BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 677—683 (1968)

Reaction of Allylbenzene with *n*-Butyllithium in Tetrahydrofuran

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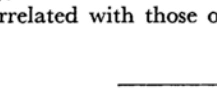
(Received September 22, 1967)

The reaction products between allylbenzene and *n*-butyllithium in tetrahydrofuran at 60°C were fractionated and investigated by elementary analysis, a molecular-weight determination, and a study of the IR, UV, and NMR spectra. The products were hydrocarbons and alcohols, the latter of which were formed by the reaction of the carbanions with tetrahydrofuran. The main products were 3-phenylheptene-2, 5-methyl-6-phenyldecane, 5-phenyl-5-heptene-1-ol, 5-phenyl-5-vinylnonane-1-ol, and 5-phenyl-5-vinylnonane-1, 9-diol. 3-Phenylheptene-1 was not obtained. In the resonance structures of allyl anions, a and b, $\mathrm{Ph{-}\bar{C}R{-}CH{=}CH_2}$ (a) ↔ $\mathrm{Ph{-}CR{=}CH{-}CH_2^-}$ (b), the reaction with tetrahydrofuran took place only in the form a. The observed results are correlated with those of the anionic polymerization of *trans*-β-methylstyrene reported previously.

Recently, the present authors have examined the anionic polymerization of *trans*-β-methylstyrene.[1] In the polymerization of this monomer with *n*-butyllithium in tetrahydrofuran at room temperature, a benzyl-type living anion (B) was easily converted into an allyl-type anion (A) by a chain-transfer reaction to the monomer. At a high temperature such as 60°C, the anions A and B further changed to inactive anions which possessed no reactivity to the monomer; this resulted in the cessation of the polymerization reaction. The anions A and B had absorption maxima at 340 and 398 mμ respectively, while the inactive anions had theirs at 510 and 570 mμ. The species having a λ_{max} at 510 mμ was supposed to be an anion C, but the species showing a λ_{max} at 570 mμ (anion D) was not confirmed.

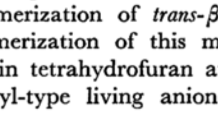
$(\mathrm{Ph{-}CH{\cdots}CH{\cdots}CH_2})^-\ \mathrm{Li}^+$

(A)



$\sim\!\mathrm{CH(CH_3){-}CH(Ph)^-\ Li^+}$

(B)



$\sim\!\mathrm{CH(CH_3){-}\overset{Li^+}{\bar{C}}(Ph){-}C(CH_3){=}CH(Ph)}$

(C)

On the other hand, only the anion D was formed in the reaction of allylbenzene with *n*-butyllithium at 60°C in tetrahydrofuran.[1]

This paper will be concerned with investigations of the reaction of allylbenzene with *n*-butyllithium carried out in order to determine the structure of the anion D.

Experimental and Results

Materials. *Allylbenzene.* This was prepared from phenylmagnesium bromide and allyl chloride,[2] and was purified by fractional distillation. Bp 72—73°C/39 mmHg. The purity was checked by gas chromatography.

Tetrahydrofuran (THF). Tetrahydrofuran was refluxed first over sodium and then over lithium aluminum hydride. The solvent was distilled onto sodium-potassium alloy and benzophenone, from where it was transferred into a reaction vessel on a vacuum line.

n-Butyllithium (n-BuLi). According to the method of Gilman,[3] *n*-BuLi was prepared in THF. The concentration was determined by double titration.[4] The presence of the unchanged *n*-butyl chloride, which was used for the preparation of *n*-BuLi, was not detected by gas chromatography, while the formation of *n*-octane was observed.

Reaction. The reaction was carried out under dry nitrogen in a glass vessel equipped with a three-way stopcock. To a solution of allylbenzene (13 g, 0.11 mol) in THF (200 m*l*), *n*-BuLi (0.11 mol) was added with a syringe over a ten minute period at room temperature. As soon as the *n*-BuLi was added, the solution turned red and generated gas and white precipitates. The reaction mixture was then allowed to stand at 60°C for 48 hr. During this time, the solution turned gradually red-purple. The reaction was terminated by adding methanol after the white precipitates

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[1] Y. Okamoto, H. Yuki and S. Murahashi, This Bulletin, **41**, 197 (1968).

[2] E. B. Hershberg, *Helv. Chim. Acta,* **17**, 351 (1934).

[3] H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957).

[4] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

had been isolated under dry nitrogen. The white precipitates must have been lithium hydride because they showed flame-test results characteristic of lithium and reacted with methanol violently. The THF was then removed from the reaction mixture. The residue was dissolved in diethyl ether and washed with water. The ethereal layer was dried over magnesium sulfate, and then the ether was removed to give 16 g of an oily product.

Fractionation of Reaction Mixture. The above product was first separated into fractions by distillation under nitrogen, and subsequently the fractions were treated by column chromatography with activated alumina, using *n*-hexane, benzene, and methanol as eluents. The results are summarized in Table 1. The fractions eluted with *n*-hexane were hydrocarbons, while those eluted with benzene and methanol were alcohols.

TABLE 1. FRACTIONATION OF REACTION PRODUCT

Fraction	Distillation			Column chromatography	
	Bp /1.5 mmHg °C	Yield g	Yield %	Eluent	Recovery %
F1H	48—52	0.3	2	Hexane	90
F2H	77—104	1.6	10	Hexane	63
F2B				Benzene	2
F2M				Methanol	33
F3H	104—114	1.4	9	Hexane	35
F3B				Benzene	46
F3M				Methanol	19
F4H	114—154	2.9	18	Hexane	56
F4B				Benzene	1
F4M				Methanol	43
F5H	154—160	2.0	13	Hexane	54
F5M				Methanol	46
F6	Residue	7.8	49	—	—

Measurement. *Molecular Weight and Elementary Analysis.* The molecular weight was measured on a Mechrolab Vapor Pressure Osmometer, Model 301 A, using a benzene solution for the hydrocarbon and an ethanol solution for the alcohol. The elementary analyses and the molecular weights of the fractions are listed in Tables 2 and 3.

TABLE 2. ELEMENTARY ANALYSES AND MOLECULAR WEIGHTS OF HYDROCARBONS

Fraction number	Elementary analysis C%	Elementary analysis H%	Molecular weight	Molecular formula
F1H	89.00	11.24	185	$C_{13}H_{19.1}$
F2H	87.64	11.88	230	$C_{17}H_{27.7}$
F3H	90.04	10.49	279	$C_{22}H_{30.5}$
F4H	89.44	10.10	300	$C_{22}H_{29.5}$
F5H	—	—	349	—

TABLE 3. ELEMENTARY ANALYSES AND MOLECULAR WEIGHTS OF ALCOHOLS

Fraction number	Elementary analysis C%	Elementary analysis H%	Molecular weight in EtOH	Molecular formula
F2M	81.43	9.57	192	$C_{13}H_{18.3}O_{1.08}$
F3B	81.91	10.68	244	$C_{17}H_{26.4}O_{1.15}$
F4M	79.01	10.27	248	$C_{17}H_{26.0}O_{1.73}$
F5M	77.56	9.90	259	$C_{17}H_{25.9}O_{2.06}$

Infrared Spectrum. The spectrum was obtained with a Nihon Bunko Model IR-S Spectrometer in a liquid state. The hydrocarbons showed the absorption bands at 1945, 1860, and 1800 cm^{-1} due to a mono-substituted benzene, at 2960 and 1380 cm^{-1} due to a methyl group, and at 2925 cm^{-1} due to a methylene group. The alcohols showed the absorptions due to a hydroxy group at 3300 and 1050 cm^{-1}, besides the absorption bands due to a mono-substituted benzene and a methylene group.

Electronic Spectrum. The measurements were made with a Hitachi EPS-2 Spectrophotometer using cyclohexane solutions for the hydrocarbons and ethanol solutions for the alcohols. The respective characteristics of the IR and UV spectra are summarized in Tables 4 and 5. In these tables, the molar extinction coefficient, ε_{max} is based on the observed molecular weight of each fraction.

NMR Spectrum. The NMR spectrum was taken in a carbon tetrachloride solution with a JNM-4H-100 Spectrometer (Japan Electron Optics Laboratory Co., Ltd.) at 100 Mc/sec, using tetramethylsilane as an internal standard. The spectra of the fractions F1H, F2H, F2M, and F3B are shown in Figs. 1, 2, 3, and 4 respectively.

TABLE 4. CHARACTERISTICS OF IR, UV, AND NMR SPECTRA OF HYDROCARBONS

Fraction number	IR[a)]		UV		NMR[b)]
	835 cm^{-1}	910 cm^{-1}	λ_{max} (mμ)	ε_{max}	H_{al}/H_{ar}
F1H	Strong	Weak	242	4300	3.4
F2H	Weak	Medium	242	1090	4.5
F3H	Weak	Weak	—	—	1.3
F4H	Weak	Weak	—	—	2.2

a) 835 cm^{-1}: $R_1R_2C=CHR_3$, 910 cm^{-1}: $CH_2=CH-$.

b) The ratio of the numbers of aliphatic proton to aromatic proton.

TABLE 5. CHARACTERISTICS OF IR, UV, and NMR SPECTRA OF ALCOHOLS

Fraction number	IR (cm^{-1})[a]			UV		NMR[b] H_{al}/H_{ar}
	835	910	3300	λ_{max}	ε_{max}	
F2M	Medium	Medium	Strong	243	6300	2.8
F3B	Weak	Strong	Strong	253	356	4.3
F4M	Weak	Strong	Strong	—	—	4.4
F5M	Weak	Strong	Strong	—	—	4.4

a) 835 cm^{-1}: $R_1R_2C=CHR_3$, 910 cm^{-1}: $CH_2=CH-$, 3300 cm^{-1}: -OH.
b) The ratio of the numbers of aliphatic proton to aromatic proton.

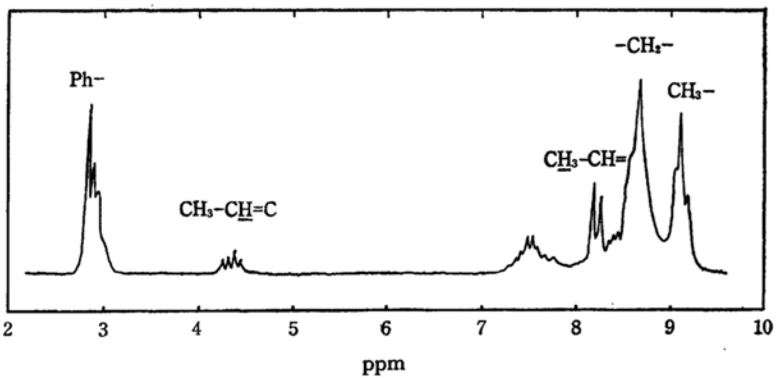


Fig. 1. NMR spectrum of fraction F1H.

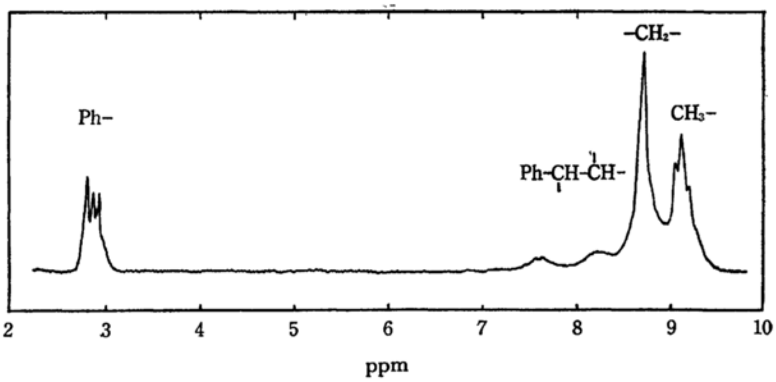


Fig. 2. NMR spectrum of fraction F2H.

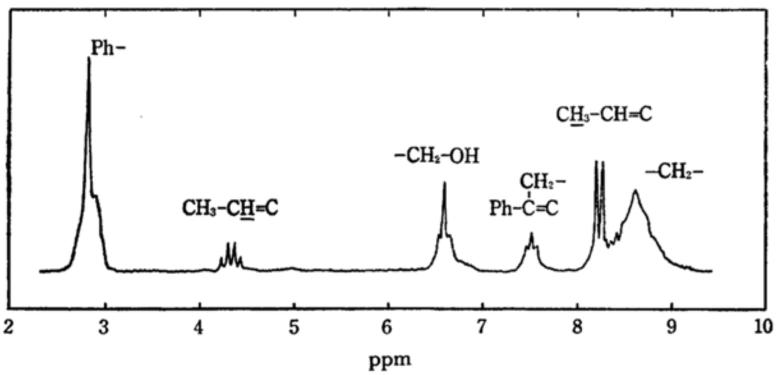
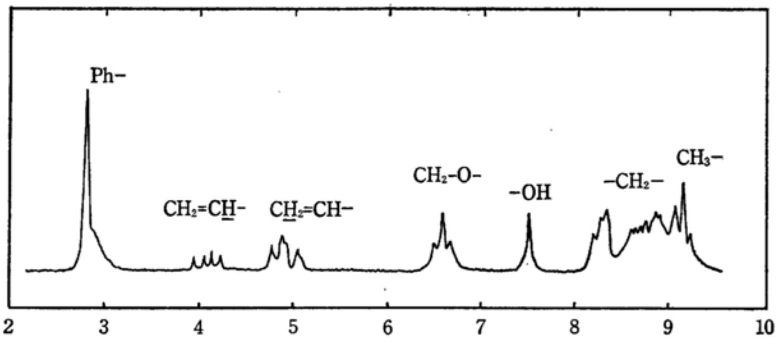


Fig. 3. NMR spectrum of fraction F2M.



ppm

Fig. 4. NMR spectrum of fraction F3B.

TABLE 6. HYDROCARBONS AS PROBABLE PRODUCTS IN THE REACTION

Molecular formula	Structural formula	Composition C%	Composition H%	Molecular weight	H_{al}/H_{ar}[a]	Remark
$C_{13}H_{18}$	$\text{Ph-}\underset{\text{C}_4\text{H}_9}{\text{CH}}\text{-CH=CH}_2$	89.6	10.4	174	2.60	Ia
$C_{13}H_{18}$	$\text{Ph-}\underset{\text{C}_4\text{H}_9}{\text{C}}\text{=CH-CH}_3$	89.6	10.4	174	2.60	Ib
$C_{17}H_{28}$	$\text{Ph-}\overset{\text{C}_4\text{H}_9}{\text{CH}}\text{-}\underset{\text{C}_4\text{H}_9}{\text{CH}}\text{-CH}_3$	87.8	12.2	232	4.60	II

a) The ratio of the numbers of aliphatic protons to aromatic protons.

TABLE 7. ALCOHOLS AS PROBABLE PRODUCTS IN THE REACTION

Molecular formula	Structural formula	Composition C%	Composition H%	Molecular weight	H_{al}/H_{ar}[a]	Remark
$C_{13}H_{18}O$	$\text{Ph-}\underset{(\text{CH}_2)_4\text{-OH}}{\text{CH}}\text{-CH=CH}_2$	82.1	9.57	190	2.60	Va
$C_{13}H_{18}O$	$\text{Ph-}\underset{(\text{CH}_2)_4\text{-OH}}{\text{C}}\text{=CH-CH}_3$	82.1	9.57	190	2.60	Vb
$C_{13}H_{18}O$	$\text{Ph-CH=CH-CH}_2\text{-(CH}_2)_4\text{-OH}$	82.1	9.57	190	2.60	Vc
$C_{17}H_{26}O$	$\text{Ph-}\overset{\text{C}_4\text{H}_9}{\underset{(\text{CH}_2)_4\text{-OH}}{\text{C}}}\text{-CH=CH}_2$	82.8	10.6	246	4.20	VIa
$C_{17}H_{26}O$	$\text{Ph-}\underset{\text{C}_4\text{H}_9}{\text{C}}\text{=CH-CH}_2\text{-(CH}_2)_4\text{-OH}$	82.8	10.6	246	4.20	VIb
$C_{17}H_{26}O_2$	$\text{Ph-}\overset{(\text{CH}_2)_4\text{-OH}}{\underset{(\text{CH}_2)_4\text{-OH}}{\text{C}}}\text{-CH=CH}_2$	77.8	9.99	262	4.20	VIIa
$C_{17}H_{26}O_2$	$\text{Ph-}\underset{(\text{CH}_2)_4\text{-OH}}{\text{C}}\text{=CH-CH}_2\text{-(CH}_2)_4\text{-OH}$	77.8	9.99	262	4.20	VIIb

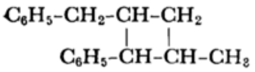
a) The ratio of the numbers of aliphatic protons to aromatic protons.

Probable Products of the Reaction. Tables 6 and 7 list some compounds which seem to be produced in this reaction. The alcohols listed in Table 7 were considered to be produced by the reactions of carbanions with THF. Their molecular formulae, structural formulae, elementary analyses, and molecular weights, and the ratios of the numbers of aliphatic protons to aromatic protons (H_{al}/H_{ar}) in them are also shown in the tables. From these characteristic features the structure of the compound contained in each fraction was estimated to be one of those included in Tables 6 and 7.

Determination of the Structure. *Fraction F1H.* The elementary analysis and the molecular weight of the fraction F1H were most similar to those of 3-phenylheptene-1 (Ia in Table 6) or 3-phenylheptene-2 (Ib). The IR spectrum showed a strong absorption due to a three-substituted olefin, $>C=CH-$, at 835 cm^{-1}; the NMR spectrum also indicated the existence of a $>C=CH-CH_3$ structure by the peaks at 8.2 and 4.3 ppm (Fig. 1). In the UV spectrum a strong absorption due to the conjugation between a benzene ring and a C=C double bond was observed at the same wavelength as that of the absorption of 3-phenylhexene-2 (λ_{max} 242 mμ, ε_{max} 4700 in cyclohexane).[5] These results showed that this fraction consisted mostly of Ib. However, the absorptions at 8.7 and 9.1 ppm in the NMR spectrum, attributed to the methylene and methyl groups respectively, are too strong if 3-phenylheptene-2 is the only component of the fraction. It seems that the fraction may also contain an other compound, probably 5-methyl-6-phenyldecane (II in Table 6); if so, the elementary analysis, the molecular weight, and the H_{al}/H_{ar} ratio show that the ratio of Ib to II will be about 2. The clear separation into these two components could not be attained by further fractionations, however.

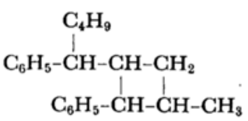
Fraction F2H. The molecular formula of the fraction F2H was consistent with that of 5-methyl-6-phenyldecane. The IR spectrum showed the absence of an olefinic double bond, and the chemical shift and the relative area of each peak (Ph : $>CH-$: $-CH_2-$: $CH_3- = 5.0 : 2.2 : 11.3 : 8.8$) in the NMR spectrum also supported the above consistence.

Fractions F3H and F4H. Both the fractions showed the absence of a C=C double bond in their IR and NMR spectra. Judging from the molecular weight and $H_{al}/H_{ar'}$, III and IV might be suggested as the components of both the fractions, whose difference may be that of the relative amounts of these compounds.



$$\begin{array}{l} C_6H_5-CH_2-\underset{|}{C}H-\underset{|}{C}H_2 \\ \quad\quad C_6H_5-CH-CH-CH_3 \end{array}$$

III



$$\begin{array}{l} \quad\quad\; C_4H_9 \\ \quad\quad\quad | \\ C_6H_5-CH-\underset{|}{C}H-\underset{|}{C}H_2 \\ \quad\quad C_6H_5-CH-CH-CH_3 \end{array}$$

IV

Fractions F5H and F6. These fractions were composed of higher-molecular-weight products, the structures of which were not determined in this study.

Fraction F2M. The elementary analysis and the molecular weight of this fraction were similar to those of 5-phenyl-6-heptene-1-ol (Va in Table 7), 5-phenyl-5-heptene-1-ol (Vb), or 7-phenyl-6-heptene-1-ol (Vc). The NMR spectrum showed the respective absorptions at around 4.3 and 8.2 ppm for an olefinic proton and methyl protons in a $CH_3-CH=C$ unit and no absorption due to a *n*-butyl group, suggesting that this fraction consisted of Vb. The relative intensities of the peaks (Ph: $C=CH-$: $-CH_2OH$: $-CH_2-C=C$: CH_3- : $-CH_2- = 5.0 : 1.0 : 3.0 : 2.0 : 2.7 : 4.4$) in the NMR spectrum were consistent with the above estimation. The IR and UV spectra also gave the same conclusion.

Fractions F2B and F3B. The molecular formula of the fraction F3B was most in accord with 5-phenyl-5-vinylnonane-1-ol (VIa in Table 7) or 7-phenyl-6-undecene-1-ol (VIb). Both IR and NMR spectra strongly suggested the existence of a vinyl group. The similarity of the UV spectrum with that of allylbenzene indicated that this fraction was VIa. The structure of VIa was also confirmed by the chemical shift and the relative intensities of the peaks (Ph : $CH_2=CH-$: $-CH_2O-$: $-OH$: $-CH_2-$: $CH_3- = 5.0 : 2.9 : 2.0 : 1.0 : 12 : 3.2$) in the NMR spectrum. The IR spectrum of the fraction F2B was very similar to that of the fraction F3B.

Fractions F3M and F5M. The structure of 5-phenyl-5-vinylnonane-1, 9-diol (VIIa in Table 7) and that of 5-phenyl-5-undecene-1, 11-diol (VIIb) might be assigned to the fraction F5M on the basis of the elementary analysis and the molecular weight. The NMR and IR spectra indicated that this fraction was compound VIIa, for it contained a C=C double bond, but only a vinyl group. The IR spectrum of the fraction F3M was similar to that of the fraction F5M.

Fraction F4M. The data suggest that this fraction consists of almost equal amounts of VIa and VIIa present in the fractions F2B and F5M respectively.

Discussion

The compounds identified as the main products in the reaction between allylbenzene and *n*-BuLi were found to be Ib, II, Vb, VIa, and VIIa, listed in Tables 6 and 7. The following reactions may be suggested as the processes by which these compounds are formed.

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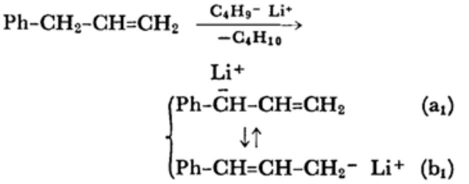
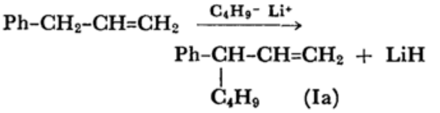
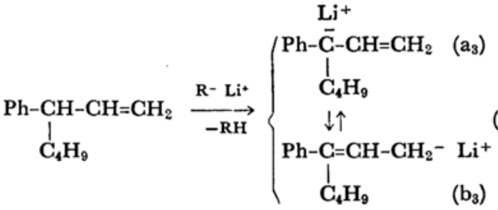
[5] D. J. Cram, F. A. Elhufez and H. Weingartner, *ibid.*, **75**, 2293 (1953).



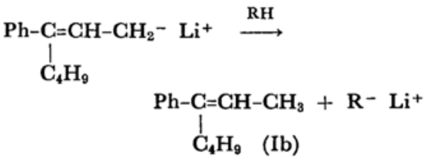
$$\mathrm{Ph\text{-}CH_2\text{-}CH{=}CH_2} \xrightarrow[-C_4H_{10}]{C_4H_9^-\,Li^+} \left\{\begin{array}{ll} \mathrm{Ph\text{-}\overset{Li^+}{\bar{C}}H\text{-}CH{=}CH_2} & (a_1)\\ \downarrow\uparrow & \\ \mathrm{Ph\text{-}CH{=}CH\text{-}CH_2^-\ Li^+} & (b_1)\end{array}\right. \qquad (1)$$



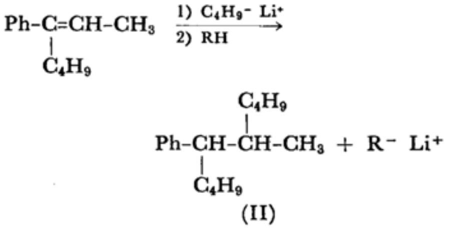
$$\mathrm{Ph\text{-}CH_2\text{-}CH{=}CH_2} \xrightarrow{C_4H_9^-\,Li^+} \mathrm{Ph\text{-}\underset{C_4H_9}{\underset{|}{C}}H\text{-}CH{=}CH_2} + \mathrm{LiH} \quad (Ia) \qquad (2)$$



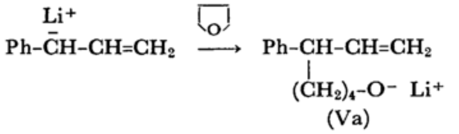
$$\mathrm{Ph\text{-}\underset{C_4H_9}{\underset{|}{C}}H\text{-}CH{=}CH_2} \xrightarrow[-RH]{R^-\,Li^+} \left\{\begin{array}{ll} \mathrm{Ph\text{-}\overset{Li^+}{\underset{C_4H_9}{\underset{|}{\bar{C}}}}\text{-}CH{=}CH_2} & (a_3)\\ \downarrow\uparrow & \\ \mathrm{Ph\text{-}\underset{C_4H_9}{\underset{|}{C}}{=}CH\text{-}CH_2^-\ Li^+} & (b_3)\end{array}\right. \qquad (3)$$



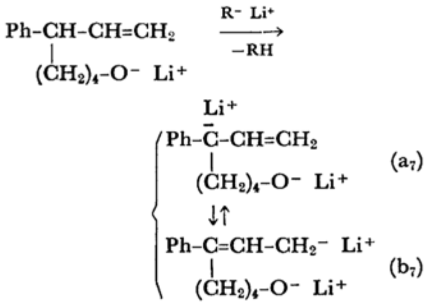
$$\mathrm{Ph\text{-}\underset{C_4H_9}{\underset{|}{C}}{=}CH\text{-}CH_2^-\ Li^+} \xrightarrow{RH} \mathrm{Ph\text{-}\underset{C_4H_9}{\underset{|}{C}}{=}CH\text{-}CH_3} + \mathrm{R^-\ Li^+} \quad (Ib) \qquad (4)$$



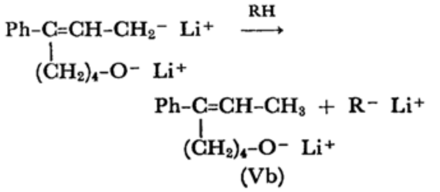
$$\mathrm{Ph\text{-}\underset{C_4H_9}{\underset{|}{C}}{=}CH\text{-}CH_3} \xrightarrow[2)\ RH]{1)\ C_4H_9^-\,Li^+} \mathrm{Ph\text{-}\underset{C_4H_9}{\underset{|}{C}}H\text{-}\overset{C_4H_9}{\overset{|}{C}}H\text{-}CH_3} + \mathrm{R^-\ Li^+} \quad (II) \qquad (5)$$



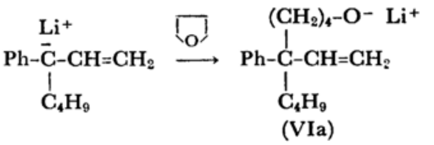
$$\mathrm{Ph\text{-}\overset{Li^+}{\bar{C}}H\text{-}CH{=}CH_2} \xrightarrow{\mathrm{THF}} \mathrm{Ph\text{-}\underset{(CH_2)_4\text{-}O^-\ Li^+}{\underset{|}{C}}H\text{-}CH{=}CH_2} \quad (Va) \qquad (6)$$



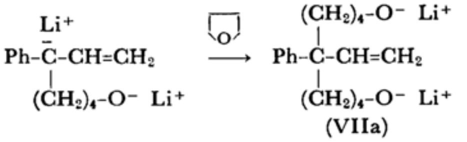
$$\mathrm{Ph\text{-}\underset{(CH_2)_4\text{-}O^-\ Li^+}{\underset{|}{C}}H\text{-}CH{=}CH_2} \xrightarrow[-RH]{R^-\,Li^+} \left\{\begin{array}{ll} \mathrm{Ph\text{-}\overset{Li^+}{\underset{(CH_2)_4\text{-}O^-\ Li^+}{\underset{|}{\bar{C}}}}\text{-}CH{=}CH_2} & (a_7)\\ \downarrow\uparrow & \\ \mathrm{Ph\text{-}\underset{(CH_2)_4\text{-}O^-\ Li^+}{\underset{|}{C}}{=}CH\text{-}CH_2^-\ Li^+} & (b_7)\end{array}\right. \qquad (7)$$



$$\mathrm{Ph\text{-}\underset{(CH_2)_4\text{-}O^-\ Li^+}{\underset{|}{C}}{=}CH\text{-}CH_2^-\ Li^+} \xrightarrow{RH} \mathrm{Ph\text{-}\underset{(CH_2)_4\text{-}O^-\ Li^+}{\underset{|}{C}}{=}CH\text{-}CH_3} + \mathrm{R^-\ Li^+} \quad (Vb) \qquad (8)$$

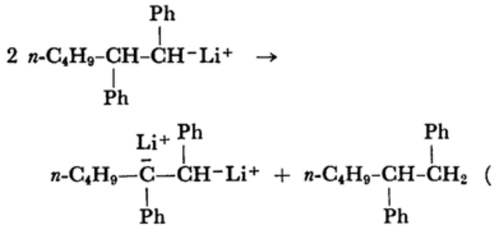


$$\mathrm{Ph\text{-}\overset{Li^+}{\underset{C_4H_9}{\underset{|}{\bar{C}}}}\text{-}CH{=}CH_2} \xrightarrow{\mathrm{THF}} \mathrm{Ph\text{-}\overset{(CH_2)_4\text{-}O^-\ Li^+}{\overset{|}{\underset{C_4H_9}{\underset{|}{C}}}}\text{-}CH{=}CH_2} \quad (VIa) \qquad (9)$$

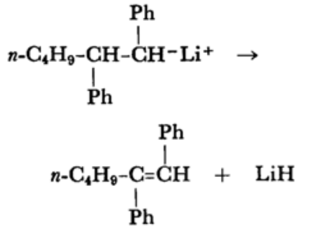


$$\mathrm{Ph\text{-}\overset{Li^+}{\underset{(CH_2)_4\text{-}O^-\ Li^+}{\underset{|}{\bar{C}}}}\text{-}CH{=}CH_2} \xrightarrow{\mathrm{THF}} \mathrm{Ph\text{-}\overset{(CH_2)_4\text{-}O^-\ Li^+}{\overset{|}{\underset{(CH_2)_4\text{-}O^-\ Li^+}{\underset{|}{C}}}}\text{-}CH{=}CH_2} \quad (VIIa) \qquad (10)$$

The process (1) is a simple hydrogen abstraction from allylbenzene by *n*-BuLi. It has been well known that the process takes place easily in diethyl ether[6] and in THF.[7] On the other hand, the process (2) is a nucleophillic replacement of the *n*-butyl anion with allylbenzene. One hydrogen is abstracted from allylbenzene as a proton in the process (1), while it is abstracted as a hydride anion in the process (2). A similar phenomenon has been observed in the reaction of *trans*-stilbene with *n*-BuLi in benzene,[8] which is shown as follows:



$$2\ n\text{-}\mathrm{C_4H_9\text{-}\underset{Ph}{\underset{|}{C}}H\text{-}\overset{Ph}{\overset{|}{C}}H^-Li^+} \rightarrow n\text{-}\mathrm{C_4H_9\text{—}\overset{Li^+}{\underset{Ph}{\underset{|}{\bar{C}}}}\text{—}\overset{Ph}{\overset{|}{C}}H^-Li^+} + n\text{-}\mathrm{C_4H_9\text{-}\underset{Ph}{\underset{|}{C}}H\text{-}\overset{Ph}{\overset{|}{C}}H_2} \qquad (11)$$



$$n\text{-}\mathrm{C_4H_9\text{-}\underset{Ph}{\underset{|}{C}}H\text{-}\overset{Ph}{\overset{|}{C}}H^-Li^+} \rightarrow n\text{-}\mathrm{C_4H_9\text{-}\underset{Ph}{\underset{|}{C}}{=}\overset{Ph}{\overset{|}{C}}H} + \mathrm{LiH} \qquad (12)$$

In the process (11), a hydrogen is abstracted as a proton; in the process (12) a hydrogen at the same position is abstracted as a hydride anion. Judging from the presence of Ib, however, the processes (3) and (4) must also have occurred during the reaction. The process (3) might occur as easily as the process (1) because of the similarity of these two processes. The presence of Ib and the absence of Ia indicate that the form b_3 exists predominantly in the equilibrium between a_3 and b_3 in the (process (3). The addition of one more molecule of *n*-BuLi to Ib gave a saturated compound, II (process (5)).

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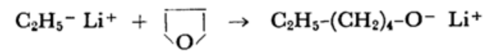
[6] H. F. Herbranderson and D. S. Mooney, *ibid.*, **79**, 5809 (1957).

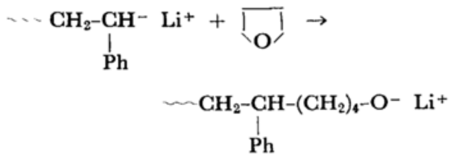
[7] R. Waack and M. A. Doran, *ibid.*, **85**, 1651 (1963).

[8] D. P. Wyman and T. Altares, Jr., *Makromol. Chem.*, **72**, 68 (1964).

Although it has been known that organolithium compounds more or less easily decompose in ether solvents at room temperature,[3] the processes have not been studied in detail. Recently several groups have found that alkyllithium compounds react with THF to give alcohols. Rembaum *et al.*[9] reported the following reaction:



Fetters *et al.*[10] investigated the reaction of polystyryl anion with THF and found it to be as follows:



In the reaction of allylbenzene with *n*-BuLi, an anion, a_1, formed by the process (1) reacts with THF to give an alcoholate, as is shown in the process (6). The alcoholate Va thus produced may isomerize to Vb through the processes (7) and (8) just the same as is isomerized Ia to Ib. On the other hand, the alcohol derived from the anion b_1 in the process (1) was not detected at all. The anions a_3 and a_7 in the processes (3) and (7) also react with THF to give alcoholates, VIa and VIIa, through the processes (9) and (10) respectively. In these cases the isomerizations of VIa and VIIa do not proceed because of the lack of a hydrogen atom at the 3-position in each compound. Moreover, the corresponding alcohols can not be derived from the anions b_3 and b_7 in the processes (3) and (7).

The above results show that, in the resonance structures of the allyl anions, a and b;

$$\underset{(a)}{\text{Ph-}\bar{\text{C}}\text{R-CH=CH}_2} \leftrightarrow \underset{(b)}{\text{Ph-CR=CH-CH}_2^-}$$

the form b is more stable than a; in other words, the form a is more reactive with THF to give an alcohol.

The allyl anions formed here reacted with THF to give alcohols in good yields, while a lot of allyllithium compounds abstract a proton from THF to yield alkanes.[11] This may be caused by the difference in the reactivity between these organolithium compounds.

At the present time, from the results of this study alone it seems to be difficult to determine the structure of the above-mentioned anion, D, having a λ_{max} at 570 mμ. However, it has been found that many of the anions derived from allylbenzene were converted into the alcoholate anions by the reaction with THF. In the anionic polymerization of *trans*-β-methylstyrene, the allyl anion, A, is formed by the chain transfer to the monomer. Therefore, the same reaction of the anion A with THF should also occur to produce alcoholate anions in this anionic polymerization at high temperatures, this reaction being one of the main causes why the polymerization ceases.

The poly-β-methylstyrene obtained by the anionic polymerization has no C=C double bond in the chain, and the structure of cyclic butane was proposed as that of the terminal unit.[1] The existence of compounds III and IV, the supposed components of the fractions F3H and F4H, may be connected with this saturated chain terminal, although the structures of III and IV have, so far, not been exactly determined.

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[9] A. Rembaum, S. P. Siao and N. Indictor, *J. Polymer Sci.*, **56**, S17 (1962).

[10] L. J. Fetters, *ibid.*, **B2**, 425 (1964).

[11] H. Gilman and G. L. Schwebke, *J. Organometal. Chem.*, **4**, 483 (1965).