A Catalytic Telomerization Reaction of Ethylene with Aromatic Hydrocarbons

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A new catalytic telomerization reaction is described with aromatic hydrocarbons as telogens and ethylene as taxogen. The primary telomerization products obtained from benzene and ethylene are straight-chain, even-numbered 1-phenyl-*n*-alkanes. From toluene and ethylene, the corresponding products are essentially the odd-numbered 1-phenyl-*n*-alkanes. The distributions of these products are in accordance with the statistical theory. The catalyst is an organolithium compound in conjunction with a tertiary aliphatic amine, particularly a chelating diamine. The reaction mechanism is suggested to involve transmetalation from aliphatic carbon to a benzylic or phenylic position of the telogen and addition of a carbon–lithium bond to ethylene. The assistance of both reactions by the amine is attributed to the formation of a coordination complex.

The term "telomerization" has been introduced to characterize the following type of reaction (eq. 1 and 2).

$$\text{X–Y} + n\text{Z} \longrightarrow \text{X–(Z)}_n\text{–Y} \quad (1)$$

$$\text{telogen} + \text{taxogen} \longrightarrow \text{telomer} \quad (2)$$

A catalyst which promotes such a reaction must be capable of propagating a taxogen unit and of facilitating a chain transfer reaction back to the telogen. The propagation and chain transfer reactions may occur by any of several mechanisms. It is necessary, however, that the rates of these two reactions are of similar magnitude; otherwise, telomerization will not occur. The proper rate ratio provided, telomeric products are obtained in a statistical distribution which can be influenced within certain theoretical limits by the variables of the system.

This report describes a new and highly active catalyst system which promotes a telomerization reaction of various aromatic hydrocarbons as telogens and ethylene as taxogen (eq. 3). The catalyst developed for

$$\text{Ar–H} + n\text{CH}_2\text{=CH}_2 \longrightarrow \text{Ar}\text{(CH}_2\text{–CH}_2)_n\text{H} \quad (3)$$

this reaction consists of an organolithium compound in conjunction with a tertiary amine.

The addition of alkyllithium compounds to ethylene (eq. 4) was previously reported by Ziegler and Gellert[1]

$$\text{RLi} + n\text{C}_2\text{H}_4 \longrightarrow \text{R}\text{(CH}_2\text{–CH}_2)_n\text{Li} \quad (4)$$

and by Bartlett and co-workers.[2] However, chain transfer did not occur; hence, only stoichiometric addition products were observed. Pines and co-workers[3] were able to effect the side-chain alkylation of alkyl aromatics (eq. 5) by using sodium or potassium

$$\text{C}_6\text{H}_5\text{CH}_3 + \text{C}_2\text{H}_4 \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3 \quad (5)$$

metal and a promoter. However, the rapid rate of chain transfer, in this case a transmetalation reaction, precluded the formation of telomeric products.

Catalyst.—The organolithium–amine complex described herein catalyzes the transmetalation and propagation reactions at comparable rates so that a smooth telomerization of ethylene with aromatic hydrocarbons is realized under reasonable operating conditions. The organolithium component of the catalyst system is conveniently chosen among commercially available materials, such as butyllithium in hexane. The amine component must be free of reactive hydrogen, which includes even aromatic, allylic and benzylic protons, and is therefore limited to tertiary, aliphatic amines.

A relationship is observed between catalytic activity and the base strength, concentration and structure of the amine. This relationship suggests the formation of a coordination complex with the lithium organic compound. Similar coordination complexes have been

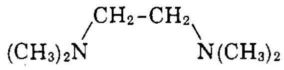
$$\text{LiR} + \text{R}_3'\text{N} \rightleftharpoons \text{RLi (NR}_3') \quad (6)$$

$$\text{R}_3'\text{N}\cdot\text{LiR} + \text{R}_3'\text{N} \rightleftharpoons \text{RLi (NR}_3')_2 \quad (7)$$

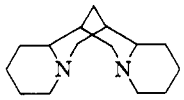
proposed by others[4] in order to explain the marked influence of amines upon the reactivity of organolithium compounds. Support for the equilibrium expressed in eq. 6 and 7 is derived from the fact that catalytic activity and catalyst stability is favorably influenced by the use of excess amine, strongly basic amines, and chelating-type diamines.

Alkyllithium compounds are known[2] to decompose at the temperature required for the telomerization reaction. The concept of Lewis base strength[5] and catalyst stability is clearly reflected in the decay of telomerization rates seen in Fig. 1. Thus, the order of catalyst stability parallels that of base strength; *viz.*, triethylamine < trimethylamine < 1,4-diazabicyclo[2,2,2]octane (DABCO). Furthermore, the concentration of DABCO is seen in Fig. 2 to influence the reaction rate as predicted by eq. 6 and 7.

The coordination of two ligands by lithium, as proposed in eq. 7, is suggested by the unusually high activity observed with bidentate ligands such as N,N,N′,N′-tetramethylethylenediamine (TMEDA, I) and sparteine (II). Furthermore, in these cases the equilibrium


I

$$(\text{CH}_3)_2\text{N–CH}_2\text{–CH}_2\text{–N(CH}_3)_2$$


II

(eq. 7) lies far to the right since the use of excess amine has no effect upon the reaction rate. The greater stability of these complexes is ascribed to the chelation capability commonly associated[6] with bidentate ligands.

The reaction rates shown in Fig. 2 are observed only initially. After some time, which depends upon temperature and catalyst concentration, the rates of telom-

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[1] K. Ziegler and H. Gellert, *Ann.*, **567**, 195 (1950).

[2] P. D. Bartlett, S. Friedman, and M. Stiles, *J. Am. Chem. Soc.*, **75**, 1771 (1953).

[3] H. Pines, J. A. Veseley, and V. N. Ipatieff, *ibid.*, **77**, 554 (1955).

[4] D. J. Cram and D. R. Wilson, *ibid.*, **85**, 1245 (1963); F. N. Jones, M. F. Zinn, and C. R. Hauser, *J. Org. Chem.*, **28**, 663 (1963); G. A. Razuvaev, *et al.*, *Zh. Obshch. Khim.*, **31**, 2347 (1961).

[5] H. C. Brown and S. Sujishi, *J. Am. Chem. Soc.*, **70**, 2878 (1948).

[6] A detailed discussion of the theory of heterocyclic ring formation involving metal ions by R. W. Parry is found in "Chemistry of Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956.

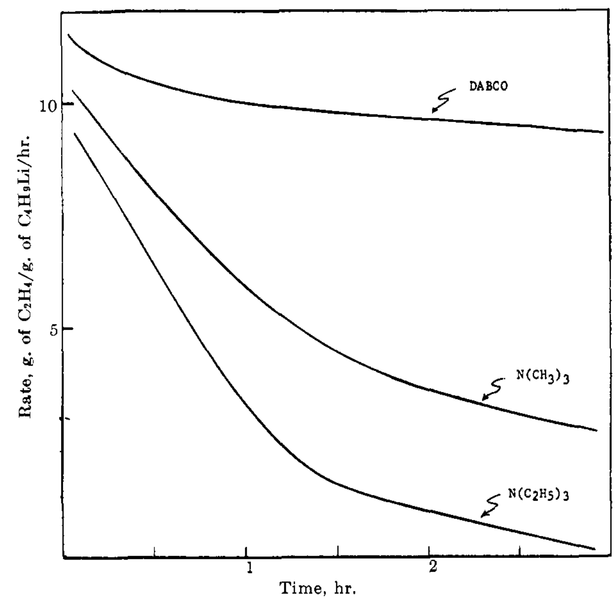


Fig. 1.—Relation of catalyst life to the structure of the amine. System: toluene and ethylene at 105° and 500 p.s.i.; 0.10 *M* RLi and 0.2 *M* amine.

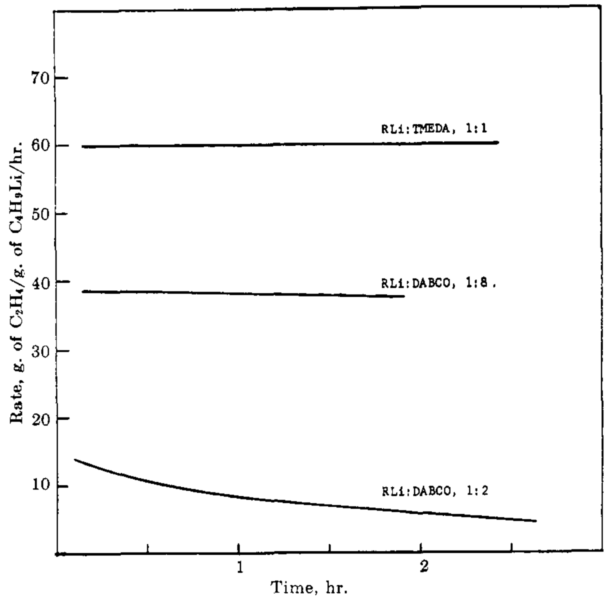


Fig. 2.—Effect of the amine structure upon rate. System: toluene and ethylene at 105° and 500 p.s.i.; 0.06 *M* RLi.

erization decrease rapidly. When sufficiently dilute catalyst concentrations are used, the rate decrease is observed even after a short reaction time (Fig. 3). This dependency of rate behavior upon catalyst concentration may be caused by catalyst association. Thus, at high concentrations, decayed catalyst may be replaced from an association reservoir which is not available at lower concentrations.

Impurities such as water, air, and carbon dioxide must be rigidly excluded since they react rapidly with organolithium compounds. Hydrogen acts as a poison since lithium hydride resulting from hydrogenolysis of the lithium–carbon bond[7] is inactive as a catalyst component.

An important route for catalyst decomposition may be the known[1,8] thermal decomposition of organolithium compounds to lithium hydride and olefins. With TMEDA as the amine component, however, hydrolysis of the thermally decomposed catalyst produced dimethylamine rather than hydrogen. Thus, cleavage of a carbon–nitrogen bond analogous to the cleavage of ethers[9] by alkyllithium compounds is the principal side reaction leading to catalyst decomposition. This decomposition may proceed *via* the six-membered transition state shown in eq. 8.

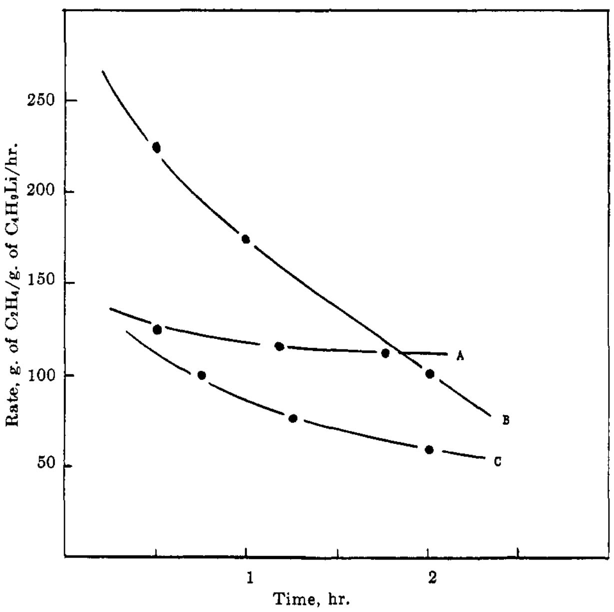
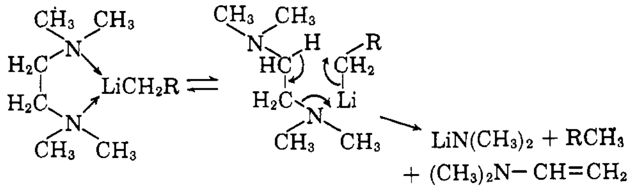


Fig. 3.—Relation of catalyst life to the temperature and amine structure. System: toluene and ethylene at 500 p.s.i.; 0.02 *M* RLi and 0.02 *M* amine. A, sparteine at 125°; B, TMEDA at 125°; C, TMEDA at 105°.



(resinifies) (8)

Such a pathway would be inhibited by a rigid structure such as that of 3,7-diazabicyclo[3,3,1]nonane. In fact, sparteine (II), a lupinane alkaloid which contains this skeleton, provided a catalyst with a considerably more steady telomerization rate (Fig. 3).

The solubility of certain organolithium–amine complexes in hydrocarbons is limited. However, at concentration levels necessary for reasonable catalytic operation, the catalyst systems discussed here are completely soluble. Despite the catalyst deactivation described, chelate-type catalysts will provide yields of 500 g. or more of telomer/gram of butyllithium.

Experimental

Transmetalation.—A 1.6 *M* solution containing 0.64 g. (0.01 mole) of butyllithium in hexane was added rapidly to a solution of 1.12 g. (0.01 mole) of DABCO (Houdry Process Corporation) in 30 ml. of toluene under an inert atmosphere. The resulting yellow solution was heated to 80° for 0.5 hr. During this period, bright yellow needles of the benzyllithium-DABCO complex precipitated from the solution. The mixture was cooled to

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[7] H. Gilman, *et al.*, *J. Am. Chem. Soc.*, **60**, 2336 (1938).

[8] D. Bryce-Smith, *J. Chem. Soc.*, 1712 (1955).

[9] A. Rembaum, S. Siao, and N. Indictor, *J. Polymer Sci.*, **56**, 17 (1962).

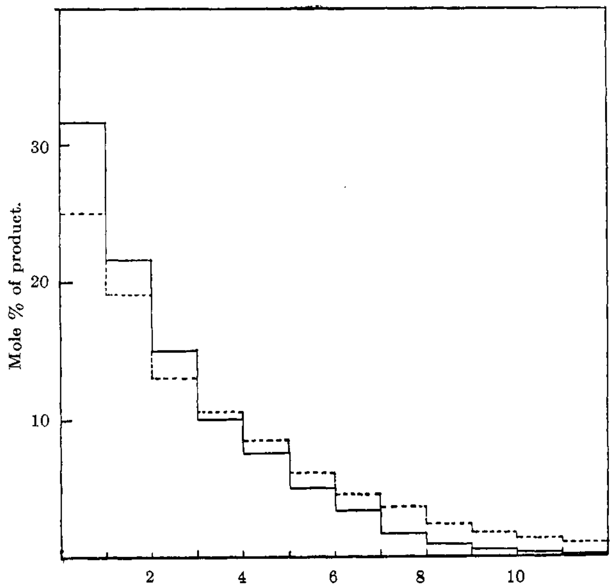

Fig. 4.—Distribution of the telomeric product obtained from benzene and ethylene at 110° with RLi·TMEDA catalyst: full line, 350 p.s.i.; broken line, 500 p.s.i.

room temperature and a solution of 1.82 g. (0.01 mole) of benzophenone in 20 ml. of toluene was added. The yellow crystals disappeared after a few minutes of agitation. The reaction mixture was washed with dilute acid and water. Upon evaporation, the toluene solution deposited benzyldiphenylcarbinol, m.p. 89°, in 85% yield.

A similar experiment was conducted with benzene as solvent and reactant, and with 1.16 g. (0.01 mole) of TMEDA as the amine component. A precipitate did not result. The clear, yellow solution was poured onto a slurry of Dry Ice in ether. The mixture was washed with dilute acid. Upon evaporation of the solvent, benzoic acid, m.p. 122°, was obtained in 90% yield.

Telomerization.—A 300-ml. stainless steel autoclave was charged under an inert atmosphere with 150 ml. of anhydrous benzene, 0.32 g. (0.005 mole) of butyllithium (10% solution in hexane). and 0.56 g. (0.005 mole) of TMEDA. The autoclave was closed and connected to a reservoir of purified, anhydrous ethylene. The autoclave was heated with rocking agitation to 110°. During the latter part of the heating period, ethylene pressure was applied at 500 p.s.i. Ethylene was rapidly consumed at the reaction temperature and was constantly replenished by the use of an in-line regulator to maintain the pressure. The extent of the reaction was conveniently determined by continuously weighing the ethylene reservoir. After 30 min., 25 g. of ethylene had reacted. At this point, the reaction was interrupted in spite of continued catalytic activity. The reactor was cooled, residual ethylene was vented, and the catalyst was deactivated by the addition of several drops of isopropyl alcohol. The product mixture was washed with dilute acid and with water. Unreacted benzene was removed by distillation. The residual telomerization product weighed 40 g. It was partially waxy at room temperature.

Rate Measurement.—The rates were determined from the weight loss or pressure drop in the ethylene reservoir during the reaction time. These measurements were easily reproducible to well within 10% of the reported values. The reaction temperature was controlled to within 1°. Ethylene pressure was maintained to within 5 p.s.i.

Product Identification.—The infrared, nuclear resonance, and ultraviolet spectra of the gross products were consistent with their identification as mixtures of arylalkanes. Telomers derived from benzene and toluene exhibited strong absorptions characteristic of *n*-alkylbenzenes; *viz.*, 6.25, 6.75, and 14.3 μ (monosubstituted aromatic) and 6.80 and 7.25 μ (unbranched aliphatic). Telomers prepared from toluene and ethylbenzene also absorbed at 12.6 μ (1,3-dialkylbenzene). Magnetic resonance spectra confirmed this identification (see Table I). The relative number of methylene protons was, in all cases, consistent with the average molecular weight of the product. Telomers derived from toluene also showed a weak signal at 2.2 p.p.m. assigned to benzylic methyl protons.

TABLE I

δ, p.p.m., TMS	Assignment	No. of protons
0.9	CH_3 (aliphatic)	3
1.3	CH_2 (aliphatic)	Variable
2.5	CH_2 (benzylic)	2
7.1	CH (aromatic)	5

The products were examined by gas–liquid partition chromatography using a silicone Chromosorb column and a linear temperature program from 50 to 300°. Authentic samples of ethyl-, propyl-, butyl-, amyl-, decyl-, and dodecylbenzene were introduced to confirm the assignments. The presence of small amounts of 1,3-dialkylbenzenes was confirmed by the use of authentic 1-ethyl-3-methylbenzene and 1,3-diethylbenzene with the toluene and ethylbenzene telomers, respectively.

Several telomers were also fractionated. The boiling points and spectra of individual fractions further confirmed the identification.

Telomers derived from the other telogens were identified in a similar manner.

Product Distribution.—The products were analyzed using partition chromatography as described above. An authentic phenylalkane was used as an internal reference and the composition was calculated from the relative areas of the peaks. Results from several known reference mixtures indicated an experimental accuracy better than 5%.

Results

Transmetalation.—The ability of sodium alkyls to undergo metal–hydrogen exchange reactions with "acidic" hydrocarbons is well known.[10] A similar reaction involving the less basic alkyllithium compounds occurs sluggishly except with the most acidic hydrocarbons[11] although Gilman and Gaj recently reported[12] the metalation of toluene by butyllithium.

Butyllithium, coordinated with DABCO or TMEDA, rapidly transmetalates to the benzylic position of toluene, to the aromatic nucleus of benzene, and analogously to other aromatic hydrocarbons. The resulting organolithium–DABCO complexes are often less soluble than the lithium–alkyls and will crystallize from sufficiently concentrated solutions. Thus, a solution of butyllithium and DABCO in toluene rapidly deposits bright yellow needles of benzyllithium–DABCO (9). The coordination complexes formed with TMEDA are generally more soluble. A solution of butyllithium and TMEDA in toluene rapidly assumes the characteristic color[13] of the benzyl carbanion.

$$C_4H_9Li\cdot N(CH_2CH_2)_3N + PhCH_3 \longrightarrow PhCH_2Li\cdot N(CH_2CH_2)_3N + C_4H_{10} \quad (9)$$

Telomerization.—Another important characteristic of the organolithium–amine complexes is their ability to propagate the polymerization of ethylene at a rapid rate in a paraffinic solvent. Olefins other than ethylene do not function as propagating units but rather as telogens. If, however, aromatic solvents such as benzene or toluene are used, the transmetalation and ethylene polymerization reactions occur concurrently and a telomerization reaction of ethylene with the aromatic solvent results. The products described

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[10] R. A. Benkeser, D. J. Foster, and D. M. Sauve, *Chem. Rev.*, **57**, 867 (1957).

[11] H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 265 (1954).

[12] H. Gilman and B. J. Gaj, *J. Org. Chem.*, **28**, 1725 (1963).

[13] R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

herein result from reactions conducted with a five- to tenfold excess of the aromatic reactant. Since the primary products can react further, the telogen must be present in large excess in order to avoid the formation of complex secondary products.

With toluene as telogen and solvent, the primary products consisted of a statistical distribution of odd-numbered homologous 1-phenyl-*n*-alkanes and 1-(methylphenyl)-*n*-alkanes in a 9:1 ratio. The infrared, ultraviolet, and proton resonance spectra were consistent with this identification as were the boiling points, elemental analyses, and mass numbers of distillate fractions. Comparison of retention times by gas–liquid partition chromatography with those of known standards supported this identification. In addition, quantitative chromatographic analysis demonstrated the statistical nature of the product distribution (Fig. 4).

The formation of 1-(methylphenyl)-*n*-alkanes as minor side products suggests the occurrence of a small amount of ring metalation in competition with metalation of the α-position. Although *m*-methyl-1-phenyl-*n*-alkane was the only isomer detected, the presence of lesser amounts of other ring isomers seems quite likely. At this time, it cannot be said whether the ring metalated intermediates are present at an equilibrium concentration or result from a kinetically controlled sequence as has been recently observed with the analogous metalation of cumene by potassium.[14]

The primary products resulting from reactions conducted in benzene as telogen and solvent were the homologous, even-numbered 1-phenyl-*n*-alkanes. With ethylbenzene, a mixture of homologous 2-phenyl-*n*-alkanes (60%) and *m*-ethyl-1-phenyl-*n*-alkanes (40%) resulted, indicating that both ring- and α-metalated species are present.

Although the rates of telomerization always decreased during the course of the reaction (Fig. 3), the initial rates were reproducible and significant trends could be observed. Within the series, toluene, benzene, and ethylbenzene, relative reaction rates of 2:3:5, respectively, were observed under identical experimental conditions. The ethylene pressure also exerted an effect upon reaction rate. Thus, in toluene solution at 105° with 0.05 *M* organolithium–TMEDA, the initial rates of ethylene reaction were 180, 230 and 390 moles of ethylene/mole of RLi/hr. at 500, 600, and 800 p.s.i., respectively. A similar pressure dependence was observed with benzene and ethylbenzene.

As expected, the initial rate of reaction was increased by raising the temperature; however, a simultaneous increase in the rate of catalyst decomposition was observed. As a result, the catalyst yields obtained from reactions conducted at higher temperatures seldom reflected the higher initial reaction rates. In fact, optimum catalyst yields were obtained at 105–115°, while, at temperatures above 125°, the yields decrease considerably.

Variations in the ethylene partial pressure had a pronounced effect upon the average molecular weight of the product. With benzene as telogen, the product consisted of 1-phenyl-*n*-alkanes with number average of 2.6 and 4.0 ethylene units incorporated into the side chain at 300 and 500 p.s.i., respectively. At 800 p.s.i., the product was largely composed of solid 1-phenyl-*n*-alkanes which were highly crystalline. Strong absorption bands noted at 13.7 and 13.9 μ have been associated with the extent of crystallinity in polyethylene side chain.[15] A similar influence of ethylene pressure upon average chain length was noted with other telogens (Table II).

Table II

Telomerization of Ethylene with Aromatic Hydrocarbons[a]

Telogen	Ethylene pressure, p.s.i.	β[b]	Structure of telomer
Benzene	350	0.50	Even-numbered 1-phenyl-*n*-alkanes
	400	0.45	
	500	0.30	
Toluene	300	1.0	Odd-numbered 1-phenyl-*n*-alkanes (90%) and 1-(methylphenyl)-*n*-alkanes (10%)
	500	0.55	
	800	0.40	
Ethylbenzene	300	0.45	2-Phenyl-*n*-alkanes (60%) and 1-ethylphenyl-*n*-alkanes (40%)
p-Xylene	500	0.48	*p*-Methyl-1-phenyl-*n*-alkanes

[a] These experiments were carried out at 110° with butyllithium–TMEDA. [b] Ratio of the rates of transmetalation and propagation, but calculated from the product distribution as described in the Discussion.

The average degree of telomerization, $\bar{n}$, was also dependent upon the temperature under otherwise-equivalent conditions (Table III). This effect could stem from a difference in the temperature dependence of the competing transmetalation and propagation rates. However, it can be equally easily explained as the result of increased solubility of ethylene at the lower temperatures.

Table III

Effect of Temperature upon Molecular Weight of Benzene–Ethylene Telomer[a]

Temp., °C.	Initial rate[b]	β	$\bar{n}$
70	122	0.19	6.3
80	190	0.35	3.9
95	275	0.50	3.0
110	380	0.70	2.4

[a] Reactions conducted at 300 p.s.i. with 0.025 *M* butyllithium–sparteine. [b] Rate expressed as moles of ethylene reacted/mole of RLi/hr.

Discussion

The products resulting from the organolithium-initiated addition of ethylene to aromatic hydrocarbons are readily explained in terms of a telomerization reaction involving an organometallic intermediate. The rapid transmetalation from the butyllithium–amine complex to the aromatic hydrocarbons observed in the absence of ethylene leaves little doubt that the alkylation proceeds *via* the aryllithium intermediate. Furthermore, the observed statistical distribution of products is consistent with a reaction path involving competitive chain growth and chain transfer reactions. The

$$C_4H_9Li + C_6H_6 \longrightarrow C_6H_5Li + C_4H_{10} \tag{10}$$

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(14) R. A. Benkeser, *et al.*, *J. Am. Chem. Soc.*, **85**, 3984 (1963).

(15) S. Krimm, C. Y. Liang, and G. B. B. M. Sutherland, *J. Chem. Phys.*, **25**, 549 (1956).

over-all reaction can be represented by the following scheme, using benzene as the chain transfer agent.

$$C_6H_5Li + C_2H_4 \longrightarrow C_6H_5CH_2CH_2Li \qquad (11)$$

$$C_6H_5CH_2CH_2Li + (n - 1)C_2H_4 \longrightarrow C_6H_5(CH_2CH_2)nLi \qquad (12)$$

$$C_6H_5(CH_2CH_2)_nLi + C_6H_6 \longrightarrow C_6H_5(CH_2CH_2)_nH + C_6H_5Li \qquad (13)$$

It should be emphasized that the amine component must be strongly coordinated with the organolithium compound throughout the reaction since neither the transmetalation steps nor the addition to ethylene occurs in hydrocarbon solvents in its absence. Coordination with the lithium has the effect of diffusing the polarizing power of the metal atom and thus weakening the carbon–lithium bond. In this manner, the carbanion is rendered more independent of the lithium and consequently more reactive. The existence of the carbanion as a discrete species is highly unlikely, however, and ion pairs or partially covalently bonded species are suggested.

In the reaction sequence suggested above, the initial transmetalation (eq. 10) is fast and irreversible as demonstrated by independent studies of the transmetalation of butyllithium to aromatic hydrocarbons in the presence of the amines. The chain-transfer step (eq. 13) is analogous to eq. 10 and would be expected to proceed at a similar rate. Likewise, the propagation step (eq. 12) must be rapid since the over-all chain life is dependent upon the rate of the competitive chain-transfer reaction. Thus, the initial addition of ethylene to the aromatic carbanion (eq. 11) must be the rate-controlling step. This is to be expected on the basis of energy considerations alone, since the aromatic carbon–lithium bond is transformed to an energetically less favorable aliphatic carbon–lithium bond.

Unlike the rate of chain transfer (eq. 13), the propagation rate (eq. 12) is dependent upon the ethylene pressure. The average number of ethylene units ($\bar{n}$) incorporated into the telomer product is therefore a function of the ethylene partial pressure for a given system. In particular, it depends on the ratio (β) of rate of chain transfer to rate of propagation where

$$\bar{n} = \frac{1 + \beta}{\beta}$$

The value of β may be readily determined experimentally by comparing the relative mole fractions of the telomer product at any successive values of n and

$$\beta = \frac{N_n}{N_{(n+1)}} - 1$$

the value of β determined in this manner may be used to calculate mole fraction of product at all values of n.

$$N_n = \frac{\beta}{(1 + \beta)^n}$$

The observed product distributions were in excellent agreement with the calculated values. The values of β for various aromatic reactants under equivalent conditions (Table III) reflect the transmetalation rates particular to the aromatic hydrocarbon involved.

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The Reactions of 1,1-Di(1-piperidinyl)ethylene with Isocyanates and Isothiocyanates

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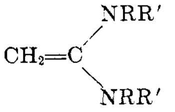
1,1-Di(1-piperidinyl)ethylene reacts with 1 or 2 moles of alkyl or aryl isocyanates and isothiocyanates to produce monoamide-, diamide-, and thioamide-substituted diaminoethylenes. The latter derivatives, as well as dipiperidinylethylene itself, react with acids and alkyl halides to give the corresponding substituted amidinium salts. Some implications of the nuclear magnetic resonance spectra with regard to the electronic structure of the various substituted diaminoethylenes and amidinium salts are discussed.

The structural relationship of the 1,1-diaminoethylenes (I) (vinylidenediamines, enediamines) to the ketene acetals[1] (II) and the enamines[2] (III) prompted a study of the reactions of these compounds with various electrophilic reagents. It had been suggested some time ago[1] that compounds of type I would show enhanced nucleophilic reactivity compared to the ketene acetals, but preparative difficulties precluded an early demonstration of this proposal. Thus, McElvain and Tate[3] did not recognize the ready availability of 1,1-di(1-piperidinyl)ethylene from the reaction of piperidine with ketene diethylacetal.[4] Similarly, Arens and Rix[5] reported that the reaction of diethylamine with ethoxyacetylene gave only a low yield of impure 1,1-bis(diethylamino)ethylene. More recent work[6] has shown that high yields of dipiperidinylethylene can be obtained from ethyl orthoacetate and piperidine under carefully controlled conditions.



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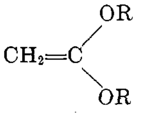

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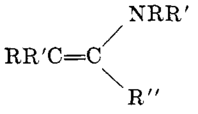

III

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[1] S. M. McElvain, *Chem. Rev.*, **45**, 453 (1949).

[2] J. Szmuszkowicz in "Advances in Organic Chemistry, Methods and Results," Vol. 4, Interscience Publishers, Inc., New York, N. Y., 1963.

[3] S. M. McElvain and B. E. Tate, *J. Am. Chem. Soc.*, **67**, 202 (1945).

[4] H. Böhme and F. Soldan, *Chem. Ber.*, **94**, 3109 (1961).

[5] J. F. Arens and Th. R. Rix, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **57B**, 270 (1954).

[6] H. Baganz and L. Domaschke, *Chem. Ber.*, **95**, 2095 (1962).