(7) P. Zuman, "Substituent Effects in Organic Polarography", Plenum Press, New York, 1967.
(8) A. Streitwieser, J. R. Murdoch, G. Häfelinger, and C. J. Chang, *J. Am. Chem. Soc.*, **95**, 4248 (1973).
(9) H. H. Freedman in "Carbonium Ions", Vol. IV, G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, 1973, Chapter 28.
(10) C. S. Marvel, J. F. Kaplan, and C. M. Himel, *J. Am. Chem. Soc.*, **63**, 892 (1941).
(11) C. D. Ritchie, "Physical Organic Chemistry", Marcel Dekker, New York, 1975, p 102ff.
(12) (a) The triphenylmethyllithium tetramethylethylenediamine complex gives twist angles for the phenyl rings of 19.7, 30.6, and 44.8°, respectively: J. J. Brooks and G. D. Stucky, *J. Am. Chem. Soc.*, **94**, 7333 (1972). (b) Triphenylmethyl perchlorate has twist angles of 31.8 ± 0.6°: A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Crystallogr.*, **18**, 437 (1965). (c) Triphenylmethyl radical investigated by electron diffraction in the vapor phase has twist angles of approximately 45°: P. Anderson, *Acta. Chem. Scand.*, **19**, 629 (1965). Crystallographic studies of the tri-*p*-nitrophenylmethyl radical gave twist angles of 40, 30, and 30° for the phenyl rings: P. Andersen and B. Klewe, *Acta Chem. Scand.*, **21**, 2599 (1967).
(13) R. Hoffmann, P. Bissell, and D. G. Farnum, *J. Phys. Chem.*, **73**, 1789 (1969), and references cited therein.
(14) L. D. McKeever and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 4544 (1966), and references cited therein.
(15) T. H. Lowry and K. S. Schueller Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, 1976, p 62ff.
(16) A. Streitweiser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1962, Chapter 7.
(17) W. E. Bachmann, "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 841.
(18) R. Hutchins, D. Hoke, J. Keough, and A. Koharski, *Tetrahedron Lett.* **40**, 3495 (1969).
(19) F. C. Whitmore and E. N. Thurman, *J. Am. Chem. Soc.*, **51**, 1491 (1929).
(20) K. Guyot, *C. R. Hebd. Seances Acad. Sci.*, **154**, 122 (1912).
(21) M. Gomberg, *Ber.*, **37**, 631 (1904).
(22) The Brown and Bell procedure in diglyme water was superior to the Me_2SO procedure: H. Bell and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 1473 (1966).
(23) K. Guyot, *Bull Soc. Chim. Fr.*, [3] **17**, 474 (1897).
(24) N. H. Tousley and M. Gomberg, *J. Am. Chem. Soc.*, **26**, 1516 (1904).
(25) M. Gomberg, *Ber.*, **35**, 2399 (1902).
(26) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(27) R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, 1969.
(28) H. Volz and W. Lotsch, *Tetrahedron Lett.*, 2275 (1969).

Kinetics of Methanolysis of and of Sodium Methoxide Induced Elimination from Substituted Benzyldimethylcarbinyl Chlorides[1]

J. F. Bunnett* and Srinivasa Sridharan[2]

Thimann Laboratories, University of California, Santa Cruz, California 95064

Received June 26, 1978

Rates of methanolysis of a series of substituted benzyldimethylcarbinyl chlorides at three temperatures obey the Hammett equation with ρ ca. −0.9. $\Delta S^{\ddagger}$ is in most cases about −4 gibbs/mol. Rates of reactions of *p*-nitro- and 3,5-dichlorobenzyldimethylcarbinyl chlorides with NaOMe in MeOH to form isomeric olefins have been measured. When taken in conjunction with literature data, our measurements for $ArCH{=}CMe_2$ formation necessitate use of σ^- for p-NO_2 to give good Hammett correlation, with ρ +1.2. For formation of $ArCH_2C(Me){=}CH_2$, ρ is essentially zero (−0.07). The data for the NaOMe reactions are successfully interpreted in terms of variable transition state E2 theory, but do not support an alternative theory that postulates attack of base on an ion pair.

The kinetics of solvolysis of benzyldimethylcarbinyl chloride (**1a**) and of elimination induced by NaOMe, both in methanol at 75.8 °C, were studied by Bunnett, Davis, and Tanida.[3] A few years later, Blackwell, Fischer, and Vaughan[4,5] extended such kinetic study to a number of ring-substituted benzyldimethylcarbinyl chlorides, all at 66.5 °C. We now report a further extension of these studies, to include two substrates not previously investigated and, for the first time, to include the influence of temperature and enable the calculation of activation parameters.

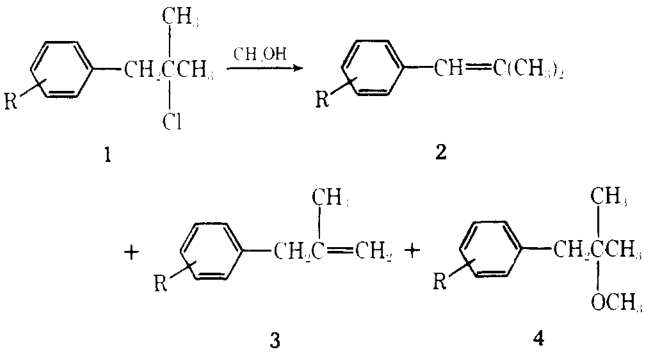
The solvolysis of substituted benzyldimethylcarbinyl chlorides in 80% aqueous ethanol has been reported by Landis and VanderWerf,[6a] Tessler and VanderWerf,[6b] and Brown and Kim.[7] However, these investigators did not determine product compositions or the kinetic effects of added bases.

Results

From either methanolysis or methoxide-induced elimination, the products are two olefins (**2** and **3**) and an ether (**4**).

Synthesis of Substrates. Although most of the substrates were obtained straightforwardly, the synthesis of one calls for special comment. *p*-Nitrobenzyldimethylcarbinyl chloride (**1f**) is conspicuously absent from the reports of Landis and VanderWerf[6a] and of Brown and Kim.[7] Blackwell et al.[4,5] mention specifically their inability to obtain it. We succeeded in synthesizing **1f** by nitration of **1a** with nitric acid in acetic anhydride at ca. 60 °C and in isolating it as a crystalline solid.

Products of types **2**, **3**, and **4** were obtained by treating the various substrates with bases in methanol. They were isolated, ultimately by gas–liquid chromatography (GLC), characterized by their NMR and other spectra, and used for qualitative and quantitative calibration of the GLC product analyses on reactions under kinetic conditions.


1 2 3 4

a, R = H
b, R = *p*-CH_3
c, R = *p*-OCH_3
d, R = *p*-Cl
e, R = 3,5-Cl_2
f, R = *p*-NO_2

Rate and Product Determinations. Inasmuch as the 1-aryl-2-methyl-1-propenes (**2**) strongly absorb ultraviolet light at about 250 nm, except that λ_{max} for **2f** is at 316 nm, while compounds of types **1**, **3**, and **4** have little absorption at these wavelengths, it was possible to estimate the yield of **2** from any reaction by spectrophotometry. In most cases the photometric estimate agreed with the GLC determination within ±2%, but the GLC yield was used for treatment of data.

We determined rate constants for solvolysis of compounds **1a–f** at three temperatures except in the case of **1a**, and our determinations are summarized in Table I. In order to avoid acid-catalyzed interconversion of products, all solvolysis re-

0022-3263/79/1944-1458$01.00/0 © 1979 American Chemical Society

Table I. Rate Constants and Product Compositions for Methanolysis of Substituted Benzyldimethylcarbinyl Chlorides[a]

substituent(s)	substrate no.	temp,[b] °C	n[c]	10^4k_s,[d] s^{-1}	products, %[d,e]		
					2	3	4
H	**1a**	56.0	5	0.28 ± 0.04	27.4	18.8	53.8
		96.0	4	15.4 ± 1.1	30.8	22.9	46.3
p-CH_3	**1b**	55.9	1	0.28	29.1	25.3	45.7
		75.8	3	2.68	32.2	30.2	37.7
		95.8	3	20.7	31.6	46.2	22.2
p-OCH_3	**1c**	55.8	2	0.36	32.9	25.0	42.0
		75.8	2	3.73	31.2	27.6	41.2
		96.2	2	25.2	31.5	29.6	39.0
p-Cl	**1d**	55.8	2	0.12	30.4	26.2	43.4
		75.8	2	1.27	32.8	23.2	44.0
		96.0	3	8.78	36.1	22.1	41.8
3,5-Cl_2	**1e**	56.0	2	0.038	26.4	20.6	53.0
		75.8	2	0.425	29.6	24.4	46.0
		96.0	5	3.51	32.0	27.4	40.6
p-NO_2	**1f**	56.0	3	0.039	25.5	21.3	53.1
		75.8	3	0.411	28.2	24.6	47.2
		96.0	3	3.25	30.6	27.5	41.8

[a] Substrate concentration ca. 0.01 M; 2,6-lutidine present in all runs, 0.01–0.08 M, as well as NaBr, 0.20 M. [b] Temperature variation ±0.1 °C at 56 and 75.8 °C, ±0.2 °C at 96 °C. [c] Number of replicate runs. [d] Averages from n replicate runs; for **1a**, the standard deviation is shown. [e] Yields by GLC.

actions were conducted in the presence of 2,6-lutidine to neutralize the HCl byproduct. It was shown earlier[3] that 2,6-lutidine does not measurably react with **1a.** Sodium bromide, 0.2 M, was also present in solvolysis runs. It was our purpose to use the solvolysis data for treatment of kinetic data concerning the reactions of NaOMe and NaSEt with the same substrates, and 0.2 M NaBr was provided to approximate somewhat the salt effects that those bases would have.

By GLC analysis of "infinity" solutions, the yields of solvolysis products of types **2, 3,** and **4** were in each case determined. These also are listed in Table I. Yields of the methyl ethers (**4**) were in the vicinity of 50% at 56 °C but in all cases diminished as the temperature increased. Yields of 1-aryl-2-methylpropenes (**2**) were in the vicinity of 30% and in most cases increased somewhat with temperature. Yields of terminal olefins (**3**) were in the vicinity of 20% and in most cases increased with temperature, sometimes steeply. These solvolyses are believed to occur via carbocation intermediates, and the changes in product yields with temperature indicate that coordination with the solvent to form ethers generally has a lower activation energy than proton abstraction, especially to form the terminal olefins.

Inasmuch as there is a statistical factor of three in favor of elimination to the terminal olefin, our results show that there is roughly a preference of fourfold for elimination to Saytzeff olefin (**2**) rather than Hofmann olefin (**3**).

Rates and product compositions were also determined for reactions of **1e** and **1f** with NaOMe at several levels of concentration at each of three temperatures. Runs were conducted with the base in great excess over the substrate, and pseudo-first-order kinetics prevailed. The techniques employed were substantially the same as used for solvolysis runs. The data obtained are presented in Table II. The conjugated olefins (**2**) were the predominant products from these reactions, with minor amounts of **3** and **4** being formed.

A potential or actual complication in the reactions with NaOMe is base-catalyzed isomerization of terminal olefin (**3**) to conjugated olefin (**2**). For the conversion of **3a** to **2a** in the presence of 1.2 M NaOMe at 114 °C, a pseudo-first-order rate constant of 2.8×10^{-6} s^{-1} has been measured.[8] Assuming that $\Delta H^{\ddagger}$ for isomerization is 25.6 kcal/mol, that ρ for rearrangement of a series of **3** to **2** is +4.0, and that σ^- prevails for p-NO_2, one reckons pseudo-first-order rate constants for rearrangement of **3f** to **2f** that somewhat exceed the k_ψ values listed for **1f** in Table II. By the same approach, isomerization rate constants <10% of the k_ψ values listed for **1e** in Table II are estimated.

Also relevant, as we report elsewhere,[9] is that **3f** on treatment with 0.42 M EtSNa and 0.21 M EtSH in methanol under the conditions of kinetic determinations with that reagent suffered partial isomerization to **2f.** Inasmuch as the basicity of NaOMe solutions is greater, the rate of **3f** to **2f** isomerization is likely to be higher in the NaOMe reactions.

We therefore deem it probable that much isomerization of **3f** to **2f** did occur in the course of the NaOMe rate measurements. Accordingly, we have not attempted to calculate k_3 values for **1f.** As for the k_2 values, they may be overestimated by as much as 20%; even the extreme 20% overestimate would not significantly affect our conclusions below concerning Hammett correlation of our data.

Our photometric observation of the reaction of **1e** with NaOMe at 96 °C did show some upward drift of absorbance, by about 6%, after ten half-lives had passed, that is, after the main reaction was essentially finished. That upward drift was probably due to slow isomerization of **3e** to **2e.** Scrutiny of our raw data has led us to conclude that our kinetic and product data for that reaction at 96 °C are partially affected by that subsequent isomerization, but we don't think that it affected our measurements at 56 and 75.8 °C very much.

It is apparent from rate data that part of the total reaction of **1e** or **1f** with NaOMe in MeOH is solvolysis. Some dissection of the rate and product data in Table II is therefore necessary in order to evaluate the rate constants and product compositions that pertain to reactions with the base itself. Such dissection has been performed previously,[3-5] and what we have done is similar to but not exactly the same as what was done before. One assumes (a) that the rate of solvolysis is the same in the presence of NaOMe as in the solvolysis determinations, (b) that the ether product (**4e** or **4f**) is derived only from solvolysis, and (c) that the product composition from solvolysis in the presence of NaOMe is the same as in its absence. Subtraction of k_ψ for solvolysis from k_ψ for the total reaction in the presence of NaOMe gives a pseudo-first-order rate coefficient pertaining only to bimolecular (E2) elimination and enables an estimate of the fraction of the total reaction that is E2. Multiplication of the yield of **4** by the **2**/**4** and **3**/**4** product ratios from solvolysis gives, respectively, estimates of the yields of **2** and **3** derived from solvolysis, and the

Table II. Rate Constants and Product Compositions for Reactions of 3,5-Dichloro- and *p*-Nitrobenzyldimethylcarbinyl Chloride with Sodium Methoxide in Methanol[a]

substituent(s)	substrate no.	temp,[b] °C	[NaOMe],[c] M	10^4k_ψ, s^{-1}	Products, %[d]		
					2	**3**	**4**
3,5-Cl_2	**1e**	56.0	0.561	0.59	91.8	5.5	2.7
			0.749	0.82	93.0	5.1	1.9
			0.935	1.04	93.7	5.0	1.3
			1.185	1.34	94.5	4.6	0.9
		75.8	0.182	1.88	84.1	8.3	7.6
			0.547	5.06	91.0	6.2	2.8
			0.730	6.55	91.9	5.7	2.4
			0.911	8.23	93.0	5.5	1.5
			1.155	10.7	93.7	5.3	1.0
		96.0	0.118	10.2[e]	77.2[e]	13.4[e]	9.4[e]
			0.237	19.8[e]	86.4[e]	8.4[e]	5.2[e]
			0.354	30.3[e]	86.6[e]	9.6[e]	3.8[e]
p-NO_2	**1f**	56.0	0.517	2.84	93.3	2.0	4.7
			0.670	4.52	96.4	1.8	1.8
			0.956	7.92	95.4	1.8	2.8
		75.8	0.064	2.57	92.2	2.3	5.5
			0.126	5.85	94.3	1.8	3.9
			0.196	10.5	94.6	3.1	2.3
			0.391	19.8	95.0	2.4	2.6
			0.652	39.0	95.2	1.8	3.0
			0.943	50.5	89.6	1.9	8.5
		96.0	0.063	16.6	92.2	2.5	5.3
			0.122	40.2	93.6	2.0	4.4
			0.635	203.0	95.8	1.9	2.3

[a] Substrate concentration ca. 0.01 M. [b] See footnote *b*, Table I. [c] Corrected for thermal expansion of methanol. [d] Yields by GLC. [e] Average from duplicate runs.

Table III. Dissection of Rates and Product Yields, Reactions of 1e and 1f with Sodium Methoxide in Methanol[a]

substituent(s)	substrate no.	temp, °C	[NaOMe],[b] M	E2 fraction of reaction		fraction of **2** in E2 olefins	10^4k_2,[b] M^{-1} s^{-1}	10^4k_3,[b] M^{-1} s^{-1}
				from rates	from products			
3,5-Cl_2	**1e**	56.0	0.561	0.94	0.95	0.952	0.94	0.047
			0.749	0.95	0.96	0.954	1.00	0.048
			0.935	0.96	0.98	0.954	0.96	0.046
			1.185	0.97	0.98	0.956	0.97	0.045
		75.8	0.182	0.77	0.84	0.949	7.6	0.41
			0.547	0.92	0.94	0.950	8.0	0.43
			0.730	0.94	0.95	0.954	8.0	0.39
			0.911	0.95	0.97	0.951	8.1	0.42
			1.155	0.96	0.98	0.951	8.5	0.43
		96.0	0.118	0.66	0.77	0.91	52	5
			0.237	0.82	0.87	0.94	65	4
			0.354	0.88	0.91	0.92	70	6
p-NO_2	**1f**	56.0	0.517	0.99	0.91	*c*	5.4	
			0.670	0.99	0.97	*c*	6.6	
			0.956	0.99	0.95	*c*	8.2	
		75.8	0.064	0.84	0.88	*c*	33.6	
			0.126	0.93	0.92	*c*	43.2	
			0.196	0.96	0.95	*c*	50.4	
			0.391	0.98	0.94	*c*	49.0	
			0.652	0.99	0.94	*c*	59.0	
			0.943	0.99	0.82	*c*	53.1	
		96.0	0.063	0.81	0.87	*c*	213	
			0.122	0.92	0.90	*c*	302	
			0.635	0.98	0.94	*c*	314	

[a] Reckoned from data in Tables I and II. [b] Concentrations and rate constants are corrected for thermal expansion of methanol. [c] Within experimental error, 100% of the olefins via E2 is **2f**.

remainder of the measured yields of **2** and **3** are ascribed to E2 reactions. These product data also enable an estimate of the fraction of the total reaction that is E2. Division of the pseudo-first-order rate coefficient for E2 by the NaOMe concentration gives a total E2 second-order rate constant, which is then separated into components k_2 (for formation of **2**) and k_3 (for formation of **3**) in proportion to the yields of these olefins from E2. What we did differs from Bunnett, Davis, and Tanida[3] and from Blackwell, Fischer, and Vaughan[4,5] in that we evaluated E2 rate constants at each concentration of NaOMe from the measured k_ψ value, whereas earlier the total k_{E2} for each compound was evaluated as the slope of a plot of k_ψ vs. [NaOMe] and was separated into k_2 and k_3 components.[10]

The results of this dissection are presented in Table III. It will be noted that the E2 fraction of the total reaction is in

Table IV. Activation Parameters

reaction	$\Delta H^{\ddagger}$, kcal/mol[a]	$\Delta S^{\ddagger}$, gibbs[a]
1a solvolysis	23.5	−8.2[b]
1b solvolysis	25.3 ± 0.1	−2.6 ± 0.2
1c solvolysis	24.7 ± 0.8	−3.8 ± 2.2
1d solvolysis	25.1 ± 0.7	−4.9 ± 2.0
1e solvolysis	26.6 ± 0.3	−2.6 ± 0.9
1f solvolysis	26.0 ± 0.3	−4.4 ± 0.8
1e + NaOMe → **2e**	24.9 ± 0.1	−1.5 ± 2.1
1f + NaOMe → **2f**	22.5 ± 0.5	−4.8 ± 1.3
1e + NaOMe → **3e**	27.2 ± 1.8	−4.9 ± 5.1

[a] The uncertainty shown in the standard deviation from linear regression analysis, unless otherwise indicated. [b] Reckoned from average rate constants at 56 and 96 °C.

Table V. Summary of Hammett Correlations

reaction series	temp, °C	log k vs. σ		log k vs. σ^-	
		ρ	r	ρ	r
1a–f solvolysis[a]	56.0	−1.0	0.972		
	66.5[b]	−0.9	0.981		
	75.8	−0.9	0.992		
	96.0	−0.9	0.998		
1 + NaOMe → **2**[c]	66.5	+1.4	0.909	+1.2	0.986
1 + NaOMe → **3**[d]	66.5	−0.07[e]	0.275		

[a] Experimental data from the present work only. [b] Based on interpolated values. [c] Data for **1e** and **1f** from the present work plus data for benzene derivatives from ref 4. [d] Data for **1e** from the present work plus data for benzene derivatives from ref 4. [e] Standard deviation ±0.08.

most cases very high, 90% or more, and that the E2 fraction as estimated from rates generally is very close to that as estimated from products. Inasmuch as the solvolysis component is small, any defects in the assumptions stated above are not likely to affect the estimates of k_2 and k_3 very much.

Discussion

Activation Parameters. Enthalpies and entropies of activation for the solvolysis reactions and the reactions of **1e** and **1f** with NaOMe are listed in Table IV. The solvolysis reactions have $\Delta S^{\ddagger}$ about −4 gibbs/mol.[11]

For the reactions of **1e** and **1f** with NaOMe to form conjugated olefins, $\Delta S^{\ddagger}$ is about the same as for the solvolyses despite the fact that the reactions with NaOMe are second order. We note that reactions of 2-hexyl bromide, iodide, and *p*-bromobenzenesulfonate with methanolic NaOMe have $\Delta S^{\ddagger}$ around −6 to −8 gibbs/mol,[12] not much different from the values we found for the E2 reaction.

Hammett Correlations. Several correlations are summarized in Table V. Our data for solvolysis of **1a–f**, inclusive, correlate satisfactorily with the usual Hammett σ constants. The ρ value is −1.0 at 56 and 66.5 °C, and −0.9 at 75.8 and 96 °C. Blackwell, Fischer, and Vaughan[4] reckoned ρ for solvolysis of compounds of structure **1** in methanol at 66.5 °C to be −1.15. Their study involved more substrates but less spread in σ values. We attempted correlation of our solvolysis data with σ^+ values, but the quality of correlation was much poorer than with σ.

For the reactions of substrates of type **1** with NaOMe to form olefins of types **2** and **3**, we have combined our data with those of Blackwell, Fischer, and Vaughan[4] (excepting only theirs for naphthalene derivatives) for correlation purposes. As reported in Table V, correlation of log k_2 for formation of conjugated olefins with σ^- is much better than with σ, and the ρ value for the superior correlation is +1.2. Combination of our data for **1e** and **1f** with those of the New Zealand workers increased the spread of σ values represented and slightly increased the ρ value (from the +1.0 that they reported). The better correlation with σ^- than with σ is entirely due to the behavior of the nitro compound; log k_2 for **1f** fits the line defined by the rest rather well when σ^- is used but poorly when σ is used.

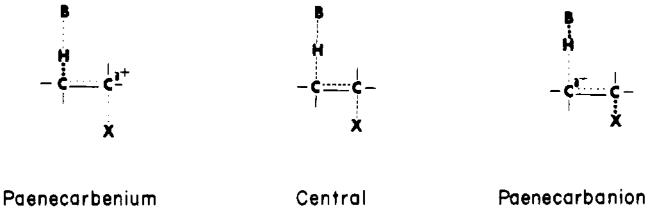


Figure 1. Extremes of variation of E2 transition-state character.

For reactions with NaOMe to form terminal olefins of type **3**, our study contributes only one additional substrate and the calculated ρ of −0.07 is not significantly different from theirs of −0.10 nor from zero.

Mechanism. Solvolyses of tertiary alkyl chlorides are generally considered[13,14b] to occur via carbocation intermediates, and we do not question that insofar as the methanolyses of **1a–f** are concerned. There is the complex question of whether or how much the elimination components of the solvolyses involve proton abstraction from solvent-separated ions or directly from carbocations in ion pairs,[15] but our data do not provide much if any insight into it.

We shall consider two mechanisms for the bimolecular eliminations observed. One is the familiar E2 mechanism, and we shall give attention especially to variation in the character of the transition state as structural and environmental features are changed.[16,17] The other, sometimes symbolized $(\mathrm{E2})_{\mathrm{ip}}$, involves attack of proton-abstracting base on the carbocation of an ion pair in virtual equilibrium with the covalent substrate.[18] The most general form of variable E2 transition-state theory focuses attention on an energy contour map which can represent variation both of the amount of carbenium character at C_α vs. carbanion character at C_β in the transition state, and of the amount reactant vs. product character.[19] However, most of the experimental evidence indicates variation in the former sense, as dealt with in an earlier form of variable E2 transition state theory,[16,17] and we shall therefore deal with the matter in those terms.

It is convenient to visualize three extremes of E2 transition state character, named as shown in Figure 1. In view of C_α being tertiary, of chlorine being a moderately good nucleofugal group, of methanol being a solvent with good capacity to hydrogen bond with chloride ion, and of methoxide ion in methanol being a moderately strong base, the transition state for transformation of substrates **1** to olefins **3** is judged to lie rather toward the paenecarbenium side with some development of positive charge on C_α in the transition state. The transition state between substrates **1** and olefins **2** is judged to have less of that character and indeed to have some paenecarbanion character[17] because of the polar effect of the β-aryl group, which will stabilize partial carbanionic character at C_β.

The observed Hammett ρ values are consistent with these views. The very small negative ρ value (−0.07) for the former reaction series (**1** + NaOMe → **3**) is consistent with the development of a small amount of positive charge at C_α and with the fact that C_α is separated from the benzene ring by a methylene group. The modest positive ρ value (+1.2) for the latter series (**1** + NaOMe → **2**) indicates some development of negative charge at C_β, but much less than in ethoxide-induced elimination from 2-phenylethyl chlorides (+2.6).[14a] It is noteworthy that even when the ρ value is so low as +1.2 the reactivity of the *p*-nitro compound (**1f**) is better correlated with σ^- than with σ. These ρ values and interpretations are similar to those of Blackwell, Fischer, and Vaughan.[4]

As discussed previously,[3] the H_β primary hydrogen isotope effects observed in methoxide-induced elimination from **1a** are difficult to reconcile with the $(E2)_{ip}$ mechanism. The Hammett ρ value for the reaction series **1** + NaOMe → **2** presents a further difficulty. In the $(E2)_{ip}$ mechanism, if overall second-order kinetics are observed, the rate-limiting step must be proton abstraction from the carbocation in the ion pair. Because such a process would be highly exoenergetic, the transition state should be reached early on the reaction coordinate and the amount of positive charge of C_α should be not much less than in the carbocation itself. It would not be expected, in terms of that mechanism, that a significant amount of negative charge would develop at C_β, certainly not enough to give a Hammett ρ value of +1.2 or to require use of σ^- to correlate the substituent effect of the *p*-nitro group.

Experimental Section

Synthesis of Benzyldimethylcarbinyl Chlorides (1). Except in the case of **1f**, the corresponding benzyldimethylcarbinols were prepared by Grignard procedures resembling those used by other workers[6b,7] for the synthesis of compounds in this series. Generally the corresponding benzyl chloride was converted to a Grignard reagent, which was then allowed to react with acetone. In synthesis of **1c**, CH_3MgI was allowed to react with methyl *p*-methoxyphenylacetate. The carbinols were treated with thionyl chloride in benzene containing about 3% of pyridine, after Bunnett, Davis, and Tanida,[3] in order to obtain compounds of type **1**. Our **1c** had mp 33–34 °C (lit.[7] 33–34 °C).

For synthesis of **1e**, *o*-toluidine was acetylated to acet-*o*-toluidide, mp 109.5–110.5 °C; chlorination gave 2′,4′-dichloro-6′-methylacetanilide, mp 185–186 °C (lit.[20a] 188 °C); hydrolysis gave 2,4-dichloro-6-methylaniline, mp 40–42 °C (lit.[20b] 57–59 °C); protodeamination by diazotization and heating the diazonium salt in ethanol after Wallingford and Krueger[21] gave 3,5-dichlorotoluene, obtained as a liquid with GLC indicating contamination probably by *m*-chlorotoluene; side-chain bromination by means of *N*-bromosuccinimide in CCl_4 gave 3,5-dichlorobenzyl bromide, first crop mp 58–60 °C (lit.[22] 57–58 °C), a larger second crop mp 38–40 °C; formation of the Grignard reagent and addition to acetone gave 3,5-dichlorobenzyldimethylcarbinol, mp 53–54 °C; and reaction with $SOCl_2$ gave **1e**, mp 26 °C. Anal. Calcd for $C_{10}H_{11}Cl_3$: C, 50.56; H, 4.67. Found: C, 50.35; H, 4.78.

For synthesis of **1f**, a solution of 9.9 g of 70% nitric acid in 20 mL of ice-cold acetic anhydride was added dropwise to a solution of 21 g (0.13 mol) of **1a** in 45 mL of acetic anhydride at 0 °C. After addition was complete, the mixture was heated at 50 °C for 11 h and then at 65 °C for nearly 2 h. The cooled reaction mixture was poured into a large volume of cold water. The yellow oil which appeared was separated and the water layer was extracted thrice with diethyl ether (150-mL portions). The yellow oil was washed with water, and the water washings were extracted with ether. The combined ether extracts were extracted thrice with water, four times with 5% aqueous NaOH, and with saturated aqueous NaCl; they were dried over anhydrous $CaCl_2$ and the ether was removed by evaporation. The remaining orange-red viscous oil (24.5 g) was dissolved in petroleum ether; the solution was passed through a column of silica gel, and the petroleum ether was removed by evaporation, yielding a yellow oil (22 g). This material was dissolved in a minimum amount of hexane; the solution was placed in a compartment at about −20 °C, and **1f** slowly crystallized. After recrystallization by the same technique, it had mp 42.5–44 °C. Anal. Calcd for $C_{10}H_{12}ClNO_2$: C, 56.21; H, 5.67. Found: C, 56.54; H, 5.68.

Proton NMR spectra were determined for the several benzyldimethylcarbinols and benzyldimethylcarbinyl chlorides (**1**), all in CCl_4. For the carbinols: δ 1.1–1.2 (s, 6 H, CH_3), 2.6–2.8 (s, 2 H, CH_2), 1.1–1.5 (br s, OH, exact shift dependent on concentration), aromatic protons 7.2–7.4 except for *p*-OCH_3, 6.8 (center of AA′BB′ pattern), and 3,5-Cl_2, 7.05 (1 H) and 7.20 (2 H), also for *p*-CH_3, 2.4 (3 H), and *p*-OCH_3, 3.7 (3 H). The ^1H NMR spectrum observed for *p*-methoxybenzyldimethylcarbinol agrees with that reported by Rappoport and Gal.[23] For substrates of structure **1**: δ 1.5–1.6 (6 H, CH_3), 2.9–3.0 except 3.2 for **1f** (2 H, CH_2); aromatic protons 7.2 (s) for **1a** and **1b**, 6.9 (center of AA′BB′ pattern) for **1c**, 7.0 (m) for **1d**, 7.2 (d, 2 H) and 7.3 (br t, 1 H) for **1e**, and 7.8 (center of AA′BB′ pattern, $J_{AB} = J_{AB'} = 8.5$ Hz) for **1f**; also for **1b**, 2.3 (*p*-CH_3), and for **1c**, 3.7 (*p*-OCH_3).

Samples of Products of Types 2, 3, and 4. Each substrate was heated at reflux (except in sealed tubes at 97–98 °C for **1e** and **1f**) in methanol containing a base, the base being $NaHCO_3$ for **1a**, **1c**, and **1e**, $NaOCH_3$ for **1b**, and 2,6-lutidine for **1d** and **1f**. The period of heating varied from 16 to 72 h. Each cooled solution was combined with water and the mixture was extracted with cyclohexane. The cyclohexane extracts were dried over anhydrous $MgSO_4$. In some cases a partial separation of the products was achieved by distillation in vacuo, with ultimate separation by GLC, while in other cases GLC separation was performed directly. A GLC column (1.21 m × 6.3 mm) of 10% SE 30 on Chromosorb G (AW-DMCS treated) at 110 °C was used, except that for the products from **1f** a column (1.21 m × 6.3 mm) of 10% Carbowax 20M on Chromosorb P operated at 190 °C was used. The products were all characterized by IR, ^1H NMR, and MS, and for the conjugated olefins (**2**) UV spectra in methanol were observed.

For the samples so obtained, the ^1H NMR spectra of **2b**,[24,25] **2c**,[23–25] **2d**,[25] **2f**,[24] and **3c**[26] agree with literature reports as cited. Also, the IR spectra of **2b**, **2c**, **2d**, **3b**, **3c**, and **3d** agree with the report of Rüchardt.[27] For **2e**: ^1H NMR (CCl_4) δ 1.8 (3 H), 1.9 (3 H), 6.1 (m, 1 H), 7.1 (m, 3 H); IR 660, 695, 790, 830, 850, 880, 930, 1100, 1115, 1225, 1375, 1405, 1550, 1580, 1650, 2920, 2945, and 2985 cm^{-1}. For olefins of type **3**: ^1H NMR (CCl_4) showed δ 1.6–1.7 (except δ 1.1 for **3f**) (br m, CH_3), 3.2 (except 3.5 for **3d** and 2.9 for **3f**) (br m, benzylic CH_2), 4.6–4.8 (except δ 4.3 for **3f**) (br m, vinylic CH_2), 6.8–7.1 (aromatic H), also 2.3 for **3b** (*p*-CH_3) and 3.7 for **3c** (OCH_3). For the methyl ethers (**4**), the ^1H NMR (CCl_4) showed: δ 1.0–1.1 (s, 6 H, CH_3), 2.5–2.8 (s, CH_2), 3.0–3.2 (s, OCH_3), and 6.8–7.1 (except δ 7.8 for **4f**) (aromatic H), also for **4b**, 2.2 (*p*-CH_3), and for **4c**, δ 3.7 (OCH_3).

For the conjugated olefins, UV λ_{max} (ϵ) observed were: **2b**, 247 nm (15 550); **2c**, 251 nm (17 590); **2d**, 251 nm (17 340); **2e**, 253 nm (13 350); and **2f**, 316 nm (12 170) (with precision in ϵ about ±1%).

Kinetic Techniques. For solvolyses, solutions in methanol (reagent grade, redried by the magnesium metal method and stored under N_2) of composition as indicated in Table I were prepared at room temperature, and measured aliquots (1, 3, or 5 mL) were dispensed into ampules which were flushed with N_2 and sealed. All the ampules for a run were placed in the thermostat bath at once. Ampules removed at recorded times were cooled immediately to 0 °C and maintained at 0 °C until further processing. The ampules were opened and their contents were transferred quantitatively to volumetric flasks and diluted to the mark with methanol. The absorbance at λ_{max} for the relevant conjugated olefin (see above or ref 3) was measured by means of a Gilford 240 spectrophotometer, the reference solution being a solution of NaBr and 2,6-lutidine in methanol at the same concentration as used for rate measurement. Plots of $\ln (A_\infty - A_t)$ vs. time were linear, and the negatives of their slopes (reckoned by linear regression analysis) were taken as the solvolysis rate constants (k_s), as listed in Table I.

For reactions with NaOMe, the technique was essentially the same. The reference solution for the photometric determinations was pure methanol inasmuch as no NaBr or 2,6-lutidine was present in the NaOMe runs. The negatives of the slopes of $\ln (A_\infty - A_t)$ vs. time were taken as k_ψ, as listed in Table II.

Product Analyses. An ampule from each kinetics run at "infinity" time was opened and the contents were transferred quantitatively into a separatory funnel containing 10 mL of redistilled cyclohexane. The mixture was extracted with 20 mL of water, and the water layer was extracted twice with 10-mL portions of cyclohexane. The combined cyclohexane extracts were washed with 10 mL of 0.5% H_2SO_4 in water, 20 mL of water, and 10 mL of saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and concentrated to a small volume by distillation. About 0.01 mmol of internal standard, accurately measured, was added and the solution was analyzed by GLC with application of freshly determined molar response factors. The internal standard was *p*-xylene for **1a** reactions, biphenyl for **1b**, **1c**, and **1d**, 1,2,4-trichlorobenzene for **1e**, and *p*-nitrotoluene for **1f**. The GLC columns were those described above in connection with the obtaining of authentic samples of the various **2**, **3**, and **4**. Also, the absorbance of "infinity" samples from the rate determinations enabled an independent evaluation of the yield of conjugated olefin (**2**) that has been formed.

Calculations. Activation parameters were reckoned according to standard procedures.[11] The σ values used for Hammett correlations were those tabulated by Bunnett.[28]

Registry No.—**1a**, 1754-74-1; **1b**, 18503-92-9; **1c**, 18503-98-5; **1d**, 18503-93-0; **1e**, 69278-41-7; **1f**, 69278-42-8; **2a**, 768-49-0; **2b**, 5916-22-3; **2c**, 877-99-6; **2d**, 19366-15-5; **2e**, 69278-43-9; **2f**, 1012-18-6; **3a**, 3290-53-7; **3b**, 40296-92-2; **3c**, 20849-82-5; **3d**, 23063-65-2; **3e**, 69278-44-0; **3f**, 18755-60-7; **4a**, 69278-45-1; **4b**, 69278-46-2; **4c**, 69278-47-3; **4d**, 69278-48-4; **4e**, 69278-49-5; **4f**, 69278-50-8.

References and Notes

(1) Research supported in part by the National Science Foundation and in part by the Petroleum Research Fund, administered by the American Chemical Society.

(2) Based on the Dissertation of S. Sridharan, University of California, Santa Cruz, March, 1974; *Diss. Abstr. Int. B*, **35**, 4399 (1975).

(3) J. F. Bunnett, G. T. Davis, and H. Tanida, *J. Am. Chem. Soc.*, **84**, 1606 (1962).

(4) L. F. Blackwell, A. Fischer, and J. Vaughan, *J. Chem. Soc. B*, 1084 (1967).

(5) L. F. Blackwell, Ph.D. Thesis, University of Canterbury, Christchurch, New Zealand, 1965.

(6) (a) A. Landis and C. A. VanderWerf, *J. Am. Chem. Soc.*, **80**, 5277 (1958); (b) M. M. Tessler and C. A. VanderWerf, *J. Org. Chem.*, **30**, 405 (1965).

(7) H. C. Brown and C. J. Kim, *J. Am. Chem. Soc.*, **90**, 2082 (1968).

(8) J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, **32**, 11 (1967).

(9) J. F. Bunnett, S. Sridharan, and W. P. Cavin, *J. Org. Chem.*, accompanying paper in this issue.

(10) Employment of the other method of dissection[3,4,5] gives estimates of k_2 and k_3 somewhat higher than listed in Table III, and in most cases negative intercepts. Employment of the slightly higher k_2 and k_3 values would only slightly affect the Hammett correlations. Naively, the intercepts in plots of log k_ψ vs. [NaOCH$_3$] should be solvolysis rate constants. The fact of negative intercepts suggests some deficiency in the assumptions that underly the dissection.

(11) J. F. Bunnett in "Investigation of Rates and Mechanisms of Reactions", Part I, E. S. Lewis, Ed., Wiley-Interscience, New York, 1974, p 404.

(12) R. A. Bartsch and J. F. Bunnett, *J. Am. Chem. Soc.*, **90**, 408 (1968).

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1969, Chapter IX.

(14) (a) W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions", Wiley, New York, 1973, p 61; (b) *ibid.*, p 210.

(15) M. Cocivera and S. Winstein, *J. Am. Chem. Soc.*, **85**, 1702 (1963); J. F. Bunnett and D. L. Eck, *J. Org. Chem.*, **36**, 897 (1971).

(16) J. F. Bunnett, *Angew. Chem.*, **74**, 731 (1962); *Angew. Chem., Int. Ed. Engl.*, **1**, 225 (1962).

(17) J. F. Bunnett, *Surv. Prog. Chem.*, **5**, 53 (1969).

(18) F. G. Bordwell, *Acc. Chem. Res.*, **5**, 374 (1972).

(19) R. A. More O'Ferrall in "The Chemistry of the Carbon–Halogen Bond", Part 2, S. Patai, Ed., Wiley, New York, 1973, p 609.

(20) (a) K. v. Auwers, A. Ernecke, and E. Wolter, *Justus Liebigs Ann. Chem.*, **478**, 154 (1930); (b) F. Asinger and G. Lock, *Monatsh. Chem.*, **62**, 344 (1933).

(21) V. H. Wallingford and P. A. Krueger, "Organic Syntheses", Collect. Vol. 2, Wiley, New York, 1943, p 353.

(22) J. D. Turner and C. K. Bradsher, *J. Org. Chem.*, **32**, 1169 (1967).

(23) Z. Rappoport and A. Gal, *J. Chem. Soc., Perkin Trans. 2*, 301 (1973).

(24) H. Rottendorf, S. Sternhell, and J. R. Wilmshurst, *Aust. J. Chem.*, **18**, 1759 (1965).

(25) E. R. Curry and D. J. Sardella, *J. Am. Chem. Soc.*, **96**, 1822 (1974).

(26) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5531 (1968).

(27) C. Rüchardt, *Chem. Ber.*, **94**, 2609 (1961).

(28) J. F. Bunnett in "Investigation of Rates and Mechanisms of Reactions", Part I, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, 1961, p 215.

Olefin-Forming Elimination Induced by Mercaptide Ions. Variation of Transition-State Character as Indicated by Substituent Effects on Rate[1]

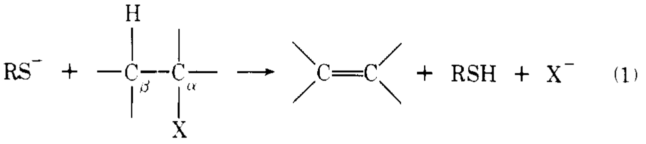
J. F. Bunnett,* Srinivasa Sridharan,[2] and William P. Cavin[3]

Thimann Laboratories, University of California, Santa Cruz, California 95064, and
Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912

Received June 26, 1978

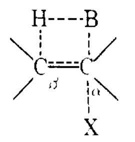
For reactions of a series of substituted benzyldimethylcarbinyl chlorides (5) with ethanethiolate ion in methanol solution, product ratios and rate constants have been measured. Dissected rate constants (k_2) for EtS$^-$-induced reaction to form substituted β,β-dimethylstyrenes (2) furnish a U-shaped Hammett plot vs. σ. The change in ρ from negative with electron-releasing to positive with strongly electron-attracting substituents is easily rationalized in terms of the theory of the variable E2 transition state; the character of the transition state is considered to change as substituents change. The reversal in sign of ρ can alternatively be rationalized in terms of a change from the (E2)$_{\mathrm{ip}}$ to the E2 mechanism. The "E2C" mechanistic hypothesis provides little insight into these phenomena. Comparison of k_2 values with two reagents shows that ethanethiolate is more reactive than methoxide ion except in the case of the p-nitro substrate.

Mercaptide ions in alcoholic solvents, despite their lesser basicity, are frequently more effective than alkoxide ions in generating olefins from secondary and tertiary alkyl halides (eq 1). This phenomenon, discovered in 1956, has been studied in several laboratories.[4–15]



$$\mathrm{RS^-} + -\overset{\mathrm{H}}{\underset{\beta}{\mathrm{C}}}-\underset{\mathrm{X}}{\underset{\alpha}{\mathrm{C}}}- \longrightarrow \mathrm{{>}C{=}C{<}} + \mathrm{RSH} + \mathrm{X^-} \qquad (1)$$

The high efficacy of the low-basicity mercaptide ions has been discussed with respect to three different mechanisms. One view is that these reactions proceed essentially by the normal E2 mechanism and that for special reasons mercaptide ion induced reactions are sometimes remarkably fast. The dependence of the mercaptide/alkoxide reactivity ratio and of the Hammett ρ value for substituted thiophenoxide ion reagents on the identity of nucleofugal group X have found interpretation in terms of the theory of the variable E2 transition state.[16,17]



1

A second view invokes covalent interaction between the reagent (which may be called a base or a nucleophile) and C_α of the substrate in the elimination transition state. Structures such as 1 have been proposed for the transition state,[18–20] and such a mechanism has been dubbed "E2C". This mechanism as originally proposed[18] would call for a high sensitivity of the reaction rate to the steric effects of α substituents, a sensitivity which is not observed. In recent discussions[20] less emphasis has been placed on covalent interaction of the base (nucleophile) with C_α.

A third view is that eliminations induced by weakly basic reagents occur via ion pair intermediates.[21,22] According to this view, such a reagent may be too weak to effect elimination from a neutral substrate molecule, but it may be quite good at taking a proton from C_β of the carbocation in an ion pair. If such an ion pair were in mobile equilibrium with the substrate, the overall process would be kinetically second order, first order in substrate, first order in base, and therefore difficult to distinguish from the E2 mechanism.

We now report a study of the effects of aromatic substitu-

0022-3263/79/1944-1463$01.00/0