46-47°; ir 3650-2500, 1720, 1695, and 1630 cm^{-1}; nmr δ 1.62 (4 H, m), 1.89 (3 H, d, J = 1Hz), 2.12 (3 H, d, J = 1 Hz), 2.40 (4 H, m), 6.03 (1 H, m), and 11.5 (1 H, br s).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.25; H, 8.72.

Sensitized Irradiation of 4. A solution of 108 mg of **4** in acetone was irradiated at 300 nm. After 46 hr no new products had been detected by vpc and removal of the solvent gave a crude product whose spectral properties indicated that it consisted mainly of starting **4**.

Registry No.—4, 51222-33-4; **5,** 51293-25-5; **6,** 51222-34-5; **7,** 51222-35-6; cyclohexa-1,2-dione, 765-87-7; 1-chloro-2-methylpropene, 513-37-1.

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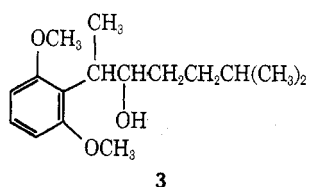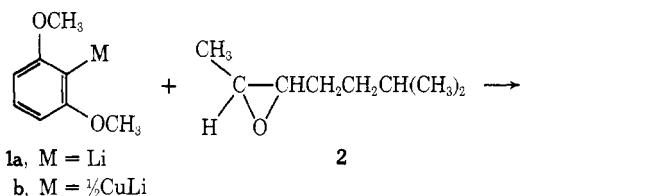

Reactions of Organometallic Derivatives of 1,3-Dimethoxybenzene[1a]

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2-(2,6-Dimethoxyphenyl)-6-methyl-3-heptanol (**3**), desired in connection with synthetic work on fumagillin,[2] was to be synthesized by the route below.


1a, M = Li   **2**
b, M = ½CuLi

3

Phenyllithium gives only the secondary alcohol with propylene oxide,[3] and it was hoped that **1** would attack the epoxide **2** at the methylated carbon rather than at the carbon carrying the larger isoamyl group.

1,3-Dimethoxybenzene is metalated by *n*-butyllithium in the 2 position,[4] with only 3–4% in the 4 position, as shown by carbonation[5] and careful examination of the acid. We have found that **1a** with propylene oxide gives a 28% yield of the secondary alcohol **4**, along with a considerable amount of 1,3-dimethoxybenzene.

4
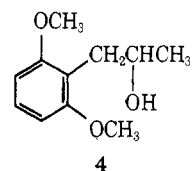
trans-2,3-Epoxy-6-methylheptane (**2**) was prepared by *m*-chlorperbenzoic acid oxidation[6] of *trans*-6-methyl-2-heptene; the latter was prepared from the corresponding acetylene, which could serve as the source of both the cis and trans ethylene.[7]

5-Methyl-1-hexyne[8] (**5**) gave 90% yield of pure 6-methyl-2-heptyne (**6**) by treatment with *n*-butyllithium at

5   **6**
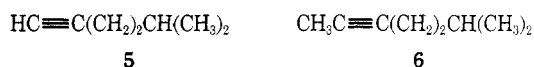
−78°, addition of a small amount of dimethyl sulfate at this temperature to react with unchanged *n*-butyllithium, and then addition of the remaining dimethyl sulfate at ice–salt temperature. Sodamide and methyl iodide in liquid ammonia gave only a 33% yield of **6**. The action of *n*-butyllithium on **5**, followed by methyl iodide at −78°, yielded some *n*-butyl iodide. The action of *n*-butyllithium at 0°, followed by dimethyl sulfate at 0°, gave mainly the monomethyl derivative **6**, but with about 10% of a higher homolog, probably $CH_3C{\equiv}CCH(CH_3)CH_2CH(CH_3)_2$, which would be the result of dianion formation from **6** by the *n*-butyllithium.[9] The method described above avoids these side products.

Reduction of **6** to the pure *trans*-6-methyl-2-heptene in 57% yield with sodium–liquid ammonia[10] was satisfactory.

2,6-Dimethoxyphenyllithium (**1a**) did not react with the epoxide **2** after 48-hr refluxing in THF. Heating the mixture in diglyme at 110–120° for 24 hr used up the organometallic,[11] but left the epoxide; a crystalline solid, mp 178–180°, isolated from the reaction mixture was shown by nmr, ir, mass spectrum, and elemental analysis to be the known[12] 2,6,2',6'-tetramethoxydiphenylcarbinol, Ar_2CH-OH, Ar = 2,6-$(CH_3O)_2C_6H_3$.

It is reported[13] that lithium dimethylcuprate and lithium diphenylcuprate in ether are better reagents for nucleophilic attack on epoxides than their lithium counterparts. The lithium cuprate of 1,3-dimethoxybenzene (**1b**), prepared from 0.5 equiv of purified cuprous bromide[14] to 1 equiv of the lithium compound **1a** in ether, gave a 45% yield of **4** from propylene oxide. Reaction of the lithium cuprate **1b** with the epoxide **2** gave no reaction after 3 hr at 0°; after 12 hr at room temperature, no disappearance of epoxide was observed, but no 1,3-dimethoxybenzene was found by hydrolysis and vpc analysis. A solid, mp 174–176°, different from the solid described above, was isolated, and from its ir and nmr spectra was shown to be the known 2,6,2',6'-tetramethoxybiphenyl.[15] The lithium cuprate compounds couple well with aryl halides.[14]

The trans epoxide **2** is apparently too highly substituted to react with the diortho-substituted organometallic **1**.

Experimental Section[16]

6-Methyl-2-heptyne (6). A 2-l., three-neck flask was fitted with a mechanical stirrer (nonsparking motor, glass blade), a condenser, and a dropping funnel fitted with a septum. In the flask were placed 52 g (0.54 mol) of 5-methyl-1-hexyne[8] in 250 ml of THF. The dropping funnel contained 0.57 mol of *n*-butyllithium, added by means of a syringe; the system had been purged with nitrogen and a nitrogen atmosphere was maintained during the reaction. The flask was cooled by a Dry Ice–acetone bath and the *n*-butyllithium was added dropwise over a 30-min period. The resulting yellow solution was stirred for an additional 45 min at this temperature. About 70 ml of dimethyl sulfate was placed in the dropping funnel, and to the yellow solution was added about 5 ml of dimethyl sulfate to remove any unreacted *n*-butyllithium. The

solution was then allowed to warm to ice–salt temperature, and the dimethyl sulfate was added at this temperature dropwise over a period of 20–30 min. The resulting solution was stirred for an additional 2 hr at room temperature. About 400 ml of water was added to the mixture and it was extracted with ether. The organic layer was washed with a saturated sodium bicarbonate solution and with water. This was dried over magnesium sulfate and the product was distilled to yield 53.8 g (90%) of a colorless liquid, bp 125°. The nmr (CCl_4) showed peaks at 0.90 (d, 6 H, CH_3CHCH_3), 1.1–1.5 (m, 3 H, CH_2CH), 1.70 (t, 3 H, $CH_3C≡C$), and 1.9–2.3 ppm (m, 2 H, $CH_2C≡C$). The ir spectrum (CCl_4) showed peaks at 2950, 2910, and 2870 (C–H stretch), 1470 (C–H bend), and 1385 and 1370 cm^{-1} (isopropyl). A mass spectrum gave a molecular ion at m/e 110.

trans-6-**Methyl-2-heptene** was prepared from the heptyne above (52 g), following the procedure[10] for the reduction of 2-octyne. Distillation yielded 37.0 g (70%) of a colorless liquid, bp 113–115°. The absorptions of the nmr spectrum (CCl_4) are 0.90 (d, 6 H, CH_3CHCH_3), 1.1–1.6 (m, 3 H, CH_2CH), 1.67 (d of d, 3 H, $CH_3C≡C$), 1.8–2.1 (m, 2 H, $CH_2C≡C$-), and 5.3–5.5 ppm (m, 2 H, $HC≡CH$). The ir spectrum (CCl_4) showed peaks at 3020, 2960, 2920, 2860 (C–H stretch), 1450 (C–H bend), 1380 and 1360 (isopropyl), and 960 cm^{-1} (characteristic of a trans-disubstituted alkene).

trans-2,3-**Epoxy-6-methylheptane** (2) was prepared from the trans olefin above (25.3 g) essentially as described.[6b] Distillation yielded 19.4 g (67%) of a colorless liquid, bp 148–150°. The absorptions of the nmr spectrum (CCl_4) are 0.9 (d, 6 H, CH_3CHCH_3), 1.25 (d, 3 H, CH_3CO), 1.3–1.9 (m, 5 H, CH_2CH_2CH), and 2.4–2.8 ppm (m, 2 H, epoxy H). An ir spectrum (CCl_4) showed peaks at 2940 and 2860 (C–H stretch), 1450 (C–H bend), and 1380 and 1360 cm^{-1} (isopropyl).

Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.80; H, 12.57.

1-(2,6-**Dimethoxyphenyl**)-2-**propanol** (4) was prepared by the general procedure described[3] by first adding 13.1 ml (0.1 mol) of 1,3-dimethoxybenzene in 70 ml of THF to 0.12 mol of n-butyllithium over a 10-min period under nitrogen. An exothermic reaction took place, heating the mixture to reflux. The mixture was refluxed for 1 hr and an aliquot gave a negative test for alkyllithium.[17] To this solution, while refluxing, was added 13.5 ml (0.2 mol) of propylene oxide. The mixture was then refluxed for 2 hr, and was hydrolyzed by dropwise addition of water while being cooled by an ice bath. The resulting solution was extracted with chloroform and dried over sodium sulfate. The solvent was removed under reduced pressure and the product was crystallized. The solid was separated by vacuum filtration and washed with petroleum ether, and diethyl ether, 5.5 g (28%), was obtained, mp 66–68°. The nmr spectrum (CCl_4) showed peaks at 1.08 (d, 3 H, $CHCH_3$), 2.38 (broad s, 1 H, OH), 2.78 (d, 2 H, $CHCH_2$), 3.75 (s, 6 H, OCH_3), 4.0 (m, 1 H, $CHOH$), 6.45 (d, 2 H, aromatic), and 7.0 ppm (m, 1 H, aromatic). The ir spectrum (KBr) showed peaks at 3420 (OH stretch), 2960 and 2930 (C–H stretch), 2840 (C–H stretch, characteristic for methoxyl),[18] and 1590 cm^{-1} (aromatic C=C stretch).

Reaction of 2,6-Dimethoxyphenyllithium (1a) **with** *trans*-2,3-**Epoxy-6-methylheptane** (2). The 2,6-dimethoxyphenyllithium (1a) was made by the procedure used in the reaction with propylene oxide starting with 1.1 g (0.008 mol) of m-dimethoxybenzene. To the refluxing organometallic solution was added 1.0 g (0.008 mol) of *trans*-2,3-epoxy-6-methylheptane (2) in about 10 ml of THF. This reaction was followed by vpc and after 48 hr reflux the vpc still showed most of the starting epoxide.

A change of solvent to diglyme was accomplished by adding diglyme (freshly distilled) to the mixture and then removing the THF and hexane by distillation until a temperature of 110–120° was reached. The mixture was then refluxed at this temperature for another 24 hr. The vpc still showed a considerable amount of epoxide, but the Michler's ketone test was negative for organometallics.[11] The mixture was hydrolyzed and worked up in the usual way, and the residue was distilled at atmospheric pressure to remove the diglyme. The fraction boiling at 145–160° gave an nmr spectrum of a mixture of *trans*-2,3-epoxy-6-methylheptane (2) and diglyme. The residue of this distillation was heated to 100° (15 mm) with no further distillation.

After standing, a crystalline substance separated from the residue. This was filtered, washed with carbon tetrachloride, and recrystallized from a mixture of chloroform and carbon tetrachloride, mp 178–180°. An nmr spectrum ($CDCl_3$) showed peaks at 3.85 (s, 12 H), 5.70 (broad d, 1 H), 6.63 (d, 4 H), 6.79 (broad d, 1 H), and 7.25 ppm (t, 2 H). An ir spectrum ($CHCl_3$) showed peaks

at 3500, 2990, 2930, 2830, 1590, 1475, and 1110 cm^{-1}. An elemental analysis gave C, 68.06; H, 6.61. A mass spectrum gave a molecular ion at m/e 304 with a large peak at m/e 286. The most probable molecular formula is $C_{17}H_{20}O_5$. The data indicate that the compound is the known 2,6,2′,6′-tetramethoxydiphenylcarbinol, mp 179°.[12]

Purification of Cuprous Bromide. The published[19] procedure as modified by Thoennes[20] was used. To 100 ml of water saturated with sodium bromide was added 20 g of cuprous bromide (green-blue) at 75°. Enough concentrated HBr was added dropwise to just clear up the cupric carbonate impurity. To this dark solution was added just sufficient sodium bisulfite to clear the color to light orange-brown. The solution was filtered and water was added to fill the container, precipitating cuprous bromide as a white solid. The suspension was filtered and water was added to the filtered solution to precipitate more cuprous bromide. This was repeated until no more precipitate was formed. The filtrate was washed with 200 ml of 0.02 M HBr (made with deoxygenated water). The filter cake was washed with 95% ethanol (200 ml), transferred to a clean, dry flask prefilled with nitrogen, and immediately evacuated, pumping for 24 hr. The solid was then transferred and stored in a nitrogen-filled jar. The yield was 13 g.

Reaction of Lithium Di-2,6-dimethoxyphenylcuprate (1b) **with Propylene Oxide.** 1,3-Dimethoxybenzene (5.2 g, 0.0375 mol) was metalated with 0.0375 mol of n-butyllithium in the usual way in THF, refluxing for 1 hr. The solution was allowed to cool to room temperature and the solvent was removed under reduced pressure after the system was purged with nitrogen. The remaining solid was dissolved in dry ether.

A 250-ml, three-neck flask was equipped with a condenser, addition funnel, and magnetic stirrer. The flask was flamed and purged with nitrogen. In the flask were placed 30 ml of ether and 2.7 g (0.0187 mol) of purified cuprous bromide. The ether solution of the above 2,6-dimethoxyphenyllithium was added dropwise while the solution was cooled in an ice bath. After 1 hr, the Michler's ketone test gave a negative result, indicating that all of the cuprous bromide had reacted.[11] The solution at this time was green. To this solution was added 1.45 g (0.025 mol) of propylene oxide in 10 ml of ether. The reaction was followed by vpc and after about 1.5 hr the reaction appeared to be complete. The reaction solution was hydrolyzed by dropwise addition of 100 ml of water, and the water was separated from the ether layer. The water was extracted several times with ether. After the combined ether solutions were dried over magnesium sulfate and the solvent was removed under reduced pressure, 2.2 g of 1-(2,6-dimethoxyphenyl)propan-2-ol (4, 45%) was obtained, mp 66–68° (ether-petroleum ether). The spectra were the same as those obtained with the product of the reaction of 2,6-dimethoxyphenyllithium (1a) with propylene oxide.

Reaction of Lithium Di-2,6-dimethoxyphenylcuprate (1b) **with** *trans*-2,3-**Epoxy-6-methylheptane** (2). Using the same procedure as for the reaction of lithium di-2,6-dimethoxyphenylcuprate (1b) with propylene oxide, 2 g (0.0156 mol) of *trans*-2,3-epoxy-6-methylheptane (2) was treated with 0.05 mol of 1b. The reaction was followed by vpc by hydrolyzing an aliquot. After 3 hr at ice temperature no reaction was observed. The solution was then allowed to stir at room temperature for 12 hr. A disappearance of m-dimethoxybenzene could be detected without any loss of 2. After hydrolysis and work-up a solid was isolated. The solid was separated and washed with carbon tetrachloride, mp 174–176°. An nmr spectrum ($CDCl_3$) showed a singlet at 3.72 ppm and a multiplet at 6.5–7.3 ppm with an integration ratio of 2:1. An ir spectrum ($CHCl_3$) showed a peak at 1590 cm^{-1} and no hydroxyl. A mixture melting point with the solid isolated from the reaction of the lithium compound with the epoxide 2 gave a range of 150–162°. The structure is most probably the known 2,6,2′,6′-tetramethoxybiphenyl, mp 175–176°.[15]

Registry No.—1a, 2785-97-9; 1b, 51065-61-3; 2, 51065-62-4; 4, 51065-63-5; 6, 51065-64-6; 5-methyl-1-hexyne, 2203-80-7; *trans*-6-methyl-2-heptene, 51065-65-7; 1,3-dimethoxybenzene, 151-10-0; propylene oxide, 75-56-9.

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Alkyl Metal Asymmetric Reduction. V.[1] Reduction of Alkyl Methyl Ketones by Chiral Organoaluminum Compounds

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In connection with studies on alkyl metal asymmetric reduction,[1,2] we have extended our investigations on the reaction of some alkyl methyl ketones with optically active 2-methylbutylaluminum derivatives to evaluate the dependence of the stereoselectivity of the reduction on the structure and on the nature of the ketonic substrate employed.

Analogously with previous findings,[2c] (+)-tris[(S)-2-methylbutyl]aluminum reacts very fast at 0° in pentane with alkyl methyl ketones too. The reduction affords the corresponding S carbinols in satisfactory yields (Table I). The results reported show that the extent of asymmetric induction increases as the steric hindrance to the carbonyl carbon atom is increased, in the order of Et < *i*-Pr < *t*-Bu.[3] The absolute S configuration of the predominant enantiomer of the carbinol recovered may be predicted on the basis of the stereochemical model previously proposed.[2c] In fact, even if in this case electronic interactions should not reasonably play an important role, in the preferred transition state of the reduction the ethyl group on the β carbon atom of the aluminum alkyl should be in an anti position with respect to the bulkiest alkyl group of the carbonyl substrate; thus the β hydrogen of the 2-methylbutyl group should be preferentially transferred to the *re* face of the ketone.[2c] This picture satisfactorily explains also the trend of the asymmetric reduction in the series (Table I). In fact, when the effective size of the groups is not a function of their rotational conformations in the transition state,[2c,4] the extent of stereoselectivity should essentially depend on the difference in steric bulk between the alkyl groups substituent to the carbonyl carbon atom.

In our previous paper,[2c] we have pointed out the role of donor solvents in the asymmetric reduction of ketones by optically active organoaluminum compounds. In this context, it was noticeable that (R)-*tert*-butylmethylcarbinol was recovered in the reduction of the corresponding ketone by (+)-tris[(S)-2-methylbutyl]aluminum diethyl etherate in benzene solution.[5] Since the other chiral groups of the organoaluminum compounds do not affect appreciably the stereoselectivity of the reduction,[2c] this result[5] seemed to indicate that the donor ligand had exerted such a control to afford a carbinol the absolute configuration of which is opposite to that observed in the reduction carried out in the absence of donor ligand (runs 5, 6).

Therefore, to get a deeper insight into the question, we have performed the reduction of *tert*-butyl methyl ketone by (+)-tris[(S)-2-methylbutyl]aluminum diethyl etherate at 0° in pentane (run 7, Table II). Although, according to previous findings,[2c] the extent of asymmetric reduction was effectively changed with respect to runs 5 and 6 (Table I), the carbinol recovered had the S configuration.

Table I
Asymmetric Reduction of Alkyl Methyl Ketones by (+)-Tris[(S)-2-methylbutyl]aluminum[a]
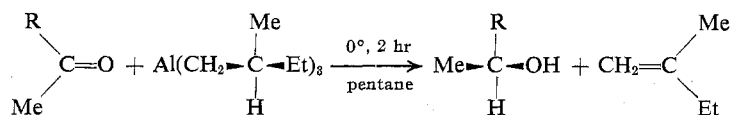
Run	R (registry no.)	Yield, %[b]	Chemical purity, %[c]	α^{25}D, deg, *l* = 1 (neat)	$[\alpha]^{25}$D	$[\alpha]^{25}$D[d]	Optical purity, %	Asymmetric reduction, %[e]
1	Et (4221-99-2)	72.2	~100	+0.51	+0.63	+0.63	4.5[f]	5.3
2	Et	87.0	~100	+0.49	+0.61	+0.61	4.4[f]	5.2
3	*i*-Pr (1517-66-4)	75.2	97	+0.60	+0.74	+0.76	14.2[f]	16.7
4	*i*-Pr	81.5	98	+0.60	+0.74	+0.75	14.0[f]	16.4
5	*t*-Bu (1517-67-5)	36.7[g]	98	+1.02	+1.26	+1.28	16.7[h]	19.6
6	*t*-Bu	66.6	95	+1.00	+1.23	+1.29	16.9[h]	19.8

[a] Optical purity 85.2%. [b] Product recovered by continuous extraction by ether and isolated by distillation. [c] Based on glpc analyses of the products, other impurities being the ketone. [d] Corrected for the per cent purity of the carbinol. [e] Corrected for the minimum optical purity of the organoaluminum compound used. [f] D. Nasipuri and G. Sarkar, *J. Indian Chem. Soc.*, **44**, 165 (1967). [g] The carbinol was not continuously extracted. [h] W. H. Foley, F. J. Welch, E. M. La Combe, and H. S. Mosher, *J. Amer. Chem. Soc.*, **81**, 2779 (1959).