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Anionic Telomerizations of Styrene with Some Aromatic Amines[1]

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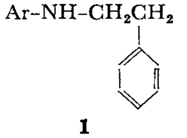
The anionic telomerizations of styrene with some aromatic amines catalyzed by sodium metal were investigated. *o*-Toluidine, *m*-toluidine, *p*-toluidine, 2,4-xylidine, 2,5-xylidine and 3,4-xylidine were used as the aromatic amines. Each amine reacted with styrene to give an addition product, which was identified as *N*-substituted 2-phenylethylamine. Though both α-hydrogen atoms on α-carbon atoms and hydrogen atoms attached to nitrogen atoms of the aromatic amines are weakly acidic, only the latter hydrogen atoms were detached by alkali species under the present experimental conditions. The formations of the products were discussed from the standpoint of anionic telomerization.

In previous papers, the base-catalyzed reactions of styrene with butylamines[2] and the telomerizations of this monomer with secondary aliphatic amines[1] were reported. Wegler and Pieper[3] investigated the reactions of styrene with various amines in the presence of alkali metal and found that aniline combined with styrene into *N*-phenyl-2-phenylethylamine. Pines and Wunderlich[4] reported that toluene and ethylbenzene react with styrene in the presence of sodium metal to form monoadducts, 1,3-diphenylpropane and 1,3-diphenylbutane, and diadducts, 1,3,5-triphenylpentane and 1,3,5-triphenylhexane, respectively. Therefore, it is interesting to study which type of compound is produced when aromatic compounds containing both α-hydrogens on α-carbons and an amino group neighboring an aromatic nuclei react with styrene in the presence of alkali matel.

In this paper the reactions of toluidines and xylidines with styrene and the structures of the products will be reported on. The reaction scheme will also be discussed.

Results and Discussion

Reactions of Styrene with Aromatic Amines. *o*-Toluidine, *m*-toluidine, *p*-toluidine, 2,4-xylidine, 2,5-xylidine, and 3,4-xylidine reacted with styrene in the presence of sodium metal to produce *N*-substituted 2-phenylethylamine **1**. The compounds



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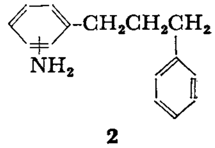

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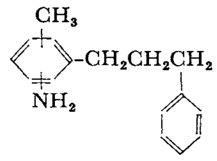
[1] Anionic Telomerizations. III. Part II of this series: T. Asahara, M. Senō, S. Tanaka and N. Den, This Bulletin, **42**, 2337 (1969).

[2] T. Asahara, M. Senō, S. Tanaka and N. Den, *ibid.*, **42**, 1996 (1969).

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

[4] H. Pines and D. Wunderlich, *J. Amer. Chem. Soc.*, **80**, 6001 (1958).

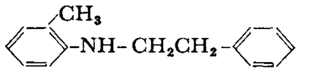
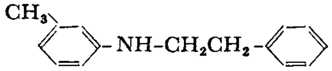
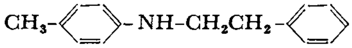
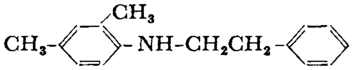
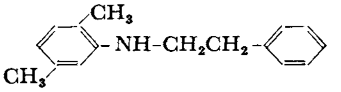
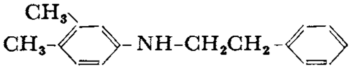


3

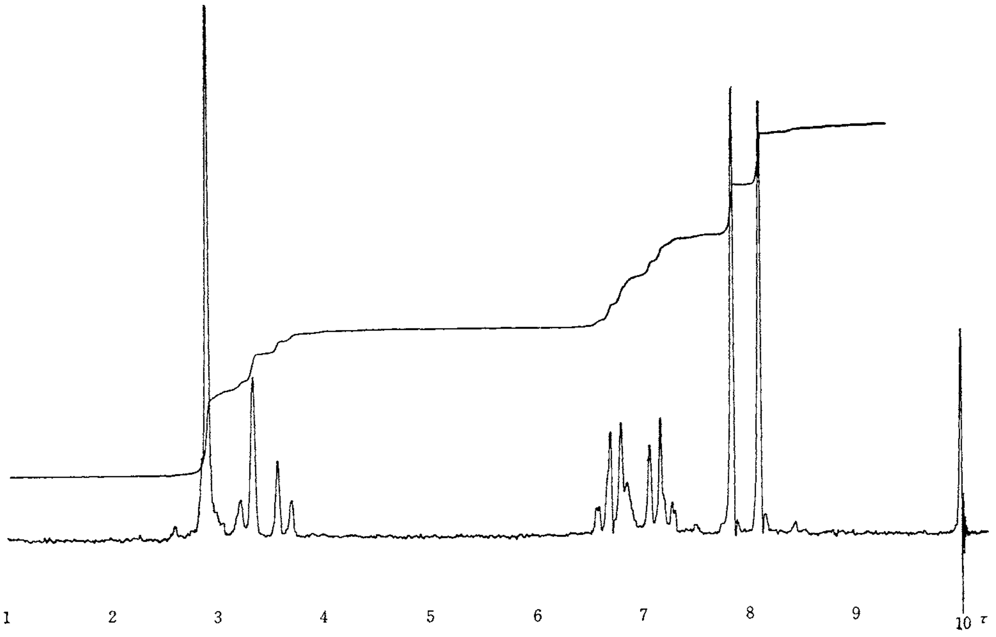
of Type **2** and **3** were not produced in the present experiment. The reaction conditions and products are listed in Table 1.

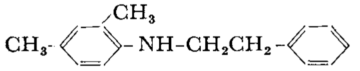
Structure of the Products. The structures of the 1 : 1 addition products obtained in the reactions of styrene with toluidines may be expressed by formula **1** or formula **2**, since both the α-hydro-

TABLE 1. REACTION PRODUCTS OBTAINED IN REACTIONS OF STYRENE WITH AROMATIC AMINES[a]

Amine	Reaction temp. and time °C	hr	Reaction product	Bp[b] °C/mmHg	Yield[c] %
o-Toluidine	150±1	3.0	 **(1a)**	161—162/4	50.1
m-Toluidine	150±1	3.0	 **(1b)**	172—173/4	72.0
p-Toluidine	150±1	3.0	 **(1c)**	180—181/4	76.3
2,4-Xylidine	150±1	4.0	 **(1d)**	160—162/2	67.1
2,5-Xylidine	150±1	2.0	 **(1e)**	159—160/2	41.8
3,4-Xylidine	150±1	4.0	 **(1f)**	175—176/2	78.8

a) The molar ratio of styrene to amine was 2 : 1. 0.7 g of sodium was used in each reaction.
b) Boiling points were uncorrected.
c) Yields were calculated on the basis of amine added.



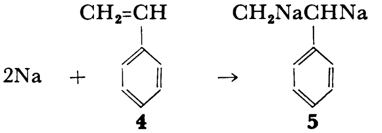


(1d)

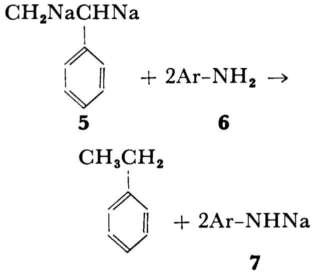
Fig. 1. The proton NMR spectrum of product **1d**.

gens attached to α-carbon atoms and those connected to the nitrogen of toluidines are weakly acidic. The proton NMR spectrum of each product showed a methyl singlet near 8τ; this is consistent with structure **1**. The reaction products derived from xylidines were analysed in the same way and were identified as **1**. Each product has still six methyl hydrogens and a hydrogen belonging to the –NH– group, whose signal (near 6.8τ) disappeared in the presence of heavy water. The proton NMR spectrum of **1d** is shown in Fig. 1 as an example.

Reaction Scheme. In the first step, sodium metal may add to styrene **4** to give an organometallic compound **5**, which then transmetalates with an aromatic amine.

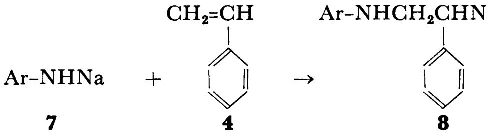


(1)

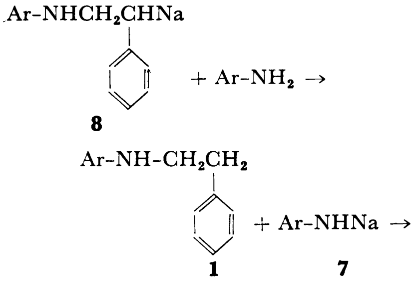


(2)

Compound **7** combines with styrene to produce an organosodium salt **8**, and **8** reacts with the amine **6**. Thus, the product **1** is obtained.

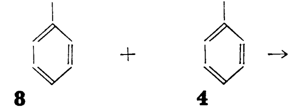


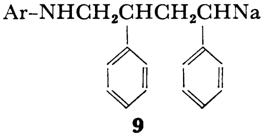
(3)



(4)

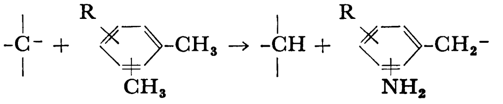
The organosodium compound **8** may react with styrene, and styrene may compete with the amine **6** for the sodium salt **8**, but the rate of reaction (5) is far slower than that of reaction (4) in the present experiment.



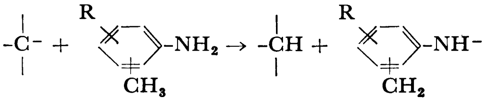


(5)

Carbanions such as **5** and **8** react more readily with hydrogen atoms attached to the nitrogen than with those of the methyl group in the following reactions:



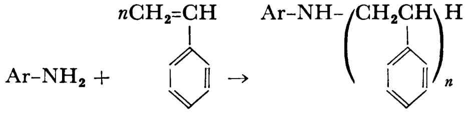
(6)



R : H or CH$_3$ (7)

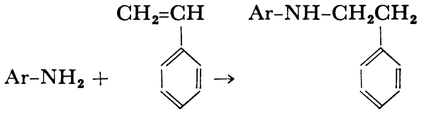
Following the concept of proton-donors and proton-acceptors, carbanions are bases and hydrogen compounds are acids, and the acid strength of the methyl hydrogens is weaker than that of the hydrogens of amino group. Therefore, reaction (7) exceeds reaction (6) in the reaction rate, and not compound **2** but compound **1** is obtained.

If an aromatic amine and styrene act as a telogen and a taxogen, respectively, the following equation of the telomerization reaction may be presented:

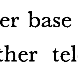


(8)

On combining Eqs. (3) and (4), we obtain Eq. (9):



(9)

Thus, reaction (9) may be regarded as a special case among anionic telomerization reactions (8). In other words, when a chain-transfer reaction is much faster than a propagation reaction, anionic telomerization reaction of the type (9) are realized. An organosodium compound, Ar–NNa–CH$_2$CH$_2$–, which is a weaker base than Ar–NHNa, may be too stable for another telomerization reaction (10) to take place.

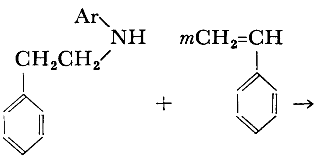
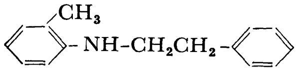
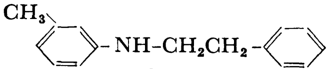
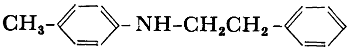
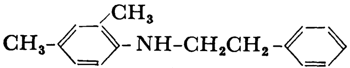
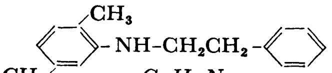
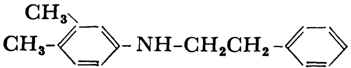
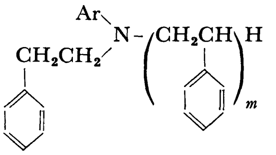


TABLE 2. CHARACTERIZATION OF REACTION PRODUCTS

Structural formula Molecular formula			Elementary analysis		Molecular weight			Refractive index (25.0°C)
			Calcd	Found	Calcd	Mass	VPO	
 $C_{15}H_{17}N$	(1a)	C	85.26	85.35				
		H	8.11	8.27	211.29	211	208	1.5883
		N	6.63	6.74				
 $C_{15}H_{17}N$	(1b)	C	85.26	85.18				
		H	8.11	8.20	211.29	211	208	1.5887
		N	6.63	6.76				
 $C_{15}H_{17}N$	(1c)	C	85.26	85.45				
		H	8.11	8.34	211.29	211	212	—
		N	6.63	6.93				
 $C_{16}H_{19}N$	(1d)	C	85.28	85.53				
		H	8.50	8.47	225.32	225	223	1.5788
		N	6.22	5.96				
 $C_{16}H_{19}N$	(1e)	C	85.28	85.40				
		H	8.50	8.34	225.32	225	220	1.5801
		N	6.22	6.28				
 $C_{16}H_{19}N$	(1f)	C	85.28	85.21				
		H	8.50	8.60	225.32	225	228	1.5849
		N	6.22	5.93				



(10)

Experimental

Physical Data. The molecular-weight determination by vapor-pressure osmometry was carried out in benzene at 37°C on a Hewlett Packard Model 302 vapor-pressure osmometer. The proton NMR spectra were recorded on a Hitachi Model R-20A spectrophotometer, using tetramethylsilane as the internal standard in carbon tetrachloride. For mass spectral analysis, a Hitachi RMU-6D mass spectrometer was employed, with the electron beam energy at 80 eV.

Material. The styrene was dried over anhydrous magnesium sulfate and was distilled under reduced pressure. All the aromatic amines except 3,4-xylidine were dried over sodium hydroxide and were distilled *in vacuo*. The 3,4-xylidine was recrystallized from ligroin.

***N*-(2,4-dimethylphenyl)-2-phenylethylamine (1d).** To 37.0 g of 2,4-xylidine and 0.7 g of finely-sliced sodium metal which had been heated to 150±1°C, 62.5 g of styrene was added, drop by drop, over a 0.8-hr; the reaction was then continued for a further 3.2 hr. After 55 m*l* of water and 50 m*l* of benzene had been added to the reaction mixture, the solution was neutralized with hydrochloric acid and washed with water, and the organic layer was separated, dried, and distilled *in vacuo* to give 45.4 g (67.1%) of the product, **1d**, at 160—162°C/2 mmHg. Some parts of the styrene and amines added were recovered unreacted by the distillation, and the residues were very small in quantity.

The other products were synthesized by similar procedures. Table 2 summarizes the results on the characterization of the compounds.