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Cationic Polymerizations by Aromatic Initiating Systems. 1. A Model for Initiation and Termination Using the p-$CH_3C_6H_4CH_2Cl/Et_3Al$ System

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The interaction between p-$CH_3C_6H_4CH_2Cl$ and Et_3Al (or Et_2AlCl) has been investigated using CH_2Cl_2 solvent in the range from −50 to −80 °C. The reaction yields three products: p-$CH_3C_6H_4CH_2Et$, p-$CH_3C_6H_4CH_2H$, and oligomeric polybenzyls. The first two arise upon ethylation and hydridation of the p-$CH_3C_6H_4{}^+CH_2$ cation by the Et_3AlCl^- counteranion while the third one is the result of self-polybenzylation. The relative amounts of termination products and polybenzyls can be controlled by temperature and reagent stoichiometry (Al/Cl ratio). Surprisingly, fastest p-$CH_3C_6H_4CH_2Cl$ disappearance was observed at low Al/Cl ratios. Kinetic studies indicate that ethylation and hydridation occur readily with Et_3Al, i.e., via the p-$CH_3C_6H_4{}^+CH_2$ Et_3AlCl^- pair, while the in situ formation of Et_2AlCl leads to the p-$CH_3C_6H_4{}^+CH_2$ $Et_2AlCl_2{}^-$ pair which in turn gives rise mainly to polybenzyls. The understanding of the mechanism of ethylation and hydridation in the p-$CH_3C_6H_4CH_2Cl/Et_3Al$ reaction is important as a model of initiation followed by immediate termination of cationic polymerizations by benzyl halide/alkylaluminum initiator systems.

During our fundamental studies on the mechanism of cationic olefin polymerizations it appeared of interest to investigate the mechanism of initiation by the use of aromatic cations, in particular to study the initiation of isobutylene polymerization by the $CH_3C_6H_4{}^+CH_2$ cation and thus to introduce a UV-active p-methylbenzyl head group into a polyisobutylene chain. Quantitative analysis of UV-active aromatic head groups promised to provide increased insight into the mechanistic details of initiation and chain breaking.

We have shown that isobutylene polymerization can be initiated readily by the use of a variety of tertiary alkyl and allyl halides in conjunction with alkylaluminum compounds,[1,2] presumably by direct alkylation of the olefin:

$$RX + Et_2AlX \rightarrow R^+Et_2AlX_2{}^- \text{ (or } R^+//Et_2AlX_2{}^-\text{)}$$

$$R^+Et_2AlX_2{}^- + C{=}C \rightarrow R{-}C{-}C^+\ Et_2AlX_2{}^-$$

$$R{-}C{-}C^+ + nC{=}C \rightarrow R{+}C{-}C{+}_n C{-}C^+$$

$$R = \text{tertiary alkyl or allyl, } X = \text{halide}$$

This paper concerns the interaction between the benzyl halide (initiator) and alkylaluminum (coinitiator) in the absence of olefin and the effect of experimental variables on the reaction. Subsequent papers of this series will deal with further model studies and polymerizations.

Because benzyl chloride in the presence of Friedel–Crafts acids readily undergoes self-benzylation and rapidly leads to polybenzyls,[6] an undesirable side reaction for our study, we used the p-methyl substituted derivate, p-methylbenzyl chloride, to afford at least some protection against para self-benzylation and to increase the reaction rate.

Results and Discussion

A. Interaction between p-Methylbenzyl Chloride and Triethylaluminum. The reaction between alkyl chlorides and alkylaluminums may be viewed as a model for initiation followed by immediate termination in carbenium ion polymerization ("polymerization without propagation").[1,2] In particular, the first step is the generation of a carbenium ion R^+

$$RCl + R_3'Al \rightarrow R^+ + R_3'AlCl^-$$

which in the absence of monomer is rapidly followed by the collapse of the cation–counterion pair by alkylation

$$R^+ + R_3'AlCl^- \rightarrow R{-}R' + R_2'AlCl$$

or by hydridation if a β hydrogen with respect to aluminum is available:[2-4]

$$R^+ + Et_3AlCl^- \rightarrow RH + CH_2{=}CH_2 + Et_2AlCl$$

With aromatic carbenium ion sources, specifically with p-methylbenzyl chloride and triethylaluminum, the following reactions are expected to occur:

$$CH_3C_6H_4CH_2Cl + Et_3Al \rightleftharpoons CH_3C_6H_4\overset{+}{C}H_2 + Et_3AlCl^- \qquad (1)$$

$$CH_3C_6H_4\overset{+}{C}H_2 + Et_3AlCl^- \nearrow CH_3C_6H_4CH_2Et + Et_2AlCl \qquad (2)$$

$$\searrow CH_3C_6H_4CH_2H + CH_2{=}CH_2 + Et_2AlCl \qquad (3)$$

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Table I. The Effect of Reaction Conditions on *p*-Methylpropylbenzene and *p*-Xylene Formation[a]

[p-$CH_3C_6H_4CH_2Cl$], M	$\frac{[\text{Alkylaluminum}]}{[p\text{-}CH_3C_6H_4CH_2Cl]}$	Temp, °C	$\frac{[p\text{-}CH_3C_6H_4CH_2Et] + [p\text{-}CH_3C_6H_6CH_2H]}{[p\text{-}CH_3C_6H_4CH_2Cl]_0} \times 100^b$	$\frac{[p\text{-}CH_3C_6H_4CH_3Et]^b}{[p\text{-}CH_3C_6H_4CH_2H]}$
	Et_3Al			
0.012	1	−50	13	3.4
0.012	1	−50	12	3.5
0.020	1	−65	17	2
0.020	1	−80	20	1.7
0.020	2	−80	35[c]	1.8
0.020	5	−80	63	1.6
0.020	10	−80	78	1.6
0.020	20	−80	90	1.8
0.0075	16	−80	75[d]	1.8
	Et_2AlCl			
0.020	5	−80	5	
0.020	10	−80	7	2.5
0.020	20	−80	10	1.9

[a] Solvent CH_2Cl_2. [b] After total p-$CH_3C_6H_4CH_2Cl$ consumption. [c] At 93% p-$CH_3C_6H_4CH_2Cl$ consumption. [d] At 72% p-$CH_3C_6H_4CH_2Cl$ consumption.

We have studied the interaction between p-$CH_3C_6H_4CH_2Cl$ and Et_3Al at Et_3Al/p-$CH_3C_6H_4CH_2Cl$ (Al/Cl) ratios ≥1 using CH_2Cl_2 solvent in the range from −50 to −80 °C. The Al/Cl ratio was changed by changing the concentration of the Et_3Al; the concentration of p-$CH_3C_6H_4CH_2Cl$ was kept constant. A few experiments with Et_2AlCl have also been carried out. Table I shows representative data. High Al/Cl ratios and low temperatures were used to minimize side reactions leading to undesirable products.

Confirming our analysis above, evidence for the presence of p-methylpropylbenzene and p-xylene has been found. Quantitative material balance determinations, however, have indicated that in addition to these two expected "termination products", other resinous materials, probably polybenzyls, have also been formed, the structure(s) of which have not been analyzed in detail. The terminology "termination products" refers to termination by ethylation and hydridation of cationic polymerization by the Et_3AlCl^- counteranion.

The yield of p-$CH_3C_6H_4CH_2Et$ and p-$CH_3C_6H_4CH_2H$ is strongly affected by the initial molar ratio of Et_3Al/p-$CH_3C_6H_4CH_2Cl$ (Al/Cl ratio). The ratio p-$CH_3C_6H_4CH_2Et$/p-$CH_3C_6H_4CH_2H$ (column 5 in Table I) reflects the relative rates of ethylation and hydridation and is affected by the temperature, i.e., it increases from 1.7 to 3.4 by raising the temperature from −80 to −50 °C. Similarly to these results, ethylation was found to be 2.3 times faster than hydridation when α-phenethyl chloride was reacted with Et_3Al using EtCl solvent at −65 °C.[5] The relative rates of ethylation vs. hydridation are probably governed by steric factors, i.e., the four-membered transition state leading to ethylation is more compressed than the six-membered one leading to hydridation.[2]

Column 4 in Table I shows the overall yield of ethylation and hydridation. Highest yields (80–90%) are obtained at Al/Cl ratios of 10–20 whereas the yields drop with decreasing Al/Cl ratios. In addition to these well-defined termination products a yellow-brown, resinous, brittle material, conceivably a mixture of oligobenzyls or polybenzyls, is formed, the structure and composition of which have not been studied. Such polybenzyls are expected to form upon mixing p-$CH_3C_6H_4CH_2Cl$ with Friedel–Crafts acids.[6] Thus in the polymerization of isobutylene using the benzyl halide/Et_3Al initiator system, the initiator consumption by Friedel–Crafts alkylation would be reduced at higher Al/Cl ratios.

A few experiments have also been carried out with Et_2AlCl. The yield of p-$CH_3C_6H_4CH_2Et$ plus p-$CH_3C_6H_4CH_2H$ (termination products) obtained with this relatively strong Lewis acid was much lower (<10%) and that of polybenzyls much higher even at high Al/Cl ratios than with the weaker Et_3Al (cf. Table I). This observation is probably due to the different nucleophilicities of the counterions: polybenzylation is more likely to occur in the presence of the less nucleophilic $Et_2AlCl_2^-$ than with the more nucleophilic Et_3AlCl^-. The lifetime of the benzyl cation is longer when it is associated with $Et_2AlCl_2^-$ and thus polyalkylation is favored; in contrast, the lifetime of the carbocation is shorter and ethylation or hydridation is favored over that of polybenzylation in the presence of the more nucleophilic Et_3AlCl^-. Differences in the tightness of these ion pairs has already been invoked by Kennedy and Rengachary[2] to explain rapid termination by Et_3AlCl^- of isobutylene polymerizations.

Finally, another important observation was the absence of p-$CH_3C_6H_4CH_2OCH_3$ among the reaction products. Since all experiments were quenched by the addition of methanol, we expected the formation of this ether; however, we did not find any evidence for the presence of p-$CH_3C_6H_4CH_2OCH_3$ among the reaction products. The mechanism discussed in the next section helps to rationalize this observation.

B. Kinetic Studies. Kinetic experiments have been carried out to study the effect of the Al/Cl ratio and temperature on the p-$CH_3C_6H_4CH_2Cl$ + Et_3Al reaction. Figure 1 summarizes our data obtained at Al/Cl = 1, 2, and 20 at −80 °C by plotting the rate of disappearance of p-$CH_3C_6H_4CH_2Cl$ and the rates of appearance of the products of ethylation and hydridation, respectively.

Surprisingly, the rate of p-$CH_3C_6H_4CH_2Cl$ disappearance is fastest at the lowest Et_3Al concentration, i.e., at Al/Cl = 1, and decreases by increasing the Al/Cl ratio from 1 to 5. Above Al/Cl ≈ 5 the rates remain essentially constant within what is considered to be experimental error. Other data (not shown) indicate that p-$CH_3C_6H_4CH_2Cl$ consumption is faster at −65 °C and that the yield of termination products is lower than at −80 °C.

The p-$CH_3C_6H_4CH_2Et$/p-$CH_3C_6H_4CH_2H$, i.e., the termination product ratio, seems to remain constant throughout the reaction; however, the amount of these products formed is a function of the Al/Cl ratio, and highest ethylation plus hydridation (~90%) occurs at highest (20) Al/Cl values. This

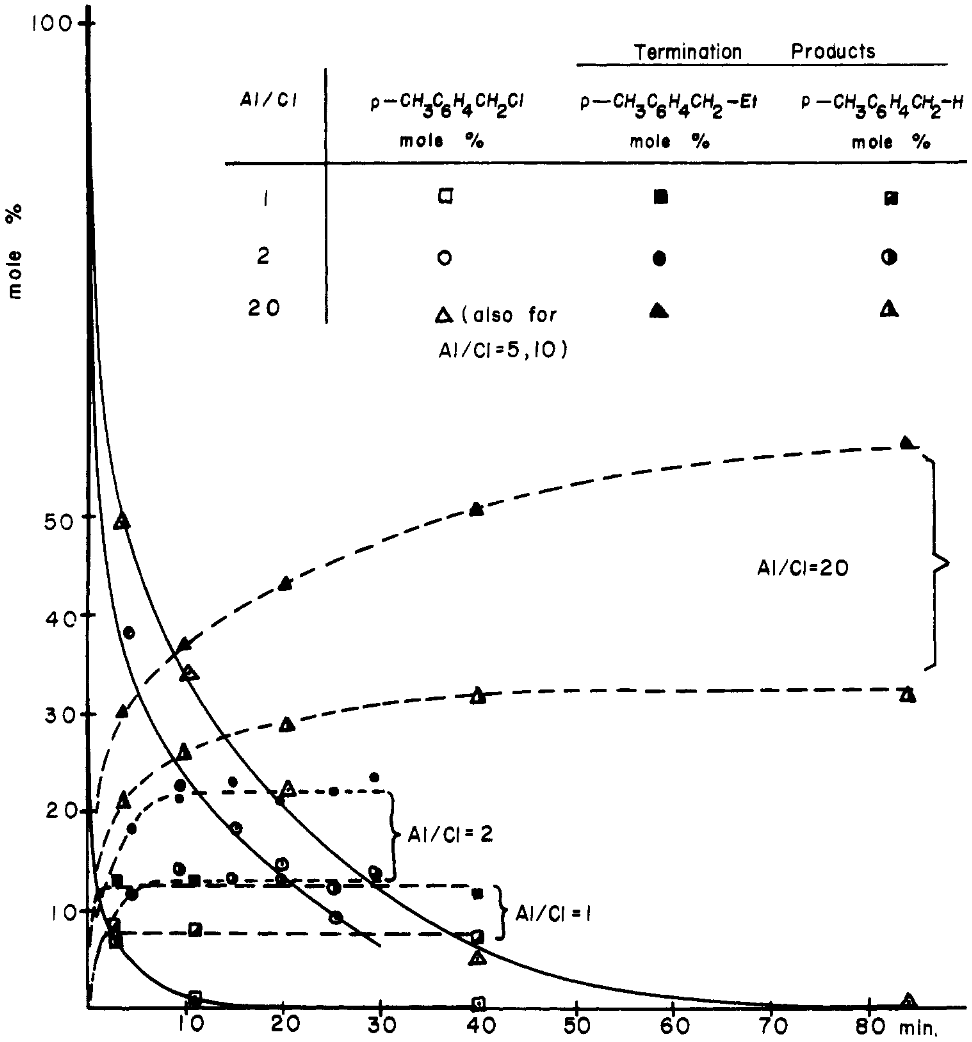

Figure 1. Effect of the Al/Cl ratio on the rate of p-$CH_3C_6H_4CH_2Cl$ disappearance and the rate of formation of p-$CH_3C_6H_4CH_2Et$ and p-$CH_3C_6H_4CH_2H$ ([p-$CH_3C_6H_4CH_2Cl$] 0.02 M, −80 °C).

statement is illustrated by Figure 2, which shows the sum of termination products (in mol % of p-$CH_3C_6H_4CH_2Cl$) and the termination products/polybenzyls ratio as a function of Al/Cl. The termination products/polybenzyls mole ratio was calculated from the analytically directly available sum of p-$CH_3C_6H_4CH_2Et$ and p-$CH_3C_6H_4CH_2H$ and the molar amount of polybenzyl that was obtained by assuming that besides the two termination products only polybenzyls formed.

On closer examination of our results it became increasingly apparent that the kinetics governing this reaction are more complex, partly because at least two of the by-products, i.e., Et_2AlCl and $CH_3C_6H_4CH_2{\cdot}C_6H_3(CH_3)CH_2Cl$, are much more reactive than the original reagents and partly because the nature and polarity of the reagents change during the reaction thus leading to unpredictable/uncontrollable changes in rates and solvation. While the extent of our data is far from sufficient for a complete kinetic analysis, indeed such an analysis is quite outside the scope of these studies, they still allow the drawing of some conservative conclusions valuable for the understanding of the mechanism of these reactions and, by inference, for the mechanism of cationic polymerization initiated by benzyl cations.

The key to the understanding of these at first glance unexpected observations described in this and the previous section is to rationalize why the rate of disappearance of p-$CH_3C_6H_4CH_2Cl$ decreases with increasing Et_3Al concentration at constant initial p-$CH_3C_6H_4CH_2Cl$ concentration. A possible explanation is provided by the following set of equations:

$$CH_3C_6H_4CH_2Cl + Et_3Al \overset{K}{\rightleftharpoons} [CH_3C_6H_4\overset{+}{C}H_2\ \ Et_3AlCl^-]$$

$$\begin{tikzcd} & CH_3C_6H_4CH_2Et + Et_2AlCl \\ {[CH_3C_6H_4\overset{+}{C}H_2\ \ Et_3AlCl^-]} \arrow[ur] \arrow[r] \arrow[dr, "n\text{-}CH_3C_6H_4CH_2Cl"'] & CH_3C_6H_4CH_2H + CH_2{=}CH_2 + Et_2AlCl \\ & CH_3C_6H_4CH_2C_6H_3(CH_3)CH_2Cl + Et_2AlCl + C_2H_6 \text{ (and similar polybenzyls)} \end{tikzcd}$$

$$CH_3C_6H_4CH_2Cl + Et_2AlCl \overset{K'}{\rightleftharpoons} [CH_3C_6H_4\overset{+}{C}H_2\ \ Et_2AlCl_2^-] \longrightarrow \text{mainly polybenzyls (cf. Table I)}$$

According to this mechanism the two reactants rapidly form an ion pair. In line with similar carbenium ion systems the equilibrium constant K which governs the concentration of the ion pair is probably quite low. This ion pair is formed from a large reservoir of $CH_3C_6H_4CH_2Cl{\cdot}Et_3Al$ molecular complex. A similar problem has already been treated in greater depth in conjunction with the t-$BuCl{\cdot}Me_3Al$ system.[1] The ion pair can either collapse to the two termination products or ring-benzylate the unreacted p-$CH_3C_6H_4CH_2Cl$ to give a mixture of polybenzyls. All these reactions, i.e., ethylation, hydridation, and polybenzylation, give rise to Et_2AlCl. This species,

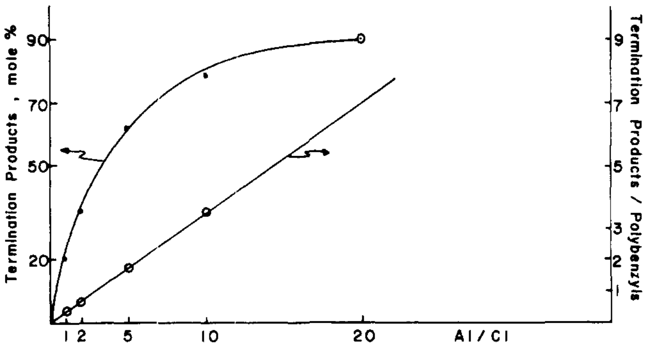

Figure 2. Termination products as a function of Al/Cl.

being a stronger Lewis acid than Et_3Al, will much more rapidly react with unconverted p-$CH_3C_6H_4CH_2Cl$ to produce polybenzyls than Et_3Al. Indeed, it is well known that Et_2AlCl rapidly converts benzyl halides to polybenzyls[6,7] and our own experiments also indicate that Et_2AlCl consumes p-$CH_3C_6H_4CH_2Cl$ much more rapidly than Et_3Al and gives almost exclusively polybenzyls (cf. Table I). In the reaction under investigation Et_3Al and Et_2AlCl compete for p-$CH_3C_6H_4CH_2Cl$; while the p-$CH_3C_6H_4{}^+CH_2$ Et_3AlCl^- ion pair rapidly collapses either by ethylation or hydridation, the p-$CH_3C_6H_4{}^+CH_2$ $Et_2AlCl_2{}^-$ pair is longer lived and produces mainly polybenzyls.

By increasing the concentration of Et_3Al relative to that of p-$CH_3C_6H_4CH_2Cl$, i.e., increasing the Al/Cl ratio, the rate of p-$CH_3C_6H_4CH_2Cl$ disappearance decreases (cf. Figure 1), most likely because the concentration of unreacted p-$CH_3C_6H_4CH_2Cl$ (and consequently the rate of polybenzyl formation) decreases. In other words, at high Al/Cl ratios the concentration of the ion pair increases while that of the free p-$CH_3C_6H_4CH_2Cl$ decreases, which results in reduced polybenzylation rates. Apparently at Al/Cl = 1.0 sufficient p-$CH_3C_6H_4CH_2Cl$ remains for rapid polybenzylation while at Al/Cl > 5 unconsumed p-$CH_3C_6H_4CH_2Cl$ is converted to the p-$CH_3C_6H_5{}^+CH_2$ cation thus reducing the rate of polybenzylation. Indeed, at Al/Cl = 20 hardly any polybenzyl is formed.

The fact that in the Al/Cl range from 1.0 to 5.0 polybenzyl formation predominates suggests that polybenzylation is extremely rapid and it is able to compete with ethylation and/or hydridation, rapid first-order reactions involving the collapse of an ion pair. In the system under investigation the ion pair may be highly solvated p-$CH_3C_6H_4{}^+CH_2//et_3AlCl^-$ and the carbenium ion may be preferentially solvated by the reagent p-$CH_3C_6H_4CH_2Cl$ rather than the CH_2Cl_2 solvent.

The fact that p-$CH_3C_6H_4CH_2OCH_3$ has not been found among the reaction products after quenching with methanol is explained by the very small equilibrium concentration of the carbenium ion pair p-$CH_3C_6H_4{}^+CH_2$ Et_3AlCl^-.

We can compare the reults obtained with the t-BuCl/Me_3Al/CH_3Cl system[1] and those of the present study with p-$CH_3C_6H_4CH_2Cl/Et_3Al/CH_2Cl_2$. The t-BuCl + Me_3Al reaction gave only the one expected termination product, t-BuMe (neopentane); however, in the present case, in addition to the expected two termination products, polybenzyls have also been obtained. The formation of polybenzyls indicates the great facility of alkylations in these systems. Since aromatic compounds lead to undesirable, complex ring alkylations, their use should be minimized in the study of the mechanism of cationic polymerization.

The overall activation energy of the p-$CH_3C_6H_4CH_2Cl$ + Et_3Al reaction was determined by carrying out a series of experiments at −49, −64, and −80 °C (p-$CH_3C_6H_4CH_2Cl$ 0.01 M, CH_2Cl_2 solvent) at Al/Cl = 20 to minimize polybenzyl formation. The accuracy of the data was not sufficient to determine unambiguously the order of the reaction with respect to p-$CH_3C_6H_4CH_2Cl$. However, assuming that the rate of p-$CH_3C_6H_4CH_2Cl$ disappearance is first order we have determined the reaction rate constants (Figure 3) and constructed the Arrhenius plot from these data. According to these results $k = 2.8 \times 10^{-3}$, 0.46×10^{-3}, and 0.037×10^{-3} at −49, −64, and −80 °C, respectively, and the overall activation energy of the reaction $\Delta E = 12 \pm 1$ kcal/mol. This value is very similar to those obtained for the *tert*-butyl halide + Me_3Al reactions using polar solvents (10 ± 1 kcal/mol) (5).

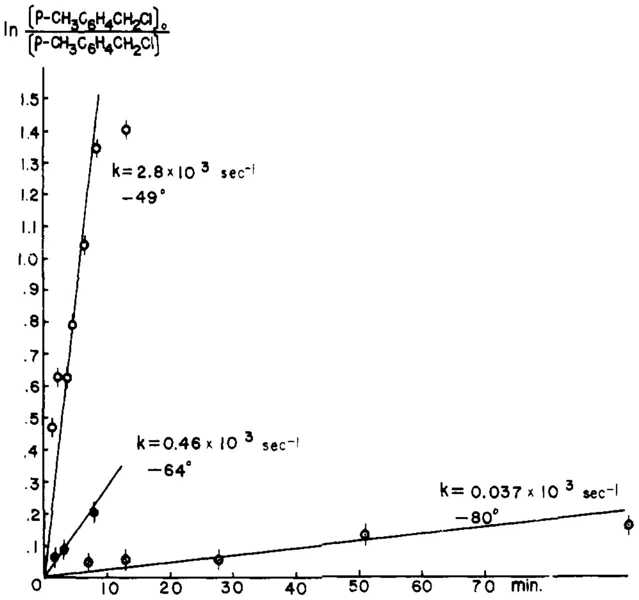

Figure 3. First-order plot of the p-$CH_3C_6H_4CH_2Cl$ + Et_3Al reaction ([p-$CH_3C_6H_4CH_2Cl$] 0.01 M).

Experimental Section

Alkylaluminium compounds (Ethyl Co.), p-methylbenzyl chloride (Aldrich), and n-nonane (Chemical Samples Co.) were commercially available. These materials were distilled in the absence of oxygen and moisture. Distilled Et_2ClAl was stored over sodium chloride to prevent the accumulation of $EtAlCl_2$. Methylene chloride (Matheson) was refluxed over Et_3Al and freshly distilled before use. All experiments and material handlings were performed in a stainless steel enclosure under N_2 atmosphere (<50 ppm moisture), using Pyrex glassware with septum caps. The glassware was dried at 140 °C for 24 h and cooled under nitrogen.

A representative experiment (line 10 in Table I) was carried out as follows. To 10 ml of CH_2Cl_2 was added 1.23 ml of Et_3Al (0.8 M Et_3Al). Of this solution 5 ml was poured into a round-bottom flask. The flask was tightly capped with a septum cap and cooled to −80 °C. A solution containing 0.57 ml of p-$CH_3C_6H_4CH_2Cl$ and 10 ml of CH_2Cl_2 was prepared in a test tube and further diluted tenfold (0.04 M p-$CH_3C_6H_4CH_2Cl$). The test tube was capped and cooled to −80 °C. After temperature equilibrium 4.5 ml of this solution at −80 °C (5 ml at room temperature) was rapidly added by a prechilled pipet to the 5 ml of 0.8 M solution Et_3Al and the round-bottom flask capped again and shaken. Subsequently, 1-ml aliquots of the mixture were withdrawn at suitable intervals by means of a prechilled syringe and poured into test tubes containing 0.5 ml of prechilled CH_3OH. Then 1 ml of 0.082% p-methylethylbenzene in CH_2Cl_2 was added as an internal standard to the quenched solution. n-Nonane was the internal standard in the three experiments illustrated in Figure 3. The aluminum oxide residues were separated from the organic phase by adding aqueous sodium–potassium tartrate at 0 °C.

After extraction, the organic layers were analyzed using a Hewlett-Packard 5750 research chromatograph with a flame detector. The column used (12 ft × 0.125 in.) contained 10% SE-30 Silicone gum as a liquid phase and helium was the carrier gas. The reaction products were identified by peak enhancement using authentic samples. Conditions when p-$CH_3C_6H_4CH_2CH_3$ was the standard: injection port 230 °C, oven 130 °C; retention times (in s) 150 (p-$CH_3C_6H_4CH_3$), 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%.

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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.

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Neopentylallyllithium. 5. Stereochemistry of Nonrearrangement Reactions with Epoxides

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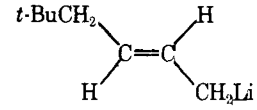
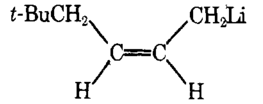
Reactions of neopentylallyllithium (NpALi), the 1:1 addition product of *tert*-butyllithium and 1,3-butadiene, with cyclohexene oxide and *cis*- and *trans*-2,3-epoxybutane are reported. In aliphatic hydrocarbon solvent each reaction is shown to consist predominantly of "normal," i.e., nonrearranged, 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 ^1H 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]

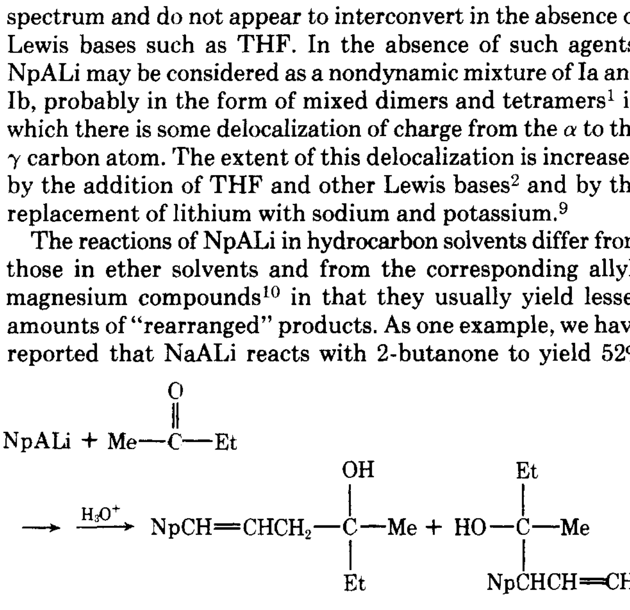


Ia



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]



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

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, ^1H 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