[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

1,3-Shifts. VI. The Kinetics of the Rearrangement of α-Benzyloxystyrene[1a]

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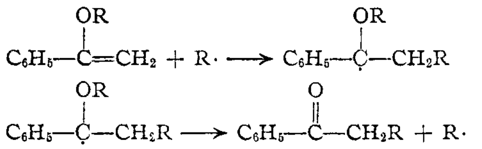
The kinetics of the azo-bis-isobutyronitrile catalyzed and of the uncatalyzed thermal rearrangement of α-benzyloxystyrene have been studied. They are in agreement with the mechanism previously proposed, involving a free radical chain process. Further information was obtained by determining the amounts of initiation and termination products *via* isotope dilution analysis.

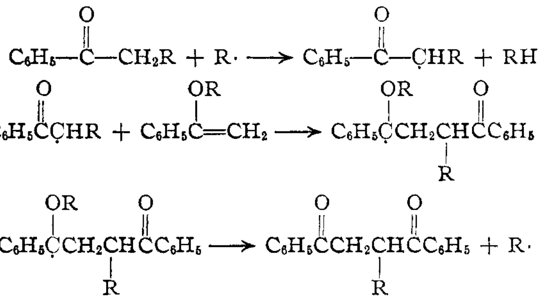
It has previously been shown that the rearrangement of optically active α-2-butoxystyrene proceeds with racemization of the migrating group,[3] that the rearrangement of α-neopentoxystyrene proceeds without concurrent rearrangement within the neopentyl group,[3] that the rearrangement of α-methoxystyrene is intermolecular,[4] and that the reactions may be catalyzed by free radicals.[3] On the basis of these observations, a free radical chain process was proposed as the mechanism with the chain propagation steps



$$C_6H_5\text{—}\overset{OR}{\overset{|}{C}}{=}CH_2 + R\cdot \longrightarrow C_6H_5\text{—}\overset{OR}{\overset{|}{\underset{\cdot}{C}}}\text{—}CH_2R$$

$$C_6H_5\text{—}\overset{OR}{\overset{|}{\underset{\cdot}{C}}}\text{—}CH_2R \longrightarrow C_6H_5\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_2R + R\cdot$$

It seemed desirable to obtain kinetic data concerning this rearrangement in order to establish more firmly a mechanism for the process. The alkoxystyrenes did not appear suitable since coupling by-products are formed.[5] These compounds appear to arise by the abstraction by a free radical of an α-hydrogen from the ketonic rearrangement product, followed by a reaction corresponding to the propagation steps in the rearrangement.



$$C_6H_5\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_2R + R\cdot \longrightarrow C_6H_5\text{—}\overset{O}{\overset{\|}{C}}\text{—}\underset{\cdot}{C}HR + RH$$

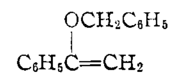
$$C_6H_5\overset{O}{\overset{\|}{C}}\underset{\cdot}{C}HR + C_6H_5\overset{OR}{\overset{|}{C}}{=}CH_2 \longrightarrow C_6H_5\overset{OR}{\overset{|}{\underset{\cdot}{C}}}CH_2\underset{\underset{R}{|}}{CH}\overset{O}{\overset{\|}{C}}C_6H_5$$

$$C_6H_5\overset{OR}{\overset{|}{\underset{\cdot}{C}}}CH_2\underset{\underset{R}{|}}{CH}\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}CH_2\underset{\underset{R}{|}}{CH}\overset{O}{\overset{\|}{C}}C_6H_5 + R\cdot$$

Support for this mode of reaction may be found in the observation than when α-methoxystyrene was heated in the presence of toluene, the product derived from the addition of benzyl radicals was found.[5]

It was observed that α-1-phenethoxystyrene rearranged essentially quantitatively to the expected product, β-phenylbutyrophenone.[3] This is in accord with the proposed mechanism since the 1-phenethyl radical would have a lower reactivity than the ordinary alkyl radicals and therefore would be less likely to abstract a hydrogen atom from the ketone. Thus, the principal side reaction should be minimized. The observation suggested that α-benzyloxystyrene would be particularly suited to the present purpose.

α-Benzyloxystyrene was prepared by the reaction of styrene with benzyl alcohol, iodine and mercuric oxide giving an iodoether which was dehydrohalogenated with alcoholic potassium hydroxide. The rearrangement was induced both thermally and using azo-bis-isobutyronitrile as a catalyst. The yield of purified rearrangement product was 80 and 88%, respectively, and the actual yield appeared to be somewhat higher. Thus the reactions appeared to be suited to a kinetic study.



$$C_6H_5CH{=}CH_2 + C_6H_5CH_2OH \xrightarrow[HgO]{I_2} C_6H_5\overset{OCH_2C_6H_5}{\overset{|}{C}}HCH_2I \xrightarrow[KOH]{alc.} C_6H_5\overset{OCH_2C_6H_5}{\overset{|}{C}}{=}CH_2$$

The azo-bis-isobutyronitrile-catalyzed reaction was studied first. It proceeded at a convenient rate at temperatures between 60 and 75°. The rate of reaction was determined by following the appearance of the 5.93 μ carbonyl band of the ketone, and also by noting the disappearance of the 8.88 μ band of the reactant. The former could be more accurately determined because of the stability of the base line in the vicinity of 6 μ from one sample to another. The variation in base line near 9 μ made the values for the ether relatively less accurate. However, within the experimental error, the rate constant for the disappearance of ether was equal to that for the appearance of ketone. All of the rate constants are based on the latter.

In order to be able to compare the rate of formation of ketone with the rate of production of free radicals from the initiator, it was necessary to measure the rate of decomposition of azo-bis-isobutyronitrile under the reaction conditions. This was done gasometrically, following the evolution of nitrogen. Good first-order plots were obtained and the data are shown in Table I.

TABLE I

RATE OF DECOMPOSITION OF AZO-BIS-ISOBUTYRONITRILE IN α-BENZYLOXYSTYRENE SOLUTION

T, °C.	[AIBN]		k_1, sec.$^{-1}$ × 10^5	k_1 (xylene) × 10^5
59.65	0.236		1.09	
59.65	.236		1.20	
59.65	.236		1.06	
		Av.	1.11	1.10
75.83	0.233		9.60	9.92

Also, the rate of decomposition of the catalyst in xylene solution[6] at the same temperature is given for comparison. The close similarity in the rate constants suggests that there was no induced decomposition of the catalyst during the reaction. From these data the activation parameters were calculated to be E_a = 31 kcal./mole, $\Delta S^{\ddagger}$ = 12 e.u. These values are typical for the decomposition of this compound in other solvents.

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[1] (1) This work was supported by the A. P. Sloan Foundation to whom we express our sincere appreciation. (b) Present address: Department of Chemistry, Yale University, New Haven, Conn.

[2] Taken from parts of theses submitted by R. R. Kintner and E. L. Motell to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree; 1957 (RRK), 1961 (ELM).

[3] K. B. Wiberg and B. I. Rowland, *J. Am. Chem. Soc.*, **77**, 1159 (1955).

[4] K. B. Wiberg, T. M. Shryne and R. R. Kintner, *ibid.*, **79**, 3160 (1957).

[5] E. H. MacDougall, W. M. Lauer and M. A. Spielman, *ibid.*, **55**, 4089 (1933); W. M. Lauer and M. A. Spielman, *ibid.*, **55**, 4923 (1933); M. A. Spielman and C. W. Mortenson, *ibid.*, **61**, 666 (1939); **62**, 1609 (1940).

[6] F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949). *Cf.* also R. Petersen, J. Markgraf and S. Ross, *ibid.*, **83**, 3819 (1961), for the effect of solvent on the rate of decomposition of azo-bis-isobutyronitrile.

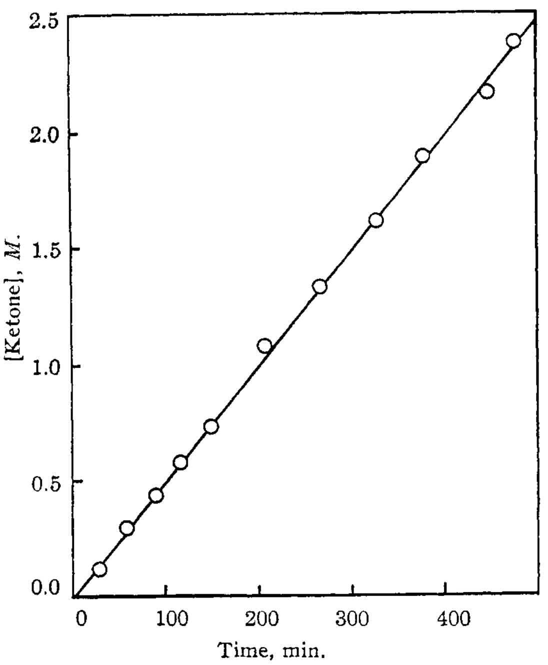

Fig. 1.—Zero-order plot for the catalyzed rearrangement of α-benzyloxystyrene.

For the catalyzed rearrangement, a plot of ketone concentration against time gave a fairly good straight line (Fig. 1). The zero-order rate constants thus obtained were useful in establishing the order of the reaction with respect to substrate and catalyst concentration and their values are given in Table II. It should be noted that the reaction is not zeroth order, but this apparent result is due to a fortuitous balancing of (unknown) effects. This is shown by the fact that the zero-order rate constants are a function of concentration.

TABLE II

RATE CONSTANTS FOR THE CATALYZED REARRANGEMENT OF α-BENZYLOXYSTYRENE

Run	[S]	[I]	*T*, °C.	$k_0 \times 10^{5a}$	$k_{3/2} \times 10^{5b}$	*m*
1	4.80	0.1234	59.65	6.00	3.56	54.3
2	4.73	.2360	59.65	8.33	3.62	38.2
3	4.73	.2360	59.75	7.90	3.44	37.1
4	4.73	.2360	59.65	8.30	3.60	36.7
5	4.61	.3579	59.65	10.4	3.78	29.9
6	3.27	.2333	59.65	5.80	3.66	26.0
7	2.32	.2331	59.65	3.87	3.47	17.6
8	4.66	.2326	75.83	55.3	24.6	27.5

[a] Units are moles l.$^{-1}$ sec.$^{-1}$. [b] Units are l.$^{1/2}$ mole$^{-1/2}$ sec.$^{-1}$.

The order of the reaction with respect to the concentrations of the reactants may be determined from a plot of log k_0 against log concentration of the compound whose concentration is being varied. This type of plot using the data from runs 2, 3, 4, 6 and 7 (neglecting the small change in catalyst concentration) gave a slope of 1.05 indicating the reaction to be first order with respect to benzyloxystyrene concentration. A similar plot using the data for runs 1, 2, 3, 4 and 5 gave a slope of 0.52 indicating the reaction to be half-order with respect to the catalyst concentration. If the benzyloxystyrene is symbolized as S, and the catalyst as I, then the rate law may be written

$$v = k_{3/2}[\mathrm{S}][\mathrm{I}]^{1/2}$$

It should be noted that the concentration of α-benzyloxystyrene was varied by diluting it with cyclohexane. Since this is undoubtedly a free radical reaction, it would be expected that this change in solvent would not affect the rate constants to a marked degree, and that the above conclusion is valid. The range over which the concentrations were varied was limited on one hand by the low solubility of the catalyst in the solutions, and on the other hand by the fact that the chain length was small, and decreased with decreasing benzyloxystyrene concentration. Thus, if too dilute solutions were used, the rates of initiation and propagation would become almost equivalent.

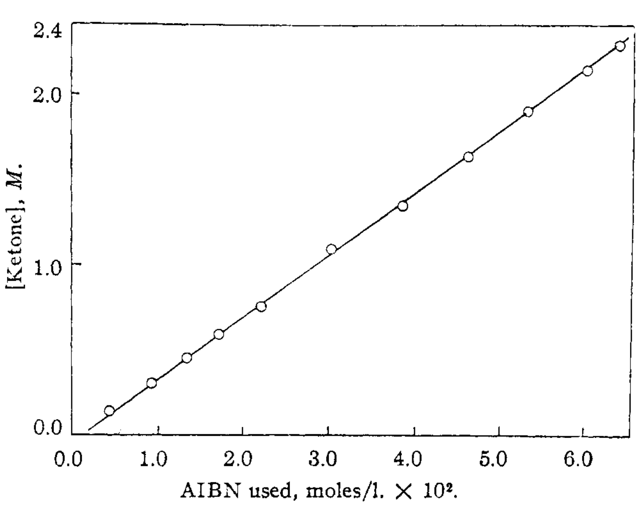

Fig. 2.—Determination of kinetic chain length.

The chain lengths may be obtained by plotting the amount of ketone formed against the amount of catalyst consumed at different times. A typical plot is shown in Fig. 2. For much of the reaction, this plot may be represented by a straight line, and the slopes of these lines are given in Table II in the column headed *m*. These slopes are twice the chain length since the initiator gives two radicals. Properly, the chain length should be the ratio of the amount of α-benzyloxystyrene consumed to the amount of catalyst consumed. This is equivalent to the values calculated above since the product of the initiation step has an infrared carbonyl absorption at the same place as the product ketone, and the two are included together in the amount of ketone formed.

Knowing the rate law for the reaction, it is desirable to obtain the three-halves-order rate constants. This requires the integration of the expression

$$\mathrm{d}y/\mathrm{d}t = k_{3/2}[\mathrm{S} - y][\mathrm{I} - x]^{1/2}$$

This may be done by substituting $[\mathrm{I}]_0{}^{1/2}e^{-kt/2}$ for $[\mathrm{I} - x]^{1/2}$ since the concentration of I is a function only of time and not of the concentration of the other reagent. If one performs the integration and expands the exponential as a series, the required plot is found to be in $[\mathrm{S} - y]$ against $t(1 - k_it/4)$, where the slope will be $-k_{3/2}[\mathrm{I}]_0{}^{1/2}$. Since the experimental data fit a zeroth-order plot, it is obvious that the above plot will be non-linear and therefore not satisfactory for establishing rate constants. However, in any case, if one takes the tangent of a plot of concentration against time at zero time, and divides by the concentrations, one will obtain the rate constant. In the present case, the tangent is easily obtained since the zero-order plot is linear. The three-halves-order rate constants given in Table II were obtained by dividing the zero-order constants by the concentrations of both reagents, and it can be seen that the values are constant. The reason for zero-order behavior in individual runs is obscure, but it may arise from any of a number of effects, such as a small autocatalytic component to the reaction.[7]

(7) Since the chain length is short, the apparent zeroth-order kinetics may in part arise from the formation of dimethylketenecyanoisopropylimine (M.

TABLE III

DETERMINATION OF INITIATOR EFFICIENCY

Reactants		Scavenger, g.						
α-Benzyloxystryene, g.	AIBN,[a] g.	β-Cyanoisovalerophenone	Act. (× 10^{-8} d.p.m./m.) 3 recryst.	4 recryst.	Init. prod. formed, g.	Av. chain length Actual[c]	Kinetic[b]	Efficiency, %
2.006	0.0677	0.5033	...	8.64	0.0670	26.6	14.9	56
2.001	.0783	.5162	10.2	10.5	.0860	20.8	13.8	66
2.075	.0807	.5146	9.82	9.78	.0790	23.4	13.8	59
2.020	.0768	.5127	...	9.82	.0790	22.7	14.0	61
							Av.	61 ± 3

[a] Activity = 1.47×10^{10} d.p.m./m. [b] Based on run 8 and the observed effect of AIBN concentration on the chain length. [c] Chain ength = moles of α-benzyloxystyrene used/mole of initiation product formed.

The activation parameters may be determined from these data and are $E_a = 27$ kcal./mole, $\Delta S^{\ddagger} = 0$ e.u.

The relationship between the observed rate law and the mechanism of the reaction may now be considered. If the previously proposed mechanism is correct, the steps including initiation and termination must be

$$\mathrm{I} \xrightarrow{k_1} 2\mathrm{R}\cdot$$

$$\mathrm{R}\cdot + \mathrm{S} \xrightarrow{k_2} \mathrm{RS}\cdot$$

$$\mathrm{RS}\cdot \xrightarrow{k_3} \mathrm{P_i} + \mathrm{B}\cdot$$

$$\mathrm{B}\cdot + \mathrm{S} \xrightarrow{k_4} \mathrm{BS}\cdot$$

$$\mathrm{BS}\cdot \xrightarrow{k_5} \mathrm{P} + \mathrm{B}\cdot$$

$$2\mathrm{R}\cdot \xrightarrow{k_6} \mathrm{R_2}$$

$$\mathrm{R}\cdot + \mathrm{B}\cdot \xrightarrow{k_7} \mathrm{RB}$$

$$2\mathrm{B}\cdot \xrightarrow{k_8} \mathrm{B_2}$$

where I is the initiator, R· is the radical derived from the initiator, S is the substrate, P_i is the product resulting from the initiation step, P is the normal product, B· is the benzyl radical, and R_2, RB and B_2 are the respective coupling products. As a first approximation, one might expect that the coupling of two benzyl radicals would be the important chain-terminating step and, if this were so, the application of the steady-state approximation would give as the rate law

$$v = 2k_i[\mathrm{I}] + \frac{(2k_1)^{1/2}k_4}{k_8^{1/2}}[\mathrm{S}][\mathrm{I}]^{1/2}$$

in which the first term would be the rate of initiation, which may be neglected in favor of the second term. This is of the form required by the kinetic experiments.

We now wish to test the assumption that coupling of benzyl radicals is the only important chain-terminating reaction. This requires that one first determine the initiator efficiency, for it is known that a significant amount of azo-bis-isobutyronitrile reacts *via* a process which does not produce radicals capable of initiating polymerization.[8]

The product of the initiation step is β-cyanoisovalerophenone, and if one were to determine the amount of this which was formed and compare this with the amount of α-benzyloxystyrene consumed, the average chain length would be known. A comparison of this with the kinetically determined chain length would give the initiator efficiency.

The rearrangement was effected under the conditions of run 8 (Table II) using azo-bis-isobutyronitrile-C^{14}, and was allowed to proceed for ten half-lives. The reaction product was treated with a known amount of unlabeled β-cyanoisovalerophenone. In order to facilitate isolation, the nitrile was hydrolyzed to the corresponding acid, separated, and purified by recrystallization. The activity of the acid was determined by liquid scintillation counting, and from the result the amount of β-cyanoisovalerophenone formed was calculated. The results are given in Table III.

The observed initiator efficiency (61%) seems quite reasonable in comparison with the results obtained in other systems using the same initiator.[8] At the same time it shows that the coupling of the cyanoisopropyl radical with some other radical is not the major chain-terminating reaction for, if it were, a lower apparent efficiency would have been observed.

The amount of dibenzyl formed was then determined, again using isotope dilution analysis. Carbon-14 labeled α-benzyloxystyrene was prepared and rearranged under the same conditions as above. Unlabeled dibenzyl was added to the reaction product, and then isolated *via* liquid chromatography. The activity of the dibenzyl was determined giving the results shown in Table IV.

TABLE IV

TERMINATION AND CHAIN TRANSFER PRODUCTS

React-ant, g. α-Benzyloxystyrene[a]	Scavenger Dibenzyl, g.	Toluene, ml.	Activity (× 10^{-7} d.p.m./m.) Dibenzyl		Toluene	Products, g. Dibenzyl	Toluene
1.949	1.948	25	8.02[b]	7.73[c]	1.38	0.0148	0.0533
1.997	1.996	25	8.04	8.24	1.48	0.0158	0.0572

[a] Activity = 5.61×10^9 d.p.m./mole. [b] After three recrystallizations. [c] After four recrystallizations.

From 2.0 g. of α-benzyloxystyrene (9.5 mmoles), and with a chain length of 23.4 (average of four determinations), there should be obtained 0.20 mmole of dibenzyl if this were the only chain termination product. The amount actually found was 0.084 mmole, or 42% of the theoretical amount. Thus, about half of the termination reaction involves the coupling of two benzyl radicals.

Since chain transfer, with the ketone as the chain transfer agent, was a common characteristic of the rearrangement of α-alkoxystyrenes, the possibility of chain transfer was examined in this case also. Scavenging the above reaction mixture with toluene, and the determination of the activity of the toluene thus obtained gave the data shown in Table IV. It can be seen that about 6% of the theoretical amount of toluene was obtained (based on *all* of the benzyl groups appearing as toluene). Thus, even in this case, chain transfer is an important step. The remainder of the termination reaction then probably involves the combination of two α-keto radicals, or of one α-keto radical and one benzyl radical.

The possibility that some of the toluene was formed by the reaction of benzyl radicals with dibenzyl was

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Talât-Erben and S. Bywater, *J. Am. Chem. Soc.*, **77**, 3710 (1955)) in the decomposition of the catalyst, and the subsequent decomposition of this intermediate to free radicals (*cf.* J. C. Bevington and H. G. Troth, *Trans. Faraday Soc.*, **58**, 186 (1962)).

(8) G. S. Hammond, J. N. Sen and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955). *Cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Ch. 3.

also examined by scavenging the reaction mixture with 1,2,3-triphenylpropane. This would be the product of the combination of a benzyl radical with the radical derived from dibenzyl, and has been observed in other reactions involving benzyl radicals.[9] The amount of triphenylpropane was less than 1% of the dibenzyl which was found, and thus reactions leading to this compound are a negligible component of the total reaction.

It was also found that in the absence of an initiator and of oxygen, the rearrangement would proceed if the temperature were raised to about 180°. The rate of this reaction was found to be reproducible and thus it appears to be an uncatalyzed, thermal reaction. The experimental data were found to give a linear plot when treated as a second-order reaction (Fig. 3) and the rate constants are given in Table V. It may be noted that the second-order rate constants were not changed when the concentration of α-benzyloxystyrene was halved, indicating again that it is a second-order reaction.

TABLE V

RATE CONSTANTS FOR THE THERMAL REARRANGEMENT OF α-BENZYLOXYSTYRENE

[Benzyloxystyrene], M	T, °C.	$k_2 \times 10^5$ l. mole^{-1} sec.$^{-1}$
4.57	158.0	1.14
4.57	158.0	1.05
4.53	174.0	3.67
4.53	174.0	3.85
2.27	174.0	3.28
2.27	174.0	3.84

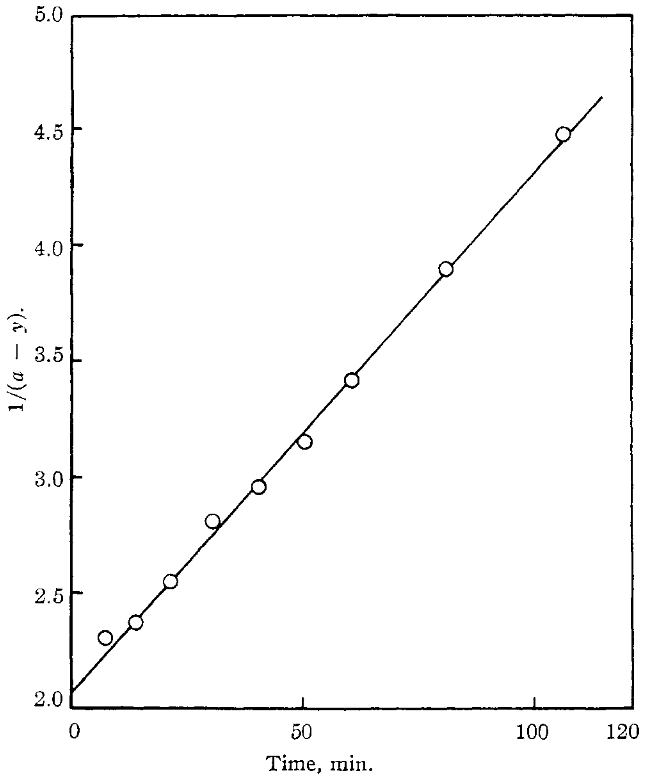

Fig. 3.—Second-order plot for the uncatalyzed rearrangement of α-benzyloxystyrene.

There are two possibilities which must be considered for this reaction. The first is a radical chain reaction whose propagation and termination steps are similar to those proposed for the catalyzed reaction. The second is a bimolecular reaction involving an eight-membered cyclic activated complex such as has been suggested by Spielman and Mortenson.[5] If a radical chain process were operative, the initiation step would have to be second order with respect to α-benzyloxystyrene. Similar behavior has been observed in the thermal polymerization of styrene[10] and thus such a process does not seem unreasonable here.

If the radical chain process were operative, then one would expect some dibenzyl to be formed as a result of the termination step. A quantitative comparison could not be made, for there is no convenient method for determining the chain length for the reaction. If, on the other hand, no dibenzyl were formed, then it would be unlikely for the free radical process to be correct. The amount of dibenzyl formed was determined as before. Starting with α-benzyloxystyrene having an activity of 1.48 × 10^8 d.p.m./mole, and scavenging with an equal amount of dibenzyl, the latter was found to have an activity of 3.50 and 3.42 × 10^5 d.p.m./mole after two and three recrystallizations, respectively. This is about one-sixth of the amount found in the catalyzed reaction. The amount is too small to be definitive, but it suggests that at least part of the thermal reaction proceeds *via* the radical chain process.

Experimental

α-Benzyloxystyrene.—Freshly distilled styrene (41.8 g., 0.4 mole) was added with stirring to a mixture of 104 g. (0.96 mole) of benzyl alcohol, 50.7 g. (0.2 mole) of iodine and 21.7 g. (0.1 mole) of mercuric oxide which was cooled in an ice-bath. The mixture was stirred overnight and was allowed to come to room temperature as the ice melted. The solution was filtered and then washed with potassium iodide solution followed by sodium bisulfite solution and water. The solution was dried over anhydrous sodium sulfate giving a product which was quite stable and which could be converted to the α-benzyloxystyrene as required. This was important since only freshly distilled samples of the benzyloxystyrene gave good results in the kinetic studies.

In a typical case, 8.8 ml. of the above material was added to a boiling solution of 2.24 g. of potassium hydroxide in 15 ml. of 95% ethyl alcohol. The solution was heated to reflux for 5 minutes and then tightly stoppered and left overnight. The solution was diluted with 10 ml. of water and extracted three times with pentane. The pentane solution was washed with water and dried over anhydrous sodium sulfate. Distillation gave 2.34 g. (51%) of α-benzyloxystyrene, b.p. 125° at 0.4 mm., n^{25}D 1.5850, d^{25} 1.058.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.7. Found: C, 85.7; H, 6.7.

Thermal Rearrangement.—α-Benzyloxystyrene (0.65 g.) was sealed in an evacuated Pyrex tube and heated to 207° for 3 hours. On cooling, the contents of the tube solidified. Recrystallization from *n*-hexane gave 0.52 g. (80%) of β-phenylpropiophenone, m.p. 70–71°; oxime, m.p. 83.4–83.8°; semicarbazone, m.p. 145.5–145.7°.[11]

Catalyzed Rearrangement.—A sealed, evacuated tube containing 3.58 g. of α-benzyloxystyrene and 0.094 g. of azo-bis-isobutyronitrile was heated to 75° for 24 hr. The solid product was recrystallized from *n*-hexane giving 3.07 g. of β-phenylpropiophenone (88%), m.p. 70–71°.

Kinetic Method.—Freshly distilled α-benzyloxystyrene was added to a tared 7-mm. glass tube sealed at one end, and the weight determined. The initiator and diluent (cyclohexane), if used, were also weighed into the tube. The tubes were degassed at less than 0.001 mm. pressure, ensuring the removal of oxygen which had been shown to have a catalytic effect on the reaction. The tubes were sealed off, wrapped in aluminum foil, and inserted into the thermostat. From 9–12 tubes were used in each run. As a check, some tubes containing only the alkoxystyrene were run simultaneously, and in all cases the amount of ketone formed was negligible.

The thermostat used for the catalyzed reaction was a standard water thermostat which could be regulated to ±0.02°. The thermometer used was checked against NBS calibrated thermometers. The thermostat used for the thermal reactions was a silicone oil-bath which could be regulated to ±0.1° using a standard mercury thermoregulator.

Analytical Methods.—A number of methods for determining the concentration of alkoxystyrene and ketone in the reaction

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[9] E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 131 (1952); E. Eliel, private communication.

[10] *Cf.* C. Walling, ref. 8, pp. 180-184.

[11] The ketone m.p. is reported as 73°; the semicarbazone, 144° ("Tables for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, Ohio, 1960).

mixtures was tried, but the only successful method was that using the infrared spectrum. Cyclohexane was found to be the most satisfactory solvent, and 0.3 *M* solutions were used throughout. Curves of % ketone against the 5.93 μ carbonyl peak intensity and of % ether against the 8.88 μ band intensity were constructed using mixtures of known amounts of ketone and ether. The analysis for % ketone was very satisfactory since the base line near 6 μ was very stable from one reaction mixture to the next. The base line near 9 μ was not as stable and led to some uncertainty about the % ether in the reaction products. For this reason, all of the rate constants are given for the appearance of ketone. In all cases, the rate of disappearance of ether and the rate of appearance of ketone (presumably both the product ketone and that formed by the initiation step since they have the same carbonyl band) was the same within experimental error.

Analysis for β-Cyanoisovalerophenone.—The rearrangement of α-benzyloxystyrene was carried out under the conditions for run 8, using azo-bis-isobutyronitrile-C^{14}, for a period of 24 hr. The contents of the tube were transferred to a flask with benzene, and a weighed quantity of β-cyano-isovalerophenone (quantities given in Table III) was added. The benzene was evaporated, and concentrated hydrochloric acid (16.5 ml.) and water (20 ml.) were added. After heating to reflux for 24 hr., the solution was made basic and was extracted three times with ether. The aqueous solution was acidified and extracted with three 30-ml. portions of ether. Evaporation of this ether solution, followed by recrystallization from petroleum ether–benzene, gave the β-benzoyl-α,α-dimethylpropionic acid, m.p. 169.5–171°; 2,4-dinitrophenylhydrazone, m.p. 197.5–198.5°.[12] The activity of the sample was determined by liquid scintillation counting[13] giving the data in Table III.

Analysis for Dibenzyl and Toluene.—α-Benzyl-C^{14}-oxystyrene was prepared by the procedure described above, except that benzyl-C^{14} alcohol was used. The rearrangement was carried out as above, and the contents of the tube were placed in a flask containing 25 ml. of toluene and a weighed quantity of dibenzyl. The mixture was warmed until the contents of the tube had dissolved, and was heated under reflux for 5 minutes. The toluene was separated by distillation, and a middle fraction was taken for C^{14} analysis. To the residue was added 15 ml. of pentane, and the precipitated β-phenylpropiophenone was removed by filtration. The pentane was added to an alumina-packed column, which was then eluted with pentane. The dibenzyl came through rapidly, and was shown to have less than 0.1% of the ketone by comparing the intensities of the ultraviolet absorption at 244 and 269 mμ. A very small amount of ketone will cause a noticeable change in the ratio of intensities at these two wave lengths. The dibenzyl was further purified by three (sample 1) or four (sample 2) recrystallizations from ethanol–water. The data for the C^{14} analyses are given in Table IV.

The thermal rearrangement was carried out at 174° for 18 hr. (about 10 half-lives) using 3.11 g. of the benzyloxystyrene. To this was added 3.11 g. of dibenzyl and the latter was isolated as described above.

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[12] E. Rothstein and M. Saboor, *J. Chem. Soc.*, 425 (1943), reported acid m.p. 173°; 2,4-dinitrophenylhydrazone, m.p. 198–199°.

[13] The C^{14} analyses were performed by the New England Nuclear Assay Co., Boston, Mass.

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Polymerization of Benzene to *p*-Polyphenyl by Aluminum Chloride–Cupric Chloride[1]

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Benzene is polymerized under remarkably mild conditions on treatment with aluminum chloride–cupric chloride–water to a solid possessing the properties of *p*-polyphenyl. Evidence for the structural assignment is based upon the C/H atomic ratio obtained from elemental analyses, infrared spectrum, X-ray diffraction pattern, pyrolysis products, oxidative degradation, insolubility, color and thermal stability. The polymer is very similar in its properties to the *p*-polyphenyl prepared previously by Marvel and Hartzell by another method. The reaction is believed to proceed by oxidative cationic polymerization of the aromatic nuclei.

Introduction

The literature appears to contain no reports on the use of benzene as a monomer in well-defined polymerizations leading to homopolymers. However, benzene is known to give resins, dark-colored solids, and other uncharacterized higher molecular weight products on treatment with aluminum chloride or aluminum bromide.[3] Usually, rather drastic conditions were employed. More than sixty years ago, Thomas[4] found that treatment of benzene with ferric chloride resulted in formation of a black solid. In a more recent investigation, Kovacic and Wu[5] reported data indicating the presence of polynuclear structures in this product, apparently formed by oxidative cationic polymerization. In a related area concerned with benzene polymerization, evidence has been presented by Stockmayer and Peebles[6] for the free radical copolymerization of benzene with vinyl acetate.

Polymers containing polyphenyl structures have been synthesized by various procedures. Marvel and Hartzell[7] prepared impure *p*-polyphenyl by chloranil oxidation of poly-1,3-cyclohexadiene which was obtained by Ziegler polymerization. In general, use was made by other investigators of the Fittig and Ullmann methods.[8] For example, treatment of *p*-dichlorobenzene with sodium–potassium alloy gave a polyphenyl which, however, possessed structural irregularities.[8a] Polymerization is also reported to occur on heating *p*-dibromobenzene with activated copper.[9] In studies involving catalytic hydrogenation of dibromobenzene in the presence of methanol, Busch and coworkers[10] isolated polyphenyls through the septiphenyl homolog in the *para* series. It is claimed that oily or waxy polyphenyls are formed in high yield from a mixture of benzene and biphenyl in the presence of sulfur at 650–950°.[11] Organometallic compounds have also been used as precursors for this type of polymer, *e.g.*, in the reaction of dilithium benzene with heavy metal halides.[12a,b] Electrolysis of phenylmagnesium bromide gave small amounts of incompletely characterized polymer presumed to be polyphenyl.[12c] Low molecular weight polyphenyls containing halogen or alkyl substituents have been prepared by the Fittig and Ullmann syntheses.[13] As an outgrowth of their

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[1] Paper II in the series, "Polymerization of Aromatic Nuclei"; an abstract of the M.S. thesis of Alexander Kyriakis, Case Institute of Technology, 1962; preliminary communication, *Tetrahedron Letters*, 467 (1962); presented at the 142nd National Meeting of the American Chemical Society.

[2] American Chemical Society–Petroleum Research Fund Fellow, 1961.

[3] C. H. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1941, p. 716.

[4] V. Thomas, *Compt. rend.*, **126**, 1211 (1898).

[5] P. Kovacic and C. Wu, *J. Polymer Sci.*, **47**, 45 (1960).

[6] W. H. Stockmayer and L. H. Peebles, Jr., *J. Am. Chem. Soc.*, **75**, 2278 (1953).

[7] C. S. Marvel and G. E. Hartzell, *ibid.*, **81**, 448 (1959).

[8] (a) G. A. Edwards and G. Goldfinger, *J. Polymer Sci.*, **16**, 589 (1955); (b) G. Goldschmiedt, *Monatsh.*, **7**, 40 (1886); (c) W. Fuchs and H. Metzl, *Ber.*, **55**, 738 (1922).

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[10] M. Busch, W. Weber, *et al.*, *J. prakt. Chem.*, **146**, 1 (1936).

[11] W. H. Williams, U. S. Patent 1,976,468 (1934).

[12] (a) G. Wittig and F. Bickelhaupt, *Ber.*, **91**, 883 (1958); (b) V. Y. Bogomolnyy and B. A. Dolgoplosk, *Akad. Nauk SSSR Izv. Otd., Khim. Nauk*, 1912 (1961); (c) W. V. Evans, R. Pearson and D. Braithwaite, *J. Am. Chem. Soc.*, **63**, 2574 (1941).

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