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Anionic Telomerizations of Styrene with Butylamines[*1]

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The anionic telomerizations of styrene with *n*-butylamine, *s*-butylamine, *t*-butylamine and isobutylamine catalyzed by sodium metal were investigated. The structures of the products were discussed by the NMR spectra obtained in carbon tetrachloride and identified to be *N*-butyl-2-phenylethylamines and *N*-butyldi(2-phenylethyl)amines. The general reaction scheme was proposed and interpreted with the concept of the anionic telomerization, where amine acts as a telogen and styrene as a taxogen.

The concept of telomerization was introduced for reactions of the type

$$XY + nM \rightarrow XM_nY$$

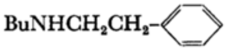
by Harmon in 1945.[1] Radical telomerizations have been actively investigated by many reseachers in the USA, Japan, USSR, Israel, *etc.*, and those of ethylene with carbon tetrachloride in particular. On the contrary, only a few papers on anionic and cationic telomerizations have appeared.

The hydrogen atoms attached to the nitrogen atom in ammonia NH_3, primary amines RNH_2 or secondary amines $RR'NH$ are weakly acidic[2] and subject to the attack of strong alkalis such as sodium metal, phenyl potassium and *n*-butyllithium to form alkali amides. Some of these can add to styrene[3] or initiate the anionic polymerization of styrene.[4] Hence it was supposed that on taking one of the amines as a telogen and styrene as a taxogen, an anionic telomerization would take place with sodium metal as a catalyst.

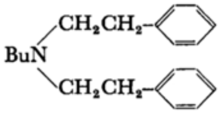
In this paper investigation in telomerization of styrene with butylamines and the NMR spectra of the resulting *N*-butyl-2-phenylethylamines and *N*-butyldi(2-phenylethyl)amines are presented. Moreover, the reaction mechanism is discussed with the proposed scheme from the standpoint of anionic telomerization.

Results and Discussion

Reaction Products. Each of the butylamines $BuNH_2$ was reacted with syrene in the presence of sodium metal as a catalyst to produce N-butyl-2-phenylethylamine (**1**) and *N*-butyldi(2-phenylethyl)amine (**2**), but *N*-butyl-2,4-diphenylbutylamine (**3**) was not obtained.



1



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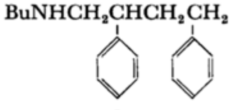
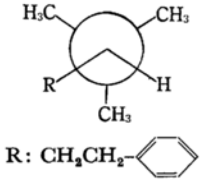


3

The reaction products are listed in Table 1, where column 1 shows the amines used and column 4 the reaction products isolated.

Structures of the Reaction Products. Figures 1, 2, 3 and 4 show the proton NMR spectra of the reaction products. The assignments of the signals to the protons are listed in Table 2. In the compound **2c** there is one conformation about a single bond between the nitrogen and the carbon (e), in which three methyl groups are not equivalent in the conformation.



The splitting of the methyl singlet of the protons (f) into two signals would be caused by the restricted rotation about the single bond between the nitrogen and the carbon (e). If the rotation is as free as in the compound **1c**, three methyl groups would become equivalent in the NMR and show a single methyl singlet. The splitting of the phenyl

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[*1] Anionic Telomerizations. I.

[1] J. Harmon, U. S. Pat. 2390099 (1945)

[2] W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936).

[3] R. Wegler and G. Pieper, *Chem. Ber.*, **83**, 1 (1950).

[4] W. C. E. Higginson and N. S. Wooding, *J. Chem. Soc.*, **1952**, 760.

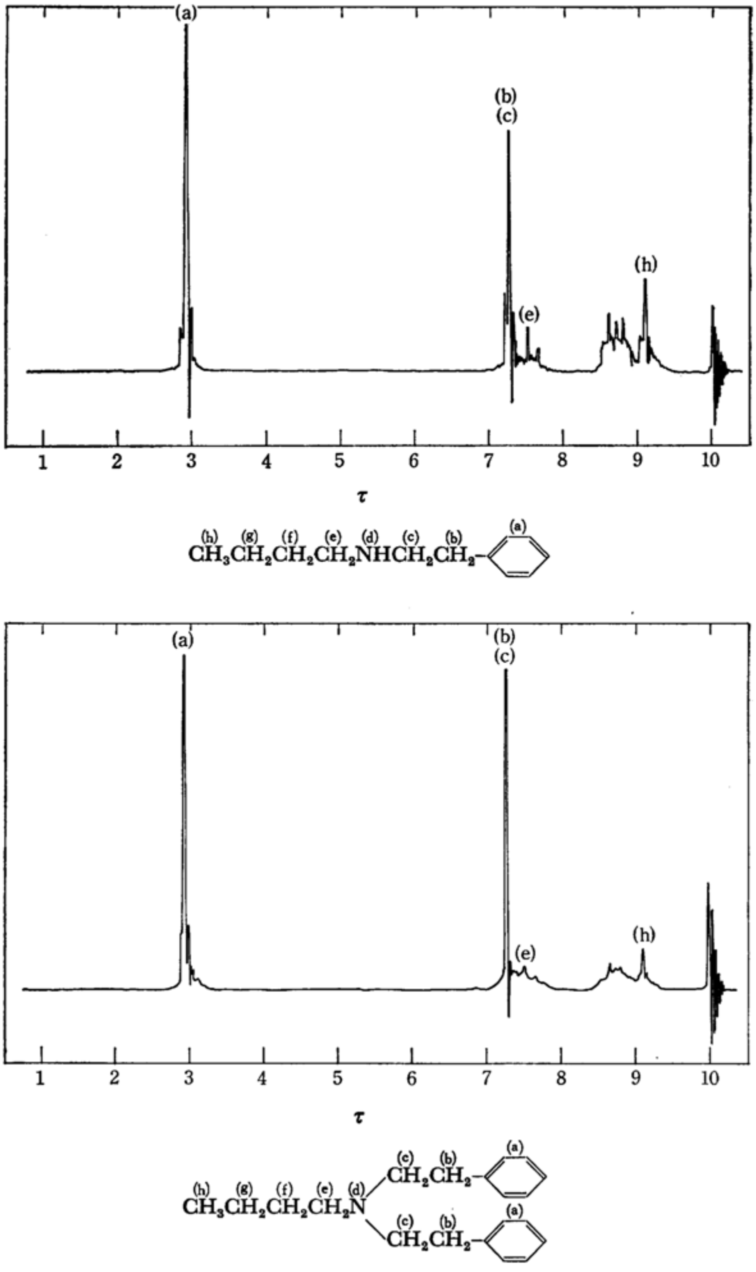


Fig. 1. NMR spectra of *n*-butyl-2-phenylethylamine and *n*-butyldi(2-phenylethyl)amine.

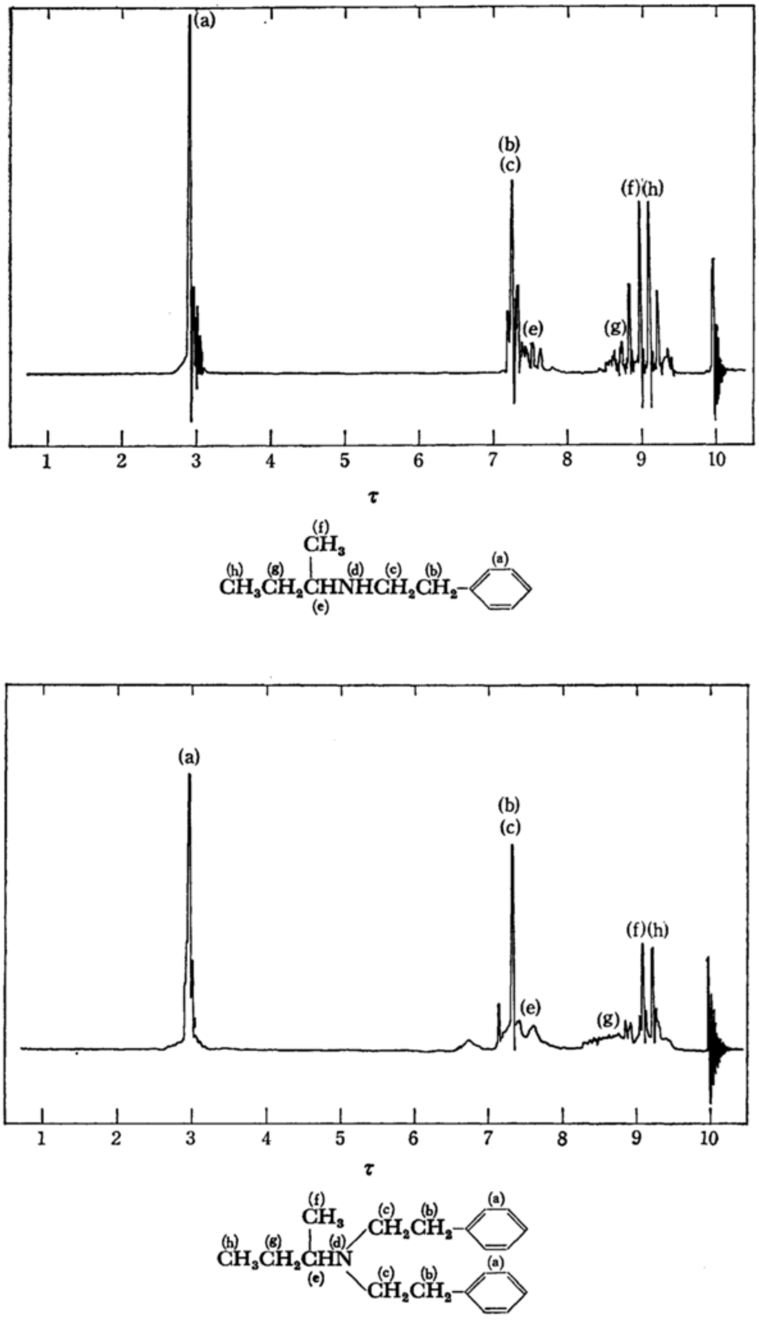


Fig. 2. NMR spectra of *s*-butyl-2-phenylethylamine and *s*-butyldi(2-phenylethyl)amine.

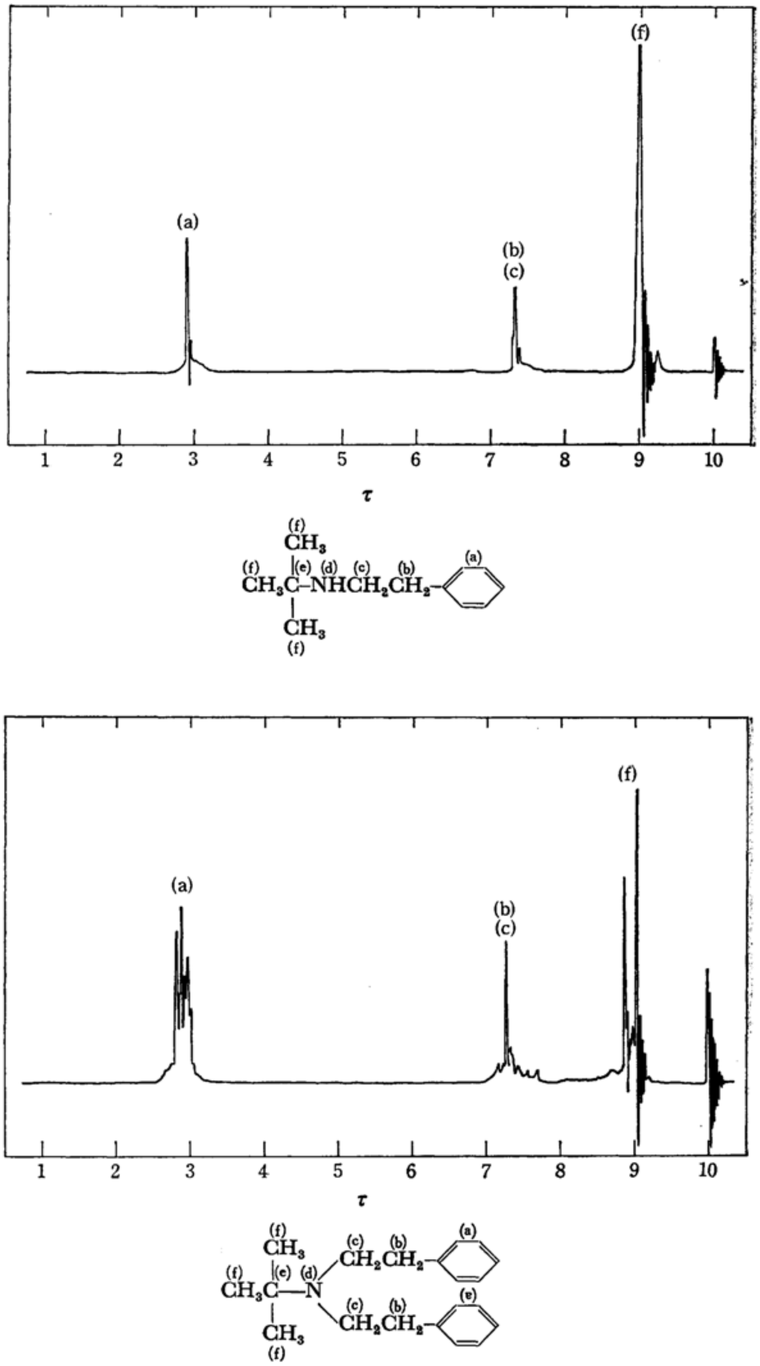


Fig. 3. NMR spectra of *t*-butyl-2-phenylethylamine and *t*-butyldi(2-phenylethyl)amine.

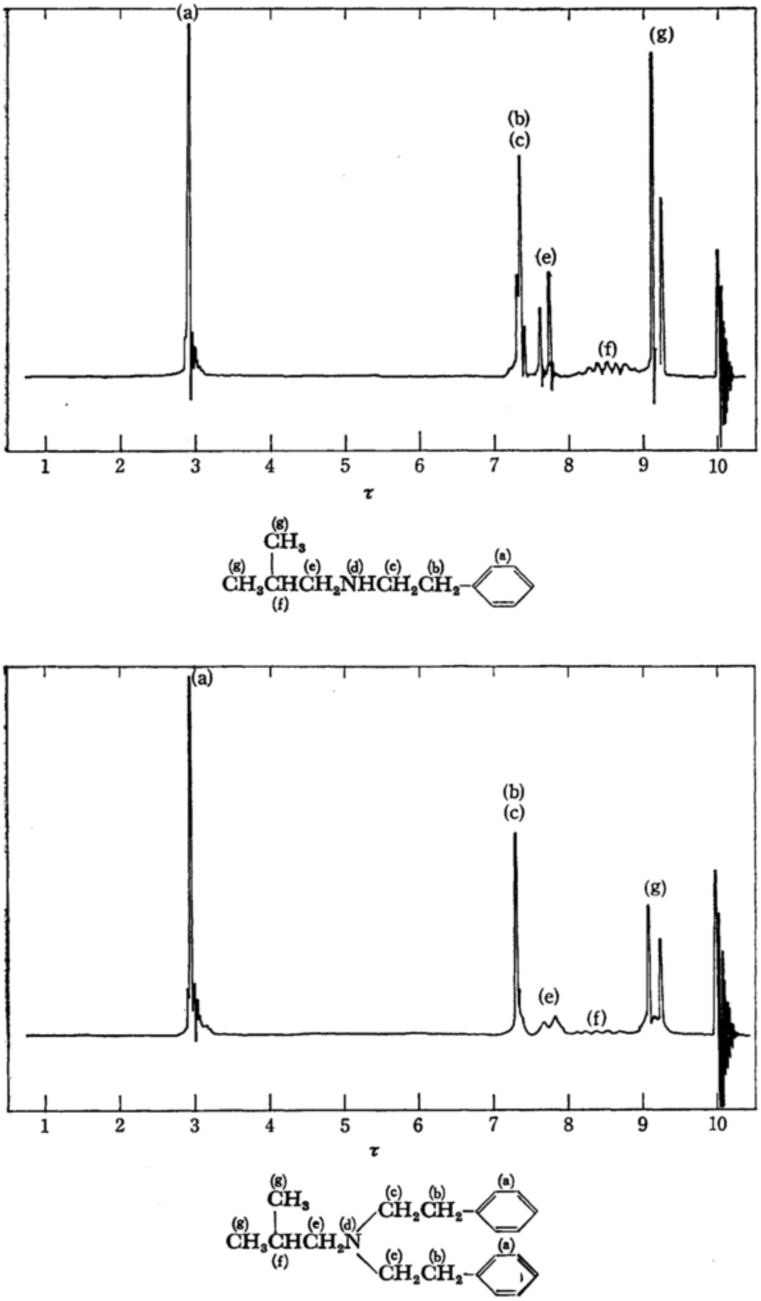
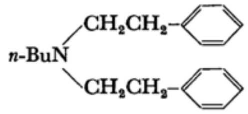
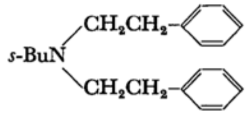
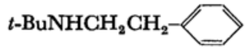
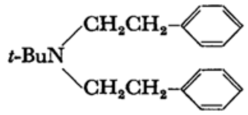
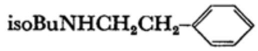
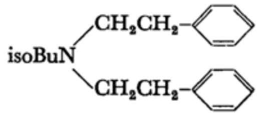


Fig. 4. NMR spectra of isobutyl-2-phenylethylamine and isobutyldi(2-phenylethyl)amine.

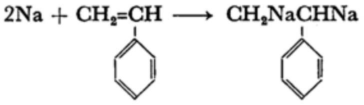
TABLE 1. REACTION PRODUCTS OBTAINED IN THE REACTIONS OF STYRENE WITH BUTYLAMINES[a)]

Amine	Reaction temp. and time °C	hr	Reaction products		Bp[b)] °C/mmHg	Yield[c)] %
n-Butylamine	46.0±0.5	3.0		**(1a)**	104—105/4	26.3
				**(2a)**	183—184/4	23.5
s-Butylamine	60.0±0.5	4.3		**(1b)**	90—91/4	11.1
				**(2b)**	179—180/4	10.8
t-Butylamine	45.0±1.0	3.9		**(1c)**	86—87/4	11.6
				**(2c)**	170—171/4	11.9
Isobutylamine	65.0±0.5	4.1		**(1d)**	91—92/4	21.5
				**(2d)**	177—178/4	49.4

a) The molar ratio of styrene to amine was unity.
b) Boiling points were uncorrected.
c) Yields were calculated on the basis of styrene added.

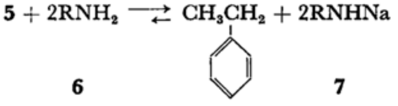
protons (a) in the compound **2c**, which does not appear in the compound **1c**, is perhaps due to the different conformations that are brought about by the restricted rotations about single bonds between carbons (b) and (c) and between carbon (c) and nitrogen. The IR spectra and the NMR spectra are consistent with the structural formulas illustrated in Table 1.

General Reaction Scheme. The reaction scheme is considered as follows. The initiation reaction may be the addition of sodium to styrene **4**, and product **5** transmetalates with the primary amine to give sodium amide **7**.



$$2Na + CH_2{=}\underset{C_6H_5}{CH} \longrightarrow CH_2Na\underset{C_6H_5}{CHNa} \quad (1)$$

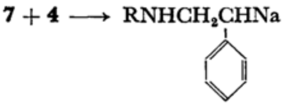
4 **5**



$$\mathbf{5} + 2RNH_2 \rightleftarrows CH_3\underset{C_6H_5}{CH_2} + 2RNHNa \quad (2)$$

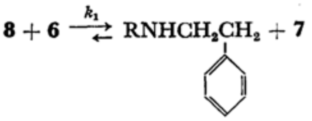
6 **7**

Sodium amide **7** is able to react with styrene, and the resulting sodium salt **8** changes into the amide **7** by reaction (4), thus a cycle of reactions is formed.



$$\mathbf{7} + \mathbf{4} \longrightarrow RNHCH_2\underset{C_6H_5}{CHNa} \quad (3)$$

8



$$\mathbf{8} + \mathbf{6} \overset{k_1}{\rightleftarrows} RNHCH_2\underset{C_6H_5}{CH_2} + \mathbf{7} \quad (4)$$

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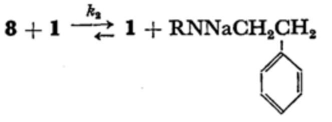
Compound **8** reacts with the secondary amine **1** as well as the primary amine **6**, and amide **9** adds to styrene.



$$\mathbf{8} + \mathbf{1} \overset{k_2}{\rightleftarrows} \mathbf{1} + RNNaCH_2\underset{C_6H_5}{CH_2} \quad (5)$$

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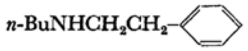
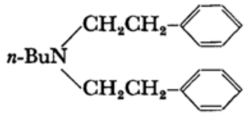
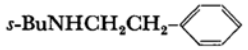
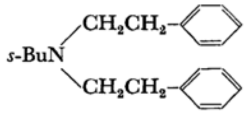
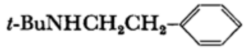
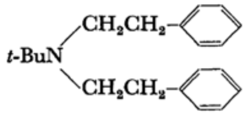
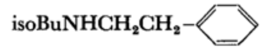
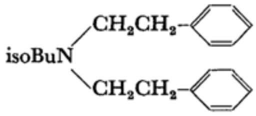
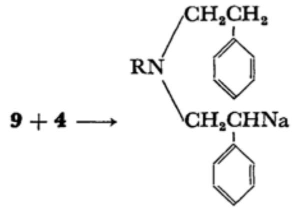
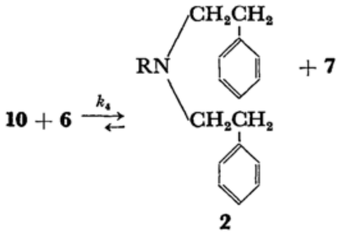
TABLE 2. ASSIGNMENTS OF THE SIGNALS TO THE PROTONS*

Reaction products		Protons							
		(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
	(**1a**)	2.89	7.27	7.27	···	7.48	···	···	9.09
	(**2a**)	2.94	7.33	7.33	—	7.53	···	···	9.12
	(**1b**)	2.91	7.29	7.29	···	7.53	9.00	8.75	9.09
	(**2b**)	2.96	7.38	7.38	—	7.50	9.07	8.76	9.17
	(**1c**)	2.90	7.29	7.29	···	—	8.99	—	—
	(**2c**)	2.84 2.90 2.93 2.94	7.28	7.28	—	—	8.93 9.04	—	—
	(**1d**)	2.89	7.30	7.30	···	7.63 7.74	8.51	9.13 9.24	—
	(**2d**)	2.91	7.33	7.33	—	7.71 7.83	8.33	9.12 9.23	—

* Figures in Table are τ values

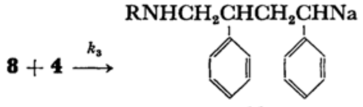

10 (6)

Compound **10** transmetalates with amines **6** and **1**.

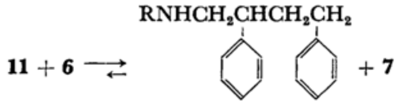

2 (7)

$$10 + 1 \overset{k_5}{\rightleftarrows} 2 + 9 \qquad (8)$$

The organometallic compound **8** has a possibility to react with **4**, besides **6** and **1**, *i.e.* the propagation reaction may also take place.


11 (9)

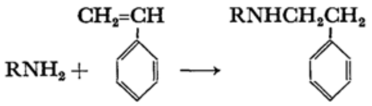
Compound **11** reacts with amines **6** and **1**.


3 (10)

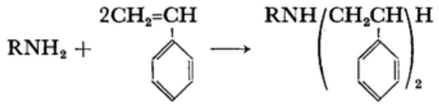
$$11 + 1 \rightleftarrows 3 + 9 \qquad (11)$$

It may be understood from the reaction scheme that compounds **1**, **2** and **3** should be prepared in the reaction of amines and styrene catalyzed by sodium metal.

Anionic Telomerization. The reactions described in the preceding section can be interpreted as follows. We obtain Eq. (12) on combining Eqs. (3) and (4),

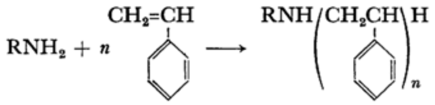

(12)

and Eq. (13) on combining Eqs. (3). (9) and (10).



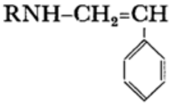
$$\mathrm{RNH_2} + 2\,\mathrm{CH_2{=}\underset{C_6H_5}{CH}} \longrightarrow \mathrm{RNH}\left(\mathrm{CH_2\underset{C_6H_5}{CH}}\right)_2\mathrm{H} \qquad (13)$$

If $\mathrm{RNH_2}$ acts as a telogen and styrene as a taxogen, the telomerization reaction may be expressed as follows,

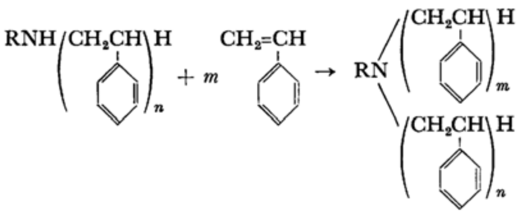


$$\mathrm{RNH_2} + n\,\mathrm{CH_2{=}\underset{C_6H_5}{CH}} \longrightarrow \mathrm{RNH}\left(\mathrm{CH_2\underset{C_6H_5}{CH}}\right)_n\mathrm{H} \qquad (14)$$

12

and the homolog **12** is obtained as a telomer. Hence, it is considered that Eqs. (12) and (13) are special cases of Eq. (14) and the products **1** and **3** are the telomers with $n=1$ and $n=2$, respectively. The secondary amine **12** has still an acidic hydrogen attached to the nitrogen atom and so **12** can react as a telogen. Therefore, another telomerization reaction may occur in  $\mathrm{RNH{-}CH_2{=}\underset{C_6H_5}{CH}}$ system,

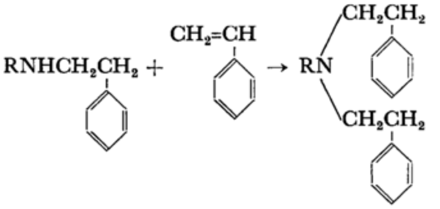
i.e.,



$$\mathrm{RNH}\left(\mathrm{CH_2\underset{C_6H_5}{CH}}\right)_n\mathrm{H} + m\,\mathrm{CH_2{=}\underset{C_6H_5}{CH}} \rightarrow \mathrm{RN}\begin{cases}\left(\mathrm{CH_2\underset{C_6H_5}{CH}}\right)_m\mathrm{H}\\ \left(\mathrm{CH_2\underset{C_6H_5}{CH}}\right)_n\mathrm{H}\end{cases} \qquad (15)$$

13 (15)

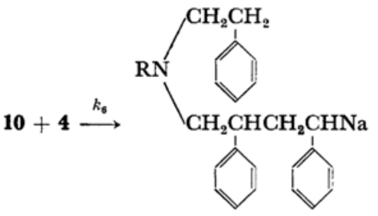
From Eqs. (6) and (8), Eq. (16) is obtained.



$$\mathrm{RNHCH_2\underset{C_6H_5}{CH_2}} + \mathrm{CH_2{=}\underset{C_6H_5}{CH}} \rightarrow \mathrm{RN}\begin{cases}\mathrm{CH_2\underset{C_6H_5}{CH_2}}\\ \mathrm{CH_2\underset{C_6H_5}{CH_2}}\end{cases} \qquad (16)$$

Reaction (16) is a special case of the telomerization reaction (15) and product **2** is one of the telomers **13**. Thus, the reaction products **1**, **2** and **3** may be interpreted as telomers in the telomerization reactions (14) and (15), and some part of the residue which remained undistilled in vacuum distillation is supposed to be a mixture of telomers **13** with $m+n\geqq 3$.

Reaction Scheme and Reactivity of Amines. Suppose k_1, k_2, k_3, k_4, k_5 and k_6 are the rate constants of reactions (4), (5), (9), (7), (8) and (17), respectivery. Compound **8** reacts with **6**, **1** and **4**, and so reactions (4), (5) and (9) are competitive each other. Other competitive reactions consist of reactions (7), (8) and (17).



$$\mathbf{10} + \mathbf{4} \xrightarrow{k_6} \mathrm{RN}\begin{cases}\mathrm{CH_2\underset{C_6H_5}{CH_2}}\\ \mathrm{CH_2\underset{C_6H_5}{CH}CH_2\underset{C_6H_5}{CH}Na}\end{cases} \qquad (17)$$

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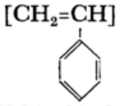
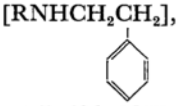
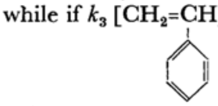
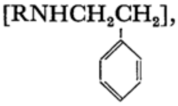
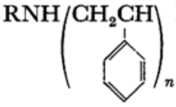
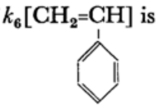
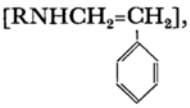
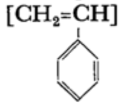
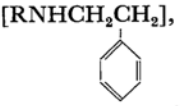
If k_3  $[\mathrm{CH_2{=}\underset{C_6H_5}{CH}}]$ is smaller than $k_1\,[\mathrm{RNH_2}]$ or k_2  $[\mathrm{RNHCH_2\underset{C_6H_5}{CH_2}}]$, the main product is not **3** but **1**, while if k_3  $[\mathrm{CH_2{=}\underset{C_6H_5}{CH}}]$ is greater than $k_1[\mathrm{RNH_2}]$ and k_2  $[\mathrm{RNHCH_2\underset{C_6H_5}{CH_2}}]$, product **3** and its higer homologs  $\mathrm{RNH}\left(\mathrm{CH_2\underset{C_6H_5}{CH}}\right)_n\mathrm{H}$ ($n=2,3,\cdots$) areformed.

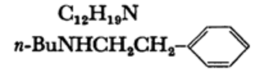
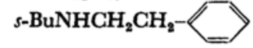
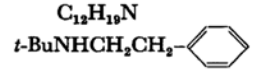
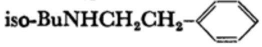
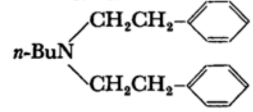
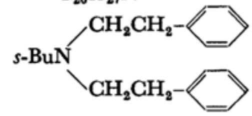
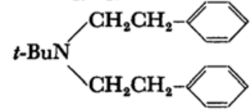
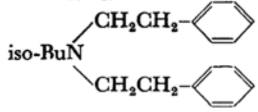
From similar consideration, if k_6  $[\mathrm{CH_2{=}\underset{C_6H_5}{CH}}]$ is smaller than $k_4[\mathrm{RNH_2}]$ or k_5  $[\mathrm{RNHCH_2{=}\underset{C_6H_5}{CH_2}}]$, product **12** is hardly prepared, but compound **2** is prepared. On the contrary, if k_6  $[\mathrm{CH_2{=}\underset{C_6H_5}{CH}}]$ is greater than $k_4[\mathrm{RNH_2}]$ and k_5  $[\mathrm{RNHCH_2\underset{C_6H_5}{CH_2}}]$, compound **12** and its higher homologs **13** are formed.

Under the reaction conditions adopted, the rate of the chain transfer reaction may be considered to be faster than that of the propagation one, since compound **2** was obtained but not compound **3**, *i.e.* the amines with acidic hydrogens reacted more easily with the organosodium compound **8** than styrene.

Experimental

Physical Data. For mass spectral analysis, a Hitachi RMU-6D mass spectrometer was employed with the electron beam energy at 80 eV. The molecular weight determination by vapor pressure osmometry was car-

TABLE 3. CHARACTERIZATION OF FRACTION PRODUCTS

Molecular formula Structural formula			Elementary analysis		Molecular weight			Ref. I. (°C)	IR cm^{-1}
			Calcd	Found	Calcd	MS	VPO		
$C_{12}H_{19}N$ 	(**1a**)	C H N	81.30 10.80 7.90	80.78 10.81 7.91	177.28	177	184	1.4951 (25.0)	3290
$C_{12}H_{19}N$ 	(**1b**)	C H N	81.30 10.80 7.90	80.75 10.99 8.11	177.28	177	171	1.4958 (24.5)	3310
$C_{12}H_{19}N$ 	(**1c**)	C H N	81.30 10.80 7.90	80.71 11.06 7.69	177.28	177	182	1.4938 (24.5)	3290
$C_{12}H_{19}N$ 	(**1d**)	C H N	81.30 10.80 7.90	81.28 10.85 7.89	177.28	177	173	1.4938 (24.5)	3315
$C_{20}H_{27}N$ 	(**2a**)	C H N	85.35 9.67 4.98	85.10 9.89 4.78	281.42	281	272	1.5319 (25.0)	—
$C_{20}H_{27}N$ 	(**2b**)	C H N	85.35 9.67 4.98	84.86 10.01 5.17	281.42	281	286	1.5281 (24.5)	—
$C_{20}H_{27}N$ 	(**2c**)	C H N	85.35 9.67 4.98	84.88 10.18 5.09	281.42	281	277	1.5298 (24.5)	—
$C_{20}H_{27}N$ 	(**2d**)	C H N	85.35 9.67 4.98	85.14 9.78 5.00	281.42	281	279	1.5299 (24.5)	—

ried out in benzene at 37°C on a Hewlett Packard Model 302 vapor pressure osmometer. IR spectra were recorded on a Hitachi Perkin-Elmer 125 grating infrared spectrophotometer. Proton NMR spectra were obtained on a Japan Electron Optics Lab. JNM C-60 HL spectrophotometer using tetramethylsilane as internal standard in carbon tetrachloride.

Materials. Styrene was dried over anhydrous magnesium sulfate for a day or two and was distilled under reduced pressure. Amines were dried over sodium hydroxide and were collected by distillation under atmospheric or reduced pressure according to their boiling points.

General Procedure for Preparation. A primary amine and finely sliced sodium were placed in a four-necked round-bottomed flask, provided with a mechanical stirrer, a reflux condenser, a dropping funnel and an inlet of nitrogen. The flask was heated to a prescribed temperature in an oil bath. The oil was agitated mechanically and its temperature was controlled by a thermostat. Styrene was added dropwise to the amine for from one hour to three, and thereafter the mixture was kept standing for reaction for a further three to five hours. Then the solution was cooled to room temperature and the alkali was decomposed by adding an equivalent amount of methanol and was neutralized by a 0.1 N hydrochloric acid. A small amount of benzene was added to this reaction mixture and the resulting solution was washed with water, dried over sodium carbonate and distilled *in vacuo*.

***N*-Butyl-2-phenylethylamine (1a) and *N*-Butyldi-(2-phenylethyl)amine (2a).** To 21.1 g of *n*-butylamine and 0.7 g of sodium which were heated to 46.0 ±0.5°C, 31.2 g of styrene was added dropwise during 3 hr and the reaction was carried out for a further 3 hr. To the reaction mixture that was cooled to room temperature were added 3.1 m*l* of methanol and 5.0 m*l* of water. Then the solution was neutralized with hydrochloric acid, diluted with 50 m*l* of benzene and washed with 50 m*l* of water, and the organic layer was separated, dried and distilled *in vacuo* to give **1a** (14.0 g, 26.3%) and **2a** (19.8 g, 23.5%). The other reactions were carried out in similar procedures.

Characterization of Reaction Products. Table 3 summarizes the results on the characterization of the reaction products. Column 1 lists the molecular formula and structural formula of these compounds. Columns 2 and 3 show the result of the elementary analysis. The weight percents were calculated for the molecular formula described in column 1. Satisfactory agreement with measured values confirms the expected structures. Columns 4, 5 and 6 report the molecular weights which were calculated, determined by the mass spectrometry and measured by the vapor pressure osmometry, respectively. The theoretical molecular weight was calculated for the molecular formula listed in column 1. These molecular weights agree with one another, and support the molecular formula proposed. The refractive indices of these compounds are listed in column 7. Whether the product has the group -NH- or not was confirmed by IR spectra. Wave numbers of the absorption peak due to the -NH- stretching vibration are described in column 8.