropane (n_D^{20} 1.4033) was 88%, but bromine titration indicated 29% olefin impurities. The hydrocarbon was treated with an excess of potassium permanganate at 5° for three days. The excess permanganate was destroyed with alcohol, and the hydrocarbon was steam-distilled, dried, and distilled at about 20-plate efficiency. Fractions amounting to about 50% of the charge distilled on a plateau, but their refractive indices progressively increased slightly. Repeated distillation of the material was ineffective in removing the small amount of impurity. The physical properties of the best sample of *n*-butylcyclopropane prepared by this method were: b.p. 99.5°, m.p. −125.8°, d_4^{20} 0.7283, n_D^{20} 1.4029 to 1.4042. A melting point determination on a mixture of this material with the previously prepared *n*-butylcyclopropane gave an intermediate value. The infrared absorption spectrogram of this hydrocarbon was virtually identical with that of the *n*-butylcyclopropane prepared from 1-ethoxy-3-bromoheptane.

1-Ethoxy-3-hydroxy-3-phenylpropane. This compound was prepared by treating 5 moles of phenylmagnesium bromide with 4 moles of 3-ethoxypropionaldehyde. The reaction mixture was hydrolyzed with dilute hydrochloric acid, and the hydroxyether was distilled under reduced pressure. The yield of 1-ethoxy-3-hydroxy-3-phenylpropane (b.p. 122°/4–126°/6 mm.; n_D^{20} 1.5093–1.5096; d_4^{20} 1.0173) was 497 g., or 69%.

1-Ethoxy-3-bromo-3-phenylpropane. 1-Ethoxy-3-hydroxy-3-phenylpropane (2 moles) was caused to react with PBr_3, at −20° by the procedure described previously; there was obtained 1.8 moles of crude 1-ethoxy-3-phenylpropane (b.p. 129–130°/13 mm.; n_D^{20} 1.5220). Redistillation reduced the yield to 65% of the bromo-ether (b.p. 135–139°/20 mm.; n_D^{20} 1.5182; d_4^{20} 1.2430), which decomposed on standing with loss of hydrogen bromide, making analysis difficult.

Anal. Calc'd for $C_{11}H_{15}BrO$: C, 54.3; H, 6.2; Br, 32.9.
Found: C, 57.3; H, 5.3; Br, 30.6.

Phenylcyclopropane. A Grignard reagent was formed from 18 g. (0.75 g.-atom) of magnesium and 180 g. (0.74 mole) of 1-ethoxy-3-bromo-3-phenylpropane. The mixture was stirred for 30 minutes, after which time titration of an aliquot portion showed 27% Grignard reagent to have formed. Dicyclohexyl (125 ml.) was added, the ether was removed by distillation, and then the mixture was heated for 3 hours. After cooling, the reaction mixture was hydrolyzed with aqueous hydrochloric acid. The organic material was separated, dried, and distilled. Only 3.8 g. of material (b.p. 165°, uncorr., n_D^{20} 1.526) was obtained; as phenylcyclopropane [lit. (11), b.p. 171°/771 mm., n_D^{20} 1.5285], this corresponds to a yield of 16% based on the Grignard reagent formed.

Trimethylene glycol monoethyl ether. This compound was prepared from the monosodium salt of trimethylene glycol and ethyl bromide by a procedure reported by Smith and Sprung (12), except that no xylene was added to the reaction mixture.

The reaction proceeded smoothly at a temperature of 100° (just above the melting point of sodium). The reaction mixture was cooled and filtered, and the filtrate was distilled under reduced pressure. After a forerun of trimethylene glycol diethyl ether, the monoethyl ether (66% yield) was collected at 70–84°/40 mm. Redistillation of this product at atmospheric pressure cut the yield to 63%: b.p. 160 to 161°, n_D^{20} 1.4158.

1-Ethoxy-3-bromopropane. This compound was prepared from trimethylene glycol monoethyl ether and phosphorus tribromide by the method described by Noyes (13). The crude bromo-ether was stripped of the by-product, ethyl bromide, by rapid distillation at atmospheric pressure and then was fractionated under reduced pressure. The product boiling at 65–75°/40 mm. then was redistilled at atmospheric pressure at about 20-plate efficiency to obtain a 58% yield of fairly pure 1-ethoxy-3-bromopropane (b.p. 149.1 to 149.4°, n_D^{20} 1.4449, d_4^{20} 1.2773).

Cyclopropane. This cycloparaffin was obtained from 1-ethoxy-3-bromopropane by the procedure described for the preparation of ethylcyclopropane, except that toluene was used in place of xylene. The cyclopropane product was distilled through a vacuum-jacketed column of about 10-plate efficiency, which was fitted with a Dry Ice-cooled reflux condenser and a vapor-phase take-off device connected to a condenser and receiver cooled by Dry Ice. The product obtained from 0.5 mole of the bromo-ether gave 10.9 g. (a 52% yield) of cyclopropane [lit. (14) b.p. −33°] boiling −33 to −30°, along with a smaller fraction (bringing the yield to 61%) boiling at −30 to −27° and containing chiefly cyclopropane. The hydrocarbon was identified by comparison of its infrared spectrum with one determined on an authentic sample of cyclopropane obtained from the Ohio Chemical Company.

2-Ethoxy-4-hydroxypentane. This compound was prepared in the same manner as trimethylene glycol monoethyl ether, from 400 g. (3.84 moles) of 2,4-pentanediol (Carbide and Carbon Chemicals Corp.), 46 g. (2 g.-atoms) of sodium, and 230 g. (2.1 moles) of ethyl bromide. The crude product was distilled at reduced pressure and there was obtained 154.6 g. (59% yield) of the mono-ether (b.p. 83–86°/35 mm.; n_D^{20} 1.4153–1.4165). Redistillation at atmospheric pressure at 10-plate efficiency reduced the yield to 50% of reasonably pure 2-ethoxy-4-hydroxypentane (b.p. 165–166°; n_D^{20} 1.4158; d_4^{20} 0.8750).

2-Ethoxy-4-bromopentane. This compound was prepared in the same manner as 1-ethoxy-

3-bromopropane from 132 g. (1 mole) of 2-ethoxy-4-hydroxypentane and 104 g. (0.38 mole) of phosphorus tribromide. The reaction mixture was hydrolyzed by pouring it into ice-water, and the organic material was separated, washed, dried over sodium sulfate, and distilled at reduced pressure. The yield of 2-ethoxy-4-bromopentane was 88.4 g. or 45%: b.p. 63–64°/15 mm., n_D^{20} 1.4390, d_4^{20} 1.1568.

In a second run the yield was increased to 54% by starting the reaction at Dry Ice temperature and then permitting the mixture to warm up and stand at room temperature for two days before hydrolysis.

1,2-Dimethylcyclopropane. This hydrocarbon was prepared from 2-ethoxy-4-bromopentane by the (now) standardized procedure. The crude 1,2-dimethylcyclopropane was fractionated at about 10-plate efficiency to obtain a 49% yield of a mixture of the geometrical isomers of the cycloparaffin (b.p. 28 to 38°, uncorr., n_D^{20} 1.3726 to 1.3832). From the distillation data it appeared that the *cis-* and *trans*-isomers were formed in almost equal amounts; Baudrenghien (15) reported the following values: *trans*-1,2-dimethylcyclopropane, b.p. 28.8–29.0°, n_D^{20} 1.3713, and *cis*-1,2-dimethylcyclopropane, b.p. 37.2–37.4°, n_D^{20} 1.3822.

1-Ethoxy-4-bromobutane. Sodium ethoxide (1 mole) in 400 ml. of absolute ethanol was added with stirring to 1.16 moles of tetramethylene dibromide in 100 ml. of absolute ethanol under reflux conditions. When the mixture became neutral, heating and stirring were discontinued, and it was cooled and filtered. The filtrate was distilled at reduced pressure to obtain a 34% yield (based on dibromide consumed) of 1-ethoxy-4-bromobutane [b.p. 63–70°/11 mm.; lit. (16) b.p. 69°/15 mm.].

Attempted preparation of cyclobutane. An unsuccessful attempt was made to prepare cyclobutane from 1-ethoxy-4-bromobutane by the same procedure which succeeded in the preparation of cyclopropane from 1-ethoxy-3-bromopropane. The only product found (40% yield) was ethyl *n*-butyl ether (b.p. 80.0–93.5°). Two other experiments at higher temperatures were equally unsuccessful in producing cyclobutane.

Attempted ring closure of 1-ethoxy-3-bromopropane with zinc in alcohols. To 200 ml. of refluxing 90% aqueous *n*-propyl alcohol and 125 g. of zinc dust was added 69.1 g. of 1-ethoxy-3-bromopropane; no evolution of gas occurred. On distillation of the resulting (liquid) organic material the only product obtained (51% yield) was ethyl *n*-propyl ether (b.p. 58–64°, n_D^{20} 1.3689, d_4^{20} 0.7244). When this reaction was repeated using 85% aqueous ethanol, the result was virtually the same.

Attempted ring closure of 1-ethoxy-3-bromopropane with zinc in molten acetamide. To 320 g. of molten (110°) acetamide and 125 g. of zinc dust was added 81 g. of 1-ethoxy-3-bromopropane. Fractionation of the organic material which had distilled from the reaction mixture gave a product (b.p. 64°, n_D^{20} 1.3691) which was identified as ethyl *n*-propyl ether (yield 35%). No evidence for the formation of cyclopropane could be found.

SUMMARY

A practical method for producing cyclopropane hydrocarbons by the action of magnesium on *gamma*-bromoethers has been developed. The method was applied to the synthesis of ethyl-, *n*-propyl-, *n*-butyl-, phenyl-, and 1,2-dimethylcyclopropane (*cis-trans* mixture), as well as cyclopropane, itself. Cyclobutane did not result from similar treatment of 1-ethoxy-4-bromobutane. The action of zinc on 1-ethoxy-3-bromopropane in various solvents produced no cyclopropane.

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