[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ionic Polymerization. VII. Relative Reactivities of Mono- and *p*-Dialkylbenzenes as Molecular Terminating Agents in the Cationic Polymerization of Styrene[1]

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It was desired to test the usefulness of molecular termination in cationic polymerization as a means of determining the relative reactivities of aromatic compounds in electrophilic substitution by carbonium ions. For this purpose, the molecular termination constants of eight mono- and *p*-dialkylbenzenes were determined in the polymerization of styrene by stannic chloride. The activating effect of alkyl groups on the aromatic nucleus was in the order methyl > ethyl > isopropyl > *t*-butyl, in agreement with their effect in other types of electrophilic aromatic substitution. This order of activation is believed to be the result largely of steric effects. The results indicate that under these conditions hydride transfer from the side chains of these compounds does not take place to a significant extent.

Previous papers in this series have described the occurrence of molecular termination by aromatic compounds in the cationic polymerization of styrene by stannic chloride. It was shown[4] that the effects of active compounds of this class on the number average degree of polymerization $\bar{P}_n$ of the resultant polystyrene are described quantitatively by the equation[5]

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_{n_0}} + \frac{k_r}{k_p} \times \frac{(R)}{(M)} \qquad (1)$$

where $\bar{P}_{n_0}$ is the degree of polymerization in the absence of the molecular terminating agent, (R)/(M) is the molar ratio of agent to monomer, and k_r/k_p (the "molecular termination constant") is the ratio of the rate constant for molecular termination to that for propagation. The relative values of the ratio for several representative aromatic-type compounds, together with the identification of fragments of the agents in the polymers, led to the conclusion that these compounds function through undergoing nuclear alkylation by the carbonium ion-anion pairs of the active polymerization centers.[1] A study of the effects of the compounds on the over-all polymerization rate indicated that hydrocarbons, at least, were chain transfer agents.[1]

It is evident that studies of molecular termination in cationic polymerization can provide quantitative relative reactivities of aromatic compounds in electrophilic substitution by carbonium ions, and the present work was undertaken in order to test further the sensitivity of the method. Since the reactivities toward other electrophilic agents of the monoalkylbenzenes, toluene, ethylbenzene, cumene and *t*-butylbenzene have received considerable study and the differences in reactivity within the series are relatively small, the molecular termination constants of these compounds have been determined. The dialkylbenzenes, *p*-cymene, *p*-*t*-butyltoluene and *p*-di-*t*-butylbenzene also have been tested.

Experimental

The purification of many of the materials used, including *p*-xylene and *p*-cymene, has been described previously.[1,4,6] Toluene, ethylbenzene, cumene and *t*-butylbenzene were Eastman Kodak Company White Label materials. After being shaken with cold concentrated sulfuric acid until a fresh portion of the acid became no more than slightly colored, the materials were washed with 10% aqueous sodium hydroxide followed by distilled water until neutral, and dried over Drierite. Distillation was carried out in 25–50 cm. glass helices-packed columns, and constant-boiling middle fractions were collected: toluene, $n^{25.9}_D$ 1.4940 (1.4932)[7]; ethylbenzene, $n^{24.9}_D$ 1.4937 (1.4934)[7]; cumene, $n^{24.8}_D$ 1.4889 (1.4890)[7]; *t*-butyltoluene, n^{24}_D 1.4908 (1.4910).[7]

p-*t*-Butyltoluene was prepared through the chloromethylation of *t*-butylbenzene, following the procedure of Bert.[8] The *t*-butylbenzyl chloride was reduced quantitatively in absolute methanol using 50 lb. hydrogen pressure over palladium on calcium carbonate. Infrared analysis of the product revealed that it was contaminated by a considerable amount of the *meta* isomer, which was not satisfactorily removed by fractional distillation through an efficient column. All but a trace of the *meta* compound was removed, however, through four crystallizations from methanol at −70°, m.p. −57°, b.p. 193° (atm.), n^{20}_D 1.4919. The removal of the *meta* compound could be followed smoothly by infrared analysis.

p-Di-*t*-butylbenzene was prepared from 1 mole of benzene and 2 moles of *t*-butyl alcohol in the presence of 1 mole of ferric chloride.[9] After two distillations under reduced pressure and three recrystallizations from methanol, the product melted at 77° (m.p. 76°).[10]

The methods used to minimize adventitious traces of water in the system and to prepare, isolate, and determine the molecular weights of the polymers were those described previously.[4,6]

No isomerization of *p*-*t*-butyltoluene was effected at 0° in the nitrobenzene–carbon tetrachloride mixture with stannic chloride without monomer present as determined by infrared analysis.

Results

Styrene was polymerized by stannic chloride in carbon tetrachloride–nitrobenzene solvent mixture at 0°, in the presence of various concentrations of the mono- and dialkylbenzenes. For each compound, control polymerizations containing no added compound were carried out and all polymerizations were stopped at low conversion. Table I lists the intrinsic viscosities of the polystyrenes obtained, together with the number average degrees of polymerization calculated from them,[4] and values of the molecular termination constant calculated using equation 1. Cumene is not included in the ta-

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[1] For the sixth paper of this series, see C. G. Overberger and G. F. Endres, *J. Polymer Sci.*, **16**, 283 (1955).

[2] This paper comprises part of a thesis presented by Gerard F. Endres in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the graduate school of the Polytechnic Institute of Brooklyn.

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[4] G. F. Endres and C. G. Overberger, THIS JOURNAL, **77**, 2201 (1955).

[5] Equation 1 is analogous to the chain transfer equation of free radical polymerization; F. R. Mayo, *ibid.*, **65**, 2324 (1943).

[6] C. G. Overberger, L. H. Arond and J. J. Taylor, *ibid.*, **73**, 5541 (1951).

[7] G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publ. Corp., New York, N. Y., 1946.

[8] L. Bert, *Bull. soc. chim.*, **37**, 1252 (1925).

[9] W. M. Potts and R. J. Dodson, THIS JOURNAL, **61**, 2553 (1939).

[10] H. Meyer and K. Bernhauer, *Monatsh.*, **53/54**, 727 (1929).

ble since reproducible data have not been obtained for this compound in carbon tetrachloride solvent.

TABLE I

EFFECTS OF AROMATIC HYDROCARBONS ON DEGREE OF POLYMERIZATION IN CARBON TETRACHLORIDE SOLVENT

Initial styrene concentration 1.95 *M;* stannic chloride concn. 0.023 *M;* solvent, carbon tetrachloride–nitrobenzene (nitrobenzene 40% vol. of total charge); $t = 0°$.

$(R)_0/(M)_0$, initial molar ratio	Conv., %	$[\eta]$, 100 cc./g.	$\bar{P}_n$	$k_r/k_p \times 10^3$
R = Toluene				
0	17	0.289	180	. .
0.176	15	.247	142	8.49
.353	13	.216	116	8.80
.530	13	.193	97.5	8.89
.704	13	.174	83.4	9.17
R = Ethylbenzene				
0	16	0.294	184	. .
0.188	13	.250	145	7.91
.374	14	.220	119	8.02
.561	12	.197	101	7.97
.746	13	.178	86.2	8.26
R = *t*-Butylbenzene				
0	11, 15	0.305, 0.300	196, 190[a]	. .
0.215	12	.268	161	4.81
.431	13	.246	141	4.46
.645	13	.226	124	4.45
.859	15	.210	111	4.44
R = *p*-Cymene				
0	16, 15	0.303, 0.300	194, 190[a]	. .
0.166	11	.270	162	5.76
.330	16	.254	148	4.70
.498	20	.242	137	4.16
.661	18	.225	123	4.42
.825	19	.214	115	4.27
.992	20	.203	106	4.31
R = *p*-*t*-Butyltoluene				
0	8	0.191[b,c]	96	. .
0.146	10	.189	94	1.5
.258	9	.182	89	3.2
.369	11	.176	85	3.6
.485	11	.173	83	3.4
.724	*ca.* 10	.167	79	3.2
R = *p*-Di-*t*-butylbenzene				
0	8–10.5	0.162[b,d]	75	. .
0.076	5	.157	71	10
.151	5	.161	74	1
.228	4	.158	72	2
.303	13	.169	78	. .
.448	7	.155	70	2

[a] The mean of the two controls was taken as $\bar{P}_{n_0}$ in equation 1. [b] Mean of three controls. [c] This value of the intrinsic viscosity is considerably lower than that normally obtained for the polymerization in the absence of added compounds, and is probably due to the presence of an unusually high concentration of adventitious water. However, equation 1 predicts that this would not affect the value of k_r/k_p, provided that the water concentration is the same in all polymerizations of the series. [d] In this series the nitrobenzene concentration was lowered to 27.5% of the total volume, because of its adverse effect on the solubility of the hydrocarbon. The resultant decrease of the dielectric constant of the medium produced polymers of lowered degree of polymerization, but it has been shown that for *p*-xylene the molecular termination constant is independent of the dielectric constant (ref. 1).

In each case the molecular termination constant is independent of the concentration of agent, showing that the effects of these compounds are described accurately by equation 1. This is also evident in plots of $1/\bar{P}_n - 1/\bar{P}_{n_0}$ *vs.* $(R)_0/(M)_0$, which are linear and pass through the origin (Fig. 1). (The points for *p*-di-*t*-butylbenzene are more scattered, owing to the relatively small reductions in degree of polymerization.)

Polymerizations were also carried out in the presence of each of the four monoalkylbenzenes with the substitution of cyclohexane for carbon tetrachloride solvent, all other conditions being the same (Table II). With this solvent, values of k_r/k_p calculated, using equation 1, are concentration dependent, and plots of $1/\bar{P}_n - 1/\bar{P}_{n0}$ *vs.* $(R)_0/(M)_0$ are linear but do not pass through the origin. The data are shown as $1/\bar{P}_n$ *vs.* $(R)_0/(M)_0$ in Fig. 2.

TABLE II

EFFECTS OF AROMATIC HYDROCARBONS ON DEGREE OF POLYMERIZATION IN CYCLOHEXANE SOLVENT

Initial styrene concentration 1.95 *M;* stannic chloride concn. 0.023 *M;* solvent, cyclohexane–nitrobenzene (nitrobenzene 40% vol. of total charge); $t = 0°$

$(R)_0/(M)_0$, initial molar ratio	Conv., %	$[\eta]$, 100 cc./g.	$\bar{P}_n$	$k_r/k_p \times 10^3$
R = Toluene				
0	9, 10	0.323, 0.319	213, 209[a]	. .
0.223	8	0.261	155	7.76
.443	9	.221	120	8.20
.663	10	.192	97.1	8.39
.882	10	.171	81.0	8.63
R = Ethylbenzene				
0	11, 11	0.323, 0.321	214, 212[a]	. .
0.238	13	0.268	161	6.39
.478	13	.225	124	7.09
.718	11	.196	100	7.38
.956	13	.173	82.4	7.77
R = Cumene				
0	9	0.322	212	. .
0.265	10	.277	169	4.59
.523	10	.238	134	5.25
.785	11	.210	111	5.48
1.05	9	.188	94.2	5.64
R = *t*-Butylbenzene				
0	10	0.329, 0.326	219, 216[a]	. .
0.272	10	0.285	176	4.00
.544	9	.251	145	4.21
.805	9	.223	122	4.52
1.07	13	.200	103	4.73

[a] The mean of the two controls was taken as $\bar{P}_{n_0}$ in equation 1.

In both carbon tetrachloride and cyclohexane, none of the molecular terminating agents significantly affect the over-all rate of polymerization as estimated from the conversions and reaction times. This is in accord with more precise rate data previously reported for *p*-xylene, *p*-cymene, and *p*-*t*-butyltoluene and indicates that these compounds are chain transfer agents.[1]

Discussion

The slopes of the plots in Fig. 1 are taken as the best values of the molecular termination constants

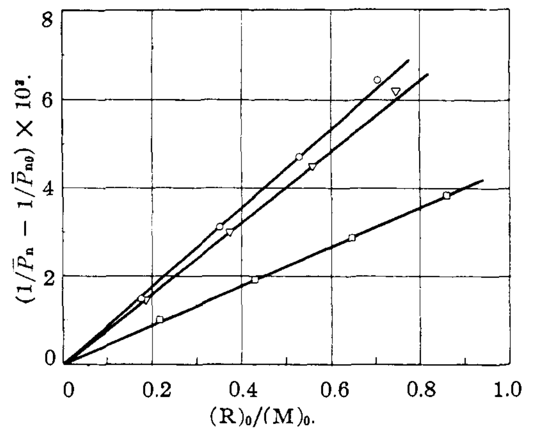


Fig. 1.—Monoalkylbenzenes in carbon tetrachloride–nitrobenzene solvent: ○, toluene; ▽, ethylbenzene; □, *t*-butylbenzene.

of the three monoalkylbenzenes in carbon tetrachloride, and these are listed in Table III. Values for the *p*-dialkylbenzenes obtained in the same way are given in Table IV, together with the previously reported value for *p*-xylene.[4] In an earlier communication[11] a higher molecular termination constant was reported for *p*-*t*-butyltoluene (6.2×10^{-3}). This is believed to have been due to the presence in the sample of considerable amounts of the *meta* isomer.[12]

TABLE III

MOLECULAR TERMINATION CONSTANTS AND RELATIVE REACTIVITIES OF MONOALKYLBENZENES

Substituent	$k_r/k_p \times 10^3$ CCl$_4$ diluent	C_6H_{12} diluent	Relative reactivity CCl$_4$ diluent	C_6H_{12} diluent	Propylation[a]	Bromination[b]
CH_3-	8.8	8.7	100	100	100	100
C_2H_5-	8.0	7.8	90	90	86	76
$(CH_3)_2CH-$	..	6.0	..	69	80	44
$(CH_3)_3C-$	4.5	5.0	50	57	67	23

[a] Reaction with propylene at 40°, aluminum chloride catalyst in nitromethane; ref. 15. [b] Reaction with bromine in 15% aqueous acetic acid at 24°; ref. 13a.

TABLE IV

MOLECULAR TERMINATION CONSTANTS AND RELATIVE REACTIVITIES OF *p*-DIALKYLBENZENES

Substituents	$k_r/k_p \times 10^3$	Relative reactivity
CH_3-, CH_3-	10.5	100
CH_3-, $(CH_3)_2CH-$	4.4	42
CH_3-, $(CH_3)_3C-$	3.3	31
$(CH_3)_3C-$, $(CH_3)_3C-$	2	*ca.* 20

From Fig. 2 it is seen that the deviation from equation 1 in cyclohexane solvent is not large but is nevertheless significant.

Although no explanation for this apparent anomaly can be offered at this time, it is believed that since the points for the experiments where molecular terminating agents were present are accurately linear, the slopes of these lines may be taken as the molecular termination constants. These are also listed in Table III, and the good agreement in the two solvents demonstrates that the k_r/k_p values are independent of the chemical nature of the non-polar solvent.

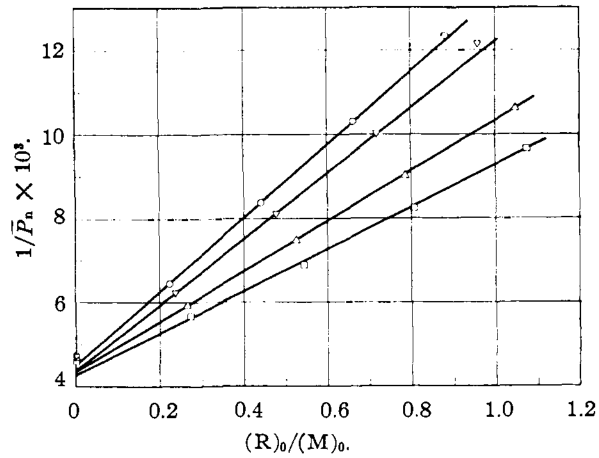
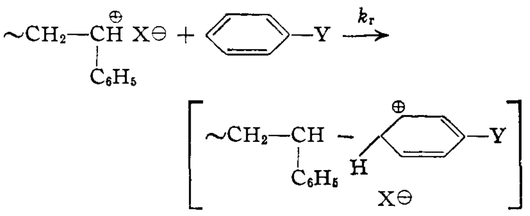


Fig. 2.—Monoalkylbenzenes in cyclohexane–nitrobenzene solvent: ○, toluene; ▽, ethylbenzene; △ cumene; □, *t*-butylbenzene.

The relative reactivities of the four monoalkylbenzenes in electrophilic aromatic substitution have been determined for halogenation,[13] nitration (toluene and *t*-butylbenzene only),[14] propylation[15] and mercuration,[16] and the *over-all* reactivity is always found to decrease in the order $CH_3- > C_2H_5- > (CH_3)_2CH- > (CH_3)_3C-$. Since in the present system the propagation rate constant k_p is presumably independent of the molecular terminating agent, k_r/k_p measures the relative reactivity of the agents toward the carbonium ion–anion pair of the active polymerization center. Such scales of reactivities are set up in Tables III and IV together with literature data for propylation and bromination, which represent the reported extremes of selectivity. The qualitative agreement supports the view that molecular termination by aromatic compounds in the present polymerization system proceeds through simple nuclear alkylation of the Friedel–Crafts type[1]



(2)

(plus other resonance forms)

Molecular termination in cationic polymerization appears to be a fairly sensitive method of determining relative reactivities of aromatic compounds toward carbonium ions, concerning which few quantitative data have been obtained in the

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(11) C. G. Overberger and G. F. Endres, THIS JOURNAL, **75**, 6349 (1953).

(12) See the Experimental section. The earlier sample was prepared by the alkylation of toluene by isobutyl alcohol in the presence of fuming sulfuric acid. It has been shown that the maximum purity of such alkylation products is 93% *para* and 7% *meta* [M. J. Schlatter and R. D. Clark, *ibid.*, **75**, 361 (1953)].

(13) (a) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943); (b) E. Berliner and F. J. Bondhus, THIS JOURNAL, **68**, 2355 (1946); (c) E. Berliner and F. J. Bondhus, *ibid.*, **70**, 854 (1948); (d) E. Berliner and F. Berliner, *ibid.*, **71**, 1195 (1949).

(14) H. Cohn, E. D. Hughes, M. H. Jones and M. G. Peeling, *Nature*, **169**, 291 (1952).

(15) F. E. Condon, THIS JOURNAL, **70**, 2265 (1948).

(16) H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2310 (1955).

past. The reactivities of a number of compounds in aluminum chloride-catalyzed acylation by acetyl chloride have been reported.[17] Alkylation studies have included the reaction of several compounds with *p*-nitrobenzyl chloride[18] or 3,4-dichlorobenzyl chloride[19] catalyzed by aluminum chloride, and with propene in the presence of boron trifluoride etherate or aluminum chloride–nitromethane.[15] The present system seems to offer selectivity comparable to the other alkylation methods, but the molecular termination constants of benzene and less reactive aromatic compounds are too small to be measured using styrene monomer under these conditions.[20] It is noteworthy that some of the most valuable data concerning reactivities toward free radicals have been obtained through similar studies of chain transfer in radical polymerization.[21]

The various alkyl groups in the mono- and dialkylbenzenes appear to activate the nucleus in accordance with their capacities for carbon–hydrogen hyperconjugation and contrary to their electrostatic inductive effects. However, the observed order could also be due to the steric effects of the groups on the *ortho* positions. From data on the isomer distribution in the bromination of toluene, it was reasoned that hyperconjugation must be operative as well as the steric effect to account for the difference in reactivity of toluene and *t*-butylbenzene.[13c] On the other hand, the distribution in the nitration of these compounds showed that in this reaction the steric effect is responsible for the decrease in over-all rate, while the rate of substitution at the *meta* and *para* positions increases in accordance with the inductive effect.[14,22] Similarly, rate decrease in propylation was shown to be largely a steric effect,[15] and most of the decrease in mercuration can be accounted for in the same way.[16]

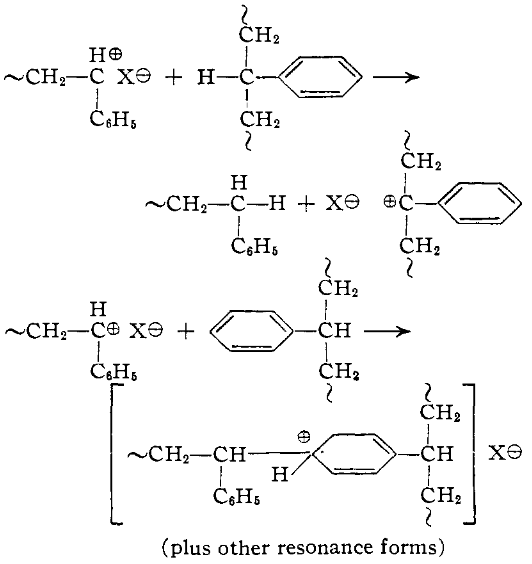
No data on isomer distribution have been obtained in the present work, but it appears probable that in molecular termination in cationic styrene polymerization the orders of reactivity of mono- and dialkylbenzenes are largely the result of the steric rather than the hyperconjugative factor. Recently, the apparently varying electronic influences of alkyl groups have been interpreted in terms of the electrophilicity of the attacking reagents.[23,24]

Highly electrophilic species, such as NO_2^+, $(CH_3)_2CH^+$, etc., are very reactive and little resonance stabilization is required for the transition state involved in their reaction with an aromatic nucleus. The low selectivity observed for these reagents may be explained from a consideration of the sites of highest electron density as determined by the inductive effect of the substituent. On the other hand, reagents of low electrophilicity such as bromine, are less reactive and resonance stabilization of the transition states (*e.g.*, hyperconjugation) is important in determining the selectivity.

The attacking species in cationic polymerization should be highly electrophilic, more similar in this respect to the nitronium ion or isopropylcarbonium ion than to bromine. This appears to be reflected in its relatively low selectivity toward the various alkyl groups compared to bromination (Table III). (In nitration by nitric acid in 90% aqueous acetic acid at 45°, the rate ratio toluene to *t*-butylbenzene is 100:64[14]).

In the above discussion it has been assumed that the aromatic hydrocarbons react only at the nucleus and there are no side-reactions at the alkyl groups. It is established, however, that carbonium ions can under certain conditions abstract hydrogen atoms and their electron pairs from tertiary aliphatic hydrocarbons.[25] In addition, attempted alkylation of *p*-cymene and similar compounds by olefins such as 4-methylcyclohexene in the presence of sulfuric acid or hydrogen fluoride results instead in hydride transfer from a tertiary or secondary side-chain carbon.[26] Hydride transfer must be unimportant in the present system, however, since neither cumene nor *p*-cymene seems to show an enhanced reactivity when compared with the other hydrocarbons in its series.

The above conclusion is of interest in connection with chain branching in the polymerization of styrene by stannic chloride, which has not been conclusively demonstrated but seems likely.[27] Polypropenes prepared with promoted aluminum bro-


(3)

(4)

(plus other resonance forms)

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[17] H. F. McDuffie, Jr., and G. Dougherty, This Journal, **64**, 297 (1942).

[18] S. C. J. Olivier and G. Berger, *Rec. trav. chim.*, **45**, 710 (1926).

[19] H. C. Brown and M. Grayson, This Journal, **75**, 6285 (1953). From the work of these authors it appears that alkylation by primary halides is a nucleophilic displacement reaction on the halide rather than simple electrophilic substitution by primary carbonium ions.

[20] Small chain transfer constants are measured precisely in free radical polymerization through high dilution of the monomer by the appropriate solvent. In the cationic polymerization of styrene, however, relatively low degrees of polymerization are obtained and dilution further reduces them so that molecular weight reductions due to compounds of low reactivity remain within the experimental error.

[21] (a) R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947); (b) J. A. Gannon, E. M. Fettes and A. V. Tobolsky, This Journal, **74**, 1854 (1952).

[22] K. L. Nelson and H. C. Brown, *ibid.*, **73**, 5605 (1951).

[23] H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).

[24] E. Berliner and F. Berliner, *ibid.*, **76**, 6179 (1954).

[25] P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1531 (1944).

[26] H. Pines, *et al.*, *ibid.*, **70**, 2123, 3859 (1948); **71**, 3534 (1949); **72**, 1563, 5521 (1950).

[27] Unpublished data obtained from light-scattering measurements by Dr. F. W. Billmeyer, Polychemical Dept., E. I. du Pont de Nemours and Co.

mide are highly branched, and isobutane has a marked lowering effect on the degree of polymerization. These effects have been attributed to tertiary hydrogen transfer from polymer chains or isobutane.[28] Branching in styrene polymerization could conceivably occur through hydride transfer (equation 3) followed by propagation from the resultant tertiary carbonium ion or alternatively through nuclear alkylation (equation 4).

The structural similarity of cumene and *p*-cymene to a segment of the polymer chain, and the expected steric hindrance toward attack on a hydrogen attached to the central carbon chain of polystyrene, make it highly probable that any branching in this system takes place through nuclear alkylation.

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BROOKLYN, N. Y.

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(28) (a) C. M. Fontana, G. A. Kidder and R. J. Herold, *Ind. Eng. Chem.*, **44**, 1688 (1952); (b) C. M. Fontana, R. J. Herold, E. J. Kinney and R. C. Miller, *ibid.*, **44**, 2955 (1952).

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

The Reaction of Thiosemicarbazide with Orthoesters

BY C. AINSWORTH

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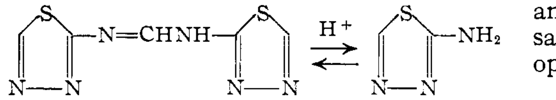
Thiosemicarbazide and excess ethyl orthoformate when heated together on the steam-bath formed N,N′-bis-(1,3,4-thiadiazole-2)-formamidine (I). The intermediates, ethyl formate thiosemicarbazone (III), 2-amino-1,3,4-thiadiazole (II) and ethyl N-(1,3,4-thiadiazole-2)-formimidate(IV), were isolated. A possible mechanism of these transformations is discussed.

Based on the report of Stolle and Bowles[1] that thiocarbohydrazide with ethyl orthoformate formed 4-amino-1,2,4-triazole-3-thiol, it was surmised that reaction of thiosemicarbazide and ethyl orthoformate might furnish a simple synthesis of 1,2,4-triazole-3(5)-thiol. The reaction, however, proved to be more complex.

When thiosemicarbazide was heated overnight on the steam-bath with excess ethyl orthoformate, a compound with the molecular formula $C_5H_4N_6S_2$ resulted. This compound was formulated as N,N′-bis-(1,3,4-thiadiazole-2)-formamidine (I). The evidence for this assignment was based on the fact that compound I on acid hydrolysis formed 2-amino-1,3,4-thiadiazole (II). The supposition that 2-amino-1,3,4-thiadiazole was an intermediate in the formation of compound I was substantiated by the fact that compound II with ethyl orthoformate yielded compound I. Further, thiosemicarbazide and only *one* mole of ethyl orthoformate when heated together on the steam-bath overnight formed 2-amino-1,3,4-thiadiazole. From the reaction of equimolar quantities of thiosemicarbazide and ethyl orthoformate, heated on the steam-bath for two hours, ethyl formate thiosemicarbazone (III) was isolated. A small yield of compound III was obtained from a mixture of thiosemicarbazide and excess ethyl orthoformate heated on the steam-bath for ten minutes.

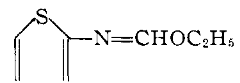
$NH_2NHCSNH_2 + HC(OC_2H_5)_3 \longrightarrow$



I II

$$C_2H_5OCH{=}NNHCSNH_2 \quad \text{III}$$

When thiosemicarbazide and excess ethyl orthoformate were heated together at about 140° overnight, a liquid corresponding to ethyl N-(1,3,4-thiadiazole-2)-formimidate (IV) was obtained. Compound IV with a one molar ratio of 2-amino-1,3,4-thiadiazole formed compound I, indicating that IV might be an intermediate in the formation of I. After compound IV had stood for several months in a loosely stoppered bottle it appeared that a change had taken place. Upon analysis of the contents the following compounds were isolated: ethyl alcohol, ethyl formate, ethyl orthoformate and compounds I and IV. In addition, when a sample of compound IV was allowed to stand in an open container overnight, compound I was formed.



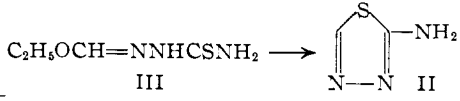
IV

The reaction of aniline with ethyl orthoformate was reinvestigated recently by Roberts and DeWolfe.[2] From physical studies they arrived at the mechanism given below for this reaction, where R equals phenyl. We believe that these reversible equations help explain our observations. The reaction of thiosemicarbazide and ethyl orthoformate likely passes through the intermediate III

$$RNH_2 + HC(OC_2H_5)_3 \underset{r}{\overset{f}{\rightleftarrows}} RN{=}CHOC_2H_5 + 2C_2H_5OH \quad (1)$$

$$RN{=}CHOC_2H_5 + RNH_2 \underset{r}{\overset{f}{\rightleftarrows}} RN{=}CHNHR + C_2H_5OH \quad (2)$$

$NH_2NHCSNH_2 + HC(OC_2H_5)_3 \longrightarrow$



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(1) R. Stolle and P. E. Bowles, *Ber.*, **41**, 1099 (1908).

(2) R. M. Roberts and R. H. DeWolfe, THIS JOURNAL, **76**, 2411 (1954).