BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 760—765 (1969)

Reaction of *trans*-Stilbene with *n*-Butyllithium in Tetrahydrofuran

Yoshio OKAMOTO, Masahiko KATO and Heimei YUKI

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka

(Received July 1, 1968)

The reaction of *trans*-stilbene with *n*-butyllithium was investigated in tetrahydrofuran at 0°C. The structures of the products fractionated by column chromatography were determined by elementary analysis, a molecular-weight determination, and a study of the IR, UV, and NMR spectra. The main products were 1,2-diphenylhexane, 1,2-diphenylethane, and 1,2,3-triphenylpropene which was formed by the cleavage of a C–C bond of a product. The reaction mixture showed an ESR signal. The observed results are explained in terms of the anionic copolymerization of *trans*-stilbene and styrene reported previously.

In a previous paper,[1] a study of the anionic copolymerization of styrene and *trans*-stilbene by *n*-butyllithium (*n*-BuLi) has been reported. The results have shown that in tetrahydrofuran (THF) a chain-transfer reaction to the *trans*-stilbene occurs, while in benzene the copolymerization proceeds without any chain-transfer. In the copolymerization, the color of the reaction mixture changes in time; it was followed spectrophotometrically.

The work reported here was carried out in order to clarify two points: the reaction mechanism of the chain-transfer and the change in the color in the copolymerization. Wyman and Altares[2] carried out the same reaction in benzene, but their results differ greatly from ours.

Experimental

Reagent. The preparations and purifications of *trans*-stilbene, *n*-BuLi, and THF were previously described.[1]

Reaction. The reaction was carried out under dry nitrogen in a glass ampoule equipped with a three-way stopcock. To a solution of *trans*-stilbene (10.0 g, 5.56×10^{-2} mol) in THF (250 m*l*), *n*-BuLi (2.83×10^{-2} mol) was added with a syringe over a three-minute period at 0°C. The color of the reaction mixture changed from red to purple in time. After 48 hr, the reaction was terminated by adding methanol (1.1 m*l*, 2.6×10^{-2} mol) until the color of the solution disappeared. The solvent was evaporated *in vacuo*, and then the residue was dissolved in diethyl ether. The ether solution was

---

[1] H. Yuki, M. Kato and Y. Okamoto, This Bulletin, **41**, 1940 (1968).

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

washed with water and dried over magnesium sulfate; then the ether was removed to give 11.6 g of an oily product.

Fractionation of Product. The fractionation of the above product was carried out by column chromatography with activated alumina, using *n*-hexane, benzene, and methanol as solvents.

Measurements. The measurements of the molecular weight, the elementary analysis, and the IR, UV, and NMR spectra were made according to methods reported previously.[1] The ESR spectrum was measured with a JES-3BX Spectrometer.

Results

Fractionation of Product. Before the fractionation of the reaction product by column chromatography, the product was submitted to sublimation in order to exclude any unchanged *trans*-stilbene. However, no *trans*-stilbene was recovered. The addition of *n*-hexane to the product gave no precipitate of *trans*-stilbene, which is almost insoluble in this solvent at 0°C. The results of the fractionation by column chromatography are shown in Table 1. Fraction 1, which is not shown in the table, was fractionated by subsequent chromatography, using *n*-hexane as a solvent, to give two fractions, 1A and 1B.

Characterization of Each Fraction. The results of the elementary analysis, the molecular weight, and the molecular formula of each fraction are listed in Table 1. The characteristics of the IR and UV spectra, and the ratio of the number of aromatic to that of aliphatic protons (H_{ar}/H_{al}) of the fraction are summarized in Table 2.

Compounds Formed in the Reaction Mixture. Table 3 shows the molecular formulae, the structural formulae, the results of the elementary analyses, the molecular weights, and the ratios of the number of aromatic to that of aliphatic protons (H_{ar}/H_{al}) of the compounds which may be supposed to be the reaction products on the basis of the results.

Structure of Each Fraction. *Fraction 1A.* This fraction was liquid; the results of its elementary analysis and its molecular weight and the molecular formula derived from them were most consistent with those of 1,2-diphenylhexane, Ia, in Table 3. In the NMR spectrum of the fraction 1A (Fig. 1), the chemical shifts of the Ph, –CH(Ph)-Ch_2Ph, –CH_2–, and CH_3-protons, and the relative areas of the peaks, 10.0 : 2.9 : 6.1 : 3.0, also support the above structure. The IR spectrum showed the absence of a C=C double bond, as was also speculated on the basis of the UV spectrum.

Fraction 1B. The melting point of the fraction 1B was 50—52°C. Its molecular formula was similar to that of 1,2-diphenylethane, Ib, in Table 3, the melting point of which is 53°C.[3] The NMR spectrum of this fraction also completely agreed with that of the authentic sample. The NMR spectrum of the fraction 1 indicated that this fraction contained only Ia and Ib in a molar ratio of 3.3.

TABLE 1. FRACTIONATION OF REACTION MIXTURE BY COLUMN CHROMATOGRAPHY

Fraction	Eluent	Recovery wt%	Elementary analysis C%	Elementary analysis H%	Molecular weight	Molecular formula
1A	*n*-Hexane	38	90.70	9.27	233	$C_{18}H_{21.9}$
1B	*n*-Hexane	9	92.28	7.72	168	$C_{14}H_{13.9}$
2	H/B(95/5)[a]	19	93.37	6.82	264	$C_{21}H_{18.3}$
3	H/B(50/50)[a]	21	92.46	7.64	345	$C_{27}H_{27.0}$
4	Methanol	6	83.27	8.77	291	$C_{22}H_{27.7}$

a) H: *n*-hexane, B: benzene.

TABLE 2. CHARACTERISTICS OF IR, UV, AND NMR SPECTRA

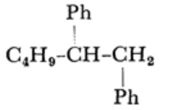
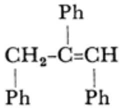
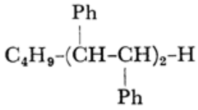
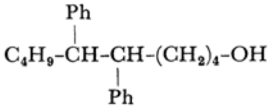
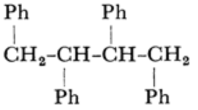
Fraction	IR (cm^{-1})[a] 870	IR (cm^{-1})[a] 1380	IR (cm^{-1})[a] 3300	UV λ_{max} (mμ)	UV ε_{max}	NMR[b] H_{ar}/H_{al}
1A	—	Medium	—	260	411	0.83
1B	—	Weak	—	260	450	2.4
2	Medium	Weak	—	272	14800	5.1
3	Weak	Weak	—	272	5490	2.4
4	Weak	Medium	Strong	—	—	0.68

a) 870: $R_1R_2C{=}CHR_3$, 1380: CH_3–, 3300: -OH.
b) The ratio of the numbers of aromatic to aliphatic protons.

---

[3] J. S. Buck and S. S. Jenkins, *J. Am. Chem. Soc.*, **51**, 2163 (1929).

TABLE 3. COMPOUNDS SUPPOSED TO BE THE PRODUCTS IN THE REACTIONS

Molecular formula	Structural formula	Composition C%	Composition H%	Molecular weight	H_{ar}/H_{al}[a]	Remarks
$C_{18}H_{22}$	 $C_4H_9\text{-}\overset{Ph}{C}H\text{-}\underset{Ph}{CH_2}$	90.76	9.24	238	0.83	Ia
$C_{14}H_{14}$	$PhCH_2CH_2Ph$	92.31	7.69	182	2.5	Ib
$C_{21}H_{18}$	 $\underset{Ph}{CH_2}\text{-}\overset{Ph}{C}\text{=}\underset{Ph}{CH}$	93.33	6.67	270	5.0	II
$C_{32}H_{34}$	 $C_4H_9\text{-}(\overset{Ph}{C}H\text{-}\underset{Ph}{CH})_2\text{-}H$	91.87	8.13	418	1.43	III
$C_{22}H_{30}O$	 $C_4H_9\text{-}\overset{Ph}{C}H\text{-}\underset{Ph}{CH}\text{-}(CH_2)_4\text{-}OH$	85.16	9.68	310	0.5	IV
$C_{28}H_{26}$	 $\overset{Ph}{CH_2}\text{-}\underset{Ph}{CH}\text{-}\overset{Ph}{C}H\text{-}\underset{Ph}{CH_2}$	92.82	7.18	362	3.3	V

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

Fraction 2. The molecular formula of the fraction 2 was in best accord with 1,2,3-triphenylpropene, II, in Table 3. In the NMR spectra (Fig. 2), the peaks at 3.65 and 6.29 τ were assigned to the methine and methylene protons, respectively, of the *cis*-isomer, judging from the NMR spectra of *cis*- and *trans*-stilbene. The peak at 5.96 τ was assigned to the methylene protons of the *trans*-isomer, while the absorption of its methine proton might overlap with those of aromatic protons near 3 τ. The IR spectrum of the fraction 2 showed an absorption due to a three-substituted olefin at 870 cm^{-1}. A further separation of this fraction by column chromatography gave the *cis*-isomer as the initial fraction; its melting point was 61—62°C (lit.,[4] 62—63°C). The fraction eluted at the later stage of the chromatography was largely composed of the *trans*-isomer, but it always contained a small portion of the *cis*-isomer. In the UV spectra, the absorption maxima of *cis*- and *trans*-1,2,3-triphenylpropene appeared at 260 mμ (ε_{max} 14200) and 273 mμ (ε_{max} 16100) respectively. The molar ratio of the *trans*- to the *cis*-isomer was 1.9; this ratio was calculated from the relative strength of the corresponding absorptions in the NMR spectrum of the fraction 2.

Fraction 3. The molecular weight of the fraction 3 was 345. This rather large value indicates that a compound composed of at least two molecules of *trans*-stilbene must have been a component of this fraction. The sharp peak at 5.96 τ in the NMR spectrum (Fig. 3) suggests that the tailing of *trans*-1,2,3-triphenylpropene, which was present in the fraction 2, is incorporated into this fraction.

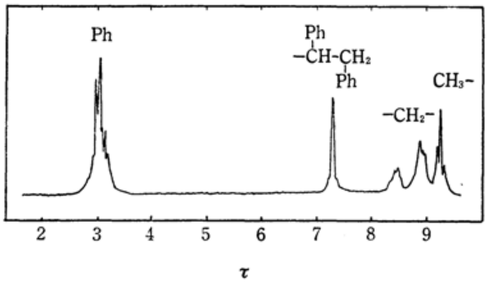


Fig. 1. NMR spectrum of fraction 1A.

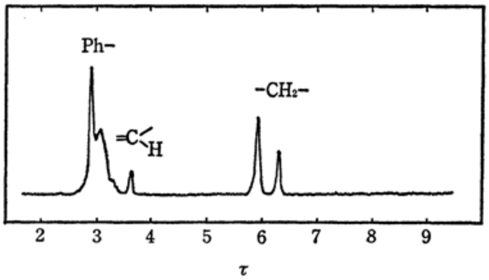


Fig. 2. NMR spectrum of fraction 2.

---

[4] A. Orechoff, *Ber.*, **47**, 89 (1914).

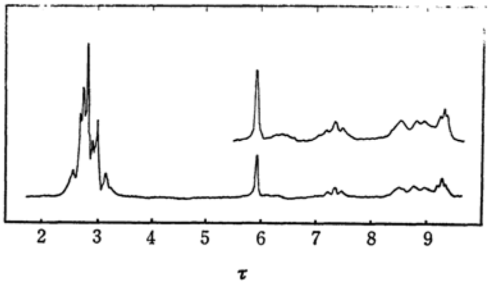


Fig. 3. NMR spectrum of fraction 3.

However, 1,2,3,4-tetraphenyloctane, III in Table 3, must be the main component of this fraction, judging from the absorption at 9.1 τ due to the methyl group and absorptions at 7.5—8.9 τ due to methylene and methine groups in the NMR spectrum, and judging from the molecular weight of this fraction.

This fraction also contained a small amount (about 100 mg) of a compound insoluble in petroleum ether at 0°C; this compound was identified as 1,2,3,4-tetraphenylbutane, V in Table 3. Its melting point was 181—183°C (lit.,[5] 182°C), and the observed H_{ar}/H_{al} ratio in the NMR spectrum was 3.5. Found: C, 92.76; H, 7.24%.

Fraction 4. Judging from the elementary analysis, this fraction consisted of a compound containing oxygen. The IR spectrum suggested the presence of an OH group by means of the strong absorption at 3300 cm^{-1}. Although the NMR spectrum was complicated, the H_{ar}/H_{al} ratio was 0.66. This small value means that there were more aliphatic protons than aromatic ones. The reaction of a carbanion with THF must have formed an alcohol containing the greater portion of the aliphatic protons. A compound such as IV in Table 3 may be proposed as one of the alcohols.

Yields of Product Compounds. The yields of the product compounds identified were calculated from the NMR spectrum of the unfractionated mixture and from the weights of the compounds fractionated by column chromatography. The results are shown in Table 4. The yields of 1,2,3-triphenylpropene (II) and 1,2-diphenylethane (Ib), after reactions of 25 and 180 min carried out under the same conditions as those shown in the Experimental section, were obtained by means of the NMR spectra of the respective reaction mixtures, as are shown in Table 4. The ratios of 1,2,3-triphenylpropene to 1,2-diphenylethane were about 2, regardless of the reaction time.

TABLE 4. YIELDS OF PRODUCT COMPOUNDS[a)]
Reaction condition: [Stilbene]/[*n*-BuLi]=2.0, in THF, at 0°C

Reaction time	Ia	Ib	II	III	V
25 min	—	6	16	—	—
180 min	—	16	34	—	—
48 hr	62	18	38	10	2

a) Yield was calculated as per cent of the product (mole) per *n*-BuLi (mole).

Electronic Spectrum of Reaction Mixture. The electronic spectra of the reaction mixtures of *trans*-stilbene and *n*-BuLi in THF at room temperature are shown in Fig. 4. In the reaction of *trans*-stilbene with an excess of *n*-BuLi, the spectrum showed a peak at 332 mμ which was stable for a prolonged time and might be based on a benzyl-type anion, $C_4H_9CH(Ph)–CH(Ph)^-Li^+$. On the other hand, when the molar ratio of *trans*-stilbene to *n*-BuLi was 6.2, new peaks appeared at 555 and 420 mμ in time. When *n*-BuLi was added to the solution of 1,2,3-triphenylpropene in THF, the peaks at 555 and 420 mμ appeared instantaneously in the UV spectrum of the solution. Then, 1,2,3-triphenylpropene-3-d_1, was recovered by terminating the reaction with deuterium oxide. This was confirmed by a study of the NMR spectrum.

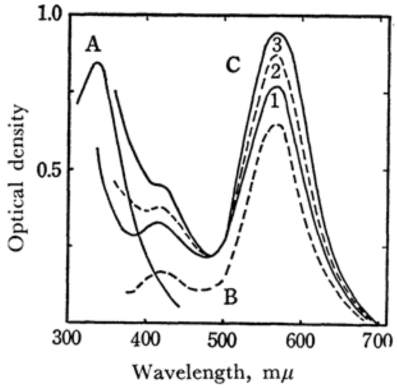


Fig. 4. Electronic spectrum of reaction mixture.
A: [Stilbene]/[*n*-BuLi]=0.25
B: 1,2,3-Triphenylpropene+*n*-BuLi (1 : 1)
C: [Stilbene]/[*n*-BuLi]=6.2
Time: (1) 46 min, (2) 1.4 hr, (3) 2.4 hr

ESR Spectrum of Reaction Mixture. The ESR spectrum of the reaction mixture in THF was

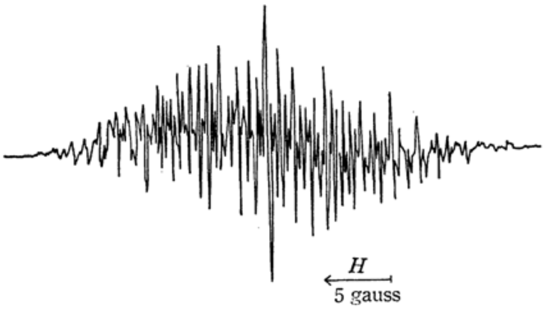


Fig. 5. ESR spectrum of reaction mixture.
[Stilbene]/[*n*-BuLi]=2.0, temp.: room temp.

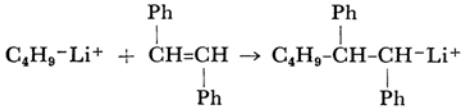
---

5) D. P. Wyman, *J. Org. Chem.*, **27**, 3712 (1962).

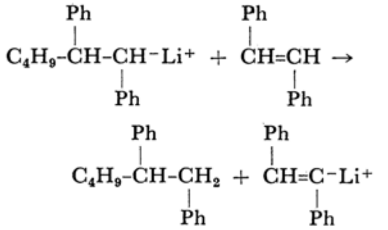
measured at room temperature, the molar ratio of *trans*-stilbene to *n*-BuLi being 2.0. The spectrum is shown in Fig. 5. In the reaction of 1,2,3-triphenylpropene with *n*-BuLi in THF, however, no ESR signal was observed.

Discussion

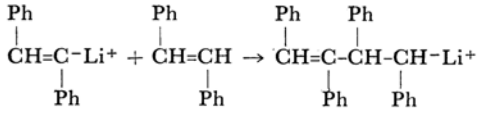
The compounds identified as the main products were 1,2-diphenylhexane (Ia), 1,2-diphenylethane (Ib), and 1,2,3-triphenylpropene (II). It is noteworthy that no *trans*-stilbene was recovered and that 1,2-diphenylethane and 1,2,3-triphenylpropene were obtained instead. The mechanisms of the formations of these two compounds cannot be explained by simple addition or abstraction reactions of carbanions. The 1,2,3-triphenylpropene can be produced only by the cleavage of a C–C bond because there is no compound with odd carbons in the starting materials. The molar ratio of the yield of 1,2,3-triphenylpropene to 1,2-diphenylethane was two, regardless of the reaction time; this suggests that the formations of these compounds are interrelated. The following processes (1)—(7) constitute our proposed mechanisms for the production of the above compounds.



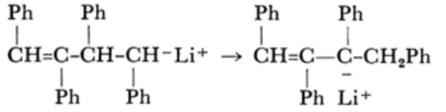
$$C_4H_9{}^-Li^+ + \overset{Ph}{CH}{=}\underset{Ph}{CH} \rightarrow C_4H_9\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH}{}^-Li^+ \tag{1}$$



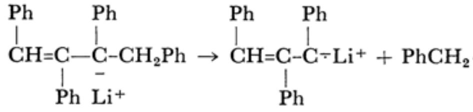
$$C_4H_9\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH}{}^-Li^+ + \overset{Ph}{CH}{=}\underset{Ph}{CH} \rightarrow C_4H_9\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH_2} + \overset{Ph}{CH}{=}\underset{Ph}{C}{}^-Li^+ \tag{2}$$



$$\overset{Ph}{CH}{=}\underset{Ph}{C}{}^-Li^+ + \overset{Ph}{CH}{=}\underset{Ph}{CH} \rightarrow \overset{Ph}{CH}{=}\underset{Ph}{C}\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH}{}^-Li^+ \tag{3}$$

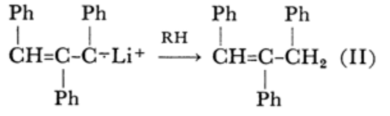


$$\overset{Ph}{CH}{=}\underset{Ph}{C}\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH}{}^-Li^+ \rightarrow \overset{Ph}{CH}{=}\underset{Ph}{C}\text{—}\overset{Ph}{\underset{-\,Li^+}{C}}\text{-}CH_2Ph \tag{4}$$



$$\overset{Ph}{CH}{=}\underset{Ph}{C}\text{—}\overset{Ph}{\underset{-\,Li^+}{C}}\text{-}CH_2Ph \rightarrow \overset{Ph}{CH}{=}\underset{Ph}{C}\text{-}\overset{Ph}{C}\overset{\cdot}{-}Li^+ + PhCH_2\cdot \tag{5}$$

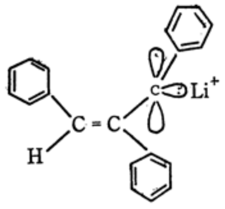
$$2\ PhCH_2\cdot \rightarrow \underset{(Ib)}{PhCH_2CH_2Ph} \tag{6}$$



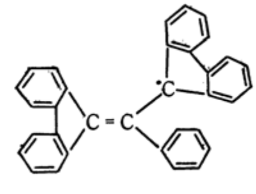
$$\overset{Ph}{CH}{=}\underset{Ph}{C}\text{-}\overset{Ph}{C}\overset{\cdot}{-}Li^+ \xrightarrow{RH} \overset{Ph}{CH}{=}\underset{Ph}{C}\text{-}\overset{Ph}{CH_2}\ (II) \tag{7}$$

The total product yield indicates that the process (1), which is an addition reaction of *n*-BuLi to *trans*-stilbene, takes place easily. As may be seen from the electronic spectrum of the reaction mixture, the benzyl-type anion formed in the process (1) is stable, if no excess *trans*-stilbene is present. However, the acidity of the methine protons of *trans*-stilbene is rather strong, as is shown by the isomerization of *cis*-stilbene to the *trans*-isomer by a base such as potassium *t*-butoxide.[6] Therefore, if excess *trans*-stilbene is present, the process (2) will occur. This process must be a chain-transfer reaction in the copolymerization of *trans*-stilbene and styrene.[1]

The new anion produced in the process (2) reacts with *trans*-stilbene to give a dimer anion, which may accompany the cleavage of a C–C bond with the production of the benzyl radical and the 1,2,3-triphenylpropenyl radical anion (the process (5)), *via* a proton shift reaction in the process (4). This radical anion may be of new type. The structure of the 1,2,3-triphenylpropenyl radical anion may be represented as shown by RA-II. This radical anion, if present, can be greatly stabilized by the delocalization of an electron on the benzene rings. It has been estabilished that the 1,3-bis(diphenyl)-2-phenylallyl radical, with a similar structure to that of RA-II, is very stable even in air.[7]



(RA-II)



(1,3-Bis(diphenylene)-2-phenylallyl radical)

The reaction mixture of *trans*-stilbene and *n*-BuLi showed an ESR signal (Fig. 5). This might be because of the mono lithium-adduct of *trans*-stilbene. However, no absorption maximum at 480 mμ (ε_{max} 62000)[8] due to the adduct in THF could be observed in the electronic spectrum of the reaction mixture (Fig. 4). The hyperfine structure of the ESR spectrum observed herein suggests the presence of a radical with a rather complicated structure, although it is not certain at present whether or not the ESR signal is due to the radical anion, RA-II. The coupling of benzyl radicals gives 1,2-diphenylethane, as is shown in the process (6).

Although the yield was rather low, 1,2,3,4-tetraphenyloctane was also obtained. This means

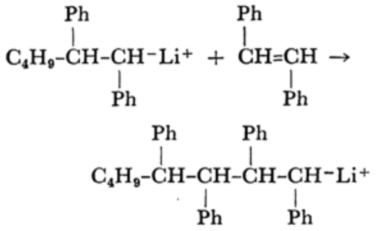
---

[6] D. H. Hunter and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 5765 (1966).

[7] W. O. Hamilton and G. E. Pake, *J. Chem. Phys.*, **39**, 2694 (1963).

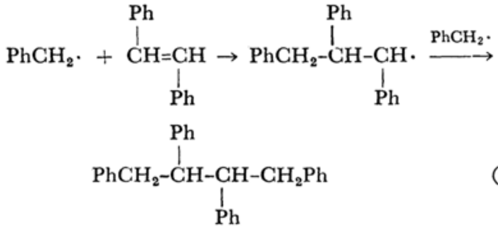
[8] E. R. Zabolotny and J. F. Garst, *J. Am. Chem. Soc.*, **86**, 1645 (1964).

that a stilbene anion can add to *trans*-stilbene to give a dimer, even if the reaction is very slow (the process (8)).



$$C_4H_9\text{-}\underset{Ph}{\overset{Ph}{CH}}\text{-}CH^-Li^+ + \underset{}{\overset{Ph}{CH}}{=}\underset{Ph}{CH} \rightarrow C_4H_9\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH}\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH^-}Li^+ \quad (8)$$

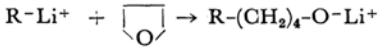
The formation of a small amount of 1,2,3,4-tetraphenylbutane can be explained by the following process:



$$PhCH_2\cdot + \overset{Ph}{CH}{=}\underset{Ph}{CH} \rightarrow PhCH_2\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH}\cdot \xrightarrow{PhCH_2\cdot} PhCH_2\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH}\text{-}CH_2Ph \quad (9)$$

(V)

The carbinol in the fraction 4 may be produced through the following process:[9,10]

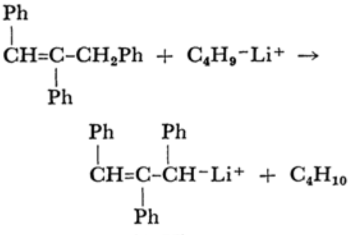


$$R^-Li^+ + \text{THF} \rightarrow R\text{-}(CH_2)_4\text{-}O^-Li^+$$

Judging from the yield of each compound obtained in this experiment, *n*-BuLi is considered to be consumed almost quantitatively in the process (1); about 49% of the 1,2-diphenylhexyl anions produced in the process reacted with *trans*-stilbene to give 1,2-diphenylhexane, 1,2,3-triphenylpropene, and 1,2-diphenylethane. About 10% of the 1,2-diphenylhexyl anions were apparently consumed in the formation of 1,2,3,4-tetraphenyloctane, while about 20% of the anions remained free from the subsequent reactions. The residual 1,2-diphenylhexyl anions and also probably a part of the 1,2,3,4-tetraphenyloctyl anions reacted with THF to yield alcohols. The absence of 1,2,3,4-tetraphenylbutene indicates that the anions produced in the processes (3) and (4) are rather unstable.

The reaction mixtures both of *trans*-stilbene with *n*-BuLi and of 1,2,3-triphenylpropene with *n*-BuLi showed the same absorption maxima, at 555 and 420 mμ. It is likely that the A-II anion, which may be produced from RA-II by the abstraction of a hydrogen from any material in the system, will be present in the reaction mixture of *trans*-stilbene and *n*-BuLi. It may be supposed that the radical anion, RA-II, shows the same absorption maxima, at 555 and 420 mμ.

The reaction of 1,2,3-triphenylpropene with *n*-BuLi proceeds as follows:

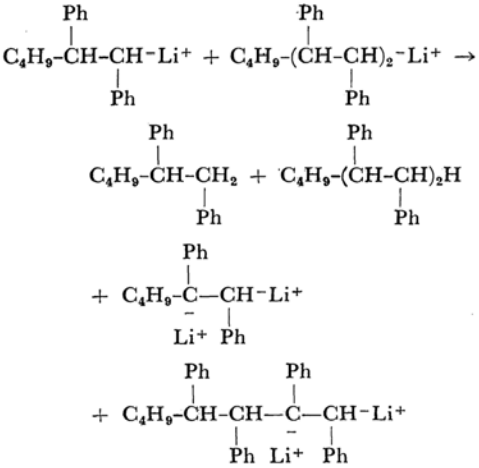


$$\overset{Ph}{CH}{=}\underset{Ph}{C}\text{-}CH_2Ph + C_4H_9^-Li^+ \rightarrow \overset{Ph}{CH}{=}\underset{Ph}{C}\text{-}\overset{Ph}{CH^-}Li^+ + C_4H_{10} \quad (10)$$

(A-II)

since the 1,2,3-triphenylpropene with a deuterium at the methylene position is recovered when the reaction is terminated by deuterium oxide.

A distinct solvent effect exists in the reaction of *trans*-stilbene and *n*-BuLi. Wyman and Altares[2] have studied the reaction of *trans*-stilbene and *n*-BuLi in benzene at 60°C. Contrary to the reaction in THF, the main process (11) was found to follow the processes (1) and (8), thus giving the dianions shown below.



$$C_4H_9\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH^-}Li^+ + C_4H_9\text{-}(\overset{Ph}{CH}\text{-}\underset{Ph}{CH})_2^-Li^+ \rightarrow C_4H_9\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH_2} + C_4H_9\text{-}(\overset{Ph}{CH}\text{-}\underset{Ph}{CH})_2H + C_4H_9\text{-}\overset{Ph}{\underset{Li^+}{\overset{-}{C}}}\text{—}\underset{Ph}{CH^-}Li^+ + C_4H_9\text{-}\overset{Ph}{CH}\text{-}\underset{Ph}{CH}\text{—}\overset{Ph}{\underset{Li^+}{\overset{-}{C}}}\text{—}\underset{Ph}{CH^-}Li^+ \quad (11)$$

The results obtained in the present study establish that the chain-transfer in the copolymerization of *trans*-stilbene and styrene occurs by means of the abstraction of a proton from the *trans*-stilbene, as is shown by the process (2), and that the change in the color observed in the copolymerization is associated with the 1,2,3-triphenylpropenyl anion or the radical anion.

---

[9] L. J. Fetters, *J. Polymer Sci.*, **B2**, 425 (1964).

[10] Y. Okamoto and H. Yuki, This Bulletin, **41**, 677 (1968).