water-cooled reflux condenser, the outlet of which was connected to a graduated trap cooled in Dry Ice followed by a series of three tubes of soda lime and finally a glass tube dipping a few millimeters below the surface of a pool of mercury. The apparatus was dried carefully before use and swept out with a stream of dry helium (or other inert gas).

In experiments with ethyl and isopropyl haloformates, where the alkyl halides produced are volatile,[5] the boron trifluoride etherate was placed in the reaction flask, and a small amount of the haloformate was added. The stirred mixture was warmed if necessary until evolution of carbon dioxide commenced and then maintained at that temperature while the remainder of the haloformate was added gradually over the course of a few hours. When gas evolution had ceased, the system was swept out briefly with helium, and the soda lime tubes were weighed to determine the amount of carbon dioxide produced. The alkyl halide collected in the cold trap was redistilled into another cold receiver and its identity checked by a determination of its molecular weight by the vapor density method. None of the volatile alkyl halides obtained contained olefin, inasmuch as they did not reduce potassium permanganate in acetone solution.[6]

In experiments with cyclopentyl and cyclohexyl haloformates, in which the halide produced remained in contact with the catalyst during the entire reaction, considerable amounts of higher boiling material were formed. The production of this apparently dimeric product could be minimized by adding to the reaction mixture a paraffin hydrocarbon, such as *n*-pentane or *n*-hexane, in which boron trifluoride etherate is insoluble. The haloformate, which is soluble in the boron trifluoride etherate, was added slowly to the stirred mixture of hydrocarbon and catalyst held at the desired temperature.[7] As the carbon dioxide was evolved, the resulting alkyl halide, which is less soluble in the boron trifluoride etherate than is the haloformate, entered the hydrocarbon layer and was removed from further contact with the catalyst. When the reaction was complete, the carbon dioxide absorption tubes were weighed, and the hydrocarbon layer containing the product was separated, washed with water, dried over sodium sulfate and distilled. The products obtained from cyclohexyl haloformates appeared to be olefin free, but with cyclopentyl haloformates some cyclopentene invariably was formed.

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[5] In the decomposition of isopropyl chloroformate the reflux condenser was not cooled so that the isopropyl chloride was carried over to the cold trap by the carbon dioxide.

[6] In testing with potassium permanganate it is necessary that all traces of boron trifluoride etherate be absent, since a mixture of this substance and acetone reduces permanganate.

[7] In the case of cyclopentyl fluoroformate, the reaction was initiated at room temperature, and the mixture was then cooled in an ice-bath whereupon smooth reaction continued.

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Mechanisms of Elimination Reactions. XV. The Reaction of Phenyllithium with *cis*- and *trans*-β-Bromostyrene[1]

BY STANLEY J. CRISTOL AND ROBERT F. HELMREICH

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Both isomers of β-bromostyrene are converted by phenyllithium in ether to phenylacetylene, the *trans* isomer reacting about twice as rapidly as the *cis* isomer. Reaction-rate studies, with *n*-butyl ether as solvent, show that the reaction is first order in phenyllithium, rather than second order in phenyllithium, as has been claimed with chlorostyrene. Under these conditions, the *trans* isomer is about six times as reactive as the *cis* isomer. The results are rationalized in terms of an α-elimination mechanism. Decomposition of the sodium salt of *trans*-cinnamic acid dichloride in water has been shown to give a mixture of isomers of β-chlorostyrene, the *cis* isomer being formed in predominant amount.

It has been reported[2] that the rate of the reaction between β-chlorostyrene and phenyllithium (equation 1) in ether is first order in the halide and second

$$\mathrm{PhCH{=}CHX + 2PhLi \longrightarrow PhC{\equiv}CLi + 2C_6H_6 + LiX} \quad (1)$$

order in phenyllithium. The order of the reaction was attributed to the dimeric nature of phenyllithium in ether solution,[3] and a mechanism was suggested involving simultaneous lithium–hydrogen exchange at both the α- and β-carbon atoms of β-chlorostyrene, followed by elimination of lithium chloride. The order of the reaction was derived from the observation that second-order rate constants drifted downward from 0.54 to 0.17 l./mole/min. at 0° over the range 14–84% reacted, whereas the same data calculated in a third-order equation (first order in styryl chloride and second order in phenyllithium) gave fairly reproducible rate constants. No other tests of order, such as variations of initial concentrations, appear to have been reported. These observations have been confirmed by Grummitt and Lucier.[4]

On the other hand, it had been shown[5] that the reactions of phenyllithium and of methyllithium with *n*- and *t*-butyl chlorides in *n*-butyl ether were first order in the halide and first order in the organolithium compound, regardless of whether substitution (coupling) or elimination occurred. In addition, the question of the *cis–trans* nature of the chlorostyrene used by Wittig and Harborth remained, no statement having been made regarding the stereochemical purity of the materials or the relative reactivities of each isomer.

The preparation of chlorostyrene followed that of Biltz[6] and involved the decomposition of sodium *erythro*-α,β-dichloro-β-phenylpropionate (salt of *trans*-cinnamic acid dichloride) in water, a medium in which the salt of the corresponding dibromo acid is known to lead to mixtures of β-bromostyrene[7-11] containing principally the *trans* isomer. We have now repeated the preparation of β-chlorostyrene by

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[1] Previous paper in series: E. Grunwald and S. J. Cristol, THIS JOURNAL, **77**, 2891 (1955).

[2] G. Wittig and G. Harborth, *Ber.*, **77B**, 315 (1944).

[3] G. Wittig, *Angew. Chem.*, **62**, 231 (1950).

[4] O. Grummitt and J. J. Lucier, Abstracts of Papers, the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March, 1952, p. 49K.

[5] S. J. Cristol, J. W. Ragsdale and J. S. Meek, THIS JOURNAL, **73**, 810 (1951).

[6] H. Biltz, *Ann.*, **296**, 263 (1897). See G. Wittig and H. Witt, *Ber.*, **74**, 1474 (1941).

[7] K. v. Auwers, *ibid.*, **45**, 2781 (1912).

[8] C. Dufraisse, *Compt. rend.*, **171**, 960 (1920); *Ann. chim.*, [9] **17**, 198 (1922).

[9] A. T. Dann, A. Howard and W. Davies, *J. Chem. Soc.*, 605 (1928).

[10] E. Grovenstein and D. E. Lee, THIS JOURNAL, **75**, 2639 (1953).

[11] S. J. Cristol and W. P. Norris, *ibid.*, **75**, 2645 (1953).

the method of Biltz, and the product appears to be a mixture of about 70% of the *cis* isomer and 30% of the *trans* isomer. This analysis was performed by studying the reaction of the product mixture with ethanolic alkali. At 91.2°, 70% of the material liberated chloride ion readily to alkali, while the remainder was substantially inert. Approximate rate constants for the reactive material were 2×10^{-5} l./sec./mole at 60.0° and 9×10^{-4} l./sec./mole at 91.2°. It has been shown that *cis*-β-bromostyrene has a rate constant of 3×10^{-3} l./sec./mole with alkali in isopropyl alcohol at 43°, being 2×10^5 times as reactive as the *trans* isomer, which has a rate constant of 2×10^{-5} l./sec./mole at 97.6°.[12] Thus the reactive chlorostyrene isomer has a reactivity intermediate between the *cis*- and *trans*-β-bromostyrenes. As elimination from chloroölefins is slower than that from bromoölefins,[13] the assumption that the fast isomer is *cis*-β-chlorostyrene appears reasonable.[14]

As the chlorostyrene which we prepared was a mixture and thus laid the conclusions of Wittig and Harborth[2] open to question, we decided to undertake an analogous study. Both isomers of β-bromostyrene were available,[11,12] while those of chlorostyrene were not, and we therefore decided to investigate the reaction of phenyllithium with bromostyrene isomers.

The first work was conducted in ethyl ether, and the measurement of rate constants was not attempted in view of the high rates of the reactions. However competitive experiments were devised in which an equimolar mixture of each of the two isomers in ethyl ether was allowed to react with an amount of phenyllithium insufficient for complete reaction of the halides. The composition of the resulting halide mixture then was determined by infrared analysis. From the extent of the reaction and the composition of the mixture (and assuming that both isomers followed the same rate law, first order in styryl halide and any order in phenyllithium), we calculated the ratio of the rate constants k_{trans}/k_{cis}, where the subscripts refer to the description of the isomer. The results of these experiments are given in Table I. Experiments also were performed with each of the pure isomers to show that no isomerization resulted by treatment of either isomer with phenyllithium.

TABLE I

COMPETITIVE REACTIONS BETWEEN EQUIMOLAR MIXTURES OF *cis*- AND *trans*-β-BROMOSTYRENE AND INSUFFICIENT PHENYLLITHIUM IN ETHYL ETHER AT 25°

[Halide] *M*	[Base] *M*	Extent of reacn., min.	Halides reacted, % Calcd.[a, b]	Obsd.[b]	Isomeric compn. of residue *trans*	*cis*	$\frac{k_{trans}}{k_{cis}}$
0.57	0.69	4.0	61	52	35	65	2.3
.46	.72	8.0	77	67	31	69	1.9
.55	.70	4.0	64	60	33	67	2.1
.49	.71	12.0	72	69	29	71	2.1

[a] Two moles of phenyllithium are required per mole of bromostyrene. [b] The discrepancy between these two values arises from the fact that the calculated value is based upon estimation of total base (phenyllithium plus by-product bases) of which only phenyllithium apparently reacts. In our experience solutions of this type have 80–95% of their total base as phenyllithium when freshly prepared. The observed value is based upon titration for bromide ion.

It will be observed from the data of Table I that phenyllithium reacts with *trans*-β-bromostyrene in ethyl ether (*cis* elimination) at a rate twice that at which it reacts with the *cis* isomer (*trans* elimination). This remarkably small difference in isomer reactivity (with sodium hydroxide in isopropyl alcohol, *trans* elimination is favored in this system[12] by a factor of 2×10^5) compels consideration of unusual mechanisms for this elimination and therefore necessitates study of the kinetic law governing the reaction.

Preliminary experiments with *n*-butyl ether as solvent indicated that the rates could be followed at 2°. Experiments were first set up to demonstrate that the reaction occurring was indeed elimination as in equation 1, and the formation of phenylacetylene in yields of 84–88% was demonstrated. The rates of reaction were followed by titration for bromide ion, and the rates were followed to 40–60% reaction. Beyond this point, the rate constants declined rapidly, and results could not be reproduced. The rate data are given in Table II. Included in Table II are the calculated second-order rate constants (rate law first order in styryl bromide and first order in phenyllithium) and approximate

TABLE II

THE ELIMINATION OF HYDROGEN BROMIDE FROM ISOMERS OF β-BROMOSTYRENE BY PHENYLLITHIUM IN *n*-BUTYL ETHER AT 2.10°

Halide, *M*	C_6H_5Li, *M*	$10^3 k_2$, l./mole/sec.	Av. devn., %	$10^2 k_3$, $l.^2$/mole^2/sec.
		cis-β-Bromostyrene		
0.0301	0.193	3.59		1.9
.0301	.193	3.48		1.8
.0301	.117	3.84		3.3
.0301	.117	3.87		3.3
.0303	.110	3.78[a]		3.4
.0303	.110	4.27[a]		3.9
	Av.	3.81	4.9	
		trans-β-Bromostyrene		
0.0304	0.123	19.1		16
.0304	.107	23.8		22
.0304	.064	20.3		32
	Av.	21.1	8.7	

[a] Calculated by the method of least squares.

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(12) S. J. Cristol and W. P. Norris, THIS JOURNAL, **76**, 3005 (1954).

(13) See, for example, S. J. Cristol and A. Begoon, *ibid.*, **74**, 5025 (1952).

(14) β-Chlorostyrene obtained by pyrolysis of chlorocycloöctatetraene[15] exhibits physical properties different from those of the product of the Biltz procedure. As the analogous decomposition of the salt of *trans*-cinnamic acid dibromide in water gives principally *trans*-β-bromostyrene,[7-9] Cope and Burg assumed that the Biltz product in the chloro series was also principally *trans*, and they therefore tentatively assigned the *cis* structure to their product. In the assignment of structure, comparisons of refractive indices of various preparations of chlorostyrene with those of known *cis*- and *trans*-β-bromostyrene seem significant. These (n^{25}D) are as follows: *cis*-β-bromostyrene,[12] 1.5983; *trans*-β-bromostyrene,[12] 1.6076; β-bromostyrene from pyrolysis of bromocycloöctatetraene,[15] 1.6055; β-chlorostyrene by procedure of Biltz, 1.5736,[6] 1.5738 (est.),[7] 1.5732,[15] 1.5729 (this work); β-chlorostyrene by pyrolysis of chlorocycloöctatetraene,[15] 1.5762; β-chlorostyrene by isomerization of pyrolysis product with phosphorus pentachloride,[15] 1.5740. Combination of refractive index data and elimination rate data lead to the conclusion that the Cope and Burg pyrolysis products (both chloro- and bromostyrenes) were principally *trans* isomers.

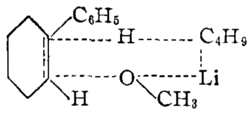
(15) A. C. Cope and M. Burg, THIS JOURNAL, **74**, 168 (1952).

third-order rate constants (first order in bromide and second order in phenyllithium). One may note that the second-order rate constants k_2 deviate from their mean by an average of 6%, with the deviations bearing no apparent relationship to the phenyllithium concentrations. On the other hand, the unsatisfactory nature of the third-order relationship, based upon k_3, is obvious.

Our results therefore lend no confirmation to the Wittig–Harborth[2] third-order mechanism proposed for β-chlorostyrene. We hope to reinvestigate this system with the pure isomers if we can prepare them.

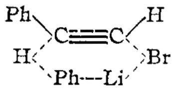
In *n*-butyl ether, the *trans* isomer reacts 5.5 times as rapidly as the *cis* isomer. Again, as in ethyl ether, *cis* elimination is preferred over *trans* elimination by a relatively small factor.

Recently Letsinger and Bobko[16] have studied elimination of methanol from the *cis*- and *trans* isomers of methyl 2-phenylcyclohexyl ether with butyllithium (ether cleavage) in a refluxing pentane–ethyl ether mixture. They observed that the *trans* isomer (*cis* elimination) gave 61% of 1-phenylcyclohexene in 21 hours, while the *cis* isomers (*trans* elimination) gave only 8% of the olefin in the same period. Letsinger and Bobko suggested the cyclic transition state (I) to explain this superiority of *cis* elimination over *trans* elimination. The observed relative reactivities of the isomers of about 10 to 1 appear to fit such a mechanism.

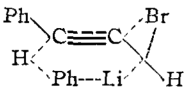


I

Although our data (*cis* elimination preferred by a small factor) are similar to those of Letsinger and Bobko, it does not appear possible to accommodate their mechanism to our results. While *cis* elimination from *trans*-β-bromostyrene may proceed *via* the analogous transition state II, the corresponding transition state III for *trans* elimination appears quite improbable in view of the difficulty of constructing a six-membered ring with an internal *trans* double bond.



II



III

While the cyclic mechanism cannot be excluded for the *cis* process, with either a concerted *trans* elimination or a carbanion process[11] for the other isomer, it would be necessary to assume that coincidence made the rates of each of the processes similar. For the present we tend to favor an α-elimination process for both isomers for the reasons outlined below. A tentatively suggested reaction path is as follows (the question of the ionic or covalent character of the carbon–lithium bonds indicated must be left open)

$$\mathrm{PhCH{=}CHBr + PhLi \longrightarrow PhCH{=}CLiBr + PhH} \quad (2)$$

$$\mathrm{PhCH{=}CLiBr \longrightarrow LiBr + \underset{IV}{PhCH{=}C:}} \quad (3)$$

$$\mathrm{PhCH{=}C: \longrightarrow PhC{\equiv}CH} \quad (4)$$

$$\mathrm{PhC{\equiv}CH + PhLi \longrightarrow PhC{\equiv}CLi + PhH} \quad (5)$$

or instead of (4) and (5)

$$\mathrm{PhCH{=}C: + PhLi \longrightarrow PhC{\equiv}CLi + PhH} \quad (6)$$

Certain of the separate steps written above may be telescoped, as for example, equations 2 and 3 may be concerted to yield the carbene IV in one step. At the present stage of knowledge, it is not practical to speculate further on the details of the mechanism, except to point out that the observed kinetics of course eliminate certain of these as rate-determining steps.[17]

The evidence which leads us to our tentative suggestion of an α-elimination is of several types. First, our own rate data, which show that the reactivities of both isomers are of similar magnitude. An α-elimination process would predict little difference in the reactivities of *cis* and *trans* isomers, whether either steps 2, 3 or telescoped 2 and 3 were rate determining.

In addition, certain facts in the literature appear almost to compel an α-elimination process. Wittig and Harborth[2] reported that β-chloro-β-methylstyrene reacted with phenyllithium only very slowly at 20°. After four days (styryl chloride reacted almost completely in one hour), 40% of pure starting material was isolated, in addition to 35% of a mixture of the starting material and the elimination product, methylphenylacetylene. An unidentified resin also was found. As we have shown that each isomer of styryl bromide is reactive, it seems likely that this also would be true of the chloride. Therefore, if β-elimination were involved, the β-methyl-β-chlorostyrene studied by Wittig and Harborth should be a reactive species, no matter which isomer was present. That this was not the case seems excellent evidence for α-elimination, as this compound, of course, has no α-hydrogen and thus cannot suffer α-elimination. Some of the weight of this argument is lost in considering that the structure(s) of their chloropropenylbenzene (mixture) was not proved. Their material was prepared by the action of potassium hydroxide in refluxing ethanol on α,β-dichloropropylbenzene and might have contained substantial amounts of α-chloro-β-methylstyrene. However, even if the material were entirely α-chloro-β-methylstyrene (*cis* or *trans*), the low reactivity lends some support to the α-elimination process, as even vinyl chloride eliminates quite rapidly with phenyllithium.[19]

A survey of the literature on the reaction of haloolefins with phenyllithium and with butyllithium *in ether*[2,19–22] suggests that elimination of hydrogen and halogen occurs readily only when a hydrogen is α to the halogen involved; when no α-hydrogen is present, either halogen–metal interchange occurs (with bromoölefins) or the compounds are very in-

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[16] R. L. Letsinger and E. Bobko, THIS JOURNAL, **75**, 2649 (1953).

[17] Curtin, Flynn and Nystrom[18] have studied elimination from radiocarbon-labeled β-bromostyrene mixture with butyllithium and have noted that no rearrangement of carbon skeleton occurs. This suggests that either the carbene IV is not an intermediate or that if it is a real intermediate, it reacts *via* hydrogen migration in equation 4, and not *via* a phenyl migration, or else it reacts according to equation 6.

[18] D. Y. Curtin, E. W. Flynn and R. F. Nystrom, private communication.

[19] G. Wittig and G. Harborth, *Ber.*, **77B**, 306 (1944).

[20] G. Wittig and H. Witt, *ibid.*, **74**, 1474 (1941).

[21] H. Gilman and A. H. Haubein, THIS JOURNAL, **67**, 1420 (1945).

[22] D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716, 4519 (1951).

ert (with chloroölefins), even though β-hydrogens (*cis* and/or *trans*) are available for elimination. However, certain key studies remain to be done.

Various examples of α-elimination are described in the literature and offer suitable analogies for the process we have described.[23-35]

Most of the previous work has been conducted with sodium or potassium amide as base and, indeed, α-elimination appears to proceed readily only in the presence of a strong base (amide ion and organolithium compounds apparently being the two known general reagents). α-Eliminations occur with weaker bases like hydroxide or ethoxide only at elevated temperatures[36-40] or when quite active hydrogens are involved.[26,32,34]

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Experimental

β-Chlorostyrene, n^{25}_D 1.5729, was prepared by the method of Biltz.[6] The product liberated over 96% of the theoretical amount of chloride when treated with sodium in isopropyl alcohol. The rates of reaction of the reactive isomer with ethanolic sodium hydroxide were measured in the usual fashion,[12] using a large excess of alkali with appropriate correction being made for the amount of reactive isomer (amount reacted in about nine half-lives of the reaction). Duplicate runs gave approximate rate constants of 2×10^{-5} and 9×10^{-4} l./sec./mole at 60.0 and 91.2°, respectively.

β-Bromostyrene isomers were prepared as described previously.[12] Solutions of phenyllithium in ethyl ether were prepared under nitrogen from bromobenzene,[41] and those in *n*-butyl ether were prepared by displacement of ethyl ether with *n*-butyl ether.[5]

Competitive Reactions of Phenyllithium in Ethyl Ether with Mixtures of *cis*- and *trans*-β-Bromostyrene.—It was found that *cis*-β-bromostyrene and the *trans* isomer had mutually exclusive infrared absorption maxima at 7.57 and 13.04 μ and at 10.65 and 13.67 μ, respectively.[42] The *cis* peak at 7.57 μ and the *trans* peak at 10.65 μ were used as points of identification to detect each isomer and the ratio of optical densities at these wave lengths was used to estimate isomer compositions quantitatively.

Each of the pure halides was treated with about 50% of the phenyllithium required for total reaction. The product was treated with water, and the ether layer was separated. The residue, after removal of the ether, was subjected to infrared study. This study indicated that no detectable isomerization occurred with either isomer.

Varying, but always less than sufficient, amounts of a solution of phenyllithium in ether were added to weighed samples of a mixture of 50% *cis*- and 50% *trans*-β-bromostyrene. After 4 to 8 minutes reaction at 25° in closed flasks, each sample was quenched with distilled water, the organic material extracted with *n*-pentane, and the extract washed with saturated salt solution to dry it. The organic solutions were distilled in such a fashion as to retain the entire bromostyrene fraction. All reaction and distillation flasks were foil-wrapped and each extraction was performed in the dark. Each aqueous layer was diluted to 100 ml. and aliquot samples were titrated by the Volhard method to determine the percentage of halides reacted. Phenylacetylene, having no peaks in the 7.6 and 10.7 μ regions, was allowed to remain in the mixture as a volume extender. Infrared analyses performed on the organic materials showed a difference in isomer concentrations indicating a reaction-rate-constant ratio of 2 to 1 for the *trans* isomer (*cis*-hydrogen and bromine) over the *cis* isomer. The results of these experiments are shown in Table I.

The reaction-rate-constant ratio was calculated from the equation

$$k_{trans}/k_{cis} = \frac{\log t^0/t}{\log c^0/c} \qquad (7)$$

where t_0 and t are initial and final concentrations of *trans* isomer and c_0 and c are initial and final concentrations of *cis* isomer. Equation 7 is derived readily from any rate law, provided that both isomers obey the same rate law and that the reaction is first-order in styryl halide.

Reaction of Phenyllithium with *cis*- and *trans*-β-Bromostyrene in *n*-Butyl Ether.—To weighed samples of about 400 mg. of β-bromostyrene isomer was added 25 ml. of *ca.* 0.7 *M* phenyllithium in *n*-butyl ether. The reaction mixture was allowed to stand at room temperature for 12 hours and then was decomposed with water. The organic layer was separated and washed with water. Phenylacetylene in the organic layer was estimated by precipitation with silver ion.[43] *cis*-Bromostyrene gave 84 and 88% of phenylacetylene, and the *trans* isomer gave 86 and 87% of phenylacetylene by this method. In our hands, pure phenylacetylene[44] gave 90–95% recovery.

Reaction rates were run in foil-wrapped volumetric flasks in a constant-temperature bath at 2.10 ± 0.03° with samples being pipetted out from time to time. Attempts were made to keep out air and moisture by conducting procedures under an atmosphere of nitrogen. The reactions were followed by Volhard titrations for bromide ion, subtracting the bromide ion carried in by the phenyllithium solution. The equation for the calculation of second-order rate constants was employed

$$\mathrm{d} \log \frac{(1 - 2a\phi/b)}{1 - \phi} \Big/ \mathrm{d}t = \frac{b - 2a}{2.303} k_2 \qquad (8)$$

where a is the initial bromostyrene concentration, b is the initial phenyllithium concentration, k_2 is the specific reaction rate constant and ϕ is the fraction reacted at various times t. The factor 2 arises from the assumption that the reaction of phenylacetylene with phenyllithium to give benzene and lithium phenylacetylide is rapid compared with the rate of formation of phenylacetylene. Values of log $(1 - 2a\phi/b)/(1 - \phi)$ were plotted against corresponding values of t; for each run the slope of the best straight line drawn by inspection through the first six or seven points was multiplied by the value of $2.303/(b - 2a)$ to give the rate constant k_2. The values are given in Table II. In separate experiments it was shown that lithium phenylacetylide does not react rapidly enough with bromostyrene to interfere with these runs.

The slopes of the lines fell off seriously after 60% reaction, and in some runs as early as 40%. The reason is not clear, but it cannot be caused by a third-order process for the reason described below, as well as for the reason that some runs contained enough excess phenyllithium such that

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[23] C. R. Hauser and W. B. Renfrow, Jr., THIS JOURNAL, **59**, 121 (1937).

[24] W. B. Renfrow, Jr., and C. R. Hauser, *ibid.*, **59**, 2308 (1937).

[25] R. D. Bright and C. R. Hauser, *ibid.*, **61**, 618 (1939).

[26] C. R. Hauser, *ibid.*, **62**, 933 (1940).

[27] C. R. Hauser, P. S. Skell, R. D. Bright and W. B. Renfrow *ibid.*, **69**, 589 (1947).

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[30] G. H. Coleman and R. D. Maxwell, THIS JOURNAL, **56**, 132 (1934).

[31] A. Michael, *ibid.*, **42**, 787 (1920).

[32] J. Hine, *ibid.*, **72**, 2438 (1950).

[33] J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

[34] C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 2357 (1929).

[35] K. Ziegler and H. G. Gellert, *Ann.*, **567**, 185 (1950).

[36] P. Fritsch, *ibid.*, **279**, 319 (1894).

[37] W. P. Buttenberg, *ibid.*, **279**, 324 (1894).

[38] H. Wiechell, *ibid.*, **279**, 337 (1894).

[39] E. E. Harris and G. B. Frankforter, THIS JOURNAL, **48**, 3144 (1926).

[40] C. Mentzer and D. Xuong, *Compt. rend.*, **222**, 1004 (1946).

[41] H. Gilman, E. A. Zoellner and W. M. Selby, THIS JOURNAL, **55**, 1252 (1933).

[42] Detailed spectra for the two isomers in the range 10–14 μ are given by Grovenstein and Lee.[10]

[43] E. C. Luce in R. H. Boundy and R. F. Bayer, "Styrene, Its Polymers, Copolymers and Derivatives," Reinhold Publishing Corp., New York, N. Y., 1952, p. 158.

[44] J. C. Hessler in H. Gilman and A. H. Blatt, "Organic Syntheses," 2nd Ed., Coll. Vol. I, John Wiley and Sons, Inc., New York N. Y., 1941, p. 438.

the decline in rate constant would not be nearly so great as that often observed. The decline in slope may have been caused by admission of air to the reaction flask when opening it to the sample. In addition, and at times which varied with each experiment, lithium chloride precipitated from the supersaturated solutions, and no more samples could be utilized. We were never able to withdraw more than seven samples without observing the decrease and in several cases the decrease occurred earlier. We therefore have used the first 40–60% of the reaction to determine the rate constants and Table II thus reports initial values of k_2.

The method of following rates in these experiments led to somewhat larger errors in individual points than are generally observed, as the bromide titration involved a difference between two values. For this reason, we have analyzed the data statistically for the two runs that appeared to have the largest deviations and have shown that the data and the correlations derived from them are statistically satisfactory. The slopes derived in these runs were placed by the method of least squares. Calculations from the least squares equations for these two runs indicate that the probable errors in rate constant were 7.3 and 8.8%. These values may be compared with values of average deviation from the mean rate constants for the *cis* isomer of 4.9% and for the *trans* isomer of 8.7% listed in Table II. Approximate values for k_3, based upon the third-order rate law (9) which were obtained by dividing k_2 by initial phenyllithium concentrations, also are given in Table II.

$$\frac{d(Br^-)}{dt} = k_3(PhLi)^2(\text{halide}) \qquad (9)$$

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Vinylation: Kinetics and Mechanism of the Methoxide-catalyzed Addition of Methanol to Phenylacetylene[1]

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As a model of the vinylation reaction we have studied the kinetics of the methoxide-catalyzed addition of methanol to phenylacetylene in the solvents methanol and dioxane. The reaction appears to be first order in phenylacetylene, first order in methoxide and zero order in methanol, with $\Delta H^* = 28.5$ kcal. mole^{-1} and $\Delta S^* = -8$ e.u. at 126°. Our data are consistent with the following general mechanism: the rate-determining step is the addition of alkoxide ion to the acetylene; this is followed by the rapid abstraction of a proton from the alcohol by the carbanion intermediate. This mechanism predicts correctly that increased electron-withdrawing power of substituents of the acetylene increases the rate of vinylation; it is also consistent with our hypothesis that increased nucleophilic power of the species attacking the acetylene increases the rate of vinylation.

The base-catalyzed addition of compounds with an acidic hydrogen to any acetylenic compound, vinylation

$$RQH + R'C{\equiv}CR'' \xrightarrow{\text{base}} R'CH{=}CR''QR \qquad (1)$$

has been widely applied in syntheses.[2,3] Some sixty years ago, in his studies of the ethoxide-catalyzed isomerization of 1-alkynes to 2-alkynes and allenes, Favorsky isolated an ethoxyalkene.[4] Later Moureu and Nef prepared β-alkoxystyrenes from phenylacetylene and alkoxide–alcohol solutions.[5,6] Related addition reactions of water, phenols, malonic ester, mercaptans, amines and possibly acetic acid to various acetylenes are scattered throughout the literature.[7–9]

Perhaps the most systematic exploitation of the vinylation reaction is found in the recent work of Reppe and co-workers at I. G. Farben.[10] Their high pressure reactions of acetylene led to whole families of vinyl compounds. Similar work has been reported in the Russian and Japanese literature.[11,12] The scope, diversity and ramifications of all of these base-catalyzed additions and their products have been ably reviewed.[7,10,13–15]

Except for the preliminary work of some Russian workers, very little was done to clarify the mechanism of these reactions.[16] As a model of the vinylation reaction we have studied the kinetics of the methoxide-catalyzed addition of methanol to phenylacetylene in the solvents methanol and dioxane

$$C_6H_5C{\equiv}CH + CH_3OH \xrightarrow{NaOCH_3} C_6H_5CH{=}CHOCH_3 \qquad (2)$$

That β-methoxystyrene is the chief product has been amply demonstrated.[5,6,17] Reaction (2) was found to be second order, first order in phenylacetylene, first order in sodium methoxide and zero order in methanol. These results allow us to

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(1) Work supported by the Office of Ordance Research.

(2) In this paper the term "vinylation" will be used only in the sense indicated by equation (1).

(3) It does not include the large group of acid-catalyzed vinylations.

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