hydroxide pellets. The aqueous portion was extracted once with ether, and, after drying the ether extract over sodium hydroxide pellets, it was combined with the oily layer and submitted for chromatography (see Table I).

B. In Absolute Ethyl Alcohol.—A solution of 17.9 g. (0.1 mole) of I in 50 ml. of absolute ethyl alcohol was reduced catalytically. After filtration from the catalyst the solution was examined (see Table I).

N′,N′-Diethyl-2-methylpropane-1,2-diamine (II).—A solution of 57.4 g. of I in 100 ml. of absolute ethyl alcohol was hydrogenated under 75-atm. pressure in the presence of 10 g. of Raney nickel. Reaction was exothermic. The temperature rose to 57° within 10 min. and uptake of hydrogen was practically complete at that time. Reaction was allowed to continue for several hours. After removal of the catalyst a sample showed the presence of 2.8% isopropylamine, 1.0% diethylamine, 2.5% N-methyldiethylamine, 90% II, and about 4% of a higher boiling component (g.l.p.c.). The remainder of the material was distilled over a long column (30 × 0.5 cm.) packed with glass helices. A constant boiling fraction, 155–156° (745 mm.), $n^{25}\mathrm{D}$ 1.4292, was obtained, 24 g. (50% yield) shown by g.l.p.c. to be 98% II and about 2% III. The remaining material, 20–25 g., was not distilled further because of the difficulty in preventing codistillation of III.

N^1,N^1-Diethyl-N^2-methyl-2-methylpropane-1,2-diamine (III).—A series of six 0.2-mole runs of I were reduced with rhodium following the description of the hydrogenation of I in acetic acid and subsequent work-up. The combined oily residues and ether extracts were distilled over a tall packed column at atmospheric pressure until no more distillate was collected. Distillation under reduced pressure of the remainder of the material through the same column yielded a fraction, b.p. 91–96° (75 mm.), which was a 60:40 mixture of II and III; one at 90° (48 mm.); and finally the last fraction, b.p. 80° (20 mm.), $n^{25}\mathrm{D}$ 1.4350. If it was not analyzed within minutes after distillation, it picked up carbon dioxide too rapidly to get good results.

Anal. Calcd. for $C_9H_{22}N_2$: C, 68.29; H, 14.01; N, 17.69. Found: C, 68.74; H, 14.26; N, 17.72.

Chromatography (g.l.p.c.) showed it to be completely free of II. It was used as a standard for g.l.p.c. along with II obtained from the high-pressure reduction of I until we were able to get very pure samples of II and III by means of a preparative chromatographic unit.

N,N-Dimethyl-2-methylpropane-1,2-diamine (V).—1-Dimethylamino-2-methyl-2-nitropropane (IV) was hydrogenated in acetic acid solution in the presence of rhodium on alumina. The product after work-up was obtained in quantitative yield. Chromatography indicated that it contained water. After drying over sodium hydroxide flakes and anhydrous magnesium sulfate, the filtered oily mass was refractionated: b.p. 116–119° (747 mm.), $n^{25}\mathrm{D}$ 1.4182 [lit.[2] b.p. 119° (755 mm.), $n^{20}\mathrm{D}$ 1.4216]. G.l.p.c. showed one component.

After hydrogenation of IV in alcohol with Raney nickel g.l.p.c. showed only one component (V) in addition to alcohol and water.

N,N-Dibutyl-2-methylpropane-1,3-diamine (VII).—The reduction of VI was carried out in acetic acid with rhodium catalyst as described for the preparation of V. Two constant-boiling fractions were obtained. The first, b.p. 80–85° (50 mm.), $n^{25}\mathrm{D}$ 1.4160, 55% yield, was identified as dibutylamine by comparison with a known standard.[6] The second fraction, b.p. 100–114° (16 mm.), $n^{25}\mathrm{D}$ 1.4437, 25% yield [lit.[2] 89–90° (6 mm.), $n^{20}\mathrm{D}$ 1.4412], was confirmed as VII by analysis.

Anal. Calcd. for $C_{12}H_{28}N_2$: C, 71.93; H, 14.08; N, 13.98. Found: C, 71.92; H, 14.04; N, 14.00.

N-(2-Amino-2-methylpropyl)piperidine.—A solution of 27.6 g. (0.148 mole) of N-(2-nitro-2-methylpropyl)piperidine in 175 ml. of ethyl alcohol was hydrogenated under 2–3-atm. pressure in the presence of 3.0 g. of Raney nickel. Reaction was exothermic. Uptake of hydrogen (108%) was complete in less than 1.5 hr. A total of 0.888 mole was reduced. The combined filtrates were concentrated under reduced pressure. The resultant residue was fractionated. A total of 101.7 g. (73.4% yield) was collected at 89–89.5° (27 mm.): $n^{25}\mathrm{D}$ 1.4565 [lit.[1] b.p. 60.5° (6 mm.)].

N-(2-Amino-2-methylpropyl)morpholine was similarly prepared. It distilled at 78–81° (6 mm.): $n^{25}\mathrm{D}$ 1.4576, 47% yield [lit.[1] b.p. 68° (6 mm.)].

G.l.p.c. showed each product to be a single component.

The Reactions of Methyl- and *n*-Butyllithium with Dichloromethyl Methyl Ether and Dichlorodiphenoxymethane

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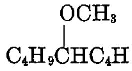
Our interest in α-alkoxycarbenes[2] prompted us to investigate the reaction of alkyllithiums with dichloromethyl methyl ether (I) in the hope of generating methoxycarbene probably as its lithium halide complex. The results we have obtained from methyllithium and I in the presence of isobutylene are in agreement with those previously published.[3]

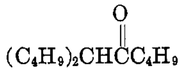
However, when an ethereal solution of I was treated with *n*-butyllithium in hexane in the presence of added cyclohexene at −35° and allowed to react for 3 hr. at −10°, and the mixture was hydrolyzed, two major products were present as shown by v.p.c. analysis. These two components were separated by distillation through a semimicro spinning-band column. The same mixture of products was obtained in the absence of cyclohexene; therefore, the trapping of carbenoid species by cyclohexene was ruled out.

The lower boiling component was shown by its infrared, n.m.r., and mass spectra and elemental analysis to be methyl 5-nonyl ether (II), the product expected by direct substitution of the chlorines in I for *n*-butyl groups. The higher boiling component was similarly analyzed along with determining its osmometric molecular weight and shown to be 6-butyl-5-decanone (III). An authentic sample of III was prepared in very low yield by the reaction of 5-nonylmagnesium bromide[4] with *n*-valeronitrile. III failed to yield a 2,4-dinitrophenylhydrazone.[5] This lack of reactivity is typical of ketones containing more than two rather long-chain alkyl groups on the α- and α′-positions. Reduction of III with lithium aluminum hydride gave an 88% yield of an alcohol whose elemental analysis and infrared and n.m.r. spectra correspond to that of 6-butyl-5-decanol.



$C_4H_9\overset{OCH_3}{\overset{|}{C}}HC_4H_9$

II



$(C_4H_9)_2CH\overset{O}{\overset{\|}{C}}C_4H_9$

III

Since a ketone present in the reaction mixture would have been expected to be consumed by reaction with *n*-butyllithium, it seemed likely that III was an artifact of the reaction and its work-up. To determine the effect of hydrolysis on the reaction mixture, the reaction between *n*-butyllithium and dichloromethyl

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[1] A portion of a dissertation presented by R. A. Krueger to the Graduate School of Kansas State University, Feb. 1965, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] R. N. McDonald and R. A. Krueger, *Tetrahedron Letters*, **No. 14**, 857 (1965).

[3] U. Schollkopf, *Angew. Chem.*, **75**, 107 (1963); U. Schollkopf and J. Paust, *ibid.*, **75**, 670 (1963).

[4] An attempt to prepare ketone III from this Grignard reagent and *n*-valeroyl chloride failed.

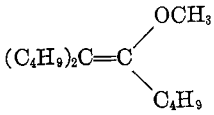
[5] A synthesis of III is reported[6] along with the fact that it does not give an oxime, semicarbazone, or bisulfite derivative.

[6] D. Bardan, *Bull. soc. chim. France*, [5] **1**, 370 (1934).

methyl ether was repeated in the same manner as before, but without the addition of water. The ether solvent was distilled directly from the reaction mixture and the residue was transferred in a drybox to a bottle fitted with a septum cap. The supernatant liquid, when analyzed by vapor phase chromatography, showed three significant peaks to be present, two of which had retention times identical with those of II and III. The third peak had not been observed in the hydrolyzed reaction product. This component had a retention time of 0.8 min. less than the ketone III and both overlapped slightly.

The addition of water to a portion of the reaction mixture and analysis of the product by v.p.c. indicated the loss of the unknown peak and a relative increase in the amount of ketone present. The v.p.c. integrated ratio of II to the sum of III plus the unknown component was 3.74:1. After hydrolysis, the ratio of II to III was 3.45:1. Since the amount of III initially present was quite small, this establishes the fact that the unknown component is the precursor of III. The aqueous solution was found to be acidic, owing mainly to the presence of excess I which is hydrolyzed by water.

The unknown component was isolated by successive collections from the vapor phase chromatograph. Even in the time required for the collection of sufficient material for spectral studies, discoloration of the sample had occurred. The infrared spectrum of this sample indicated the presence of a vinyl ether. The n.m.r. spectrum was quite complex but did have a strong peak at τ 6.42, typical of methoxy groups. A drop of the n.m.r. sample gave a small amount of a white precipitate when allowed to react with silver nitrate. When the n.m.r. sample was rechromatographed, the presence of a very small amount (1~%) of II, and approximately equal amounts of the unknown component and III were indicated. On the basis of this information structure IV has been assigned to the ketone precursor.



$(C_4H_9)_2C{=}C(OCH_3)(C_4H_9)$

IV

It has been reported that this type of vinyl ether is readily hydrolyzed to a ketone, requiring only a trace of acid.[7] In the present case it appears that the presence of chloride ion results from impurities, such as I, which could not be removed by vapor phase chromatography and which catalyze the decomposition of IV in the presence of moisture.

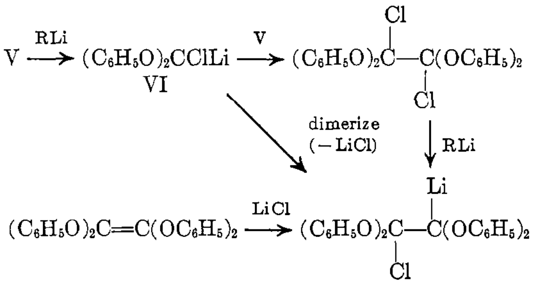
One could speculate on the formation of IV, but it is of little value in this paper.[1] Suffice it to say that several routes can be postulated involving the organolithium reagent derived from I condensing with I, substitution reactions by n-butyllithium, and eliminations of lithium methoxide and hydrogen chloride.

When n-butyllithium was added to I in 2-methylpropene at $-35°$, II and III were isolated in 24 and 3% yields, respectively. These lower yields may well be a consequence of the change in solvent.

Treatment of dichlorodiphenoxymethane[8] (V) with n-butyllithium in ether–cyclohexene solvent at $-70°$ gave as the only isolated product tetraphenoxyethylene in 23% yield. The reaction of V with methyllithium under similar conditions gave tetraphenoxyethylene in 88% yield. No cyclopropane products could be isolated.

$$\underset{\text{V}}{(C_6H_5O)_2CCl_2} \xrightarrow{\text{RLi}} (C_6H_5O)_2C{=}C(OC_6H_5)_2$$

The formation of the observed product can be explained by initially allowing halogen–metal exchange to give chlorodiphenoxymethyllithium (VI). VI can then react in either of two ways, not differentiating between VI and a free diphenoxycarbene. One path requires the reaction of VI with V to give 1,2-dichlorotetraphenoxyethane which undergoes a second halogen–metal exchange to give the organolithium compound VII from which tetraphenoxyethylene is obtained by the loss of lithium chloride. Intermediate VII might also be formed by the reaction between 2 moles of VI followed by loss of lithium chloride. This second path is in effect the mechanism used to explain the formation of tetraphenylethylene from the reactions of dichlorodiphenylmethane with phenyllithium[9] and dibromodiphenylmethane with lithium alkyls.[10]



VII

As pointed out earlier, whether or not a free carbene is formed in the α-elimination reaction of halogen compounds with alkyllithiums is as yet undetermined.[11] The fact that cyclopropane adducts are not found in the reaction product from V, resulting either from the free carbene or its organolithium precursor, may well be due to the decreased electrophilicity of the carbenoid resulting from the presence of the two adjacent oxygen atoms. This reasoning has been used to explain the lack of reactivity in dialkoxy-[12a] and dialkylthiocarbenes.[12b]

Experimental Section[13]

Reaction of Dichloromethyl Methyl Ether and n-Butyllithium in the Presence of Cyclohexene.—A solution of 33.6 g. (0.3 mole)

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(7) W. M. Lauer and M. A. Spielman, *J. Am. Chem. Soc.*, **53**, 1533 (1931).

(8) H. Gross, A. Reiche, and E. Hoft, *Ber.*, **94**, 544 (1961).

(9) G. Wittig and H. Witt, *ibid.*, **74**, 1471 (1941).

(10) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

(11) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

(12) (a) D. M. Lemal, E. P. Gosselink, and A. Ault, *Tetrahedron Letters*, 579 (1964); (b) U. Schöllkopf and E. Wiskott, *Angew. Chem.*, **75**, 725 (1963).

(13) All melting points were taken in a Kofler hot stage and are corrected. Boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 double-beam recording spectrophotometer. N.m.r. spectra were determined on a Varian A-60 recording spectrometer using carbon tetrachloride as solvent (unless otherwise stated) and tetramethylsilane as the internal standard. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weights were obtained with a Mechrolabs Osmometer, Model 301A, or with a Bendix Time-of-Flight mass spectrometer.

of dichloromethyl methyl ether and 97.8 g. (1.2 mole) of cyclohexene in 400 ml. of dry ether was cooled to −35°. To this solution was added dropwise with rapid stirring, 227 ml. of 1.32 *N* (0.3 mole) of *n*-butyllithium in hexane. The reaction mixture was held at −10° for 3 hr. following the completion of the addition and then allowed to warm to room temperature. The reaction mixture was diluted with water and the ether layer was removed. The wash water was acidic to pH paper. The aqueous layer was extracted twice with ether, and the etheral solutions were combined and dried over anhydrous sodium sulfate. Distillation of the residue through a spinning-band column yielded two main fractions. The lower boiling fraction, 12.5 g. (53%), b.p. 56–58° (6 mm.), $n^{20}\mathrm{D}$ 1.4142, was shown by its infrared (major absorption peaks at 3.42, 3.50, 6.85, 7.24, 8.63, and 9.07 μ), n.m.r. [τ 6.77 (singlet, 3), 6.97 (multiplet, 1), and 8.50–9.20 (multiplet, 18)], and mass spectra to be methyl 5-nonyl ether.

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.88; H, 14.01; mol. wt., 158. Found: C, 75.32; H, 14.18; mol. weight, 158 (mass spectrometer).

The higher boiling fraction, 7.6 g. (36%), b.p. 64–86° (0.6 to 0.9 mm.), was redistilled, b.p. 66–68° (0.03 mm.), $n^{20}\mathrm{D}$ 1.4360, and was identified as 6-butyl-5-decanone [lit.[6] b.p. 155–185° (23 mm.), $n^{20}\mathrm{D}$ 1.4414] by its infrared, n.m.r., and mass spectra.

Anal. Calcd. for $C_{14}H_{28}O$: C, 79.18; H, 13.29; mol. weight, 212. Found: C, 78.89; H, 12.96; mol. wt., 211 (osmometer, carbon tetrachloride solvent), 212 (mass spectrometer).

Reaction of *n*-Butyllithium and Dichloromethyl Methyl Ether.—The procedure used was identical with the same reaction carried out in the presence of cyclohexene with the exception that the *n*-butyllithium was prepared in 250 ml. of ether from 3.6 g. (0.5 g.-atom) of lithium wire and 27.4 g. of *n*-butyl bromide. The *n*-butyllithium solution was added to 12.9 g. (0.115 mole) of dichloromethyl methyl ether. Distillation of the reaction product gave 4.9 g. (31%), b.p. 69–70° (8 mm.), of methyl 5-nonyl ether and 3.3 g. (23%), b.p. 63–65° (0.07 mm.), of 6-butyl-5-decanone. The retention times of these products were identical with those of the products from the same reaction in the presence of cyclohexene.

5-Nonanol.—This alcohol was prepared by the procedure of Coleman and Craig,[14] b.p. 94–96° (19 mm.), 68% yield [lit.[14] b.p. 97–98° (20 mm.), 83–85% yield].

5-Nonyl Bromide.—To 114.0 g. (0.42 mole) of well-stirred phosphorus tribromide maintained at −10°, 60.6 g. (0.42 mole) of 5-nonanol was added over a period of 4 hr. The cooling was maintained for an additional 2 hr., and the reaction was then allowed to warm to room temperature with continued stirring. After standing overnight the reaction mixture was cooled in an ice bath, and 100 ml. of ice–water was added. The lower organic layer was removed and the upper layer was extracted with ether. The etheral extracts were combined with the organic layer, washed with dilute sodium carbonate, and dried over sodium sulfate. The ether was distilled off and the fraction with b.p. 98–99° (20 mm.) was collected, 52.5 g. (60%), $n^{20}\mathrm{D}$ 1.4537 [lit.[15] b.p. 83–85° (15 mm.), $n^{20}\mathrm{D}$ 1.4532].

6-Butyl-5-decanone.—A solution of 10.3 g. (0.05 mole) of 5-nonyl bromide in 75 ml. of dry ether was added dropwise to a well-stirred mixture of 1.3 g. (0.054 g.-atom) of magnesium turnings in 50 ml. of ether under a nitrogen atmosphere, and the stirring was continued overnight. The ethereal solution was filtered under nitrogen. To the resulting solution was added dropwise 2.49 g. (0.03 mole) of valeronitrile dissolved in 50 ml. of ether. The mixture was stirred for 2 days and a solution of 12 ml. of concentrated hydrochloric acid in 500 ml. of ice–water was added. After stirring for 5 hr. the etheral layer was separated. The aqueous layer was extracted with two 150-ml. portions of ether and the combined ethereal solutions were dried over sodium sulfate. The ether was distilled, leaving a residue weighing 8.29 g. The residue was vapor phase chromatographed on a 6 ft. × 0.25 in. Silicone Oil 220 on firebrick column. The presence of less than 2% of 6-butyl-5-decanone was indicated. This peak was collected and its infrared and n.m.r. spectra were obtained. They were identical with those reported for 6-butyl-5-decanone earlier in this paper.

6-Butyl-5-decanol.—A solution of 1.0 g. (0.005 mole) of 6-butyl-5-decanone in 6 ml. of ether was added dropwise to a suspension of 0.17 g. (0.0045 mole) of lithium aluminum hydride in 10 ml. of ether. After the addition was complete and the mixture had stirred for 5 min., water was carefully added until the excess hydride had been decomposed. The resulting mixture was poured in 25 ml. of a 10% sulfuric acid–ice–water mixture and the etheral layer was separated. The aqueous layer was extracted twice with ether and the combined ethereal solutions were dried over sodium sulfate. The ether solvent was removed by distillation and the residue (1.02 g.) was analyzed by vapor phase chromatography which indicated by integration (Disc integrator) of the peaks present that the residue contained 0.88 g. (88%) of alcohol. The chromatography was carried out on a 6 ft. × 0.25 in. Versamid 900 on Chromosorb W column. A collected sample had the following infrared spectrum: 3.02 (m), 3.48 (s), 3.52 (s), 6.83 (m), 7.26 (w), 8.76 (w), 8.94 (w), 9.72 (w), 9.88 (w), 10.52 (w), and 13.68 (w) μ. The n.m.r. spectrum (neat) of this compound using an external tetramethylsilane standard showed τ 6.32 (singlet) (1), 6.53 (multiplet) (1), 8.78 (multiplet), and 9.18 (multiplet). The last two peaks together integrated for 28 protons.

Anal. Calcd. for $C_{14}H_{30}O$: C, 78.43; H, 14.08. Found: C, 78.31; H, 13.86.

1-Chloropentyl Methyl Ether.—Anhydrous hydrogen chloride was bubbled through a solution of 43.0 g. (0.5 mole) of *n*-valeraldehyde and 16.0 g. (0.5 mole) of methanol in 200 ml. of ether cooled to 0° for 2.5 hr. As two layers formed, care was taken to bubble the hydrogen chloride only through the upper layer. The lower layer was then removed. The upper layer was dried over calcium chloride and distilled, yielding 48.9 g. (72%) of product, b.p. 50–51.8° (20 mm.). The distillate had the following n.m.r. spectrum: τ 4.57 (triplet) (1), 6.53 (singlet) (3), 8.05 (multiplet) (2), 8.61 (multiplet) (4), 9.08 (triplet) (3). Its infrared spectrum showed no carbonyl absorption and strong methoxy absorption.

Reaction of 1-Chloropentyl Methyl Ether and *n*-Butyllithium in the Presence of Cyclohexene.—To a solution of 13.6 g. (0.1 mole) of 1-chloropentyl methyl ether and 33 g. (0.4 mole) of cyclohexene in 150 ml. of ether cooled to −35° was added dropwise 75.7 ml. (0.1 mole) of 1.32 *N* *n*-butyllithium in hexane. After the addition was complete, stirring was continued while the mixture came to room temperature. The mixture was diluted with water and the ethereal layer was separated. The aqueous layer was extracted twice with ether and the ethereal solutions were combined and dried over anhydrous sodium sulfate. The ether solvent and all products boiling below 120° were distilled from the dried ether extracts, leaving a residue weighing 13.1 g., which vapor phase chromatography showed to be 56% (Disc integrator) methyl 5-nonyl ether or 7.3 g. (93% yield). Distillation yielded a fraction, b.p. 63.9° (9.5 mm.), $n^{20}\mathrm{D}$ 1.4144, having an infrared spectrum identical with the ether product from the reaction of *n*-butyllithium and dichloromethyl methyl ether under similar conditions.

Vapor phase chromatographic analysis gave no indication of the ketone III being present. Also, there was no carbonyl absorption in the infrared spectrum of the reaction products.

Reaction of *n*-Butyllithium and Dichloromethyl Methyl Ether without Hydrolysis.—To a solution of 11.2 g. (0.1 mole) of dichloromethyl methyl ether in 150 ml. of dry ether maintained at −35 to −30° under dry nitrogen was added dropwise with rapid stirring 62 ml. (0.1 mole) of 0.162 *N* *n*-butyllithium. Following the addition the reaction mixture was allowed to warm to −10° and held there for 2 hr. The ether solvent was then distilled from the reaction mixture. The remaining mixture was transferred in a drybox to a bottle fitted with a rubber septum. The supernatant liquid was analyzed by vapor phase chromatography using a 6 ft. × 0.25 in. Silicone Oil 220 on firebrick column. The major peaks, 8.8 and 13.5 min., and a minor peak at 14.2 min., were observed and their ratios of areas as shown by a Disc integrator were 10:10:1, respectively. An admixture of the supernatant liquid and methyl 5-nonyl ether resulted in the attenuation of the other peaks in the sample relative to the peak at 8.8 min. When 6-butyl-5-decanone was added to the sample, a similar result was observed for the 14.2-min. peak.

In another run following the same experimental procedure, but without distillation of any solvent from the reaction mixture, the ratio of the 8.8-min. peak to the combined 13.5- and 14.2-min. peaks was 3.74:1. After mixing a small portion of the reaction mixture with water and passing a part of the ethereal

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(14) G. H. Coleman and D. Craig, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 179.

(15) J. A. King and F. H. McMillian, *J. Am. Chem. Soc.*, **68**, 1369 (1946).

solution through the vapor phase chromatograph, the 13.5-min. peak had disappeared, and the ratio of the 8.8-min. peak to the 14.2-min. peak was 3.45:1.

The 13.5-min. peak was collected by vapor phase chromatography, and its n.m.r. and infrared spectra were obtained. This sample became brown during the time required to collect a sufficient sample for the spectra. When the n.m.r. sample was rechromatographed, the presence of a small amount of methyl 5-nonyl ether and approximately equivalent amounts of the 13.5-min. component and 6-butyl-5-decanone was indicated.

Reaction of Dichloromethyl Methyl Ether and *n*-Butyllithium in the Presence of 2-Methylpropene.—In the same manner as in the reaction of dichloromethyl methyl ether and *n*-butyllithium in the presence of cyclohexene, 11.5 g. (0.1 mole) of dichloromethyl methyl ether, 94 g. of 2-methylpropene, and 65 ml. (0.1 mole) of 1.5 *N* *n*-butyllithium in hexane were added together to yield, according to the integrated vapor phase chromatographic analysis, 2.9 g. (24%) of methyl 5-nonyl ether and 0.3 g. (3%) of 6-butyl-5-decanone.

Reaction of Dichloromethyl Methyl Ether and Methyllithium in the Presence of 2-Methylpropene.—To 20.7 g. (0.18 mole) of dichloromethyl methyl ether in 90 g. of 2-methylpropene maintained at -10 to $-15°$ was added with rapid stirring 200 ml. (0.18 mole) of 0.905 *N* methyllithium in ether over a period of 1 hr. Cooling was continued for an additional 2 hr. after which time the reaction mixture was allowed to warm to room temperature. Water was added to the mixture, the ether layer was separated, and the aqueous layer was extracted twice more with ether. The ethereal solutions were combined and dried over anhydrous sodium sulfate. The ether was distilled from the solution, leaving a residue weighing 16.0 g., which on vapor phase chromatography using a 6 ft. × 0.25 in. γ,γ-nitromethylpimelonitrile-on-firebrick column was shown to contain 8.5 g. (53.8% yield) of 2,2-dimethylmethoxycyclopropane. The n.m.r. spectrum of a sample collected from the vapor phase chromatograph showed peaks at τ 6.74 (singlet) (3), 7.21 (multiplet) (1), 8.90 (singlet) (3), 9.04 (singlet) (3), and 9.73 (multiplet) (2). This agrees with the spectrum published.[3]

Dichlorodiphenoxymethane.—The procedure of Gross and coworkers[8] was followed for the preparation of this compound, b.p. 164–167° (6 mm.), 49% yield [lit.[8] b.p. 183–185° (12 mm.), 63% yield].

Reaction of Dichlorodiphenoxymethane and *n*-Butyllithium in the Presence of Cyclohexene.—To a solution of 24.6 g. (0.3 mole) of cyclohexene and 33.0 g. (0.089 mole) of dichlorodiphenoxymethane in 200 ml. of dry ether cooled to $-70°$, 100 ml. (0.13 mole) of 1.28 *N* *n*-butyllithium in hexane was added dropwise over a period of 2 hr. Stirring of the mixture was continued overnight as the mixture was allowed to come to room temperature. The reaction mixture was filtered, the precipitate was dissolved in water and extracted with chloroform, and the chloroform extracts were dried over calcium chloride. The chloroform was removed from the solution under reduced pressure yielding 3.7 g. of tetraphenoxyethylene, m.p. 163–167°. Recrystallization from chloroform gave colorless crystals, m.p. 166.5–168° (lit.[16] m.p. 168°), which were further identified by their infrared and n.m.r. (multiplet centered at τ 2.98) spectra.

Distillation of the filtrate gave only a small amount of phenol after removal of the solvents. The residue from the distillation yielded an additional 0.40 g. of tetraphenoxyethylene, giving a total of 4.1 g. (23% yield).

Reaction of Dichlorodiphenoxymethane and Methyllithium in the Presence of Cyclohexene.—A solution of 16.4 g. (0.2 mole) of cyclohexene and 13.5 g. (0.05 mole) of dichlorodiphenoxymethane in 300 ml. of anhydrous ether under nitrogen was cooled to $-72°$. To this was added dropwise over a period of 1 hr. with rapid stirring, 0.104 mole of methyllithium [prepared from 2.3 g. (0.33 g.-atom) of lithium in 50 ml. of ether and 21.33 g. (0.15 mole) of methyl iodide]. While the stirring was continued, the reaction mixture was allowed to warm. During this period the reaction mixture began to turn red and was maintained at -40 to $-35°$ for 30 min. The dark color was found to be due to iodine and was removed by washing the reaction mixture with aqueous sodium thiosulfate. This procedure was repeated several times over a period of 2 days. The ethereal solution was dried over sodium sulfate and the ether then was distilled off, leaving 7.9 g. of crystalline material which was recrystallized from ethanol to give 6.98 g. (88%) of tetraphenoxyethylene, m.p. 168–169°.

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Cycloheptanol. Steric Influence of the 4-*t*-Butyl Group

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The *t*-butyl group, by acting as a remote but compelling control, has been used extensively to confer conformational stability to a 1-substituent on a cyclopentane,[1] cyclohexane,[2–4] and cyclooctane[5] ring. The ability of a *t*-butyl group to impart analogous steric control on a 1-substituted cycloheptane ring remains to be studied.

Based on the computed *A* value,[2] the equatorial position of the *t*-butyl group on a cyclohexane ring is favored over the axial position by 5.4–5.8 kcal./mole, a value sufficiently large to compel the *t*-butyl group to be equatorial. A similar equatorial preference for the *t*-butyl group would be expected on the cycloheptane ring in a pseudo-chair form; however, if the seven-membered ring is predominantly in the twist-chair form,[6] it is to be expected that slight conformational preference would be exerted by a *t*-butyl group bonded to an axis carbon.

The purpose of this paper is to measure the degree of conformational stability imparted by a 4-*t*-butyl group on cycloheptanol. To this end, gas chromatographic (including capillary column g.c.), n.m.r., and kinetic methods have been applied.

Results

4-*t*-Butylcycloheptanone (**2**) was prepared by the diazomethane ring expansion of 4-*t*-butylcyclohexanone (**1**). The reduction of ketones **1** and **2** with three reducing reagents is summarized in Table I. The 4-*t*-butylcyclohexanol (**3**) compositions were determined by gas chromatography at 160° using three 5-ft. columns packed with (1) 40–60-mesh Tide soap, (2) 20 wt. % 1,2,3-tris(2-cyanoethoxy)propane on 30–60-mesh Chromosorb, and (3) 20 wt. % diethylene glycol succinate on 30–60-mesh Chromosorb. Excellent separation was obtained for all epimeric mixtures of 4-*t*-butylcyclohexanol.

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