2-norbornanone, 497-38-1; cyclohexylidenemethyl *p*-fluorophenyl sulfone, 40583-00-4; chloromethyl *p*-fluorophenyl sulfide, 459-27-8; cyclohexanone, 108-94-1; methyl 2-butyloctyl sulfone, 40583-02-6; *p*-chlorophenyl 1,2-dimethyloctyl sulfone, 40583-03-7; *p*-chlorophenyl 2-(3-ethoxycarbonylcyclohexyl)propyl sulfone, 40583-04-8; *p*-chlorophenyl 2-(3-ethoxycarbonylcyclohexyl)hexyl sulfone, 40583-05-9; *p*-chlorophenyl neopentyl sulfone, 40583-06-0.

Asymmetric Additions of Organolithium Reagents to Allylic Alcohols

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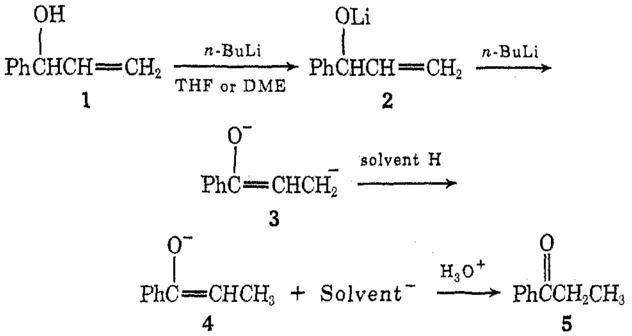
The reaction of α-vinylbenzyl alcohol (**1**) with *n*-butyllithium in hexane–TMEDA affords 1-phenyl-2-methyl-1-hexanol (**6**) and 5-benzyldecane (**7**) in an 3:1 ratio. The hydroxyl group in **1** induces the *n*-butyllithium to attack the double bond in a highly stereospecific manner, such that only one pair of enantiomers (**6a** and **6b**) are formed from **1** (*dl*). Addition to the double bond of **1** is also observed with *tert*-butyllithium except that in this case the addition is exclusively to the terminal end of olefin. The corresponding methyl ether of α-vinylbenzyl alcohol (**12**) does not react with *n*-butyllithium in an addition manner, but rather undergoes 1,2 and 1,4 Wittig rearrangements.

The reaction of 2 equiv of *n*-butyllithium in hexane–THF or hexane–DME (dimethoxyethane) with α-vinylbenzyl alcohol (**1**) gives a good yield of propiophenone (**5**).[1] The mechanism of this rearrangement has been established to be that shown in Scheme I.

SCHEME I



$$\underset{\mathbf{1}}{\mathrm{PhCH(OH)CH{=}CH_2}} \xrightarrow[\text{THF or DME}]{n\text{-BuLi}} \underset{\mathbf{2}}{\mathrm{PhCH(OLi)CH{=}CH_2}} \xrightarrow{n\text{-BuLi}} \underset{\mathbf{3}}{\mathrm{PhC(O^-){=}CH\bar{C}H_2}} \xrightarrow{\text{solvent H}} \underset{\mathbf{4}}{\mathrm{PhC(O^-){=}CHCH_3}} + \text{Solvent}^- \xrightarrow{\mathrm{H_3O^+}} \underset{\mathbf{5}}{\mathrm{PhC({=}O)CH_2CH_3}}$$

The dianion intermediate **3** never reaches a large concentration, because, soon after it forms, it abstracts a proton from the solvent. Organic dianions have proven to be useful synthetic intermediates;[2] consequently, we sought ways to increase the effective yield of this highly reactive species and possibly others like it.

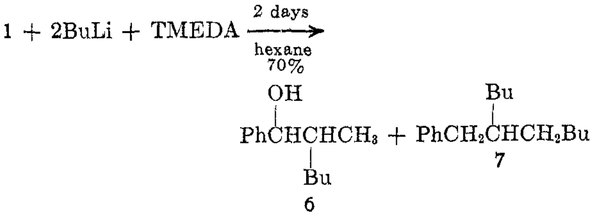
An ideal solvent for running these reactions would be pure hexane, since it has no acidic hydrogens; however, *n*-butyllithium loses much of its metalation powers in nonoxygenated solvents.[3] Thus, it was not surprising to find that α-vinylbenzyl alcohol was recovered "unchanged" when treated with excess *n*-butyllithium in pure hexane. Since tertiary amines are known[3,4] to enhance the reactivity of alkyllithium compounds, we repeated the later reaction in the presence of *N*,*N*,-N^1,N^1-tetramethylethylenediamine (TMEDA) and found that a completely different reaction had occurred—the butyllithium added to the double bond.

Although one would not normally expect an electron-rich organometallic reagent to add to nonconjugated olefins, there are several reported cases that this kind of reaction can occur.[5] Most of the reported organometallic additions to olefins have involved allylic alcohols. There appears to be a complex formed between lithium alkoxides and alkyllithium reagents which can subsequently deliver the RLi to an adjacent olefin in an intramolecular fashion. It is known that the solubility of lithium butoxide in *n*-heptane increases proportionately with increasing *n*-butyllithium concentration.[6] This suggests that a complex is formed between butoxide and lithium alkyl by the interaction of an oxygen unshared electron pair with a vacant hybridized orbital of lithium.[6,7]

The role that TMEDA plays is not clear. Some organolithium additions to allylic alcohols are known to occur in the absence of this reagent. It seems reasonable that the increased reactivity of organolithium reagents in the presence of TMEDA is due to complexation of the lithium atom with one or more amine sites.[8] Since the TMEDA does not interfere with addition of RLi to the allylic alkoxide, the alkoxide must either join with TMEDA to give a tetrahedral complex of the RLi or displace one of the amino groups of the bidentate ligand.

Results

The reaction of 2 equiv of *n*-butyllithium with 1 equiv of α-vinylbenzyl alcohol in hexane in the presence of 1–4 equiv of TMEDA for 2 days produced a 70% yield of three products: 1-phenyl-2-methyl-1-hexanol (**6**), 68%, 5-benzyldecane (**7**), 22%, and an unidentified



$$\mathbf{1} + 2\mathrm{BuLi} + \mathrm{TMEDA} \xrightarrow[\substack{\text{hexane}\\70\%}]{\text{2 days}} \underset{\mathbf{6}}{\mathrm{PhCH(OH)CH(Bu)CH_3}} + \underset{\mathbf{7}}{\mathrm{PhCH_2CH(Bu)CH_2Bu}} \quad (1)$$

component, 10%. When only 0.5 equiv of TMEDA was used over a reaction period of 1 day, the yield

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[1] D. R. Dimmel and S. B. Gharpure, *J. Amer. Chem. Soc.*, **93**, 3991 (1971).

[2] T. M. Harris and C. M. Harris, *Org. React.*, **17**, 155 (1969).

[3] J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69**, 693 (1969).

[4] R. J. Crawford, W. F. Erman, and C. D. Broaddus, *J. Amer. Chem. Soc.*, **94**, 4298 (1972), and references cited therein.

[5] J. K. Crandall and A. C. Clark, *J. Org. Chem.*, **37**, 4236 (1972), and references cited therein.

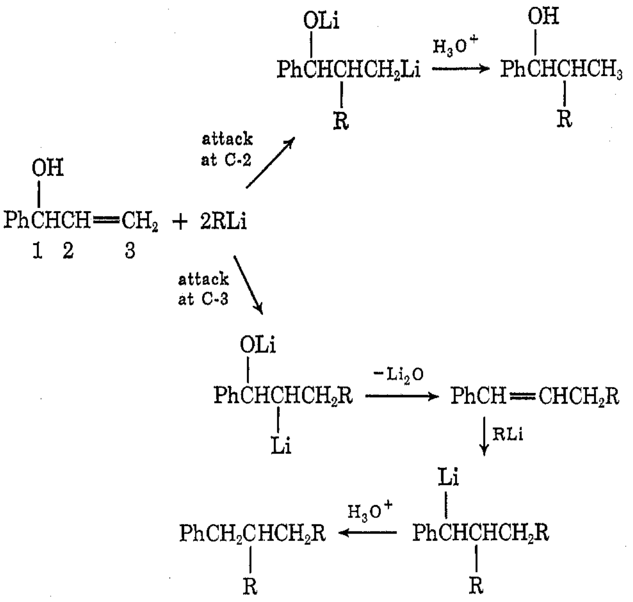
[6] C. W. Kamienski and D. H. Lewis, *ibid.*, **30**, 3498, 3502 (1965).

[7] T. L. Brown, J. A. Ladd, and G. N. Newman, *J. Organometal. Chem.*, **3**, 1 (1965).

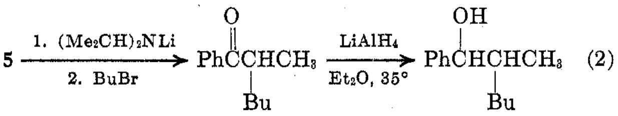
[8] G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964).

dropped to 36% but the product distribution remained the same. The products were characterized mainly by spectral means (see the Experimental Section). A probable mechanism which explains the formation of **6** and **7** is shown in Scheme II.

SCHEME II



To verify the structure of **6**, the synthesis shown in eq 2 was carried out. The two samples of **6** were not



$$5 \xrightarrow[2.\ \mathrm{BuBr}]{1.\ (\mathrm{Me_2CH})_2\mathrm{NLi}} \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\underset{\underset{\mathrm{Bu}}{|}}{\mathrm{CH}}\mathrm{CH_3} \xrightarrow[\mathrm{Et_2O},\ 35^\circ]{\mathrm{LiAlH_4}} \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{H}\underset{\underset{\mathrm{Bu}}{|}}{\mathrm{CH}}\mathrm{CH_3} \qquad (2)$$

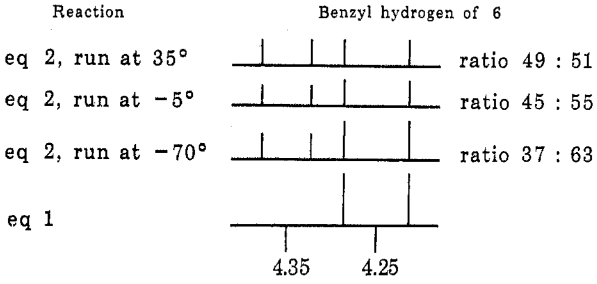
8 **6**

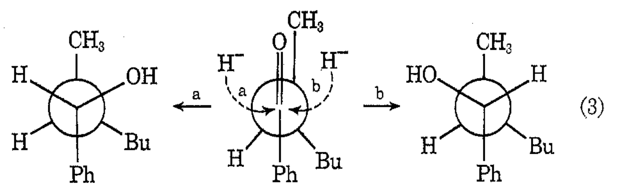
identical. For **6** prepared from **8** the benzyl proton in the 100-MHz nmr spectrum appeared as two separate, equally intense doublets, one at δ 4.25 (J = 6.5 cps) and the other at δ 4.35 (J = 5.5 cps). The sample of **6** derived from **1** showed only the δ 4.25 (J = 6.5 cps) doublet. The two benzyl proton doublets correspond to the two diastereomeric enantiomer pairs which **6**, with its two asymmetric carbons, could possess. The fact that **6** derived from *n*-butyllithium addition to **1** gives just the one doublet means that the addition is highly stereoselective (at least 98%).

Since there is an asymmetric carbon next to the carbonyl of **8**, one might expect the hydride reduction of this ketone to give an imbalance of diastereomeric products. Under the conditions of refluxing ether, the hydride reduction of **8** gave nearly an equal mixture of diastereomers. However, reduction of **8** at lower temperatures[9] gave a greater percentage of the δ 4.25 doublet (Chart I). According to the rules set down for asymmetric reductions of ketones,[10] the δ 4.25 doublet would correspond to the major set of enantiomers **6a** and **6b** and the δ 4.35 doublet to the minor set of enantiomers **6c** and **6d**. Consequently, the principal product of *n*-butyllithium addition to **1** is the enantiomer pair **6a**, **6b**.

CHART I

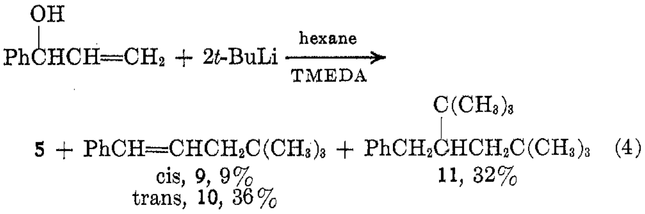
THE APPEARANCE OF THE BENZYL PROTON REGION IN THE NMR SPECTRA OF 6 PREPARED IN SEVERAL WAYS





6a, 6b **8** (*dl*) **6c, 6d**

To test how general this reaction is, several other alkyllithium reagents were screened. Methyllithium in hexane–TMEDA and phenyllithium in THF seemingly had no effect on α-vinylbenzyl alcohol; no addition or dianion products were observed. In contrast, *tert*-butyllithium in hexane–TMEDA reacted rapidly with α-vinylbenzyl alcohol to give both dianion and addition products (eq 4). In the case of *tert*-butyllithium all of the observed addition products, **9–11**, result from RLi attacking the terminal carbon of the double bond of **1**, *i.e.*, attack at C-3 (see Scheme II).



$$\mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HCH{=}CH_2} + 2t\text{-BuLi} \xrightarrow[\text{TMEDA}]{\text{hexane}}$$

$$5 + \underset{\substack{\text{cis, } 9,\ 9\% \\ \text{trans, } 10,\ 36\%}}{\mathrm{PhCH{=}CHCH_2C(CH_3)_3}} + \underset{11,\ 32\%}{\mathrm{PhCH_2}\overset{\mathrm{C(CH_3)_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_2C(CH_3)_3}} \qquad (4)$$

The importance of the hydroxyl group of **1** to direct attack at the allylic double bond is shown by the following results. Compound **1** was treated with base and methyl iodide to afford the methyl ether **12**. Reaction of **12** with 2 equiv of *n*-butyllithium in hexane–TMEDA gave, according to vpc analysis, the following mixture of volatile products: **5** (2%), **13** (46%), **14** (22%), and **15** (28%). If the reaction was done in THF as the solvent the same set of products resulted except that the ratios of volatile products were now different: **5** (35%), **13** (24%), **14** (27%), **15** (2%), and two unidentified components of 10 and 2% intensities. The reaction appears to be an example of a Wittig rearrangement, in which the 1,2 Wittig rearrangement product **13** predominates in hexane, while both 1,2 and 1,4[11] processes are occurring to about the same extent in THF. The ketone **5** more than likely arises from

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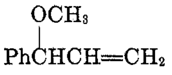
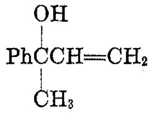
[9] The ratio of diastereomers produced in an asymmetric reduction is known to increase with decreasing temperatures: Y. Gault and H. Felkin, *Bull. Soc. Chim. Fr.*, 1342 (1960).

[10] (a) D. J. Cram and F. A. Abd Elhafez, *J. Amer. Chem. Soc.*, **74**, 5828 (1952); (b) G. J. Karabatsos, *ibid.*, **89**, 1367 (1967); (c) M. Cherest, H. Felkin, and N. Prudent, *Tetrahedron Lett.*, 2199, 2205 (1968).

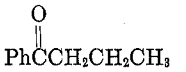
[11] For another example of 1,4 Wittig rearrangement see H. Felkin and A. Tambuté, *ibid.*, 821 (1969).


$\mathrm{Ph\overset{OCH_3}{C}HCH{=}CH_2}$

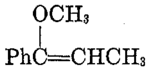
12


$\mathrm{Ph\underset{CH_3}{\overset{OH}{C}}CH{=}CH_2}$

13


$\mathrm{Ph\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3}$

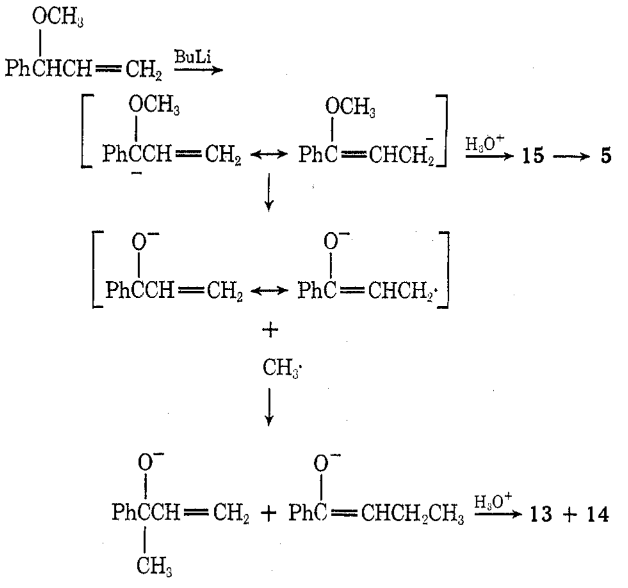
14


$\mathrm{Ph\overset{OCH_3}{C}{=}CHCH_3}$

15

hydrolysis of the vinyl ether **15** during work-up. A possible mechanism is shown in Scheme III.[12]

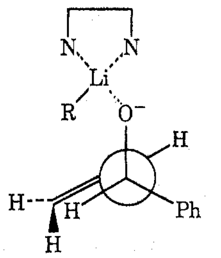
SCHEME III



Structural variations of the allylic alcohol can have a profound effect on the course of the reaction. For example, the tertiary alcohol **13** showed no observable addition or rearrangement products upon treatment with *n*-butyllithium in hexane–TMEDA.

Conclusions

Assuming a conformational preference where the phenyl group is in the least hindered environment and the alkoxide is perpendicular to the plane of the olefin group, the stereochemistry of the *n*-butyllithium addition to α-vinylbenzyl alcohol can be explained by the intermediacy of a structure like **16**.



16

Felkin and coworkers[13] have also observed some stereospecific additions of lithium alkyls to secondary allylic alcohols. In fact, they have added ethyllithium to α-vinylbenzyl alcohol (**1**) and got a compound similar to **6** (ethyl instead of butyl) in 30% yield and a 6:1 preference of diastereomers. Exactly why the butylation of **1** goes in better yield and is more stereoselective than the ethylation is not clear.

Except for cyclic alcohols, the principal attack of a RLi reagent on an allylic alcohol occurs at the olefinic carbon closest to the alcohol.[5,13] However, in the case of *tert*-butyllithium addition to **1**, the only addition products result from attack at the olefinic carbon furthest from the alcohol group. In direct contrast to this is the observation by Crandall[5] that *tert*-butyllithium exclusively adds to C-2 of allyl alcohol. It is obvious that steric factors play an important role in these additions. This is especially borne out by the fact that the tertiary alcohol **13** gives no addition products with *n*-butyllithium. The failure of this latter reaction may be a consequence of the intermediate species not preferentially existing in a conformation, such as **16**, that is essential for reaction.

Experimental Section

Boiling points are uncorrected. Proton magnetic resonance spectra were obtained with a Varian A-60D spectrometer using tetramethylsilane as the reference. Infrared spectra were recorded on a Perkin-Elmer Model 137B Infracord. Mass spectra were taken on a Consolidated Electrodynamics Corp. 103C mass spectrometer. Analytical and preparative analyses of liquid products were performed on a 6 ft × 0.25 in. aluminum column packed with 20% SE-30 on 80–100 mesh Chromosorb W, a 13 ft × 0.25 in. aluminum column packed with 20% diethylene glycol succinate (DEGS) on 80–100 mesh Chromosorb W, and a 8 ft × 0.25 in. aluminum column packed with 20% Reoplex 400 on 60–80 mesh Chromosorb W using an F & M Model 700 gas chromatograph equipped with a thermal conductivity detector. The thermal responses of the components in the vpc traces were not calibrated; thus, the relative areas on the traces, as reported, may not represent the relative molar proportions of the volatile components.

Dimethoxyethane and tetrahydrofuran were distilled from Na/K alloy before use. Commercial anhydrous reagent grade ethyl ether and hexane were used without further purification. Concentrated solutions of *n*- and *tert*-butyllithium in hexane were purchased from Alfa Inorganics, Inc.

***n*-Butylation of α-Vinylbenzyl Alcohol (1).**—To a stirred, cold (0°) solution of 5.0 g (37.3 mmol) of α-vinylbenzyl alcohol (**1**)[14] and 4.34 g (37.3 mmol) of TMEDA in about 60 ml of hexane was added, over a 15-min period, 36 ml (79 mmol) of a solution of *n*-butyllithium. The resulting solution was stirred at room temperature for 2 days under a nitrogen atmosphere and then added to 30 ml of ice–water. Ether was added and the organic layer was separated. The aqueous layer was extracted with ether several times. The combined ether extracts were successively washed with 10% HCl, 5% NaOH, and water, dried over $\mathrm{MgSO_4}$, filtered, and concentrated on a rotary evaporator to leave 5.1 g of liquid products. The two major components were separated by preparative vpc (SE-30, 180°, He flow 75 ml/min).

1-Phenyl-2-methyl-1-hexanol (6) (69%) had retention time 26 min; ir (neat) 3600 $\mathrm{cm^{-1}}$ (OH); nmr ($\mathrm{CCl_4}$) δ 0.6–1.6 [m, 13, $\mathrm{-CH(CH_3)C_4H_9}$], 3.62 (s, 1, OH), 4.28 (d, 1, J = 6.5 Hz, PhCH), and 7.18 (s, 5, Ph); 100 MHz nmr ($\mathrm{CCl_4}$) δ 4.25 (d, 1, J = 6.5 Hz, PhCH); mass spectrum (70 eV) m/e 192 (molecular ion), 174, 154, 107 (base peak), 105, 91, 79, and 77.

5-Benzyldecane (7) (25%) had retention time 39 min; ir, only aromatic and aliphatic hydrocarbon absorptions; nmr ($\mathrm{CCl_4}$) δ 0.89–1.55 [m, 21, $\mathrm{-CH(C_4H_9)CH_2(C_4H_9)}$], 2.52 (d, 2, J = 7 Hz, $\mathrm{PhCH_2}$), and 7.18 (s, 5, Ph); mass spectrum (70 eV) m/e 232 (molecular ion), 92, 91 (base), 85, 77, 71, 57, 55, 43, and 41.

The same reaction when done with 4 equiv of TMEDA per 1 equiv of **1** afforded 5.1 g of liquid residue composed of 65% **6**, 22% **7**, and 13% of an unidentified product. When the re-

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[12] Recent evidence suggests that the Wittig rearrangement involves radical anion intermediates: (a) P. T. Lansbury, V. A. Pattison, J. D. Siller, and J. B. Bieber, *J. Amer. Chem. Soc.*, **88**, 78 (1966); (b) H. Schäfer, U. Schöllkopf, and D. Walter, *Tetrahedron Lett.*, 2809 (1968).

[13] H. Felkin, G. Swierczewski, and A. Tambuté, *ibid.*, 707 (1969).

[14] R. Delaby and L. Lecomte, *Bull. Soc. Chim. Fr.*, **4**, 738 (1937).

action was done with 0.5 equiv of TMEDA for 1 day, 2.7 g of a mixture of 69% **6**, 21% **7**, and 10% of an unknown component was obtained.

2-Methylhexanophenone (8).—To a stirred solution of 55 ml (110 mmol) of a solution of *n*-butyllithium in 300 ml of DME, and cooled to −50°, 16.0 ml (110 mmol) of diisopropylamine was added dropwise.[15] The resulting solution was stirred at −50 to −20° for a few minutes and then 30 ml of a solution containing 12.7 g (95 mmol) of propiophenone in DME was added dropwise and with stirring over 30 min, during which time the temperature of the solution was kept between −20 and 0°. The resulting solution was rapidly warmed to 30° with stirring and then 40 g (300 mmol) of *n*-bromobutane was added rapidly (15 sec). The temperature of the resulting mixture rose to 50° and then began to fall. The mixture was stirred at reflux for 2 hr and at room temperature for 15 hr, and then poured into 300 ml of cold, saturated $NaHCO_3$ and extracted with ether. The ether extract was washed successively with 5% HCl and 5% $NaHCO_3$ and then dried over $MgSO_4$, concentrated, and vacuum distilled to give 14.2 g (78% yield) of a liquid: bp 113–115° (2 mm) [lit.[16] bp 107–110° (2 mm)]; analysis by vpc (Reoplex 400) showed a purity of 96%; ir (film) 1690 cm^{-1} (C=O); nmr (CCl_4) δ 0.82 (t, 3, J = 5.0 Hz, $-CH_2CH_3$), 1.15 (d, 3, J = 7 Hz, $-CHCH_3$), 1.57 [m, 6, $-(CH_2)_3-$], 3.49 (m, 1, –CH–), 7.3–8.0 (m, 5, Ph); 2,4-DNP mp 74–76° (lit.[16] mp 74.5–76.0°).

1-Phenyl-2-methyl-1-hexanol (6) from Reduction of 2-Methylhexanophenone (8).—Into a dry 250-ml round-bottom flask was placed 1 g (26 mmol) of $LiAlH_4$ and 150 ml of anhydrous ether. From the top of the condenser, 10 g (52 mmol) of 2-methylhexanophenone was added dropwise. The solution was refluxed with stirring for 7 hr and then cooled in an ice bath. Saturated Na_2SO_4 was added dropwise (no excess) until the gray solution turned white. The mixture was filtered and the filtrate was dried over $MgSO_4$. After the ether was removed on a rotary evaporator, the residue was vacuum distilled to give 7.2 g (70% yield) of 1-phenyl-2-methyl-1-hexanol, bp 126–129° (6.2 mm) [lit.[17] bp 130–132° (5 mm)], 98% pure by vpc (Reoplex 400) analysis. The vpc retention time was identical with that of **6** prepared from butylation of **1**. Spectral properties were also quite similar except for the nmr appearance of the benzyl protons, which in this case showed a triplet-like signal at δ 4.3 in the 60-MHz spectrum and two equally intense doublets in the 100-MHz spectrum, one at δ 4.25 (J = 6.5 Hz) and the other at 4.35 (J = 5.5 Hz).

Repeating the reaction as described above except for cooling the flask during the reaction in an ice-salt bath gave a 55:45 ratio of the δ 4.25 to 4.35 doublets. Repeating the reaction again in a Dry Ice bath (−68 to −72°) gave a product showing a 63:37 ratio of the δ 4.25 to 4.35 doublets.

***tert*-Butylation of α-Vinylbenzyl Alcohol (1).**—To a 250-ml three-neck round-bottom flask fitted with a dropping funnel, N_2 inlet, and drying tube was added 3.4 g (25 mmol) of compound **1**, about 70 ml of hexane, and 1.5 g (14 mmol) of TMEDA. To the cool solution, 45 ml (55 mmol) of a solution of *tert*-butyllithium was added dropwise. After stirring at room temperature for 36 hr and refluxing for 2 hr, the solution was cooled to room temperature and quenched with water. A work-up similar to the *n*-butylation of **1** afforded 2.3 g of a liquid.

Analysis by vpc (SE-30) showed several components. The major components were collected by preparative vpc. The properties of the four major components collected are reported in the following way—compound (no.) (per cent of the mixture, retention time on a SE-30 at 170°, He flow 150 ml/min), then ir; nmr; uv; mass spectral data.

Propiophenone (5) (23%, 7 min) was identical in retention time, nmr, ir, and mass spectral properties with an authentic sample.[18]

cis-β-**Neopentylstyrene (9)** (9%, 9 min) had ir (CCl_4) 1370 and 1390 cm^{-1} (*t*-Bu); nmr (CCl_4) δ 0.91 (s, 9, CH_3), 2.21 (d, 2, J = 7 Hz, CH_2), 6.18–6.4 (m, 2, –CH=CH), 7.23 (s, 5, Ph); uv λ_{max} (EtOH) 240 nm (ϵ_{max} 17,200);[19] mass spectrum (70 eV) m/e 174 (molecular ion), 159, 118, 117, 115, 91, 77, 65, 63, 57 (base), 51, 43, 41, 39, 29, and 27.

trans-β-**Neopentylstyrene (10)** (35%, 13 min) had ir (CCl_4) 1370 and 1390 (*t*-Bu) and 970 cm^{-1} (trans RCH=CHR); nmr (CCl_4) δ 0.94 (s, 9, $-CH_3$), 2.19 (d, 2, J = 6 Hz, CH_2), 6.3–6.7 (m, 2, –CH=CH–), 7.26 (s, 5, Ph); uv λ_{max} (EtOH) 248 nm (ϵ_{max} 30,000);[19] mass spectrum (70 eV) m/e 174 (molecular ion), 159, 118, 117, 115, 91, 77, 65, 63, 57 (base), 51, 43, 41, 39, 29, and 27.

3-Benzyl-2,2,5,5-tetramethylhexane (11) (23%, 28 min) had ir (CCl_4) 1370 and 1400 cm^{-1} (*t*-Bu), plus strong aliphatic and aromatic absorptions; nmr (CCl_4) δ 0.82 (s, 18, CH_3), 0.95–1.68 (m, 3, $-CHCH_2-$), 2.6–2.88 (m, 2, $PhCH_2$), and 7.20 (s, 5, Ph); mass spectrum (70 eV) m/e 232 (molecular ion), 176, 141, 140, 120, 119, 117, 105, 91 (base), 85, 77, 71, and 41.

Rearrangement of Methyl 1-Phenylallyl Ether (12).—The starting material, **12**, was prepared by methylation of α-vinylbenzyl alcohol (**1**),[1] bp 69–75° (3.5 mm) [lit.[20] bp 88–90° (10 mm)]. To a 150-ml three-neck round-bottom flask was added 5.0 g (34 mmol) of **12**, about 50 ml of hexane, and 2.2 g (20 mmol) of TMEDA. The mixture was placed in an ice bath and agitated by means of a magnetic stirrer. From a dropping funnel, 18 ml (36 mmol) of a solution of *n*-butyllithium was added over a period of a few minutes. The color of the solution changed from light yellow to dark red. After stirring for 42 hr, the reaction was cooled in an ice bath and quenched with 10 ml of water. The mixture was extracted with several portions of ether. The water layer was acidified with 10% HCl, then extracted with ether, and the ether layer was washed with 5% NaOH and water. The combined ether extracts were dried over Na_2SO_4, concentrated, and vacuum distilled to afford 2.4 g of crude product, bp 107–116° (10 mm). Analysis by vpc (Reoplex 400) showed several components, the major of which were collected by preparative vpc. The properties of the four components collected are reported in the following way—compound (no.) (per cent of the mixture, retention time on a Reoplex 400 at 160°, He flow 100 ml/min), then ir; nmr; mass spectral data.

1-Phenyl-1-methoxypropene (15) (28%, 4 min) had nmr (CCl_4) δ 1.75 (d, 3, J = 7 Hz, CCH_3), 3.50 (s, 3, OCH_3), 5.28 (q, 1, J = 7 Hz, =CH), 7.18–7.42 (m, 5, Ph); mass spectrum (70 eV) m/e 148 (molecular ion), 147 (base), 117, 105, 91, 77, 55, and 51. Literature[21] nmr reports δ 1.75 (d, 3, J = 7 Hz), 3.45 (s, 3), 5.22 (q, 1, J = 7 Hz), and 7.04–7.48 (m, 5) for **15** with cis related methyl and methoxy and δ 1.66 (d, 3, J = 7 Hz), 3.54 (s, 3), 4.67 (q, 1, J = 7 Hz), and 7.26 (s, 5) for **15** with trans related methyl and methoxy. Thus, it appears that the **15** derived from **12** is the cis isomer (methyl–methoxy).

Propiophenone (5) (2%, 7.5 min) was identical in retention time, ir, nmr, and mass spectral properties with an authentic sample.[18]

n-**Butyrophenone (14)** (22%, 9.5 min) was identical in retention time, ir, nmr, and mass spectral properties with an authentic sample.[18]

2-Phenyl-3-buten-2-ol (13) (46%, 11 min) had ir (CCl_4) 3400 (OH), 1650, 995, and 925 cm^{-1} ($-CH=CH_2$); nmr (CCl_4) δ 1.50 (s, 3, $-CH_3$), 2.59 (s, 1, OH), 4.89–5.35 (m, 2, $-C=CH_2$), 6.07 (doublet of doublets, 1, J_{trans} = 17, J_{cis} = 10 Hz, –CH=C), 7.05–7.50 (m, 5, Ph); mass spectrum (70 eV) m/e 148 (molecular ion), 133, 121, 119, 105, 91, 77, 55, 51, and 43 (base peak); identical with a sample of **13** prepared by treating acetophenone with vinyllithium.

The reaction was repeated using THF as the solvent, and no TMEDA, to give the same set of products except that the ratios were different: **15** (2%), **5** (35%), **14** (27%), **13** (24%), and two unidentified peaks of longer retention times with intensities of 10 and 2%.

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[18] Purchased from Aldrich Chemical Co., Milwaukee, Wis.

[19] It is well recognized that cis β-substituted styrenes absorb at lower wavelengths and exhibit smaller extinction coefficients than the corresponding trans isomers; for example, *cis*-β-methylstyrene shows λ_{max} 242 nm (ϵ 13,200) and *trans*-β-methylstyrene shows λ_{max} 249 nm (ϵ 16,000) as reported by C. G. Overberger, D. Tanner, and E. M. Pearce, *J. Amer. Chem. Soc.*, **80**, 4566 (1958).

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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]

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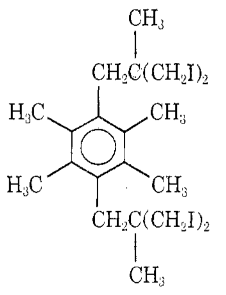
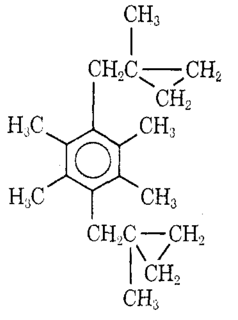
Treatment of 2-benzyl-2-methyl-1,3-diiodopropane (**3a**) with lithium aluminum hydride in ether or chromous sulfate in dimethylformamide yields mainly 1-benzyl-1-methylcyclopropane (**5**), whereas, when tri-*n*-butyltin hydride is used, solvent-dependent mixtures of **5** and neopentylbenzene (**6**) 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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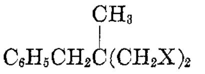
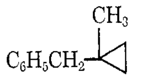

$C_6H_5CH_2\overset{CH_3}{\overset{|}{C}}(CH_2X)_2$

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

$C_6H_5CH_2CH(CH_2X)_2$

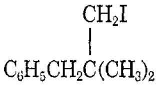
4a, X = I
b, X = Br
c, X = Cl

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


$C_6H_5CH_2\overset{CH_2I}{\overset{|}{C}}(CH_3)_2$

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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(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.

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