$-OCH_2CH_3$). No analytical results were sought for this compound since it would not crystallize even after prolonged standing.

1,2,3,4,4a,5,6,8,9,10-Decahydro-7H-7-aminobenzo[*c*]quinolizinium Iodide (31).—A saturated solution of ammonia in 10 ml of acetonitrile was added to the crude product **30** prepared from 0.4 g of **13** as described above. The acetonitrile was removed after 30 min yielding an oil. Crystallization from acetonitrile–ether gave 0.45 g (53%) of **31**: mp 164–165°; uv (EtOH) 328 mμ; ir ($CHCl_3$) 3.04, 3.19, and 6.01 μ; nmr ($CDCl_3$) τ 2.20 (s, 1 H, $-NH_2$) and 2.84 (s, 1 H, $-NH_2$).

Anal. Calcd for $C_{13}H_{21}N_2I$: C, 47.00; H, 6.37; N, 8.43. Found: C, 46.96; H, 6.30; N, 8.41.

Registry No.—Methyl iodide, 74-88-4; **12** (n = 1), 18121-40-9; **14**, 18650-05-0; **14a**, 19029-86-8; **15**, 18670-19-4; **16**, 18670-20-7; **17**, 18650-06-1; **20**, 18670-21-8; **25** (n = 2), 19039-34-0; **25** (n = 3), 19029-91-5; **26** (n = 2), 19029-92-6; **26** (n = 3), 19029-93-7; **26** (n = 4), 19029-94-8; **29**, 19029-95-9 **31**, 19029-96-0.

Mechanisms of Elimination Reactions. XXVI. Potassium *t*-Butoxide Promoted Dehydrochlorinations of the Isomeric Chlorodiphenylethenes[1]

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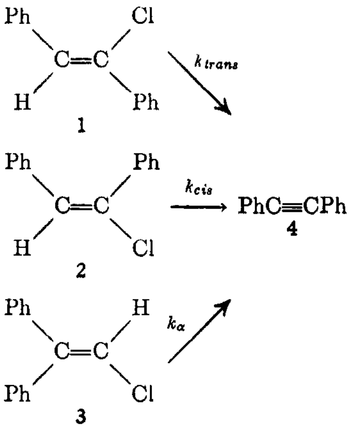
The isomeric chlorostilbenes have been subjected to potassium *t*-butoxide induced dehydrochlorination in *t*-butyl alcohol, in 5 *M* dimethyl sulfoxide in *t*-butyl alcohol, and in dimethyl sulfoxide (DMSO). The kinetics of these dehydrochlorinations were studied in the first two of these solvents, and competitive reactivities were measured in DMSO. In addition, the rates of potassium *t*-butoxide induced dehydrochlorination–rearrangement[3] of 2-chloro-1,1-diphenylethene in 5 *M* DMSO–*t*-BuOH and in DMSO[4] and a competition experiment with 1-chloro-*cis*-1,2-diphenylethene and 2-chloro-1,1-diphenylethene was performed in DMSO. The changes in reactivity ratios are discussed briefly.

A previous paper in this series[5] described the phenyllithium-induced dehydrochlorination of **1**, **2**, and **3**, all of which gave tolan (**4**) as product (Scheme I), and contrasted the relative rates of these processes, found to be $k_\alpha > k_{cis} > k_{trans}$, with the opposite order when sodium hydroxide in 92.6 wt% ethanol was used to effect the dehydrochlorination.[5b] Because of the large change in both the base strengths[6] and in the dielectric constants of the solvents,[8] the reversal in the relative rates seemed to deserve further investigation.

SCHEME I



Therefore, we undertook a study of the dehydrochlorination of the three isomers in which the base was to be held constant and the solvent was changed. The base chosen was potassium *t*-butoxide to avoid the formation of vinyl ethers as had been observed with ethoxide[3b] and also to make use of the capability to effect drastic changes in kinetic base strength[10] by changing solvent.

Experimental Section

Reagents and Solvents. *t*-Butyl Alcohol.—Eastman White Label *t*-butyl alcohol was allowed to react with cleansed potassium metal (10 g/l.) at reflux. The alcohol was then distilled into a flask containing molecular sieves (Linde, Type 4A). The alcohol was then redistilled through a 930 × 8 mm vacuum-jacketed, spiral-wire column under a stream of prepurified nitrogen (Mathieson). The material boiling at 76–77.5° (630 mm) was collected in a 4-l. serological bottle provided with a ground-glass stopper. The alcohol thus distilled had mp 25–25.5°, and 20 ml of alcohol would not decolorize 0.02 ml of Karl Fischer reagent. Immediately prior to use in the kinetic experiments, the alcohol was deoxygenated by evacuating while frozen and thawing under an atmosphere of nitrogen. A three-time repetition of this deoxygenation procedure seemed to be adequate for kinetic purposes as no color developed in the

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[1] Previous paper in series: S. J. Cristol and P. Pappas, *J. Org. Chem.*, **28**, 2066 (1963).

[2] This work was reported in the Ph.D. Dissertation of C. A. Whittemore, University of Colorado, 1963.

[3] (a) P. Fritsch, *Ann.*, **279**, 319 (1894); (b) W. P. Buttenburg, *ibid.*, **279**, 324 (1894); (c) H. Weichell, *ibid.*, **279**, 337 (1894).

[4] The kinetics of the dehydrochlorination of 2-chloro-1,1-diphenylethene for the system KO-*t*-Bu/*t*-BuOH have been reported by J. G. Pritchard and A. A. Bothner-By, *J. Phys. Chem.*, **64**, 1271 (1960).

[5] (a) S. J. Cristol and R. S. Bly, Jr., *J. Amer. Chem. Soc.*, **83**, 4027 (1961); (b) R. S. Bly, Jr., Ph.D. Thesis, Department of Chemistry, University of Colorado, 1958.

[6] The pK_A for benzene is variously reported as 36 to 40,[7] while those for water and ethanol are 14 and 18, respectively.

[7] (a) W. K. McEwen, *J. Amer. Chem. Soc.*, **58**, 1124 (1936); (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 19.

[8] Benzene, D. = 2.3;[9] ethanol, D. = 24.2.[9]

[9] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1958, p 193.

[10] Reference 7b, p 32.

kinetic samples and there were only small deviations in the rate plot (pseudo first order).

Dimethyl Sulfoxide.—The commercial material (Crown Zellerbach Corp.) was passed through a 850 × 50 mm column of molecular sieves (Linde, 4A) directly into a distillation flask and distilled through a 14 × 850 mm spiral-wire column under a stream of nitrogen. The fraction boiling at 61–62° (6.5 mm) was collected and stored in a 5-l. glass-stoppered flask until immediately prior to use when it was again passed over molecular sieves and distilled at 6.5 mm through a 25 × 40 mm Vigreux column. The material was then deoxygenated by the procedure outlined for the *t*-butyl alcohol. Such material had mp 18–18.5°, and 20 ml would not decolorize 0.05 ml of Karl Fischer reagent (Mallinckrodt, 5 mg of H_2O/ml).

Nitrogen.—Mathieson prepurified nitrogen was used after passage through a column of mixed molecular sieves and ascarite.

Potassium *t*-Butoxide in *t*-Butyl Alcohol.—These solutions were prepared by dissolving cleaned, rinsed potassium in the deoxygenated *t*-butyl alcohol. Care was taken to prevent moisture, carbon dioxide, or air from contaminating the solutions during and after preparation.

Potassium Metal.—Baker and Adamson lump potassium was cleaned of oxide under mineral oil, washed with pentane, and quickly introduced into the alcohol. Base solutions prepared from such material showed little inclination to discolor or form precipitates but any that did was discarded.

Potassium *t*-Butoxide for 5 *M* DMSO-*t*-Butyl Alcohol or DMSO Solutions.—The commercial material (MSA Corp., 95% pure) was resublimed at 200° (1 mm) and stored in a stoppered bottle in a nitrogen-atmosphere glove box. Immediately prior to the kinetic experiment, an approximate amount of material was weighed into a glass-stoppered volumetric flask and the flask was filled to the mark with the appropriate solvent. All solutions were titrated immediately prior to use. The sublimed base, when titrated against standard acid, showed an average purity of 99.5%.

5 *M* DMSO in *t*-Butyl Alcohol.—This solvent mixture was prepared by carefully weighing the required amount of dry DMSO into a dried stoppered flask and placing this in a drybox where the DMSO was transferred to a volumetric flask and diluted approximately to the mark with *t*-butyl alcohol. After transfer to the thermostat at the temperature of the kinetic run, the solution was made up to the mark.

1-Chloro-*cis*- and -*trans*-1,2-diphenylethenes were prepared by the procedures described earlier.[5a] The 1-chloro-*cis*-1,2-diphenylethene (**2**) used was that material boiling at 90–92° (0.10 mm); $n^{20}\mathrm{D}$ 1.6284 [lit. bp 97–99° (0.25 mm),[5a] 160–162° (12 mm);[11] $n^{20}\mathrm{D}$ 1.6280[5a]]. The 1-chloro-*trans*-1,2-diphenylethene (**1**) used melted at 52–54° (lit. mp 52–54°,[5a] 52°[11]).

2-Chloro-1,1-diphenylethene (**3**) was prepared by the method described in the previous paper.[5a] The material melting at 39.6–41.3° (lit.[5a] mp 39.5–42°) was used for the kinetic runs although periodic recrystallization from ethanol[5a] was necessary as the material seems to be somewhat unstable at room temperature.

Standardization and Analytical Procedure.—The potassium *t*-butoxide solutions were standardized against standard acid after dilution into a large excess of water, using phenolphthalein as indicator. The aliquots for the standardization were taken using a calibrated automatic pipet or calibrated hypodermic syringe[12] and were usually taken before, during, and after ampoule charging.

Determination of Products of Reaction.—The product of the reactions of the isomeric chlorodiphenylethenes was established to be tolan (**4**) in *t*-butyl alcohol. This agrees with the results of Pritchard and Bothner-By[4] who found that tolan was produced from 2-chloro-1,1-diphenylethene in at least 90% yield, according to ultraviolet analysis. In the case of DMSO, the product analysis was somewhat complicated by the presence, in addition to tolan, in the gas chromatogram of a minor constituent (<5%) which did not correspond to the chlorodiphenylethenes or to tolan. However, it is believed that this material might arise *after* the dehydrochlorination, for the same substance is found in a gas chromatogram of a mixture of potassium *t*-butoxide and tolan. This product was deemed to be of little importance because of its low yield and rate constants were not corrected for its formation.

Kinetic Procedure for Determination of Rate Constants in *t*-Butyl Alcohol.—The kinetic samples were prepared by pipeting the required volumes of substrate and base solutions, thermostated at 30°, into Pyrex ampoules which had previously been flushed with nitrogen. The contents of the ampoules were quickly frozen to prevent reaction, sealed with a flame, and kept in an ice bath until introduction into a thermostated oil bath. Approximately 15 min after being placed in the oil, the samples were vigorously shaken to ensure mixing of the now-melted contents and a sample was withdrawn, quenched, and titrated for liberated chloride as a zero-time sample. Thereafter samples were taken at calculated times, utilizing the rate nomographs of Smith and Stevens.[13] The extent of reaction (ϕ) for the samples were determined by titration of liberated chloride.[14] A large excess of base was used, allowing the reactions to be run pseudo first order. The rate constants were calculated by taking the slope of a straight line drawn by inspection through the points of a log $(1 - \phi)$ *vs.* time plot, and multiplication of the negative slope by the factor 2.303/$[\mathrm{BuO}^-]$. These values were then corrected for solvent expansion in the cases where the reactions were performed at elevated temperatures.

All of the reactions were followed to at least one half-life and many considerably beyond that. The pseudo-first-order rate plots showed no important deviations from linearity.[2] The second-order rate constants for the reactions in *t*-butyl alcohol are given in Table I.

The same general procedures were used for the determination of the rate constants for the reactions of potassium t-butoxide with 2-chloro-1,1-diphenylethene in 5 *M* DMSO-*t*-BuOH. The rate constants are given in Table II.

Kinetic Procedure for Dehydrohalogenations in 5 *M* DMSO in *t*-Butyl Alcohol.—Because of the rapidity with which the potassium *t*-butoxide induced dehydrochlorinations of the *cis*- and *trans*-1-chloro-1,2-diphenylethenes occurred, the rate constants in this solvent system were determined by performing a series of separate kinetic experiments utilizing the same base and substrate concentrations. Aliquots of the substrate solution, held at temperature in the thermostat, were transferred *via* a calibrated hypodermic syringe[12] to 50-ml volumetric flasks[15] which had been flushed with nitrogen. The substrate flasks were then allowed to come to equilibrium in the thermostat. Base aliquots from a solution held at temperature were then forcefully injected into the substrate solutions.[16] At the time that the collar was snapped from the hypodermic syringe, an electric timer was started. The reaction was quenched by then injecting 5 ml of 1.5 *M* nitric acid, the contents were analyzed for liberated chloride ion, and the data were treated in the same manner as the data for the dehydrochlorinations in *t*-butyl alcohol. The individual points on the line in the log $(1 - \phi)$ *vs.* time graph thus represent separate kinetic experiments performed with the same reagents. As with the *t*-butyl alcohol experiments, all reactions were run pseudo first order, using a large excess of base. This procedure was used for the potassium *t*-butoxide induced dehydrochlorination of 1-chloro-*trans*-1,2-diphenylethene and 1-chloro-*cis*-1,2-diphenylethene. Sample plots are given in ref 2.

After determination of the slope of the line through the points on the log $(1 - \phi)$ *vs.* time plots, the second-order rate constants were calculated as described above. The rate constants are given in Table II.

An examination of the data in Tables I and II indicates only a slight variation in the calculated second-order rate constants with differing base concentrations. The variations are small enough that it appears that one may readily assume that the reactions are first order in base and first order in chloro olefin.

The Arrhenius activation energies were calculated from a plot of log k_2 *vs.* $1/T$.[2,17] The entropies of activation were cal-

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[11] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

[12] T. G. Traylor and R. A. Crane, *Experentia*, **17**, 35 (1961).

[13] S. G. Smith and I. D. R. Stevens, *J. Chem. Educ.*, **38**, 574 (1961).

[14] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 3rd ed, 1952, p 546.

[15] The long necks and small bulbs for these flasks are a hindrance to air inclusion and allow good mixing of the base and substrate solution.

[16] This ensured quick, complete mixing of the base and substrate solutions. When possible, the flasks were shaken following the addition of the base solutions.

[17] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, N. Y., 2nd ed, 1961, p 23.

TABLE I

RATE DATA FOR THE DEHYDROCHLORINATION OF THE ISOMERIC 1-CHLORO-1,2-DIPHENYLETHENES IN *t*-BUTYL ALCOHOL

Temp, °C	[KO-*t*-Bu], *M*	[RCl], *M*	10^4k_2, l./mol/sec	10^4k_2, l./mol/sec (cor)	10^4k_2, l./mol/sec (ave)
		1-Chloro-*cis*-1,2-diphenylethene			
59.88	0.358	0.0104	0.827	0.862	
	0.358	0.0104	0.857	0.894	0.877
	0.346	0.0103	0.840	0.876	
71.56	0.250	0.0104	2.89	3.06	
	0.240	0.0106	2.80	2.97	3.06
	0.128	0.0114	2.70	2.86	
	0.139	0.0106	3.12	3.30	
83.40	0.227	0.0102	10.1	10.9	11.6
	0.247	0.0103	11.3	12.2	
		1-Chloro-*trans*-1,2-diphenyethene			
36.76	0.260	0.0106	0.724	0.730	
	0.260	0.0106	0.717	0.723	0.730
	0.208	0.0103	0.722	0.728	
	0.208	0.0103	0.735	0.741	
47.97	0.232	0.0109	2.37	2.43	
	0.232	0.0109	2.40	2.46	2.44
59.88	0.255	0.0100	7.72	8.04	
	0.255	0.0100	7.79	8.12	
	0.126	0.0102	8.05	8.39	8.19
	0.126	0.0102	7.89	8.22	

TABLE II

RATE DATA FOR THE DEHYDROCHLORINATION OF THE ISOMERIC CHLORODIPHENYLETHENES IN 5 *M* DIMETHYL SULFOXIDE IN *t*-BUTYL ALCOHOL

Temp, °C	[KO-*t*-Bu], *M*	[RCl], *M*	10^4k_2, l./mol/sec	10^4k_2, l./mol/sec (ave)
	1-Chloro-*trans*-1,2-diphenylethene			
0.41	0.274	0.0103	355	368
	0.274	0.0103	381	
12.50	0.222	0.0101	1660	1685
	0.222	0.0101	1710	
	0.128	0.0102	2000	
	0.128	0.0102	2020	2010
24.91	0.217	0.0104	4180	4250
	0.232	0.0102	4330	
	1-Chloro-*cis*-1,2-diphenylethene			
12.50	0.247	0.0102	3.23	3.14
	0.122	0.0101	3.05	
	0.122	0.0101	3.12	
	0.242	0.0106	3.15	
	0.242	0.0106	3.16	
24.91	0.217	0.0104	14.5	14.8
	0.231	0.0106	15.1	
36.72	0.315	0.0101	82.6	85.6
	0.315	0.0101	89.0	
	2-Chloro-1,1-diphenylethene[a]			
83.25	0.240	0.0101	0.0864	0.0884
	0.240	0.0101	0.0903	
93.55	0.203	0.0102	0.277	0.276
	0.203	0.0102	0.275	
105.29	0.248	0.0102	1.01	
	0.248	0.0102	1.02	
	0.131	0.0101	0.995	1.01
	0.131	0.0101	1.02	
116.00	0.220	0.0100	3.42	
	0.220	0.0100	3.28	
	0.133	0.0100	3.14	3.22
	0.133	0.0100	3.05	

[a] These reaction rate constants are corrected for solvent expansion.

culated using Eyring's equation.[18] These are tabulated in Table III.

Competition Experiments in Dimethyl Sulfoxide.—These were performed by the method of Lee.[19] A slight modification was made in the determination of the k_{cis}/k_{α} ratio for ease of analysis by gas chromatography. These experiments are summarized in Tables IV and V. The ratios of the rate constants, when used in conjunction with an initial rate constant for the potassium *t*-butoxide induced dehydrochlorination of 2-chloro-1,1-diphenylethene in DMSO,[20] gives approximate rate constants for all three isomers in DMSO. The constants so derived are included in Table VI.

Discussion

In the earlier work,[5] it was noted (see Table VI) that, while ethoxide-promoted elimination followed the anticipated order, *trans* elimination faster than *cis* faster than α, the phenyllithium-induced reactions were exactly reversed in order. The unusual reactivity order in the latter case was consistent with the reactivities of the isomers of β-bromostyrene toward phenyllithium,[22] and cyclic mechanisms or hydrogen–metal interchange mechanisms were proposed to rationalize these results. Certain of these conclusions have been confirmed and extended in the elegant work of the Heidelberg school.[23,24]

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[18] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 199.

[19] T. S. Lee in "Technique of Organic Chemistry," Vol. VIII, S. L. Friess and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1953, p 107 ff.

[20] A single kinetic run, using second-order techniques, gives an initial rate constant of 3.0 l./mol/sec. This quickly decreased to 0.85 l./mol/sec after *ca.* 50% reaction, which value could be roughly duplicated by adding a small amount of *t*-butyl alcohol to make a solution corresponding to the 50% reaction in pure DMSO. Similar decreases in rates with small amounts of added *t*-butyl alcohol have been observed in other systems by Schriesheim and Rowe.[21]

[21] A. Schriesheim and C. A. Rowe, Jr., *J. Amer. Chem. Soc.*, **84**, 3160 (1964).

[22] S. J. Cristol and R. F. Helmreich, *ibid.*, **77**, 5034 (1955).

[23] G. Köbrich, H. Trapp, and I. Hornke, *Chem. Ber.*, **100**, 2011 (1967); G. Köbrich and F. Ansari, *ibid.*, **100**, 961 (1967); G. Köbrich, *Angew. Chem. Intern. Ed. Eng.*, 640 (1967), and references cited therein.

[24] M. Schlosser and V. Landenberger, *Chem. Ber.*, **100**, 3877, 3893, 3901 (1967).

TABLE III

ACTIVATION PARAMETERS FOR THE DEHYDROCHLORINATION OF THE ISOMERIC CHLORODIPHENYLETHENES USING POTASSIUM *t*-BUTOXIDE AS BASIC REAGENT

Diphenylethene	Solvent	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	10^4k_2, l./mol/sec (temp, °C)
1-Chloro-*trans*-1,2- (1)	*t*-BuOH	21.5	−10.5	8.05 (60)
1-Chloro-*cis*-1,2- (2)	*t*-BuOH	25.9	−1.5	0.886 (60)
1-Chloro-*trans*-1,2- (1)	5 *M* DMSO-BuOH	16.2	−3.4	4280.0 (25)
1-Chloro-*cis*-1,2- (2)	5 *M* DMSO-BuOH	24.0	3.3	18.5 (25)
2-Chloro-1,1- (3)	5 *M* DMSO-BuOH	30.3	0.3	0.602 (100)

TABLE IV

COMPETITIVE REACTIONS BETWEEN THE ISOMERIC 1-CHLORO-1,2-DIPHENYLETHENES USING POTASSIUM *t*-BUTOXIDE IN DIMETHYL SULFOXIDE AT 19.17 ± 0.02°

Initial composition				Final composition		
% *cis*	% *trans*		% reaction obsd	% *cis*	% *trans*	Ratio of k_{trans}/k_{cis}
49.5	50.5		43.1	72.7	27.3	6.4
49.5	50.5		43.5	73.1	26.9	6.5
49.5	50.5		43.0	70.6	29.4	5.3
		Ave	43.2	72.1	27.9	6.0\6.0[a]
14.8	85.2		44.6	24.7	75.3	8.9
14.8	85.2		44.8	22.6	77.4	4.1
		Ave	44.7	23.7	76.3	5.7\6.5[a]
14.8	85.2		66.4	36	64	6.8
14.8	85.2		64.9	36	64	8.4
14.8	85.2		64.9	32	68	4.6
14.8	85.2		65.9	35	65	6.2
14.8	85.2		65.3	35	65	6.7
14.8	85.2		66.5	37	63	7.8
		Ave	65.7	35.2	64.8	6.6\7.8[a]

[a] Average value obtained by average percentages\arithmetical averages of ratios.

TABLE V

COMPETITIVE REACTIONS BETWEEN 1-CHLORO-*cis*-1,2-DIPHENYLETHENE AND 2-CHLORO-1,1-DIPHENYLETHENE USING POTASSIUM *t*-BUTOXIDE IN DIMETHYL SULFOXIDE AT 19.17 ± 0.02°

Initial composition		% reaction obsd	Final composition		
% *cis*	% α[a]	(from chloride titration)	% *cis*	% α	k_{cis}/k_{α}
97.8	2.18	76.6	91	9	44
97.8	2.18	79.0	90	10	42

[a] 2-Chloro-1,1-diphenylethene.

TABLE VI

RATE CONSTANTS FOR DEHYDROCHLORINATION OF THE ISOMERIC CHLORODIPHENYLETHENES

	10^4k_2, l./mol/sec				
Base/solvent	*trans*-β	*cis*-β	α	Temp, °C	Comments
NaOH/92.6 wt % ethanol	9.04	0.0435	0.0004	97	Ref 5b
C_6H_5Li/*n*-Bu_2O	7.71	170	1200	50	Ref 5a
KO-*t*-Bu/*t*-BuOH	184	33.4	0.064	95	*a*
KO-*t*-Bu/(5 *M* DMSO–*t*-BuOH)	4300	18.0	2.8×10^{-5}	25	This work
KO-*t*-Bu/DMSO	7.7×10^6	1.3×10^6	3×10^4	19	*e*

[a] The values for the *trans*-β and *cis*-β eliminations are from the Arrhenius plot at the temperature indicated. The value for the α elimination was obtained from the work of Pritchard and Bothner-By[4] by assuming second-order kinetics.[b] [b] This assumption was made for the purposes of comparison, but definitive statements as to the base order will have to await further data. Our data seem to indicate a fair fit for first-order base participation. The kinetic base order as found by others either has been three halves,[4] first,[c] or has not been determined.[d] [c] T. Thippeswamy, Ph.D. Thesis, University of Cincinnati, 1963; D. F. Bender, Ph.D. Thesis, University of Cincinnati, 1967. [d] W. M. Jones and R. Damico, *J. Amer. Chem. Soc.*, **85**, 2273 (1963). [e] Obtained by taking the rate of the α elimination as given above and multiplying by the preference factors as given by the competition experiments.

The present work was undertaken at a time[2] when it was felt that it might be informative to use an alkoxide base (potassium *t*-butoxide) of sufficient steric requirement to obviate the possibility of alkoxide substitution[25] and yet would allow a substantial increase in the apparent base strength.[10]

Over the range ethanol to DMSO, rate enhancements of 10^9 to 10^{11} were observed, with somewhat larger increases for *cis* and α eliminations than for *trans* elimination. However, inspection of the data in Table VI (excluding the phenyllithium-induced reactions) shows that the relative rate increases for *trans*, *cis*, and α eliminations do not vary in a monotonous understandable fashion. Thus, in ethanol (at 97°), $k_{trans}:k_{cis}:k_\alpha = 2 \times 10^4:100:1$; in *t*-butyl alcohol (at 95°), the ratios change to 3000:600:1; in 5 *M* DMSO–*t*-butyl alcohol (at 25°), to $10^8:6 \times 10^5:1$; and finally in DMSO (at 19°), to 250:40:1.

It has been suggested[26] that alkaline dehydrohalogenations in *trans* coplanar systems (such as in **1**) are concerted reactions while those in *cis* systems (such as in **2**) have carbanion intermediates. The data available[27] make it clear that, if the assumption is correct for *cis* elimination, the carbanion-formation step is usually the rate-limiting step; that is, the carbanion generally tends to lose halide ion (or other nucleofuge) rather than reprotonate to regenerate starting material. The assumption regarding carbanion intermediates in *cis* systems has been criticized, at least for saturated compounds in which the proton and nucleofuge may have *syn* eclipsed conformation,[28–30] although calculations have been performed[31] which appear to indicate the efficiency of the concerted *anti* coplanar elimination. Discussion of the concept of *syn* coplanar concerted eliminations to olefinic systems has not been extensive.[30] It has been shown[32] that the *trans* elimination in the closely allied styryl system proceeds without deuterium–hydrogen exchange and it seems reasonable to assume such is the case for **1**, and that this elimination is concerted.

On the other hand, **3** has been shown[4,33] to undergo proton exchange very rapidly compared with loss of chloride ion and rearrangement to give **4**. This, of course, means that **3** is in equilibrium with its carbanion, and that the rate-determining step with **3** is quite different from that of **1** and **2**.

We had hoped that the modifications in solvents utilized might change all of the eliminations to carbanion or "carbanionlike" situations or at least reduce the differences in energy requirements of the concerted and carbanion processes. (Since this work was completed,[2] it has been reported[34] that saturated compounds react by concerted processes, even in DMSO.) We thought then that increasing the base strength might telescope the reactivity differences between *cis* and *trans* elimination, even if, in view of the more complicated situation in the α elimination, less capability for prediction seemed assured. In fact, however, the ratio of k_{trans}/k_{cis} of 200 in aqueous ethanol was reduced to 6 in *t*-butyl alcohol, increased again to 240 in 5 *M* DMSO–*t*-butyl alcohol, and decreased again to 6 in DMSO. The k_{trans}/k_{cis} ratio change in going from aqueous ethanol to *t*-butyl alcohol might be explainable by a "*syn* mechanism" such as those proposed by Sicher,[29] for potassium *t*-butoxide is certainly present as a tight ion pair in *t*-butyl alcohol.

However, this then leaves the divergence of relative rates in the mixed solvents and in DMSO unanswered. The results may be caused by the peculiar nature of the mixed *t*-butyl alcohol–DMSO solvent, where a carbanion process,[26] followed by chloride ion loss, might be disfavored (compare especially the very small increase in rate for **3** in this medium compared with *t*-butyl alcohol).[35] Parker[36] has discussed the specific solvation of anions in dipolar aprotic solvents, and it appears likely that such effects (plus general dielectric constant effects) are responsible for the results we have observed, but we are not in a position to discuss these in depth at the present time. There appears to us to be no reason at present to assume that mechanisms described above (both concerted and carbanionic) are not possible in each of the solvent systems studied.

Registry No.—**1**, 948-99-2; **2**, 948-98-1; **3**, 4541-89-3; **4**, 501-65-5; potassium *t*-butoxide, 865-47-4; dimethyl sulfoxide, 67-68-5; *t*-butyl alcohol, 75-65-0.

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