A Nonlinear Hammett Plot. Substituent Effects in the Substitution and Elimination–Rearrangement Reactions of 1,1-Diaryl-2-bromoethenes with Potassium *t*-Butoxide in an Aprotic Solvent[1]

DANIEL F. BENDER,[2] THUDUMA THIPPESWAMY,[3] AND WILLIAM L. RELLAHAN

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45220

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A series of 1,1-diaryl-2-bromoethenes was synthesized and allowed to react with potassium *t*-butoxide in anhydrous diglyme at 0°. The substitution products were isolated by solvent extraction and column chromatography and identified by nuclear magnetic resonance spectrometry and elemental analysis. The elimination–rearrangement products were identified by ultraviolet spectrophotometry. The rate constants for the rearrangements step were calculated by the time-ratio method. An increase in electron-withdrawing character of the substituent caused the elimination–rearrangement reaction to proceed slower and the substitution reaction to proceed faster. None of the compounds tested underwent both reactions. The Hammett reaction constant, ρ, was found to be -1.3 for elimination–rearrangement and $+9$ for substitution. This produces a nonlinear Hammett plot which is concave. An unusually large solvent effect was noted when anhydrous *t*-butyl alcohol was added to the anhydrous diglyme. This is tentatively explained in terms of a cage of *t*-butyl alcohol molecules solvating the attacking *t*-butoxide anion, thus altering its character.

A change in the mechanism of a reaction owing to a change in the substituents on the substrate is known to affect the linearity of a Hammett plot, producing a curve which is concave.[4-6] Subtle changes in mechamism do not affect the sign of the Hammett reaction constant, ρ. Abupt changes in mechanism change the sign of ρ, yielding a minimum in the curve.[5] This last generalization was based on the mechanistic change from acyl oxygen fission to alkyl oxygen fission in the solvolysis of substituted ethyl benzoates by 99.9% sulfuric acid as the substituent increases in electron-withdrawing character.[7] Since both reactions are addition–elimination reactions, we thought that it would be desirable to have two completely different mechanisms operative to test this generalization.

The reaction of 1,1-diaryl-2-haloethenes ($Ar_2C{=}CHX$) with alkali-metal alkoxides (M^+, OR^-) leads to two entirely different products.[8-10] Rearrangement (reaction 1) proceeds by a preequilibrium proton abstraction producing a configurationally stable anion, followed by rearrangement of the aryl group *trans* to the bromine atom with simultaneous elimination of bromide, to produce diarylacetylene.[11,12]

$$Ar_2C{=}CHBr + {}^-O\text{-}t\text{-}Bu \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ar_2C{=}CBr^- + HO\text{-}t\text{-}Bu \quad (1a)$$

$$Ar_2C{=}CBr^- \xrightarrow{k_1} ArC{\equiv}CAr + Br^- \quad (1b)$$

Substitution (reaction 2) proceeds by addition of the alkoxide anion to the number 2 carbon followed by elimination of bromide to produce a diaryl alkyl vinyl ether.[13-18]

$$(Ar)_2C{=}CHX + OR^- \rightleftharpoons (Ar)_2C^-{-}CH(X)OR \quad (2a)$$

$$(Ar)_2C^-{-}CH(X)OR \longrightarrow (Ar)_2C{=}CHOR + X^- \quad (2b)$$

An examination of available data concerning substituent effects on the elimination–rearrangement[15,17-19] and our work on the substitution reactions indicates that a minimum could be obtained in the Hammett plot. The effect of substituents on the elimination–rearrangement reaction and the substitution reaction are described and the combined substituent effects are examined in terms of their effect on the Hammett plot.

Experimental Section

Syntheses. A. 1,1-Diaryl-2-bromoethenes.—These were prepared from the aryl bromides and ethyl acetate using previously described procedure.[20,21] The synthetic procedures and methods of characterization are shown in Table I.

B. 2,2-Bis(*p*-trifluoromethylphenyl)vinyl *t*-Butyl Ether.—A large excess (*ca.* 3 g) of potassium *t*-butoxide was dissolved in dry diglyme (see below) in the drybox, filtered, stoppered with a serum rubber cap, and brought into the room. *Ca.* 1 g of bis-(*p*-trifluoromethylphenyl)-2-bromoethene was dissolved in dry diglyme and injected into the potassium *t*-butoxide solution at ambient temperature. The reaction was followed roughly by taking samples with a syringe, quenching with 95% ethyl alcohol, and examining the ultraviolet spectrum. The reaction appeared to be over after 30 sec but was allowed to continue for several days.

The reaction mixture was diluted with water and extracted with carbon tetrachloride until no fluorescence was found in the CCl_4 wash. The combined CCl_4 portions were washed with water, dried over $CaSO_4$, and evaporated. Three crystallizations from pentane of the orange-red crystals obtained yielded slightly yellowish rods, mp 103.5-105°.

Proton nuclear magnetic resonance spectroscopy (Varian A-60) in carbon tetrachloride showed three sharp peaks with the expected relative areas: aliphatic, 1.49 ppm; vinyl, 6.8 ppm; aromatic, 7.35-7.51 ppm; relative areas, 9:1:8. The ultraviolet spectrum (Beckman DB) in 95% ethyl alcohol showed an absorption maximum at 297 mμ and a shoulder at 234 mμ.

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[1] Taken in part from the Ph.D. dissertations of T. Thippeswamy, 1963, and D. F. Bender, 1967, University of Cincinnati, Cincinnati, Ohio.

[2] Career Development Program, U. S. Department of Health, Education and Welfare, U. S. Public Health Service, 1964-1966. To whom correspondence should be addressed: U. S. Public Health Service, 222 East Central Parkway, Cincinnati, Ohio 45202.

[3] Lowenstein-Twitchell Fellow, 1961-1962; Laws Fellow, 1962-1963.

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TABLE I

SYNTHESIS AND CHARACTERIZATION OF SYMMETRICALLY SUBSTITUTED 1,1-DIARYL-2-BROMOETHENES

Substituent	Registry no.	Ref to synthetic procedure	Characterization[a]
H	13249-58-6	*b*	Recrystn from pentane, mp 42° (lit. mp 49–50°,[c,d] 41–49°[e])
p-CH_3	7208-11-9	*f*	Recrystn from pentane and then methanol, mp 55–57° (lit. mp 55–56°,[g] 53–54°[h–j])
p-OCH_3	2132-64-1	*b*	Recrystn from ethanol and then pentane, mp 80–82° (lit.[k] mp 85°)
p-F	23349-10-2	*b, l*	Bp 138–145° (5 mm). *Anal.*[m] Calcd: C, 57.00; H, 3.07; Br, 27.07; F, 12.86. Found: C, 57.65; H, 3.09; Br, 26.51; F, 12.75
m-CH_3	23349-11-3	*f*	Bp 145–151° (2 mm) [lit.[n] bp 186–191° (10 mm)]
p-Cl	23349-12-4	*l, o*	Recrystd from ether and then pentane, mp 71–72° (lit. mp 71–73°,[g] 72°[p])
m-F	23349-13-5	*b, l*	Bp 120–125° (3 mm). *Anal.*[m] Calcd: C, 57.00; H, 3.07; Br, 27.07; F, 12.86. Found: C, 57.11; H, 3.68; Br, 27.08; F, 12.13
p-CF_3	23349-14-6	*f*	Bp 116–121° (2.5 mm). *Anal.*[m] Calcd: C, 48.63; H, 2.30; F, 28.85; Br, 20.22. Found: C, 49.01; H, 2.41; F, 27.94; Br, 20.64
m-CF_3	23349-15-7	*b*	Bp 120–125° (3 mm). *Anal.*[m] Calcd: C, 48.63; H, 2.30; F, 28.85; Br, 20.22. Found: C, 49.09; H, 2.35; F, 28.61; Br, 19.95

[a] Recrystallizations were carried out several times. [b] Reference 20. [c] E. Hepp, *Chem. Ber.*, **7**, 1410 (1874). [d] G. Wittig and R. Kethner, *ibid.*, **69**, 2078 (1936). [e] P. Lipp, *ibid.*, **56**, 567 (1923). [f] Reference 21. [g] D. Y. Curtin and E. W. Flynn, *J. Amer. Chem. Soc.*, **81**, 4714 (1959). [h] F. Bergmann, S. Israelashvili, and D. Gottlieb, *J. Chem. Soc.*, 2522 (1952). [i] O. Fischer and L. Castner, *J. Prakt. Chem.*, **282**, 280 (1910). [j] R. Anschütz and A. Hilbert, *Chem. Ber.*, **57**, 1697 (1924). [k] E. E. Harris and G. B. Frankforter, *J. Amer. Chem. Soc.*, **48**, 3144 (1926). [l] Bromination–dehydrobromination carried out in CS_2. [m] Analysis performed by Mikroanalytisches Laboratorium, Stablistrasse 25, Brugg, Switzerland. [n] G. H. Coleman, W. H. Holst, and R. D. Maxwell, *J. Amer. Chem. Soc.*, **58**, 2310 (1936). [o] Prepared from reaction of 4,4′-dichlorobenzophenone with methylmagnesium iodide, dehydrated to 1,1-bis(*p*-chlorophenyl)ethenes by refluxing in 20% H_2SO_4. [p] W. Tadros, A. B. Sakla, and Y. Akhookh, *J. Chem. Soc.*, 2701 (1956).

Anal.[22] Calcd: C, 61.85; H, 4.67; F, 29.35. Found: C 61.69; H, 4.80; F, 29.61.

C. 1,1-Bis-(*m*-trifluoromethylphenyl)vinyl *t*-Butyl Ether.—This compound was prepared as above except that the crude product was chromatographed on a neutral aluminum oxide column with pentane. An impure liquid was obtained which absorbed at 271 mμ. Its nuclear magnetic resonance spectrum showed sharp peaks at 1.25, 6.65, and 7.27–7.48 ppm with approximate area ratios of 9:1:8 in addition to smaller aliphatic and aromatic peaks owing to impurities. The presence of impurities which could not be separated cast a shadow on the significance of elemental analyses and of molar absorptivity determination for the kinetic determinations. The molar absorptivity was therefore calculated from the infinity kinetic readings, as described below.

Bis-(*m*-fluorophenyl)acetylene.—Reaction conditions like those for the *p*-trifluoromethyl isomer were employed. The crude product was chromatographed on silica gel with pentane. Evaporation of the first 200-ml fraction gave white crystals which melted at 55.5–58°. The nuclear magnetic resonance spectrum showed only highly split aromatic protons. The ultraviolet spectrum was characteristic of a diarylacetylene with maxima at 299, 290, 271, and 263 mμ.

Reagents. A. Diglyme (diethylene glycol dimethyl ether, Ansul ether 141) was twice refluxed over sodium and distilled under nitrogen into dried, 500-ml, round-bottomed flasks in *ca.* 300-ml aliquots. The flasks were immediately stoppered with serum rubber caps which were then fastened with copper wire and transferred into a dry box containing an argon atmosphere.

B. *t*-Butyl alcohol was distilled into a 100-ml, round-bottomed flask which was immediately stoppered with a serum rubber cap. Potassium *t*-butoxide was added *ca.* 10 min before use and the flask was restoppered and swirled to ensure dryness. In later experiments the *t*-butyl alcohol was distilled from a solution of potassium *t*-butoxide in *t*-butyl alcohol to ensure dryness of the solvent and eliminate the possibility of the presence of hydroxide ions; no difference in the reproducibility of previous kinetic constants was obtained.

C. Preparation of Potassium *t*-Butoxide Solution.—Scoops of solid potassium *t*-butoxide (M.S.A. Research Corp., Evans City, Pa.) on a spatula, depending upon the base concentration range desired, were placed in a 250-ml, round-bottomed flask, and *ca.* 150 ml of diglyme was added. The glass-stoppered flask was swirled and then allowed to sit for *ca.* 10 min. The solution was then filtered under vacuum through glass wool and filter paper, transferred to another 250-ml, round-bottomed flask, and stoppered with a serum rubber cap for transfer into the room. Some nitrogen was introduced through a 20-gauge needle to produce a positive pressure in the base flask and thereby allow withdrawal of the necessary volume of base. The solution was then incubated at 0° for 30 min, and 5-ml portions were withdrawn with a syringe and placed in 25-ml volumetric flasks containing water for determination of the base concentration.

D. Standardization of Potassium *t*-Butoxide Solution.—The base solution was titrated conductometrically with standard hydrochloric acid.

E. Preparation of 1,1-Diaryl-2-bromoethene Solution.—A 100-ml stock solution (10^{-3} *M*) of each bromodiarylethene was prepared with diglyme. (Rigorously maintained anhydrous conditions were used throughout.) Exactly 20 ml of a solution was prepared by diluting *ca.* 2 ml of stock solution to 28 ml. The 20-ml solution was thermostated in the reaction flask for 30 min. The zero time absorbance was obtained by diluting 5 ml of the remaining 8 ml with 5 ml of diglyme followed by a 1:10 dilution with 95% alcohol.

Kinetics. A. Kinetic Procedure and Aliquot Sampling.—Exactly 20 ml of thermostated base solution was added to the bromoethene solution (see above). *Ca.* 1-ml aliquots were withdrawn and diluted to 10 ml with 95% alcohol. Absorbances were determined at two wavelengths on a Beckman DU spectrophotometer. (Since the *ratio* of absorption measurements was used, extremely accurate aliquots were not needed.) The final absorbances were constant for at least 24 hr (a successive reaction has been shown to occur under other conditions[23]). *t*-Butyl alcohol (5%) was added to the stock base solution to prevent rearrangement in the case of the *m*-fluorophenyl derivative and to study the solvent effect on other derivatives.

B. Kinetic Procedure with Alcohol Present.—It was necessary to have *t*-butyl alcohol present to prevent rearrangement in

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(22) Analysis performed by Galbraith, Laboratories, Knoxville, Tenn.

(23) P. Beltrame, P. L. Beltrame, O. Sighinolfi, and M. Simonetta, *J. Chem. Soc., B*, 1103 (1967).

TABLE II

KINETIC DATA FOR THE REACTION OF SYMMETRICALLY SUBSTITUTED 1,1-DIARYL-2-BROMOETHENES WITH POTASSIUM *t*-BUTOXIDE–DIGLYME

A. Substitution in Diglyme

Substituent	Substituent constant	$c_i \times 10^4$ [a]	[B], M[b]	$k_{exp}' \times 10^3$ [c]	$k_S \times 10^2$ [d]	Avg $k_S \times 10^2$	Std devn
p-Trifluoromethyl	0.551	2.02	0.055	9.5	15.9		
		3.09	0.057	7.4	12.7	13.8	1.1
		3.70	0.057	7.9	13.8		
		4.51	0.055	8.5	12.7		
m-Trifluoromethyl	0.415	3.13	0.154	4.3	2.8		
		3.13	0.154	4.3	2.8	2.9	0.1
		3.22	0.125	3.9	3.1		
		3.60	0.064	1.8	2.8		

B. Rearrangement in Diglyme

Substituent	Substituent constant	$c_i \times 10^4$	[B], M	$k_{exp} \times 10^3$ [e]	$k_R \times 10^2$ [f]	Avg $k_R \times 10^2$	Std devn
m-Fluoro	0.337	3.34	0.179	1.2	0.69		
		3.78	0.092	0.42	0.42	0.62	0.13
		4.80	0.179	1.3	0.74		

[a] c_i is the initial concentration of 1,1-diaryl-2-bromoethene in moles per liter. [b] [B], M is the potassium *t*-butoxide concentration. [c] k_{exp}' is the pseudo-first-order rate constant for the substitution reaction. [d] k_S is the second-order rate constant for substitution. [e] k_{exp} is the pseudo-first-order rate constant for the rearrangement reaction. [f] k_R is the second-order rate constant for rearrangement.

TABLE III

KINETIC DATA FOR THE REACTION OF SYMMETRICALLY SUBSTITUTED 1,1-DIARYL-2-BROMOETHENES WITH POTASSIUM *t*-BUTOXIDE IN 3% *t*-BUTYL ALCOHOL–DIGLYME

Substituent	Substituent constant	$c_i \times 10^4$ [a]	[B], M[a]	$k_{exp}' \times 10^3$ [a]	$k_S \times 10^2$ [a]	Avg $k_S \times 10^2$	Std devn
m-Fluoro	0.337	3.51	0.119	0.042	0.035		
		3.54	0.129	0.051	0.040	0.039	0.002
		3.65	0.081	0.033	0.041		
m-Trifluoromethyl	0.415	3.50	0.113	0.69	0.63		
		3.72	0.202	2.6	1.32	0.77	0.36
		4.28	0.113	0.40	0.37		

[a] See footnotes to Table II.

the case of the *m*-fluorophenyl derivative and to study the solvent effect of the alcohol with the other derivatives in order to correct the *m*-fluorophenyl value. For this purpose the distilled and stoppered *t*-butyl alcohol was further dried by adding some potassium *t*-butoxide. Since this procedure probably produced some hydroxide ions, later kinetic runs were carried out using *t*-butyl alcohol which had been distilled from a potassium *t*-butoxide–*t*-butyl alcohol solution. However, no change in the reproducibility of the results resulted. Enough of this solution to make a 5% *t*-butyl alcohol–diglyme base solution was transferred by syringe to the base solution in diglyme before the aliquot of base was withdrawn for titration.

C. Kinetic Calculations. Substitution Reaction.—The raw data obtained consisted of time readings and absorbance readings at two wavelengths, one at the absorption maximum of the starting material, which decreases with a decrease of starting material, and the other at the absorption maximum of the product, which increases with an increase of product. The wavelengths were so close together that there was some overlap; therefore, simultaneous equations were needed to find relative concentration data. There were not two separate maxima, but rather one continuously shifting maximum, so that readings were taken on the sides of this maximum, thereby contributing to scatter among the points. A discussion of this phenomenon can be found in the literature.[24]

D. Kinetic Calculations. Elimination–Rearrangement Reaction.—The appearance of the diarylacetylene was followed spectrophotometrically at the longest wavelength band (unsubstituted, 297 mμ; *p*-methyl, 303.5 mμ; *p*-methoxy, 311.5 mμ; *p*-fluoro, 295 mμ; *m*-methyl, 300.8 mμ; and *p*-chloro, 307 mμ). The kinetic calculations were based upon the time-ratio method,[25] with certain assumptions explained in the next section.

Results and Discussion

Solvent Choice.—In order to reduce the importance of the preequilibrium step (reaction 1a) in the rearrangement and to ensure that the identity of the base was known, an aprotic solvent was desired. This solvent also had to be able to dissolve the base, potassium *t*-butoxide. Investigations showed that anhydrous "diglyme" had the necessary properties.

Kinetics. Substitution Reaction.—Tables II and III contain the concentrations used and the kinetic results obtained. An examination of the data indicates that the reaction is probably overall second order, first order in 1,1-diaryl-2-bromoethene and probably first order in base in agreement with previously reported results.[13] The rate constants for p-CF$_3$ and m-CF$_3$ were obtained in anhydrous diglyme at 0°; however, for *m*-F, rearrangement occurred under these conditions. A "corrected" rate constant[26] for substitution when *m*-F was used is given.

The positive-sloped line in Figure 1 is the Hammett plot using the second-order rate constants for the sub-

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(24) H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, p 111 ff.

(25) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1966, p 170 ff.

(26) The preequilibrium of the rearrangement reaction was suppressed by the addition of *t*-butyl alcohol, which lead to a surprisingly large solvent effect. The correction

$$k_S(m - \mathrm{F}) = k_S'(m - \mathrm{F})[k_S(m - \mathrm{CF_3})/k_S'(m - \mathrm{CF_3})]$$

was used, where k_S is the second-order rate constant for the reaction in anhydrous diglyme and k_S' is the second-order rate constant for the reaction in anhydrous diglyme containing 3% anhydrous *t*-butyl alcohol. Hydrogen bonding between the alcohol and the anion is suggested as being responsible for altering the attacking power of the anion.

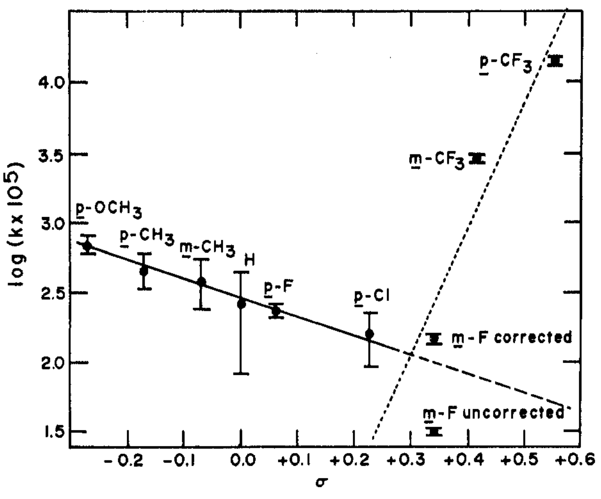

Figure 1.—Hammett plot for the elimination-rearrangement and substitution reactions of 1,1-diaryl-2-bromoethenes with potassium *t*-butoxide in dry diglyme at 0°; k is $(k_S + k_1)/(k_S^0, + k_1^0)$, as explained in the discussion.

stitution reaction of the three compounds, including the corrected and uncorrected value for the *m*-fluoro substituent. The Hammett reaction constant (ρ) is +9. A positive value was expected because electron-withdrawing groups in the *meta* or *para* position would be expected to stabilize the intermediate anion by dispersing the negative charge. The magnitude of the ρ value is interpreted as evidence that an anionic intermediate forms in the rate-determining step from a neutral substrate molecule, making the reaction sensitive to electron-withdrawing groups. Large ρ values have been obtained for aromatic nucleophilic substitution,[27,28] although of the order of +5. Even larger, though negative, values of ρ have been reported for aromatic electrophilic substitution,[29] of the order of −11. The electrophilic protonation of *para*-substituted 1,1-diarylethenes to form 1,1-diarylethyl cations yields a Hammett reaction constant value of +8 when K is plotted *vs.* σ^+. This is equilibrium data and is therefore interpreted as a measure of the stability of the cation.[30] The acid hydration of styrene, which yields a Hammett reaction constant of −4, is also an equilibrium reaction.[31] If the corrected value for the *m*-fluoro derivative were ignored, the ρ value would be in the +5 or +6 range; however, only two points would be available to obtain this value. Beltrame[23,32] has used the additive σ values in the Hammett plot for this reaction, thereby producing a ρ value which is regarded as a lower limit. Doing so would give a ρ value of *ca.* +4.5 in this case. Beltrame also points out that steric hindrance would prevent coplanarity of the aromatic moieties and the ethylenic plane for strong resonance contribution. We feel that the total effect of both moieties would be closer to the σ than to 2σ because of this steric hindrance. Therefore, the "true" value of the reaction constant, if it could be assessed, would be closer to +9 than to +4.5 with +9 itself being the upper limit.

Kinetics. Elimination-Rearrangement Reaction.—In the only previously reported example of a concave, nonlinear Hammett plot, the solvolysis of substituted ethyl benzoates, the rate-determining step involves the *breaking* of nonidentical carbon-oxygen bonds.[7] In the reaction of 1,1-diaryl-2-halogenoethenes with strong base, the rate-determining step involves the *formation* of a carbon-carbon bond *vs.* a carbon-oxygen bond while the same carbon-bromine bond breaks.[33] In this case the shape of the nonlinear Hammett plot depends upon which bond is established. In order to get the kinetic constant for the step in which the formation of the carbon-carbon bond is rate determining (eq 1b) and not have any contribution from the preequilibrium (eq 1a), we applied the time-ratio method[25] to the kinetic data obtained.

A plot of log(concentration) *vs.* time presents a typical, consecutive reaction curve. The assumption was made that the initial slope represents that time before k_r of the preequilibrium (eq 1a) becomes significant. According to this interpretation it is possible to consider the reaction as two consecutive first-order reactions and thus separate k_f of the preequilibrium (eq 1a) from k_1, the rate constant for the rearrangement step (eq 1b). However, since the initial slope changed significantly after *ca.* 30% of the starting material was consumed, and the time-ratio method involves data obtained after 15, 35, and 70% of the starting material is consumed, it was necessary to extrapolate the initial slope line. The validity of extending this line is another assumption. Since most plots of concentration *vs.* time are somewhat curved, there is error inherent in the assumption as well.

A study of the order of the reaction showed that, with a 15-fold excess of base, the reaction was pseudo-first-order. The second-order rate constant for 1,1-diphenyl-2-bromoethene at 0° held constant at 0.01 l. mol^{-1} sec^{-1} while concentrations of the enthene of 1×10^{-4}, 5×10^{-4}, and 7.5×10^{-4} mol/l. were used at constant base concentration, and while concentrations of potassium *t*-butoxide of 0.63×10^{-2}, 1.25×10^{-2}, and 3.1×10^{-2} mol/l. were used with a constant concentration of 1,1-diphenyl-2-bromoethene. The order in potassium *t*-butoxide has been reported[32] as $^3/_2$ when *t*-butyl alcohol was the solvent, rather than one, as we found with anhydrous diglyme as the solvent.

The results given in Table IV and plotted as the negative-sloped line in Figure 1 against Hammett substituent constants show a ρ of −1.3. The slope and general magnitude obtained under these conditions agree in general with the results of others,[15,17-19] as expected when one examines the electronic demands of the rate-determining step. Considerations of the nature of these electronic demands in relation to the sign of ρ have already been presented.[15,17-19]

Nonlinear Hammett Plot.—The Hammett plot for the overall reaction over a wide range of substituents can be drawn using the data shown in Tables II-IV. Figure 1 shows that a concave curve with a minimum value exists. The uncorrected point shown in the figure does not belong on the curve but was obtained

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[27] J. F. Bunnett and R. F. Snipes, *J. Amer. Chem. Soc.*, **77**, 5422 (1955).

[28] A. M. Porto, L. Altieri, A. J. Castro, and J. A. Brieux, *J. Chem. Soc., B*, 963 (1966).

[29] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957).

[30] N. C. Deno, P. T. Groves, and G. Saines, *ibid.*, **81**, 5790 (1959).

[31] J. Durand, M. Davidson, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 152 (1966).

[32] P. Beltrame, D. Pitea, and M. Simonetta, *J. Chem. Soc., B*, 1108 (1967).

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TABLE IV

KINETIC DATA FOR THE REACTION OF SYMMETRICALLY SUBSTITUTED 1,1-DIARYL-2-BROMOETHENES WITH POTASSIUM *t*-BUTOXIDE–DIGLYME[a]

Substituent	Substituent constant	[B], M[b]	$k_{exp} \times 10^3$ [c]	$k_1 \times 10^3$ [d]	Avg $k_1 \times 10^3$
p-Methoxy	−0.268	0.0175	9.4	8.0	
		0.0135	7.8	8.0	7.1
		0.0149	8.2	5.3	
p-Methyl	−0.170	0.0243	1.3	6.0	
		0.0197	7.5	3.1	4.6
		0.0169	6.7	3.4	
		0.0259	1.1	5.9	
m-Methyl	−0.069	0.0083	2.6	1.5	
		0.0198	5.6	5.4	3.9
		0.0165	5.0	4.8	
None	0.000	0.0310	6.6	1.6	
		0.0125	2.5	1.7	2.6
		0.0495	1.0	4.5	
p-fluoro	+0.062	0.0265	5.5	2.0	
		0.0264	4.7	2.4	2.4
p-Chloro	+0.227	0.0227	2.7	1.2	
		0.0170	2.0	1.0	1.6
		0.0255	2.1	2.6	

[a] c_i, the initial concentration of 1,1-diaryl-2-bromoethene, was 1×10^{-3} mol/l. [b] [B], M is the potassium *t*-butoxide concentration. [c] k_{exp} is the pseudo-first-order rate constant for the elimination–rearrangement reaction. [d] k_1 is the second-order rate constant for the rearrangement step of the elimination–rearrangement reaction by the time-ratio method.

as explained above and was included to illustrate where it appears in relation to the overall graph. Figure 1 is a plot of log k *vs.* σ; however, it mathematically represents a plot of log $[(k_S + k_1)/(k_S^0 + k_1^0)]$ *vs.* σ.[6] Since either k_S or k_1 is zero and k_S^0 is always zero, the two slopes of the curve represents data obtained in two slightly different ways, the time-ratio method for k_1 and simple kinetic calculations[34] for k_S, unified by the equation shown above. The substituent constant, σ, was used rather than additive σ values as Beltrame[23,32] used, for the reasons pointed out above.

By-Products of Substitution Reaction.—Chromatographic separation of the extracted material from the preparative-scale substitution reaction yielded other material having various ultraviolet absorption maxima. These by-products were present in very small amounts, and were not isolated and characterized. They could not be detected by ultraviolet spectrophotometry in the kinetic runs, nor in the preparative-scale runs until after chromatographic separation, owing to concentration effects. It was not known if these resulted from the room-temperature reaction or from subsequent reactions on the chromatographic columns. Their minute concentrations were considered to have no significant effect on the kinetics.

Color Changes.—A series of interesting color changes occurred in the preparative-scale reactions. When the clear solution of 1,1-bis-(*p*-trifluoromethylphenyl)-2-bromoethenes was added to the clear solution of potassium *t*-butoxide at ambient temperature, an immediate orange color was observed. The color rapidly became green, then so dark that it appeared to be black with a green tinge at higher concentrations. The same occurred for the bis-*m*-trifluoromethylphenyl derivative. When the bis-*m*-fluoro derivative was used to synthesize bis-(*m*-fluorophenyl)acetylene, the color change was from an immediate, short-lived orange color to red, then back to a more stable orange. These results lead to the speculation that the intermediate anion in the substitution reaction is green in anhydrous diglyme, and the intermediate anion in the rearrangement reaction is orange in anhydrous diglyme. If this proves correct, an interesting and useful "handle" may be available to determine the kinetic constants of the various steps of each reaction.

Conclusion

The reaction of symmetrically substituted 1,1-diaryl-2-bromoethenes with potassium *t*-butoxide in anhydrous diglyme produces two different products as a function of substituents on the aromatic ring.

The overall Hammett plot obtained is nonlinear and concave with a minimum at a σ of *ca.* +0.3. This provides another example of the type of nonlinear Hammett plot expected when an abrupt change in mechanism occurs as a result of a change in the substituents on an aromatic ring in the substrate molecule.

The Hammett plot of the substitution reaction is interpreted to indicate that a carbanion intermediate forms in the rate-determining step.

The large solvent effect on the substitution reaction when *t*-butyl alcohol is present has been tentatively explained in terms of a cage of hydrogen-bonded *t*-butyl alcohol molecules around the anion which alters the character of the anion. It was assumed, for the present, that this alteration can be linearly corrected.

The fact that substitution occurs at all in aprotic solvent rules out the *necessity* of proton addition to the intermediate anion followed by elimination of HX. Previously this had been considered a *possibility* in a *t*-butyl alcohol system.[13] The suggested[13] mechanism shown in eq 2a and 2b is most likely occurring under aprotic conditions. This is probably true for the reaction in the presence of *t*-butyl alcohol as well, since the simplest, most consistent paths that are available will usually be followed despite minor changes in a reaction system.

Registry No.—*t*-Butoxide anion, 16331-65-0; bis-(*m*-fluorophenyl)acetylene, 23349-16-8; 2,2-bis(*p*-trifluoromethylphenyl)vinyl *t*-butyl ether, 23349-17-9.

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