210 (p-$CH_3C_6H_4CH_2CH_3$), 320 (p-$CH_3C_6H_4CH_2CH_2CH_3$), 420 (p-$CH_3C_6H_4CH_2Cl$). Using *n*-nonane as a standard: injection port 230 °C, oven 110 °C for 4 min, raised to 148 °C at 30 °C/min and held at limit; retention times (in s) 190 (p-$CH_3C_6H_4CH_3$), 215 (*n*-nonane), 390 (p-$CH_3C_6H_4CH_2CH_2CH_3$), 450 (p-$CH_3C_6H_4CH_2Cl$).

The accuracy of the determination of p-$CH_3C_6M_4CH_2Cl$ concentration was estimated to be ±5%.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also wish to thank Professor M. Litt for his valuable comments.

Registry No.—p-$CH_3C_6H_4CH_2Cl$, 104-825; Et_3Al, 97-93-8; Et_2AlCl, 96-10-6; *p*-methylpropylbenzene, 1074-55-1; *p*-xylene, 106-42-3.

References and Notes

(1) J. P. Kennedy, N. V. Desai, and S. Sivaram, *J. Am. Chem. Soc.*, **95**, 6386 (1973).
(2) J. P. Kennedy, *J. Org. Chem.*, **35**, 532 (1970).
(3) J. P. Kennedy and S. Rengachary, *Adv. Polym. Sci.*, **14**, 1 (1974).
(4) A. Priola, S. Cesca, and G. Ferraris, *Makromol. Chem.*, **160**, 41 (1972).
(5) D. B. Miller, *J. Org. Chem.*, **31**, 908 (1966).
(6) J. P. Kennedy and R. B. Isaacson, *J. Macromol. Chem.*, **1**, 541 (1966).
(7) N. Grassie and I. G. Meldrum, *Eur. Polym. J.*, **7**, 1253 (1971).
(8) G. Montaudo, P. Finocchiaro, S. Caccamese, and F. Bottino, *J. Polym. Sci., Part A-1*, **8**, 2475 (1970).

Neopentylallyllithium. 5. Stereochemistry of Nonrearrangement Reactions with Epoxides

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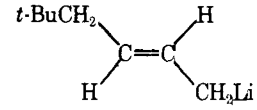
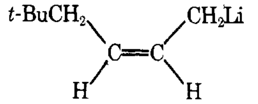
Reactions of neopentylallyllithium (NpALi), the 1:1 addition product of *tert*-butyllithium and 1,3-butadiene, with cyclohexene oxide and *cis*- and *trans*-2,3-epoxybutane are reported. In aliphatic hydrocarbon solvent each reaction is shown to consist predominantly of "normal," i.e., nonrearranged, addition of the allylic system to the epoxide. The products are shown to be those arising from trans ring opening of the epoxide.

In previous papers in the series, we have examined some of the spectra[1,2] and reactions[3,4] of neopentylallyllithium I (NpALi), the 1:1 addition product of *tert*-butyllithium and 1,3-butadiene. NpALi exists as a "partially delocalized" species in hydrocarbon solvents,[1,5–7] but the evidence presently available speaks against the existence of a dynamic allyl equilibrium of the classical type.[8] Thus, cis and trans isomers of NpALi (Ia and Ib) are directly observable in the ^{1}H NMR spectrum and do not appear to interconvert in the absence of Lewis bases such as THF. In the absence of such agents, NpALi may be considered as a nondynamic mixture of Ia and Ib, probably in the form of mixed dimers and tetramers[1] in which there is some delocalization of charge from the α to the γ carbon atom. The extent of this delocalization is increased by the addition of THF and other Lewis bases[2] and by the replacement of lithium with sodium and potassium.[9]

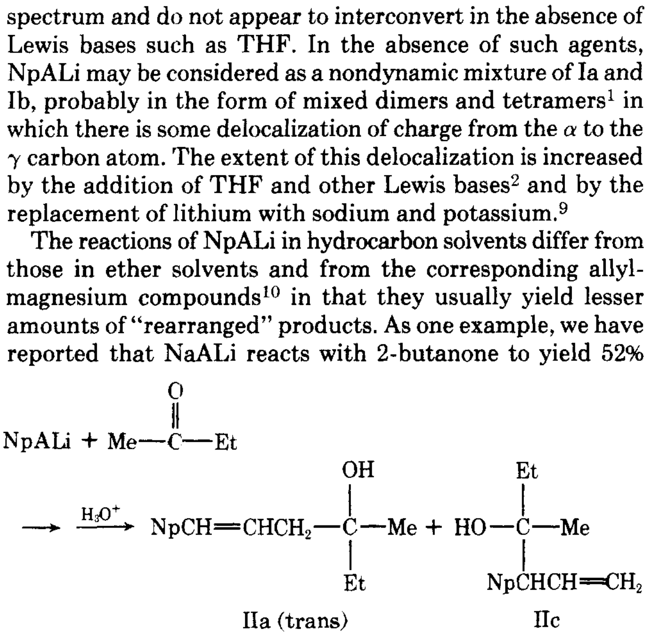


Ia



Ib

The reactions of NpALi in hydrocarbon solvents differ from those in ether solvents and from the corresponding allylmagnesium compounds[10] in that they usually yield lesser amounts of "rearranged" products. As one example, we have reported that NaALi reacts with 2-butanone to yield 52% rearranged product IIc in pentane[3] and 78% in THF[4] as compared to 70% and 96% of the same product from bis(neopentylallyl)magnesium in pentane and diethyl ether solvents, respectively.[11]



$$\mathrm{NpALi} + \mathrm{Me{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Et} \xrightarrow{\mathrm{H_3O^+}} \mathrm{NpCH{=}CHCH_2{-}\underset{\displaystyle Et}{\overset{\displaystyle OH}{C}}{-}Me} + \mathrm{HO{-}\underset{\displaystyle NpCHCH{=}CH_2}{\overset{\displaystyle Et}{C}}{-}Me}$$

IIa (trans)
IIb (cis)

IIc

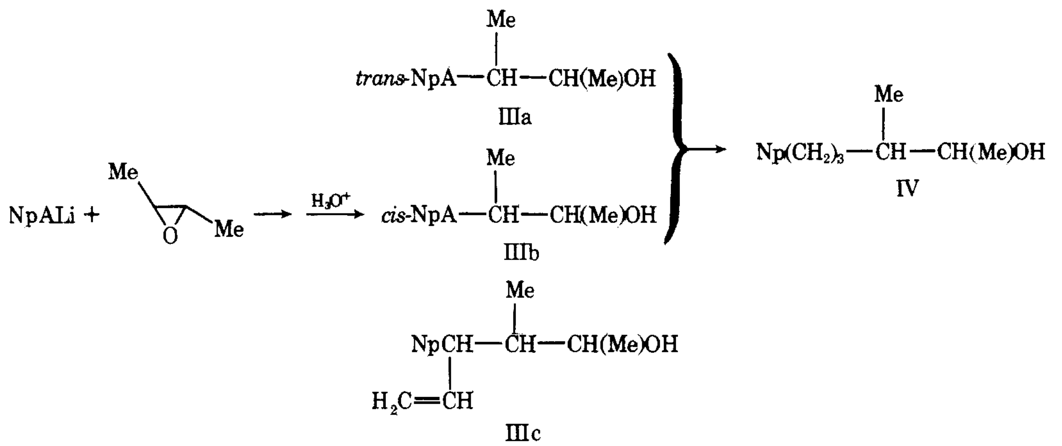
We now report on the reactions of NpALi in THF and pentane with another class of reagents, namely epoxides. Allyl metal compounds are known to add to epoxides to yield secondary carbinol salts, and such reactions have been the subject of numerous papers. Recently, Courtois and Miginiac have reviewed this reaction for zinc, cadmium, lithium, sodium, magnesium, and aluminum allylic compounds.[12] However, the present work represents the first report on the reaction of epoxides with an allylic lithium species in hydrocarbon solvent and is the first to establish the stereochemistry of the nonrearrangement process leading to products analogous to IIa and IIb.

Results and Discussion

Reaction of NpALi with 2,3-Epoxybutanes. NpALi prepared in pentane as described before[3] consists of a mixture of trans and cis isomers in 3:1 ratio. Upon reaction with *trans*-2,3-epoxybutane (and subsequent hydrolysis), NpALi yields a mixture of three compounds identified as IIIa–c (eq 1). The relative amounts of the products are shown in Table I; absolute yields totaled approximately 90% (internal standard GC). The identity of the three compounds IIIa–c was established by a combination of IR, ^{1}H NMR, MS, and elemental analyses (see Experimental Section for details).

Likewise, *cis*-2,3-epoxybutane yields compounds IIIa′–c′ as shown in Table I. However, the GC retention times of the products from the cis and trans epoxides were observed to be different. This observation was not unanticipated, since the two epoxides were expected to give different diastereomeric alcohols which would probably be separated by GC.

The identification of IIIa,b and IIIa′,b′ as the "nonrearranged" diastereomeric alcohols resulting from trans addition of NpALi to the corresponding epoxides was accomplished

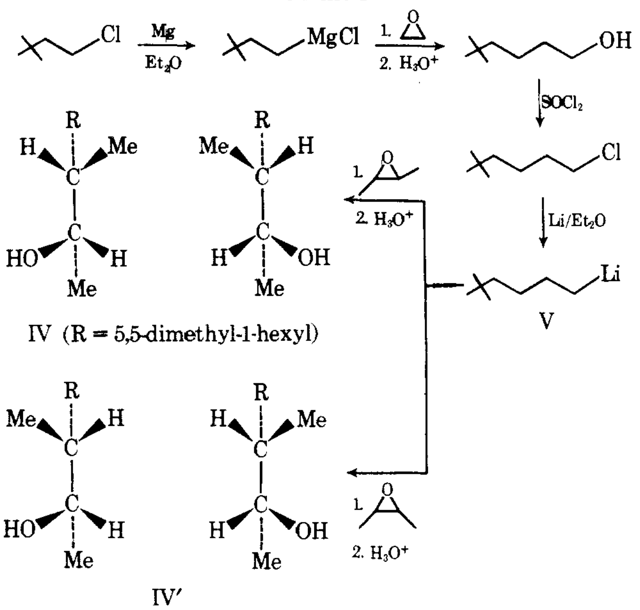


(1)

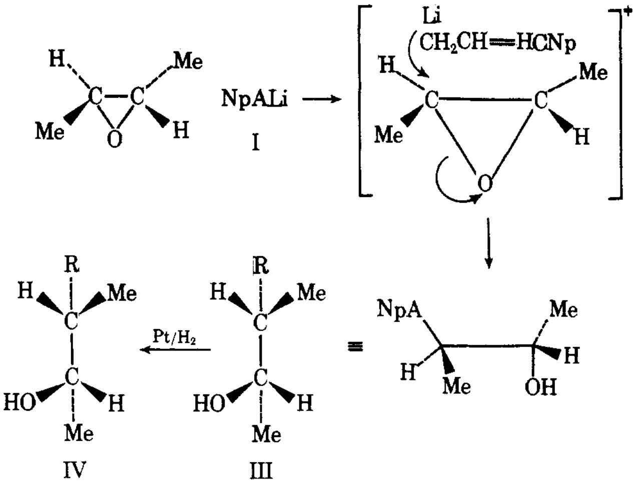
by a method originally employed by Felkin and co-workers.[13] IIIa and IIIb were collected by preparative GC and hydrogenated with platinum black catalyst to IV, shown by GC to be a single compound. Subsequently, IV was shown to be 2-(*R*,*S*)-hydroxy-3-(*R*,*S*)-8,8-trimethylnonane by the alternate synthetic route shown in Scheme I. In a similar manner, IV′ from the cis epoxide was shown to be 2-(*R*,*S*)-hydroxy-3-(*S*,*R*)-8,8-trimethylnonane.

The critical step in the alternate route to IV and IV′ shown in Scheme I involves the addition of 5,5-dimethyl-1-hexyllithium (V) to *cis*- and *trans*-2,3-epoxybutanes. We assume this reaction to be a trans addition process on the basis of the work of Malenovskii and co-workers.[13] In their work, *n*-propyllithium and *n*-butyllithium were shown to add to epoxides in a trans process. We assume that the saturated lithium alkyl V is analogous to the reagents used by Malenovskii et al., thus establishing the reaction of I with both epoxides to be a trans addition process as well (Scheme II). An S_E2 process such as that shown in Scheme II would account for the present observations. However, we have no evidence to exclude a prior dissociation of the lithium compound I to form an allylic anion which then attacks the epoxide in a trans addition process. Indirect evidence in favor of such an ionic mechanism may be inferred from the fact that the same products are observed in THF, a solvent in which the predominant organometallic species are ion pairs.[2,9] As expected, the product corresponding to allylic rearrangement (IIIc) is enhanced in THF, but it is still the minor product. This is in sharp contrast to reports of similar reactions of allylic Grignard reagents wherein the rearranged product is usually formed in yields greater than 80%.[13] It should also be noted that the relative yield of the cis olefinic addition product (IIIb or IIIb′) is substantially increased upon the addition of THF solvent to the reacting system. We have previously noted that this effect occurs in all reactions of NpALi in THF vs. hydrocarbon solvents[4] and parallels an observed increase in the relative concentration of the *cis*-NpALi species as observed by ^{1}H NMR.[2] That the cis anion is more stable than the trans form is corroborated by recent work on the analogous sodium compound[9] in which the cis/trans ratio is even higher than that for the lithium allyl.

Scheme I



Scheme II



Reaction of NpALi with Cyclohexene Oxide. This reaction yields three products which have been identified as VIa–c. Again, the major products are IVa and VIb, the products which correspond to normal, i.e., nonrearranged, addition (Table I). The ^{1}H NMR spectra of compound VIa, the major

Table I. Product Yields from NpALi–Epoxide Reactions in Pentane and THF[a]

	Solvent	
Epoxide	Pentane	THF
trans-2,3-Epoxybutane	IIIa (80); IIIb (11); IIIc (9)	IIIa (34); IIIb (39); IIIc (27)
cis-2,3-Epoxybutane	IIIa′ (68); IIIb′ (13); IIIc′ (18)	IIIa′ (29); IIIb′ (32); IIIc′ (39)
Cyclohexene oxide	VIa (65); VIb (15); VIc (20)	VIa (30); VIb (41) VIc (29)

[a] Roman numerals refer to structures on text; figures in parentheses refer to relative yields of isomeric alcohols as determined by GLC.

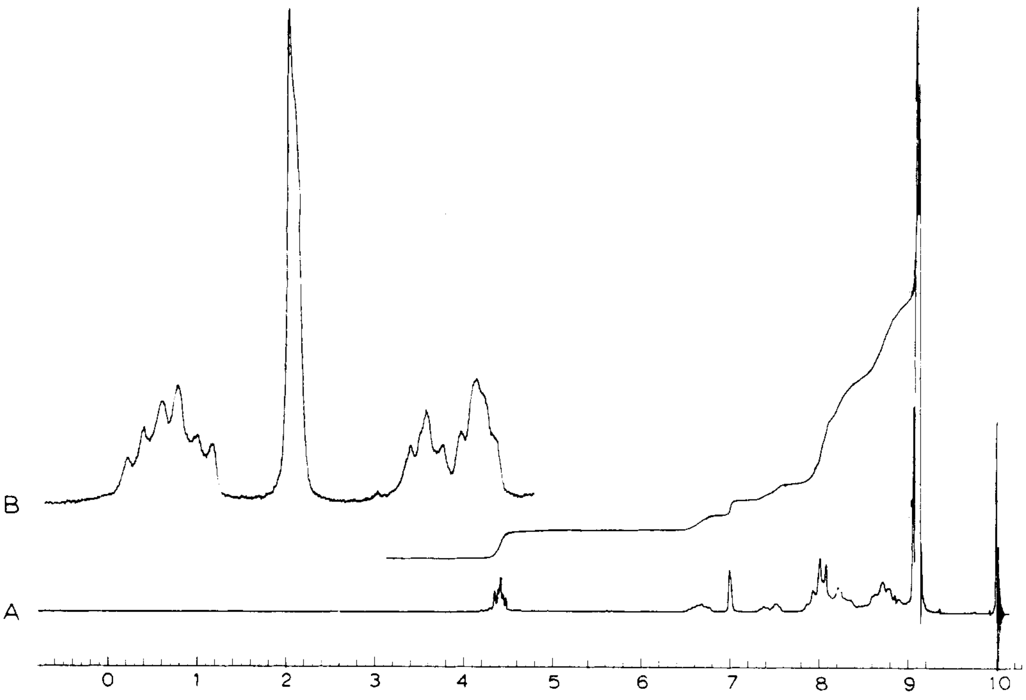
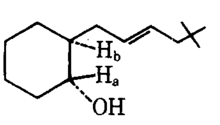
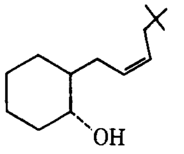


Figure 1. ^1H NMR spectrum (100 MHz) of VIa, the principal product from 3-neopentylallyllithium and cyclohexene oxide. Trace B offset 500 Hz and expanded × 10.

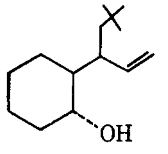
product, are shown in Figure 1. Most significant is the coupling pattern at τ 6.7 of the proton H_a, geminal to the hydroxyl



VIa



VIb



VIc

group. The pattern is that to be expected from an axially disposed proton with an axially disposed H_b in a position vicinal to H_a. A similar pattern was observed for the corresponding proton H_a in VIc. The spectra are not consistent with other structures in which the hydroxyl and NpA groups are in axial–equatorial or equatorial–equatorial orientations with regard to one another. Unless one rejects the chair conformation of the cyclohexane ring,[14] then one is forced to conclude that structures VIa and VIc predominate, and that both "normal" and "rearrangement" addition processes occur in a trans fashion.

The data in Table I also show the effect of THF solvent on the product distributions of addition of NpALi to cyclohexene oxide. The effect is the same as that observed with the acyclic epoxides; namely, that the percentage of rearranged product increases slightly, but less so than the yield of the cis olefinic product (VIb). The latter reflects the increased concentration of the cis allylic lithium compound (NpALi) in THF,[2] where at 0 °C it is present in 35% excess over the trans species. The identity of the three alcohols obtained in THF and pentane solvents shows that in both cases the trans addition process prevails.

Conclusion

Neopentylallyllithium has been shown to react with *cis*- and *trans*-2,3-epoxybutane and with cyclohexene oxide in a trans addition process. Unlike the corresponding Grignard reagents, NpALi yields a predominance of the "normal", i.e., "nonrearranged", addition products. That both types of processes occur in a trans fashion, both for the Grignard and lithium allyls and in a variety of solvents, is evidence for the strong preference of this mechanism over other alternatives.

Experimental Section

^1H NMR and IR spectra were recorded on JEOL PS-100 and Perkin-Elmer 237 spectrometers, respectively, with tetramethylsilane as the internal ^1H NMR reference. Analyses were performed by C. F. Geiger, Ontario, Calif. Gas chromatography was performed on a Varian Model 1800 with thermal conductivity and flame ionization detectors.

Neopentylallyllithium was prepared as described previously[1-4] using rigorously dried solvents and inert gas atmospheres. *trans*-2,3-Epoxybutane and 1-chloro-3,3-dimethylbutane were used as received from Chemical Samples Co., Columbus, Ohio. A mixture of *trans*- and *cis*-2,3-epoxybutane was obtained from the same source and separated by preparative gas–liquid chromatography using a 6 ft × 0.25 in. EDO-1 (Supelco, Bellefonte, Pa.) glass column at 25 °C and 30 ml/min helium flow. The epoxides collected were shown to be >99% chromatographically pure. Cyclohexene oxide was used as obtained from MCB, Cincinnati, Ohio.

Reaction of NpALi with *trans*-2,3-Epoxybutane in *n*-Pentane. To a stirred solution of 1 M NaALi (44 mmol) in *n*-pentane under argon, 3.3 g (46 mmol) of *trans*-2,3-epoxybutane was added while cooling the flask with dry ice. After stirring overnight at ca. 25 °C, the mixture was quenched with water and acidified, and the organic layer spearated and dried over magnesium sulfate. The majority of the solvent was evaporated and the mixture analyzed by GLC (13 ft × 0.25 in. FFAF at 70 °C, 29 ml He/min). Three peaks other than solvent were observed, IIIa–c (diastereomers of IIIc not resolved). Each was collected by preparative GLC and analyzed by various spectral methods. IIIa: IR (neat) 3350 (b, OH^-), 3010 (w, $=CH$), 1650 (w, $C=C$), 965 cm^{-1} (trans $CH=CH$); ^1H NMR ($CDCl_3$) τ 4.62 (m, 2 H, $CH=CH$), 6.31 (m, 1 H, $C\mathbf{H}OH$), 7.83 (m, 2 H, $=CHC\mathbf{H}_2CH$), 8.15 (d, 2 H, J = 6 Hz, t-$BuC\mathbf{H}_2CH=$), 8.37 (s, 1 H, OH), 8.47 [m, 1 H, $CH_2C\mathbf{H}(CH_3)$], 8.87 (d, 3 H, J = 6 Hz, $C\mathbf{H}_3CHOH$), 9.13 (d, 3 H, $C\mathbf{H}_3CHCH_2$), 9.15 (s, 9 H, t-Bu); MS (70 eV) m/e 184 (parent ion), 166 ($M - H_2O$). IIIb: IR (neat) 3350 (b, OH), 3010 (w, $=CH$) 1620 (w, $C=C$), 760 cm^{-1} (cis $CH=CH$); ^1H NMR ($CDCl_3$) τ 4.53 (m, 2 H, $CH=CH$), 6.29 (m, 1 H, $C\mathbf{H}OH$), 7.89 (m 2 H, $=CHC\mathbf{H}_2CH$), 8.08 (d, 2 H, J = 6 Hz, t-$BuC\mathbf{H}_2CH=$), 8.3 [m, 1 H, $CH_2C\mathbf{H}(CH_3)$], 8.56 (s, 1 H, OH), 8.88 (d, 3 H, J = 6.5 Hz, $C\mathbf{H}_3CHOH$), 9.18 (d, 3 H, J = 6 Hz, $C\mathbf{H}_3CHCH_2$), 9.18 (s, 9 H, t-Bu); MS (70 eV) m/e 184 (parent ion), 166 ($M - H_2O$). IIIc: IR (neat) 3350 (b, OH), 3030 (s, $=CH$), 1620 (w, $C=C$), 995, 900 cm^{-1} (m, $CH=CH_2$); ^1H NMR ($CDCl_3$) τ 4.4 (m, 1

H), 5.12 (m, 2 H) ($CH{=}CH_2$), 6.32 (m, 1 H, $C\mathbf{H}OH$), 7.92 (d, 2 H, t-Bu$C\mathbf{H}_2CH$), 9.13 (s, 9 H, t-Bu), other peaks too overlapping to be resolved; MS (80 eV) m/e 184 (parent ion), 166 ($M - H_2O$).

Anal. Calcd for $C_{12}H_{24}O$: C, 78.20, H, 13.12. Found (mixture of IIIa and IIIb): C, 78.29, H, 13.13. Found (IIIc): C, 77.73; H, 12.68.

Reaction of NpALi with *cis*-2,3-Epoxybutane in *n*-Pentane. The procedure used was similar to that for the trans epoxide. GLC separation yielded four isomeric olefinic alcohols, IIIa′–c′ (two diastereomers of IIIc′). IIIa′: IR (neat) 3330 (b, OH) 3005 (w, $=CH$), 1620 (w, $C{=}C$), 965 cm^{-1} (m, trans $CH{=}CH$); ^1H NMR ($CDCl_3$) τ 4.62 (m, 2 H, $CH{=}CH$), 6.38 (m, 1 H, $C\mathbf{H}OH$), 7.25 (s, 1 H, OH), 7.86 (m, 2 H, $=CHC\mathbf{H}_2CH$), 8.14 (d, 2 H, J = 6 Hz, t-Bu$C\mathbf{H}_2CH{=}$), 8.46 [m, 1 H, $CH_2C\mathbf{H}(CH_3)$], 8.90 (d, 3 H, J = 6.5 Hz, $C\mathbf{H}_3CHOH$), 9.16 (s, 9 H, t-Bu), 9.20 (d, 3 H, $C\mathbf{H}_3CHCH_2$); MS (70 eV) m/e 184 (parent ion), 166 ($M - H_2O$). IIIb′: IR (neat) 3330 (b, OH) 3040 (w, $=CH$) 1650 (w, $C{=}C$), 763 cm^{-1} (w, cis $CH{=}CH$); ^1H NMR (neat) τ 4.56 (m, 2 H, $CH{=}CH$), 6.32 (m, 1 H, $C\mathbf{H}OH$), 6.27 (s, 1 H, OH), 7.83 (m, 2 H, $=CHC\mathbf{H}_2CH$), 8.05 (d, 2 H, J = 6 Hz, t-Bu$C\mathbf{H}_2CH{=}$), 8.49 [m, 1 H, $CH_2C\mathbf{H}(CH_3)$], 8.90 (d, 3 H, J = 6 Hz, $C\mathbf{H}_3CHOH$), 9.09 (s, 9 H, t-Bu), 9.15 (d, 3 H, $C\mathbf{H}_3CHCH_2$); MS (70 eV) m/e 184 (parent ion), 166 ($M - H_2O$). IIIc′: IR (neat) 3350 (b, OH), 3040 (s, $=CH$), 1625 (w, $CH{=}CH_2$), 995, 910 cm^{-1} (s, $CH{=}CH_2$);.^1H NMR ($CDCl_3$) τ 4.50 (m, 1 H), 5.06 (m, 2 H) ($CH{=}CH_2$), 6.28 (s, 1 H, OH), 6.52 (m, 1 H, $C\mathbf{H}OH$), 7.27 (m, 1 H, $C\mathbf{H}CH{=}CH_2$), 8.68 (m, 3 H, t-Bu$C\mathbf{H}_2$ and $CH_3C\mathbf{H}$), 8.82 (d, 3 H, $C\mathbf{H}_3CH$, J = 6 Hz), 9.06 (s, 9 H, t-Bu), 9.32 (d, 3 H, $C\mathbf{H}_3CHOH$, J = 6 Hz).

Anal. Calcd for $C_{12}H_{24}O$: C, 78.20 H, 13.12. Found (mixture of IIIa′ and IIIb′): C, 78.01, H, 13.02. Found (mixture of diastereomers of IIIc′): C, 77.96, H, 13.21.

Hydrogenation of IIIa,b and IIIa′,b′. A mixture of IIIa and IIIb (8:1 ratio), collected by preparative GLC (FFAP column, 70 °C), was hydrogenated in cyclohexane solvent using a rocking bomb apparatus with platinum oxide catalyst. The resulting product contained only one GLC peak (IV), which was subsequently collected for analysis. IV: ^1H NMR ($CDCl_3$) no olefin peaks, τ 6.32 (m, 1 H, $C\mathbf{H}OH$), 7.70 (s, 1 H, OH), 8.78 (b, H, CH_2), 8.87 (d, 3 H, $C\mathbf{H}_3CHOH$, J = 6 Hz), 9.11 (d, 3 H, $C\mathbf{H}_3CHCH_2$, J = 6 Hz), 9.17 (s, 9 H, t-Bu). IV′ was similarly prepared by hydrogenation of a mixture of IIIa′ and IIIb′ (5:1 ratio). IV′: ^1H NMR ($CDCl_3$) no olefin peaks, 6.38 (m, 1 H, $C\mathbf{H}OH$), 8.11 (s, 1 H, OH), 8.92 (d, 3 H, $C\mathbf{H}_3CHOH$, J = 6 Hz), 9.16 (s and overlapping doublet, 12 H, t-Bu and $C\mathbf{H}_3CHCH_2$).

Alternate Route to IV and IV′. Preparation of 5,5-Dimethyl-1-hexanol. To 11 g (0.46 mol) of magnesium turnings covered with dry ether under argon, 10 ml of a 50% solution of 1-chloro-3,3-dimethylbutane in ether was added to initiate the reaction. After initiation, the remaining chloride solution (total amount 0.41 mol) was added dropwise over a period of 2 h. The reaction mixture was stirred at room temperature for an additional 2 h. Ethylene oxide was bubbled into the solution until all visible signs of the very exothermic reaction had disappeared. After hydrolysis and acidification, the ether layer was separated and dried with anhydrous magnesium sulfate. GLC (FFAP column, 70 °C) showed only one product which was verified by IR and ^1H NMR as 5,5-dimethyl-1-hexanol: IR (neat) 3270 (s, b, OH), 1460 (m) (CH_2), 1385 (w), 1360 (m) t-Bu, 1050 cm^{-1} (m, b, OH); ^1H NMR ($CDCl_3$) τ 6.32 (t, 2 H, $C\mathbf{H}_2OH$, J = 7.5 Hz), 7.30 (s, 1 H, OH), 8.3–8.8 (m, 6 H, CH_2), 9.10 (s, 9 H, t-Bu).

Preparation of 1-Chloro-5,5-dimethylhexane. 5,5-Dimethyl-1-hexanol (10 g, 0.077 mol) obtained by preparative GLC was reacted with $SOCl_2$ after the manner of Whitmore.[17] The alcohol was dissolved in 6.3 g (0.08 mol) of dry pyridine and treated with 10.7 g (0.09 mol) of $SOCl_2$ at −5 °C. The reaction mixture was warmed to 104 °C over a 4-h period and held at that temperature for an additional 2 h. The mixture was extracted with dilute HCl and then with bicarbonate solution. The organic layer was distilled, yielding a product of ca. 85% purity by GLC (bp 160–180 °C). The desired product (4.8 g) was obtained by preparative GLC (20 ft FFAP column, 140 °C, 110 ml He/min): IR (neat) no OH peak, 1460 (m, CH_2), 1395 (w), 1370 (m, t-Bu), 725 cm^{-1} (m, b, CCl); ^1H NMR ($CDCl_3$) τ 6.48 (t, 2 H, CH_2Cl, J = 6.7 Hz), 8.23 (t, 2 H, CH_2CH_2Cl, J = 6 Hz), 8.35–8.95 (m, 4 H, CH_2), 9.10 (s, 9 H, t-Bu).

Preparation of 5,5-Dimethylhexyllithium (V). To 0.6 g (0.086 mol) of lithium sand in ether under argon was added dropwise 0.031 mol of 1-chloro-5,5-dimethylhexane as a 10% solution in ether. After initiation with approximately 10% of the solution, the remainder was added over a period of 2 h, and then refluxed for 2 h more. The reaction mixture was filtered in a helium-filled drybox yielding 55 ml of 0.090 M RLi by the Gilman titration.[18]

Reaction of 5,5-Dimethylhexyllithium (V) with *cis*- and *trans*-2,3-Epoxybutane. The solution of the lithium alkyl V was halved in the drybox and reacted individually with the trans (5.5 mmol) and the cis epoxide (3.4 mmol). GLC of the reaction mixture from the trans epoxide and V after workup showed a single peak with retention time identical with that of IV prepared by hydrogenation of IIIa and IIIb within. A mixture of IV prepared by the two methods showed only a single GLC peak. Likewise, GLC of the product from the cis epoxide and V yielded a peak with identical retention time with that of IV′ prepared from IIIa′ and IIIb′ and not identical with IV. GLC conditions: 6 ft × 0.125 in. FFAP, 96 °C, 63 ml He/min. Retention times: IV, 23.7 min; IV′, 25.3 min.

Reaction of NpALi with Cyclohexene Oxide. To 40 ml of a 0.14 M solution of NpALi in n-pentane was added 4.0 g of cyclohexene oxide while keeping the solution in a dry ice–acetone bath. The reaction mixture was allowed to warm to room temperature and at that temperature was stirred for 1 h. Following hydrolysis the organic layer was separated and dried with anhydrous $MgSO_4$. The pentane, evaporated in a stream of nitrogen, yielded approximately 5 g of crude product. GLC on a 10 ft × 0.25 in. SE-30 column at 100 °C showed three products subsequently shown to be VIa–c in the ratio 65:15:20. IVa and VIb were collected together since they were poorly resolved. Anal. Calcd for $C_{14}H_{26}O$: C, 80.00; H, 12.38. Found: C, 80.19; H, 12.42. ^1H NMR ($CDCl_3$) τ 4.42 (m, 2 H, $CH{=}CH$), 6.66 (m, 1 H, $C\mathbf{H}OH$), 7.00 (s, 1 H, OH), 7.48 (m, 1 H, $C\mathbf{H}CH_2CH{=}$), 7.8–8.4 (m, 7 H), 8.5–8.9 (m, 5 H), 9.08, 9.11 (s, 9 H, cis and trans t-Bu). Likewise VIc was collected by GLC. Anal. Calcd for $C_{14}H_{26}O$: C, 80.00; H, 12.38. Found: C, 79.81; H, 12.12. ^1H NMR ($CDCl_3$) τ 4.36 (1 H), 5.08 (2 H) ($CH{=}CH_2$), 6.68 (1 H, $C\mathbf{H}OH$), 7.40 (m, 1 H), 8.18 (s, 1 H, OH), 8.0–8.2 (m, 2 H), 8.2–8.5 (m, 3 H), 8.5–9.0 (m, 6 H), 9.14 (s, 9 H, t-Bu). Analysis of axial CHOH multiplet for VIa with ca. 20% VIb (X portion of A_2BX): $J_{AX} = J_{\text{axial–axial}}$ = 9.0 Hz; $J_{BX} = J_{\text{axial–equatorial}}$ = 2.4 Hz.

Reactions of NpALi in THF. In each case dry THF was added to the n-pentane solution in large excess over of lithium species, and the solution allowed to equilibrate for a few minutes at 0 °C before reagent was added. Workup was the same as with n-pentane solvent.

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Registry No.—Ia, 39056-16-1; Ib, 39056-17-2; IIIa, 60967-62-6; IIIa′, 60967-63-7; IIIb, 60967-64-8; IIIb′, 60967-65-9; IIIc, 60967-66-0; IV, 60967-67-1; IV′, 60967-68-2; V, 60967-69-3; VIa, 60967-70-6; VIb, 61009-14-1; VIc, 60996-33-0; *trans*-2,3-epoxybutane, 21490-63-1; *cis*-2,3-epoxybutane, 1758-33-4; 1-chloro-3,3-dimethylbutane, 2855-08-5; ethylene oxide, 75-21-8; 5,5-dimethyl-1-hexanol, 2768-18-5; 1-chloro-5,5-dimethylhexane, 60996-32-9; cyclohexene oxide, 286-20-4.

References and Notes

(1) W. H. Glaze, J. E. Hanicak, M. L. Moore, and J. Chaudhuri, *J. Organomet. Chem.*, **44,** 39 (1972).

(2) W. H. Glaze, J. E. Hanicak, J. Chaudhuri, M. L. Moore, and D. P. Duncan, *J. Organomet. Chem.*, **51,** 13 (1973).

(3) W. H. Glaze, J. E. Hanicak, D. J. Berry, and D. P. Duncan, *J. Organomet. Chem.*, **44,** 49 (1972).

(4) W. H. Glaze, D. J. Berry, and D. P. Duncan, *J. Organomet. Chem.*, **52,** 233 (1973).

(5) F. Schué, D. J. Worsfeld, and S. Bywater, *J. Polym. Sci., Part B,* **7,** 821 (1969); *Bull. Soc. Chim. Fr.*, 271 (1970); *Macromolecules,* **3,** 509 (1970).

(6) M. Morton, R. D. Sanderson, and R. Sakata, *Polym. Lett.*, **9,** 61 (1971).

(7) F. E. Naylor, H. L. Hsieh, and J. C. Randall, *Macromolecules,* **3,** 486 (1970).

(8) D. A. Hutchison, K. R. Beck, R. A. Benkeser, and J. B. Grutzner, *J. Am. Chem. Soc.*, **95,** 7075 (1973).

(9) W. H. Glaze and D. P. Duncan, *J. Organomet. Chem.*, **99,** 11 (1975).

(10) R. A. Benkeser, *Synthesis,* **3,** 347 (1971).

(11) W. H. Glaze and C. R. McDaniel, *J. Organomet. Chem.*, **51,** 23 (1973).

(12) G. Courtois and L. Miginiac, *J. Organomet. Chem.*, **69, 1** (1974).

(13) H. Felkin, C. Frayerman, and G. Roussi, *Bull. Soc. Chim. Fr.*, 3704 (1970).

(14) Other conformational investigations of *trans*-2-alkyl-substituted cyclohexanols analogous to VI have established that such compounds exist predominantly in the trans diequatorial conformation.[15] Thus, 3,3,6,6-tetradeuterio-2-thiomethylcyclohexanol was shown to exist 80% in the trans diequatorial conformation.[16]

(15) E. Eliel, N. Allinger, S. Angyal, and G. Morrison, "Conformational Analysis", Interscience, New York, N.Y., 1965.

(16) E. A. Vorob'eva, L. G. Gurvich, N. S. Zefirov, M. Z. Krimer, and V. A. Smit, *Zhr. Org. Khim.*, **10,** 883 (1974).

(17) F. C. Whitmore, F. A. Karatz, and A. H. Popkin, *J. Am. Chem. Soc.*, **60,** 2540 (1938).

(18) H. Gilman and F. K. Cartledge, *J. Organomet. Chem.*, **2,** 44 (1964).