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]

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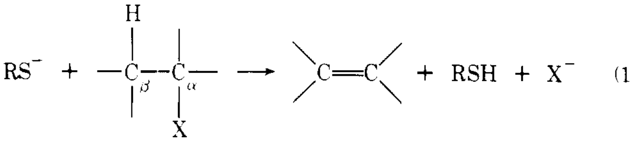
For reactions of a series of substituted benzyldimethylcarbinyl chlorides (5) with ethanethiolate ion in methanol solution, product ratios and rate constants have been measured. Dissected rate constants (k_2) for EtS$^-$-induced reaction to form substituted β,β-dimethylstyrenes (2) furnish a U-shaped 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 $(\mathrm{E2})_{\mathrm{ip}}$ 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.

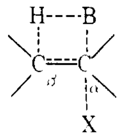
Mercaptide ions in alcoholic solvents, despite their lesser basicity, are frequently more effective than alkoxide ions in generating olefins from secondary and tertiary alkyl halides (eq 1). This phenomenon, discovered in 1956, has been studied in several laboratories.[4–15]



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

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]

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



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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-

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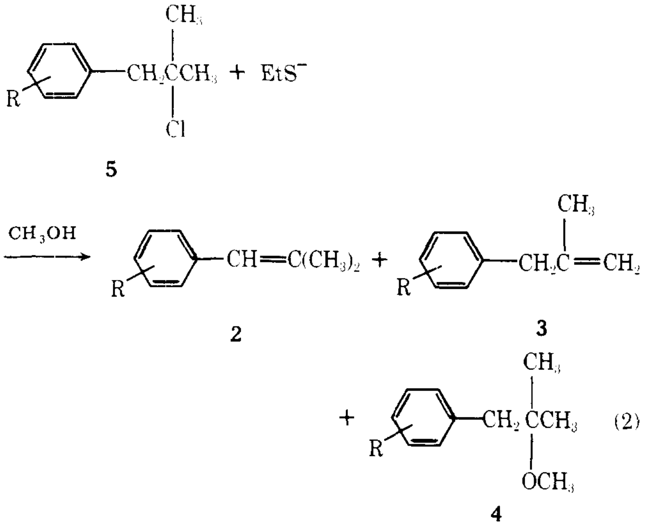
ents on the rate of elimination from benzyldimethylcarbinyl chloride (eq 2) induced by ethanethiolate ions in methanol solution. From each substrate, two olefins (2 and 3) are formed



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
g, R = m-Cl

as well as a solvolysis product, ether **4**. It is possible to subtract from the total measured rate the small contribution from solvolysis and, with attention to product composition, to evaluate rate constants for the formation of each olefin.

Elimination reactions in the benzyldimethylcarbinyl system have received previous attention in various ways. Studies of solvolysis rates without attention to products have been made.[23] The kinetics of reactions of **5a** with methanolic NaOMe and NaSEt were studied intensively by Bunnett, Davis, and Tanida.[6] Studies of the same thorough sort have been made for reactions of a series of substituted benzyldimethylcarbinyl chlorides with methanolic NaOMe,[24,25] and Hammett ρ values of ca. +1.2 and −0.1 have been evaluated, respectively, for the E2 reactions leading to the conjugated (**2**) and terminal (**3**) olefins. The relative reactivities of ethanethiolate and methoxide ions in causing elimination from **5a** and two analogous substrates with sulfur nucleofugal groups have been determined;[7] the EtS^-/MeO^- reactivity ratio is 6.5 when the nucleofugal group is Cl, 0.8 when it is $-SMe_2^+$, and 0.05 when it is $-SO_2CH_3$. Kinetics and products of elimination from **5a** and the corresponding bromide as induced by halide ions in acetone have also been studied.[26]

Results

For each of the seven substrates (**5a–g**) studied, overall reaction rate with various concentrations of EtSNa in methanol was determined, mainly by photometric measurement but sometimes by potentiometric titration of chloride ion, as discussed below. The products formed were olefins of types 2 and 3 and ethers of type 4, and the product composition was determined for each set of conditions involved in the rate study. Our rate and product data are summarized in Table I.

The rate and product data were dissected for the purposes of identifying the product composition attributable to E2 reaction, apart from solvolysis, and of evaluating second-order rate constants (k_2 and k_3, respectively) for the E2 reactions leading to olefins of types **2** and **3**. The rate measurements were conducted with the base in large excess over the substrate, and pseudo-first-order kinetics were observed. Plots of the resulting k_ψ values against [EtSNa] were linear with intercepts approximating the solvolysis rates reported in the accompanying paper.[25] The slopes represent second-order rate constants for the total ethanethiolate-induced component of the reaction.

For dissection purposes, it was assumed that the ether products stem only from the solvolysis component of the overall reaction, and that the product ratio from solvolysis in the presence of EtSNa (with EtSH) is the same as in the presence of 0.2 M NaBr but absence of EtSNa. From the amount of ether formed, the amounts of the two olefins stemming from solvolysis were reckoned and subtracted from the respective total amounts of those olefins which had been formed. The remaining amount of each olefin was attributed to reaction with EtSNa, and the fraction of conjugated olefin (**2**) in the olefins stemming from the EtSNa reaction (the "E2 olefins") was easily calculated. Multiplication of the second-order rate constants by the fractions of **2** and **3** in the E2 olefins gave, respectively, k_2 and k_3. The computed fractions of **2** in the E2 olefins and k_2 and k_3 values are listed also in Table I.

From the kinetic data, the E2 fraction of the total reaction could be estimated as $(k_2 + k_3)$ [EtSNa]/k_ψ. From the product data, the same quantity could also be estimated. In general the two estimates were in fair agreement. For example, for the third entry for **5a** at 96 °C in Table I, the E2 fraction was estimated to be 76% from product data and 86% from kinetic data. For the third entry for **5c** at 55.8 °C, the E2 fraction was estimated to be 78% from product data and 80% from kinetic data.

Complications, Actual or Conceivable. The validity of the employed photometric method for following the progress of reactions was verified by Bunnett, Davis, and Tanida[6] for elimination from **5a** by comparing the photometric rate constant with one determined by titration of chloride ion. A similar verification was carried out in the present work for elimination from **5c** at 75.8 °C with 0.475 M EtSNa and 0.198 M EtSH; k_ψ was 11.1×10^{-4} by photometric and 10.3×10^{-4} by titration measurements (both in units of s^{-1}).

The possibility that the reagent might bring about some interconversion of products was considered. In a test of that possibility, a mixture of 53.7% of **2b**, 26.0% of **3b**, and 20.3% of **4b** was exposed to 0.86 M EtSNa and 0.26 M EtSH in methanol for periods of 24 and 48 h at each of the three temperatures used for kinetics. The composition of this mixture is quite far from the probable equilibrium composition; for **2a**, **3a**, and **4a** at 75.7 °C, the equilibrium mixture is about 54% **2a**, 3% **3a**, and 43% **4a**,[6] and the p-methyl group is unlikely to affect it much. Even during 48 h at 96 °C, the change in composition was scarcely more than the uncertainty in GLC analyses. At least for reactions of **5b**, the product composition is clearly kinetically controlled.

Conceivably part of the elimination brought about by EtSNa might be due to methoxide ion in acid–base equilibrium with it. In EtSNa-catalyzed ketone isomerizations in methanol medium, a recognizable component of the overall rate is due to methoxide ion.[27] In the present study, EtSH was always present with EtSNa, in order to depress the concentration of methoxide ion. That any methoxide ion component of overall elimination rate was negligible is shown by data for the reaction of **5e** with EtSNa at 75.8 and 96 °C; see Table I. The overall rate was scarcely changed, and even apparently increased, by augmentation of [EtSH] as much as fourfold while [EtSNa] was held constant.

Complications were encountered in both kinetic and product studies on the reaction of the p-nitro substrate, **5f**, with EtSNa. It was observed that the absorbance measured for samples taken during a kinetic run increased in seemingly normal fashion during approximately the first 7 half-lives, but then dropped slowly during the next 7 half-lives to about $^5/_7$ of its peak value. Even when observations were taken only

Table I. Rate Constants and Product Compositions for Reactions of Substituted Benzyldimethylcarbinyl Chlorides with Sodium Ethanethiolate in Methanol[a]

substituent(s)	substrate no.	temp,[b] °C	[NaSEt],[c] M	[EtSH],[c] M	10^4k_ψ, s^{-1}	products, %			fraction of **2** in E2 olefins	10^4k_2,[d] $M^{-1} s^{-1}$	10^4k_3,[d] $M^{-1} s^{-1}$
						2	**3**	**4**			
H	**5a**	56.0	0.194	0.097	0.57	57.2	25.5	17.3	0.71	1.21	0.46
			0.387	0.194	0.86	62.6	26.5	10.9	0.72		
			0.582	0.291	1.25	66.1	26.7	7.2	0.72		
			0.775	0.387	1.52	69.0	24.4	6.6	0.75		
		96.0	0.092	0.045	18.0	47.0	29.0	24.0	0.64	61.6	31.8
			0.184	0.092	24.0	53.0	30.6	16.4	0.65		
			0.367	0.184	39.7	58.3	30.5	11.2	0.67		
			0.551	0.276	60.8	61.7	30.0	8.3	0.68		
p-CH_3	**5b**	55.9	0.409	0.172	1.02	54.6	33.6	11.8	0.63	0.97	0.52
			0.613	0.257	1.32	58.3	32.4	9.3	0.66		
			0.818	0.343	1.63	59.6	31.6	8.8	0.67		
		75.8	0.171	0.089	4.58	50.5	25.1	24.4	0.84	11.2	3.20
			0.233	0.116	5.30	53.6	26.2	20.2	0.78		
			0.294	0.143	6.30	55.2	26.6	18.2	0.77		
			0.405	0.206	8.43	58.4	25.7	15.9	0.78		
			0.557	0.285	9.88	61.4	28.3	10.3	0.72		
		95.8	0.098	0.029	22.8	40.9	45.6	13.5	0.55	62.5	50.5
			0.196	0.058	35.4	44.6	45.6	9.8	0.55		
			0.391	0.116	56.1	47.4	44.7	7.9	0.56		
p-OCH_3	**5c**	55.8	0.122	0.051	0.56	45.4	28.1	26.5	0.67	1.50	0.75
			0.244	0.101	0.87	51.6	28.5	19.9	0.68		
			0.488	0.203	1.38	58.2	32.7	9.1	0.65		
			0.732	0.304	1.95	60.8	31.7	7.5	0.67		
		75.8	0.119	0.049	4.46[e]	46.2	33.1	20.7	0.61	13.4	7.52
			0.238	0.099	7.16	51.6	32.3	16.1	0.65		
			0.475	0.198	11.1	56.4	33.4	10.2	0.65		
			0.713	0.296	17.2	59.4	33.8	6.8	0.65		
		96.2	0.116	0.048	27.5	43.2	35.0	21.8	0.58	75.6	48.4
			0.231	0.096	38.8	48.7	35.1	16.2	0.61		
			0.462	0.192	69.7	54.4	35.0	10.6	0.63		
			0.694	0.288	98.3	56.0	36.8	7.2	0.62		
p-Cl	**5d**	55.8	0.219	0.112	0.61	65.1	24.4	10.5	0.76	1.15	0.30
			0.438	0.224	0.92	69.2	23.4	7.4	0.77		
			0.658	0.336	1.25	74.1	20.0	5.9	0.81		
			0.877	0.448	1.56	76.8	17.3	5.9	0.84		
		75.8	0.212	0.101	5.11	63.5	24.7	11.8	0.75	8.79	2.81
			0.423	0.200	7.21	69.8	24.7	5.5	0.75		
			0.641	0.327	10.4	68.7	23.3	8.0	0.77		
			0.845	0.401	12.2	71.5	23.5	5.0	0.76		
		96.0	0.206	0.098	30.2	61.1	24.7	14.2	0.74	59.6	21.7
			0.412	0.195	42.9	68.3	24.1	7.6	0.75		
			0.624	0.318	62.5	68.6	27.4	4.0	0.72		
			0.822	0.390	79.5	68.7	27.5	3.8	0.72		
3,5-Cl_2	**5e**	56.0	0.561	0.233	1.10	80.4	17.8	1.8	0.82	2.27	0.48
			0.749	0.377	1.51	81.4	17.3	1.3	0.83		
			0.935	0.521	2.13	82.4	16.6	1.0	0.83		
		75.8	0.243	0.125	4.46	77.8	18.8	3.5	0.82	14.3	3.31
			0.243	0.508	4.72	77.4	19.5	3.1	0.81		
			0.364	0.192	6.29	78.6	19.0	2.4	0.81		
			0.364	0.508	6.35	78.4	19.3	2.3	0.81		
			0.547	0.227	9.14	79.2	19.0	1.8	0.81		
			0.547	0.508	9.18	79.6	18.8	1.6	0.81		
			0.730	0.367	13.3	79.9	18.8	1.3	0.81		
			0.730	0.508	13.0	80.0	18.8	1.2	0.81		
			0.911	0.508	16.2	80.4	18.5	1.1	0.82		
		96.0	0.237	0.121	29.2	77.1	19.4	3.4	0.81	68.9	15.7
			0.237	0.494	29.1	76.4	20.4	3.2	0.80		
			0.354	0.187	32.9	80.8	16.6	2.6	0.83		
			0.354	0.494	42.3	78.3	19.3	2.4	0.81		
			0.532	0.221	60.5	80.0	17.9	2.1	0.83		
			0.532	0.494	57.0	79.8	18.1	2.1	0.82		
			0.710	0.357	66.1	78.7	19.7	1.6	0.81		
			0.710	0.494	68.3	78.6	20.0	1.4	0.80		
p-NO_2	**5f**	56.0	0.201	0.100	0.48				f	1.58[g]	0.18[g]
			0.402	0.202	0.88				f	1.41[h]	0.35[h]
			0.816	0.404	1.57				f	1.23[i]	0.53[i]
		75.8	0.196	0.098	4.13	70.0[j]	13.7[j]	3.6[j]	f	14.0[g]	1.6[g]
			0.391	0.196	7.18				f	12.5[h]	3.1[h]
										10.9[i]	4.7[i]
m-Cl	**5g**	75.8	0.20	0.10	3.40	68.1	23.6	8.3	0.77	8.74	2.61

[a] Substrate concentration ca. 0.01 M, except for **5f**. [b] Temperatures precise to ±0.1 °C at ca. 56 and 75.8 °C, and to ±0.2 °C at ca. 96 °C. [c] Concentrations corrected for thermal expansion of methanol. [d] The one k_2 or k_3 entry for each substrate and temperature reflects average E2 olefin composition for the several relevant runs. [e] Average of two concordant runs. [f] Uncertain; see text. [g] Based on assumption that product ratio **2f**/**3f** = 9:1. [h] If **2f**/**3f** = 8:2. [i] If **2f**/**3f** = 7:3. [j] Product percentage approximate, and not used for dissection of rate datum; ca. 12.6% of a fourth product also present.

Table II. Activation Parameters for Elimination Reactions of 5a-f with Sodium Ethanethiolate in Methanol[a]

		For $5 \rightarrow 2$		For $5 \rightarrow 3$	
substrate	substituent(s)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, gibbs/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, gibbs/mol
5a	H[b]	23.0	−6.7	24.9	−3.0
5b	p-CH_3	24.5 ± 1.7	−2.4 ± 5.0	26.8 ± 4.1	+2.9 ± 11.9
5c	p-OCH_3	22.8 ± 0.9	−6.9 ± 2.7	24.2 ± 0.9	−3.9 ± 2.4
5d	p-Cl	23.0 ± 0.3	−6.9 ± 0.8	25.0 ± 0.1	−3.4 ± 0.3
5e	3,5-Cl_2	19.9 ± 0.4	−14.9 ± 1.1	20.4 ± 0.7	−16.5 ± 2.1
5f	p-NO_2	24.5	−2.0 ± 0.2[c]		

[a] Standard deviations are shown, unless otherwise noted. [b] Reckoned from measurements in the present work only. [c] $\Delta S^{\ddagger}$ is calculated to be −1.8, −2.0, or −2.3 gibbs/mol if the **2f**/**3f** ratio is, respectively, 9:1, 8:2, or 7:3.

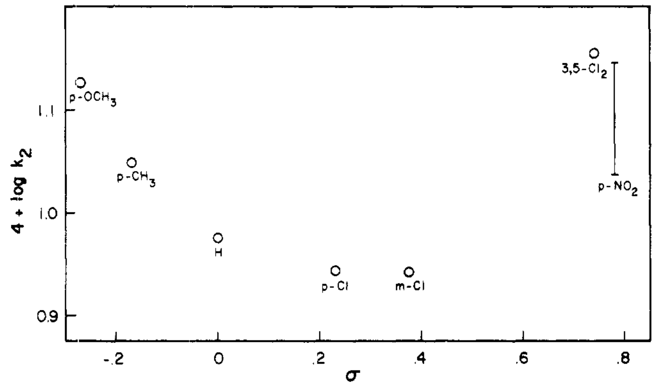


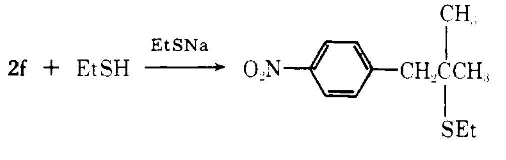
Figure 1. Hammett plot of log k_2 (for **5** + EtS^- → **2**) vs. σ for 75.8 °C. The bar for p-NO_2 indicates the range resulting from different assumptions about the **2f**/**3f** product ratio.

during the first 2 or 3 half-lives and the data were treated by the Guggenheim method,[28a] the rate constants based on photometric measurements considerably exceeded those based on potentiometric titration of chloride ion. The rate data listed in Table I for **5f** are based entirely on analysis by potentiometric titration.

GLC analysis of a sample of a **5f**–NaSEt reaction mixture, taken late and during the phase of declining absorbance, is reported in Table I for one run at 75.8 °C. Besides the expected **2f**, **3f**, and **4f**, there was a fourth product with retention time longer than for the others. In further study of the system, mixtures of authentic **2f**, **3f**, and **4f** were exposed to EtSNa and EtSH under conditions typically used for kinetics, and the appearance of a fourth substance with retention time identical to the fourth product from the **5f** reaction was observed. It appears that one or more of the normal products underwent further reaction to form the fourth product.

Samples of authentic **2f**, **3f**, and **4f** were then separately exposed at temperatures used for rate studies to 0.42 M EtSNa in methanol. The ether, **4f**, was unaffected. The terminal olefin, **3f**, underwent partial change, and a new GLC peak with retention time characteristic of **2f** appeared. The conjugated olefin, **2f**, also underwent some reaction: a new peak appeared with retention time the same as the fourth product from the rate studies.

The "fourth product" was not identified. Possibly it is a thioether formed by conjugate addition of EtSH to **2f**, as in eq 3.[29]



(3)

Because of evidence both that **3f** is converted into **2f**, and **2f** into a fourth product under conditions of the rate studies, no attempt was made to dissect the rate data for **5f** as was done for the other substrates. Instead, the total second-order rate constant was apportioned between reactions forming **2f** and **3f** on the basis of three alternative assumptions, namely, that the product ratios, **2f**/**3f**, from the E2 reaction were 9:1, 8:2, or 7:3. The resulting values of k_2 and k_3 are listed in Table I. Intuitively, we feel that the true **2f**/**3f** ratio is closer to 9:1 than to the other ratios.

Activation Parameters. Enthalpies and entropies of activation, calculated from the k_2 and k_3 values of Table I, are listed in Table II. The standard deviations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for reactions of **5b** are rather large, and the values for **5e** deviate considerably from the rest. Most of the $\Delta S^{\ddagger}$ for reactions to form conjugated olefins (**2**) are about −7 gibbs/mol, and for reactions to form terminal olefins (**3**) about −3 gibbs/mol.[28b] About half of the difference must be attributed to a statistical factor of 3 favoring formation of the terminal olefin.

Discussion

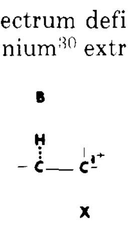
Hammett Plots. In Figure 1, we present a plot of log k_2 (at 75.8 °C) vs. σ. The plot is U-shaped, with nadir between p-Cl and m-Cl. By linear regression analysis, ρ for the left wing is reckoned as −0.4 and for the right wing as +0.4 or +0.5 (the latter depending on what assumption is made about the **2f**/**3f** product ratio).

Plots of log k_3 at 56 or 75.8 °C vs. σ are also U-shaped, although the right wing is upheld only by the 3,5-dichloro point. ρ values are about −0.7 for the left wing and +0.3 for the right wing.

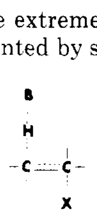
Thioethoxide/Methoxide Reactivity Ratios. Using interpolated k_2 values for EtS^--induced reactions from the present work and k_2 values for MeO^--induced reactions from elsewhere,[24,25] we reckon $k_2(EtS^-)/k_2(MeO^-)$ ratios at 66.5 °C as a function of the ring substituent as follows: p-OCH_3, 16.7; p-CH_3, 8.8; H, 7.7; p-Cl, 4.2; m-Cl, 2.7; 3,5-Cl_2, 2.1; and p-NO_2, ~0.25. Similarly, $k_3(EtS^-)/k_3(MeO^-)$ ratios are calculated to be: p-OCH_3, 18.5; p-CH_3, 8.5; H, 9.6; p-Cl, 5.2; m-Cl, 8.2; and 3,5-Cl_2, 9.2. (In both series, the data for m-Cl pertain to 75.8 °C.) It is noteworthy that, except with the p-nitro substrate (**5f**), thioethoxide is a more effective reagent than methoxide ion. For reactions leading to conjugated olefins (**2**), the EtS^-/MeO^- reactivity ratio is highest for the strongest electron-releasing substituent (p-OCH_3) and declines steadily as substituents have more positive σ values. However, for reactions leading to terminal olefins (**3**) the ratio is mostly about 9, with only p-OCH_3 at 18.5 being remarkably different.

We shall examine each of the three mechanistic models mentioned at the outset, as well as a fourth seldom if ever considered, in order to see how it accommodates the Hammett plots and the EtS^-/MeO^- reactivity ratios, and in the process take note of some relevant observations from the recent literature.

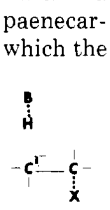
Interpretation with Respect to the E2 Mechanism and Variation of Transition State Character. Early presentations of the theory of the variable E2 transition state[16,17] focused on variation of transition state character within a spectrum defined by three extremes. One is the paenecarbenium[30] extreme, represented by structure **6**, in which the bond between C_α and the nucleofugal group is extensively sundered, some positive charge has developed at C_α, the base has made little progress in detaching H_β from C_β, and there is little double-bond character. Opposite is the paenecarbanion extreme (**8**), in which extensive bonding of base to H_β has occurred with extensive development of negative charge on C_β, but with very little breaking of the C_α–X bond and again very little development of double-bond character. The other "extreme" is a central transition state (**7**) in which breaking of the C_β–H_β bond is fully synchronized with breaking of the C_α–X bond, there is extensive double-bond character, and no development of charge on either C_α or C_β.



Paenecarbenium
6



Central
7



Paenecarbanion
8

A more recent and more comprehensive treatment of transition state variation, due to More O'Ferrall,[32,33] takes into account also variation between reactant-like and product-like extremes, and focuses attention on a contour map showing energy as a function of transition-state geometry and on the way in which those contours change with change in substrate structure and reaction conditions. It incorporates and utilizes the earlier version of the theory. Actually, most of the available experimental evidence indicates variation between the paenecarbenium and paenecarbanion extremes. Therefore we will employ the earlier form of the theory[16,17] in the present discussion.

Several features of the present system should be conducive to a transition state toward the paenecarbenium side of the spectrum. These include the facts that C_α is tertiary, that chlorine is a moderately good nucleofugal group, that methanol is moderately favorable to separation of chlorine as an anion, and that ethanethiolate ion is a rather weak base. The presence of a β-aryl substituent, for transition states leading to conjugated olefins (**2**), exerts however an opposing influence. On balance, a transition state somewhat on the paenecarbenium side might be expected.

In such a case, the Hammett ρ value for the reaction should be negative. Electron-releasing substituents should not seriously retard reaction insofar as their effect on the removal of H_β is concerned because there is no development of negative charge on C_β in a paenecarbenium transition state. But they should facilitate reaction through their energetically favorable interaction with a positively charged C_α. The observed negative ρ for the left wing of Figure 1 thus finds interpretation.

It must be noted, however, that the meta and para substituents of substrates **5b–g**, inclusive, are more than mere probes of transition-state structure. They are themselves components of the respective substrates, and as such they are expected to have some influence on transition-state character. Electron-attracting substituents should favor the development of negative charge at C_β, and it is conceivable that at some point this influence will overcome those that favor paenecarbenium character so that on balance the transition state will lie somewhat to the paenecarbanion side. In the data of Figure 1, the 3,5-dichloro and *p*-nitro substituents appear to have done just that, for ρ is positive for the right wing.

In the transition states leading to terminal olefins (**3**), the meta and para substituents are now components of substituted benzyl substituents on C_α. In this situation the aryl groups are expected to offer less resistance to the other factors that favor paenecarbenium character. A negative ρ of larger magnitude would therefore be anticipated, and indeed the observed ρ for the left wing is larger (−0.7) for formation of **3** than for formation of **2** (−0.4). However, the greater k_3 for formation of **3e** than for **3d** or **3g** is not anticipated and seems anomalous.

In regard to the thioethoxide/methoxide reactivity ratio, certain data from the literature are relevant. The pK_a for ethanethiol in water[34] is 10.50, and for methanol in water[35] 15.54. The difference of 5.04 pK units corresponds to $\Delta\Delta G°$ of 6.9 kcal/mol. In the gas phase, methoxide ion is again the more basic, but the margin is much greater; $\Delta\Delta G°$ for dissociation into proton and anion at 25 °C is 22.9 kcal/mol.[36] These differences mean that the relative basicity of methoxide ion vs. ethanethiolate is diminished on transfer from the gas phase to water solution by 16.0 kcal/mol. Assuredly the main reason for such a substantial decrement in relative basicity is that the free energy released on solvation of methoxide ion is much greater than that of thioethoxide ion. The difference in the free energies of solvation of methanol and ethanethiol will make some contribution, but a minor one.

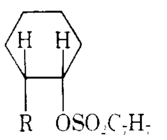
The quoted data refer to transfer from the gas phase into water solution. Because of the similarity of methanol to water as a solvent, the situation for transfer from the gas phase into methanol is much the same.[27]

When a base enters an E2 transition state, it must release some of its solvent sheath. Since the free energy released on solvation of methoxide ion is much greater than on solvation of thioethoxide ion, the free energy which must be supplied for a certain fraction of desolvation should also be much greater. This factor operates to make MeO^- less reactive than EtS^-.

A contrary factor is release of free energy on partial bonding of the base to H_β in the transition state.[37] In a paenecarbanion transition state, this is the major and predominating factor. However, in a paenecarbenium transition state, this factor is of reduced significance because there isn't much bonding of the base to H_β.

The balance between these two factors determines which reagent is the more reactive. Methoxide ion is the more reactive for paenecarbanion E2 reactions, thioethoxide is more reactive for paenecarbenium reactions, and there is a gradation of relative reactivity as the detailed character of the transition state varies along the variable transition state spectrum. Such variation is evident in the present results, as in previous studies.[7,9,17]

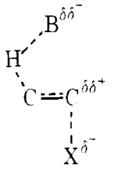
This type of interpretation has been offered previously,[7,17] and it has been criticized[38] on grounds that the reactivity order, $RS^- > RO^-$, persists in dipolar aprotic solvents. The data cited in support of this criticism do not actually concern alkanethiolate/alkoxide ion reactivity ratios in dipolar aprotic solvents, but rather arenethiolate/aryloxide ion ratios. They are less comprehensive than one would wish, and in a strict sense they do not support the criticism offered. The most complete set of data shows that PhS^- is about 3.5-fold more reactive than PhO^- in inducing elimination *from tert-butyl bromide in ethanol*,[14a] but only about ⅝ as effective in causing elimination *from cyclohexyl bromide in acetone*.[39] Closely related is the fact that in reactions with *tert*-butyl bromide in acetone,[14d] the *p*-nitrobenzenethiolate/*p*-nitrophenoxide reactivity ratio is 0.73. The foregoing data suggest that the RS^-/RO^- reactivity ratio does indeed change from >1 to <1 with change from protic to dipolar aprotic solvent, as one might expect from desolvation energy considerations. It is to be noted, however, that in reactions with both cyclohexyl (**9a**) and *cis*-2-methylcyclohexyl (**9b**) *p*-toluenesulfonates in acetone solution, the PhS^-/PhO^- and the ArS^-/ArO^- (Ar = *p*-nitrophenyl) reactivity ratios exceed unity,[39] ranging from 3.0 to 8.1.



9a, R = H
9b, R = CH_3

In identifying the desolvation energy factor as a major one contributing to EtS^-/MeO^- reactivity ratios in excess of unity, we do not mean to assert that it is solely responsible. Perhaps one or more others are also significant.

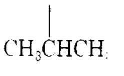
Interpretation with Respect to the "E2C" Mechanism. A key feature of the "E2C" mechanism in its original version was substantial bonding interaction of the base with C_α in the transition state. Transition-state structures such as **1** were proposed,[18] and it was suggested that the type of bonding, charge distribution, and stereochemistry were very similar to those in S_N2 transition states.[19,40] In a 1976 discussion,[20] less emphasis was placed on covalent interaction of the base with C_α, but it was stated: "... the fact that RS^- causes β-elimination faster than does RO^- ... is regarded as strong evidence against bonding to hydrogen in many E2 transition states." McLennan[38] has suggested that the base interacts mainly with H_β but slightly and rather remotely with C_α, sketching the transition state as **10**.



10

Insofar as thiolate ions are concerned, the primary rationale for invoking covalent interaction of the base with C_α was that it seemed to provide an interpretation of the superior elimination-inducing reactivity of thiolate ions over alkoxide ions in some reactions. It was believed that thiolate ions are categorically stronger nucleophiles toward carbon, but weaker toward hydrogen. It has since been found, however, that MeO^- is more reactive than MeS^- with methyl halides in the gas phase[41] and more reactive than PhS^- with some substrates in methanol.[42]

Steric implications of "E2C" transition states are also troublesome. Whereas isopropyl bromide (**11**) reacts with EtS^- in methanol to give ethyl isopropyl sulfide in nearly quantitative yield, the reaction of **12** with EtS^- gives about 97% of olefin **13**, the only byproducts being small amounts of rearranged olefins attributed to a minor solvolysis component.[8] Since no propene could be detected as a product from **11**, only a maximum elimination rate could be assigned; the maximum possible rate constant, statistically corrected, is at most 2.2-fold greater than the measured rate constant for conversion of **12** to **13**. Thus the introduction of three α-methyl substituents in **11** absolutely blocks the otherwise predominent S_N2 reaction with EtS^-, but has little if any effect on the rate of elimination to form **13**. The interference with the S_N2 process is due to steric hindrance, and the fact that the elimination is immune to steric hindrance shows that its transition state has a geometry with EtS^- remote from C_α.[8]



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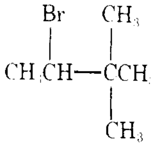
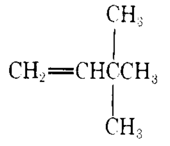
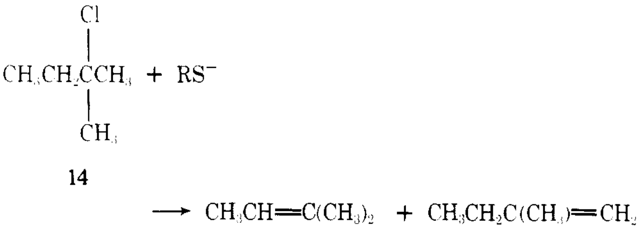


12



13

The reactions of 1-butanethiolate ion (n-BuS^-), 2-butanethiolate ion (sec-BuS^-), and 2-methyl-2-propanethiolate ion (t-BuS^-) with 2- chloro-2-methylbutane (**14**) in ethanol at 55.2 °C all give virtually the same olefin product ratio (73.2 ± 1.2% of **15**), and there is little variation in rate as the thiolate ion is changed.[13] The relative rates are: n-BuS^-, 1.2; sec-BuS^-, 1.1; t-BuS^-, 1.0. However, substitution reactions of the same three thiolate ions with 2-bromobenzothiazole[43] (eq 4) proceed at rates strongly dependent on the identity of the thiolate ion; the relative rates are: n-BuS^-, 50; sec-BuS^-, 15; t-BuS^-, 1. In the substitution reaction the thiolate ions attack C-2 of the benzothiazole framework, and the rate differences reflect steric problems associated with the requisite close approach. In **14**, tertiary C-2 is buried deep within the molecule, in contrast to C-2 of 2-bromobenzothiazole, and a much more serious set of steric oppositions would operate if the thiolate ions approached closely to it in the elimination transition state. Again the conclusion is that the thiolate ion cannot closely approach C_α. On the other hand, the different steric requirements of the three thiolate ions should matter little if the thiolate ion interacts only with H_β.[44]



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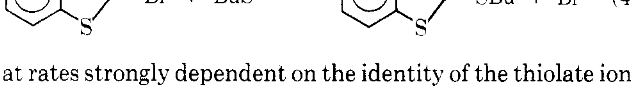
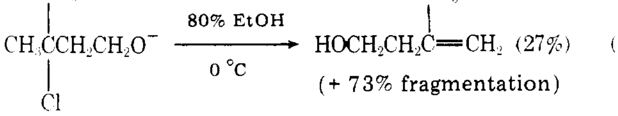


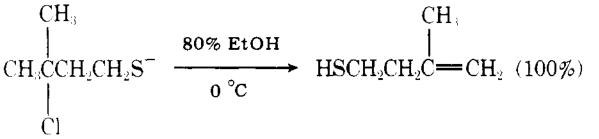
(4)

Grob and co-workers[45] have observed a pair of intramolecular elimination reactions brought about by analogous oxyanion and sulfanion bases, **16** and **17**. The observed thiolate ion/alkoxide ion rate ratio, k_{17}/k_{16}, is 14.4. It is similar to the RS^-/RO^- reactivity ratios found for intermolecular eliminations from tertiary alkyl halides,[6,9b,13] and is consistent with cyclic transition states such as **18**, as proposed.[45] However, the "E2C" hypothesis would assign a highly strained transition state of type **19** to thiolate reaction 6 while allowing oxyanion reaction 5 to proceed via an unstrained transition state analogous to **18**, and therefore would require that k_{17}/k_{16} be substantially lower than for corresponding intermolecular



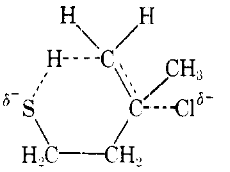
(5)

16



(6)

17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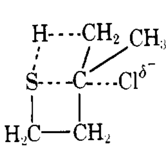

19

reactions. The "E2C" hypothesis calls for behavior not substantiated by observation.

Presentations of the "E2C" hypothesis[19,20] have suggested that there exists a spectrum of transition states, varying from an "E2C" extreme (of type 1) to an "E2H" extreme, the latter being a standard E2 transition state usually represented as 7. As to factors governing the position of a particular transition state within that spectrum, principal emphasis has been placed on the H basicity vs. C nucleophilicity of the base, the acidity of the β-hydrogen, and the identity of the leaving group. How would the present reactions of **5a–g** with EtS^- and the analogous reactions with MeO^- be viewed with regard to that hypothesis? First, the reactions with EtS^- would be classed as E2C-like, and those with MeO^- as E2H-like. Second, the variation of ring substituents within the set of substrates, **5a–g,** would be considered to affect the acidity of H_β and thereby to shift the reactions toward the E2C extreme as substituents become more strongly electron releasing, and vice versa. Probably the observed variation in EtS^-/MeO^- reactivity ratio could thereby be rationalized. However, the "E2C" hypothesis is insensitive to the effects of substituents in a β-aryl group on reaction rate. Thus, it has been stated: "... it makes virtually no difference to the rate of E2C-like reactions whether the β substituents are methyl, phenyl, *p*-anisyl, or a combination of these."[14c] The "E2C" hypothesis appears to provide no basis for judging the substituent effects on elimination to olefins **2** and **3,** which are the main concern of the present work.

In summary, the "E2C" hypothesis has difficulty in accommodating recent experimental evidence concerning thiolate ion induced elimination and provides little insight into the kinetic data we have obtained.

Interpretation in Terms of Thiol Catalysis of Chloride Departure. We consider now an elaborated E2 mechanism in which lyate ion attacks H_β concerted with electrophilic catalysis by ethanethiol of nucleofuge departure, as sketched in Scheme I. Elimination to form **2** is depicted; a similar representation of the formation of **3** can be visualized. The kinetic expression appropriate to this mechanism is that of

$$d[2]/dt = k_2'[5][MeO^-][EtSH] \qquad (7)$$

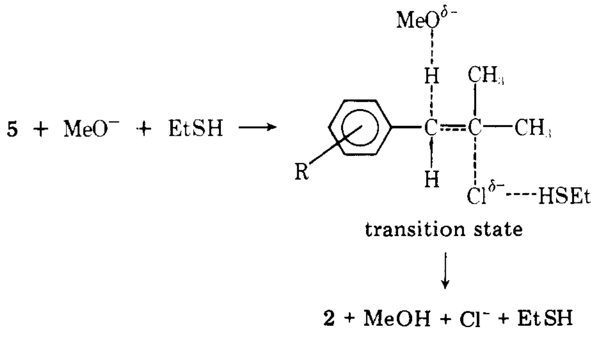
For the acid–base reaction of ethanethiolate ion with methanol, the equilibrium constant is given by

$$K_{eq} = [EtSH][MeO^-]/[EtS^-] \qquad (8)$$

from which it is plain that eq 7 can be written as

$$d[2]/dt = k_2'K_{eq}[5][EtS^-] \qquad (9)$$

Scheme I



Thus this mechanism calls for a rate law of the same mathematical form as for direct attack of EtS^- on substrate. The value of K_{eq} was estimated by Bunnett and Retallick[27] to be about 1/270. It is implied that the indirect mechanism of Scheme I should be competitive with direct attack if k_2' is about 270 times as great as k_2, which is a conceivable possibility. Moreover, this mechanism would be compatible with the experimental fact that the steric requirements of thiolate-induced elimination are not much different than those of alkoxide-induced elimination.

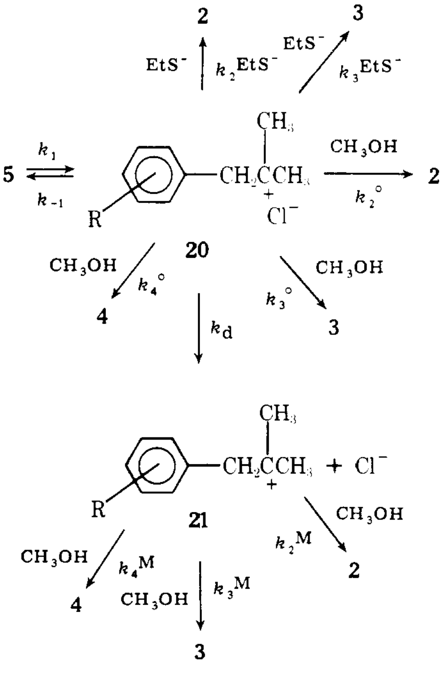
However, this mechanism is unable to give a satisfactory account of certain other observations. One of them is the fact[7] that the EtS^-/MeO^- reactivity ratio with (benzyldimethylcarbinyl)dimethylsulfonium ion, $PhCH_2CMe_2SMe_2^+$, is 0.7. Ethanethiol would not be expected to render any assistance to the departure of a dimethylsulfonio group as dimethyl sulfide, and therefore by this mechanism a reactivity ratio of about 1/270 would have been anticipated. Another is the fact[45] that elimination from **17** (eq 6) is kinetically first order; the mechanism of Scheme I would call for it to be second order in substrate.

The mechanism of Scheme I is therefore dismissed.

Interpretation in Terms of an Ion Pair Mechanism. The mechanistic model which we now consider is sketched in Scheme II. Substrate **5** ionizes first to form contact ion pair **20** for which seven pathways of reaction are provided: reversion to **5**, reaction with EtS^- to form **2** or **3**, reaction with or without solvent to form **2** or **3**, reaction with solvent to form **4**, and diffusive separation into carbocation **20** and chloride ion.[46] (Reaction of **20** without solvent to form **2** or **3** implies proton abstraction from the carbenium ion of **20** by the chloride ion.) Free carbocation **21** may react with solvent to form **2**, **3**, or **4**. This type of model, dubbed $(E2)_{ip}$ by Bordwell,[21] has been considered several times in the past. For reactions kinetically first order in base as well as in substrate, it has been favored by some authors[21,22,47] and disfavored by others.[6] Saunders[48] has discussed it.

If one makes the usual steady-state assumption that the rates of formation and consumption of ion pair **20** are equal, and the further assumption that **5** and **20** are in mobile equilibrium, that is, that $k_{-1} \gg (k_2{}^\circ + k_3{}^\circ + k_4{}^\circ + k_d + k_2{}^{EtS^-}[EtS^-] + k_3{}^{EtS^-}[EtS^-])$, one may obtain the following expression for the rate of formation of **2**:

Scheme II



$$\frac{d[2]}{dt} = \frac{k_1}{k_{-1}}[\mathbf{5}]\left\{k_2{}^{\circ} + k_2{}^{\mathrm{EtS^-}}[\mathrm{EtS^-}] + \frac{k_{\mathrm{d}}k_2{}^{\mathrm{M}}}{k_2{}^{\mathrm{M}} + k_3{}^{\mathrm{M}} + k_4{}^{\mathrm{M}}}\right\} \quad (10)$$

This expression is consistent with the observed kinetic behavior.

A significant feature of eq 10 is that the solvolytic component of the rate of formation of **2** is composite of contributions from the $k_2°$ term and the k_d term. Whereas $k_2°$ may well depend on the isotope of hydrogen that is being removed from the carbocation of **20** and on substituent effects in the carbocation, k_d should be virtually independent of those factors. Since the isotope and substituent effects called for by this mechanism, insofar as the solvolytic component of elimination is concerned, would represent an average of contributions from $k_2°$ and k_d terms of unknown relative magnitude, one cannot predict from this mechanism how large these effects would be. One therefore cannot argue from the observed magnitudes of these effects for the solvolytic part of elimination whether or not this mechanism obtains for the part of the overall reaction induced by ethanethiolate ion.[6]

If the $(E2)_{ip}$ mechanism were to obtain for elimination induced by EtS^- or MeO^-, the observed ρ for formation of **2** should be composite of a negative contribution for the **5** $\rightleftarrows$ **20** equilibrium and a positive contribution for proton removal from **20**. Inasmuch as removal of H_β from a carbocation by EtS^- or MeO^- would be highly exothermic, the transition state for the proton abstraction step should be attained very early on the reaction coordinate and the associated positive contribution to ρ should be very small. The overall ρ for formation of **2** by this mechanism should therefore be negative. This mechanism is thus compatible with the left wing of Figure 1, but not with the right wing. If it prevails for the left wing, the change in slope must be attributed to a change in mechanism, to the E2 mechanism for the right wing.

If the negative slope of the left wing of Figure 1 is indeed due to the operation of the $(E2)_{ip}$ mechanism, the same mechanism should in principle be available to methoxide ion, but the uniformly positive slope for the Hammett plot for methoxide-induced formation of **2**[24,25] indicates that the E2 mechanism operates throughout for it. It would then be implied that reaction of **20** with MeO^- were very much slower than with EtS^-. If so, the lower desolvation energy of EtS^- than of MeO^- would probably be responsible, as discussed above.

It is to be noted that the reaction of **5e** with EtS^- to form **2e** falls on the right wing of Figure 1, and therefore goes by the E2 mechanism, but is nevertheless about twice as fast as the same transformation induced by MeO^-. Invoking the $(E2)_{ip}$ mechanism thus does not dismiss the problem of rationalizing the fact that EtS^- surpasses MeO^- in E2 reactions with some substrates.[49]

Concluding Comments. We have seen that the present results are accounted for satisfactorily in terms of the E2 mechanism with transition states quite far to the paenecarbenium side. They can also be rationalized in terms of a combination of the $(E2)_{ip}$ and E2 mechanisms, but such a model would necessitate proposing higher elimination reactivity for EtS^- than for MeO^- for reactions by both mechanisms. The "E2C" mechanism doesn't really deal with phenomena such as explored in the present study, but runs into trouble with results for closely related reactions.

Experimental Section

Materials. Substrates and authentic samples of products were obtained as described in the preceding paper.[25]

Kinetics by Photometric Measurement. In a volumetric flask, enough substrate to give an approximately 0.01 M solution was weighed directly. The appropriate volume of freshly made and standardized NaOMe solution was added with external cooling by ice, and the appropriate volume of a standard solution of ethanethiol (Aldrich) in methanol (stored under dinitrogen) was added. The amount of ethanethiol added was enough to neutralize the $NaOCH_3$ and to be present in excess as indicated in Table I. The solution was then diluted to the mark with magnesium-dried methanol at room temperature. Measured aliquots (1, 3, or 5 mL) were dispensed by pipet 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, their contents were transferred quantitatively to volumetric flasks which contained methanolic acetic acid in amount slightly greater than enough to neutralize the NaSEt originally present, and the ampules were diluted to the mark with methanol. The absorbance of each solution was measured as described in the preceding paper[25] for kinetics with NaOMe, the reference solution being a solution of all the reactants but the substrate, sampled and diluted in the same way. Plots of ln $(A_\infty - A_t)$ vs. time were linear, and the negatives of their slopes were taken as k_ψ, as listed in Table I.

Kinetics by Potentiometric Titration. The procedure of Bunnett, Davis, and Tanida[6] was employed. Initial substrate concentration was on the order of 0.02–0.05 M.

Product Analysis. An ampule from each kinetics run at "infinity" time was opened and the contents was transferred quantitatively into a separatory funnel containing 10 mL of redistilled cyclohexane. The mixture was extracted with two 10-mL portions of water, three 15-mL portions of 2 M aqueous NaOH, and finally with one 20-mL portion of water. The cyclohexane layer was dried over anhydrous Na_2SO_4, and the dried solution was analyzed by GLC with use of the same methods described for analogous determinations on solvolyses of the same substrates.[25]

Registry No.—2a, 768-49-0; **2b,** 5916-22-3; **2c,** 877-99-6; **2d,** 19366-15-5; **2e,** 69278-43-9; **2f,** 1012-18-6; **2g,** 64781-39-1; **3a,** 3290-53-7; **3b,** 40296-92-2; **3c,** 20849-82-5; **3d,** 23063-65-2; **3e,** 69278-44-0; **3f,** 18755-60-7; **3g,** 53483-21-9; **4a,** 69278-45-1; **4b,** 69278-46-2; **4c,** 69278-47-3; **4d,** 69278-48-4; **4e,** 69278-49-5; **4f,** 69278-50-8; **4g,** 69291-95-8; **5a,** 1754-74-1; **5b,** 18503-92-9; **5c,** 18503-98-5; **5d,** 18503-93-0; **5e,** 69278-41-7; **5f,** 69278-42-8; **5g,** 3762-41-2; ethanethiolate, 20733-13-5.

References and Notes

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(2) This paper is based in part on the Dissertation of S. Sridharan, University of California, Santa Cruz, March, 1974; *Diss. Abstr. Int. B*, **35**, 4399 (1975).

(3) National Science Foundation Science Faculty Fellow at Brown University, 1965–1966, on leave from Wofford College, Spartanburg, South Carolina.

(4) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 41 (1956).

(5) E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5995 (1957); E. L. Eliel and R. G. Haber, *ibid.*, **81**, 1249 (1959).

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

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

(8) J. F. Bunnett and D. L. Eck, *J. Am. Chem. Soc.*, **95**, 1900, 4473 (1973).

(9) (a) D. J. McLennan, *J. Chem. Soc. B*, 705 (1966); (b) *ibid.*, 709 (1966).

(10) B. D. England and D. J. McLennan, *J. Chem. Soc. B*, 696 (1966).

(11) D. J. McLennan, *Aust. J. Chem.*, **22**, 1905 (1969); D. J. McLennan and R. J. Wong, *J. Chem. Soc., Perkin Trans. 2*, 279 (1972); 526, 1818 (1974).

(12) W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Am. Chem. Soc.*, **87**, 3401 (1965).

(13) D. S. Bailey and W. H. Saunders, Jr., *J. Org. Chem.*, **38**, 3363 (1973).

(14) (a) E. C. F. Ko and A. J. Parker, *J. Am. Chem. Soc.*, **90**, 6447 (1968); (b) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *ibid.*, **92**, 115 (1970); (c) G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, **93**, 4735 (1971); (d) A. J. Parker, M. Ruane, D. A. Palmer, and S. Winstein, *ibid.*, **94**, 2228 (1972).

(15) W. T. Ford and R. J. Hauri, *J. Am. Chem. Soc.*, **95**, 7381 (1973).

(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) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968).

(19) A. J. Parker, *CHEMTECH*, **1**, 297 (1971).

(20) A. J. Parker, *Proc. R. Aust. Chem. Inst.*, 105 (1976).

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

(22) W. T. Ford, *Acc. Chem. Res.*, **6**, 410 (1973).

(23) A. Landis and C. A. VanderWerf, *J. Am. Chem. Soc.*, **80**, 5277 (1958); M. M. Tessler and C. A. VanderWerf, *J. Org. Chem.*, **30**, 405 (1965); H. C. Brown and C. J. Kim, *J. Am. Chem. Soc.*, **90**, 2082 (1968).

(24) L. F. Blackwell, A. Fischer, and J. Vaughan, *J. Chem. Soc. B*, 1084 (1967); L. F. Blackwell, Ph.D. Thesis, University of Canterbury, Christchurch, New Zealand, 1965.

(25) J. F. Bunnett and S. Sridharan, *J. Org. Chem.*, preceding paper in this issue.

(26) J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, **35**, 76 (1970).

(27) J. F. Bunnett and L. A. Retallick, *J. Am. Chem. Soc.*, **89**, 423 (1967).

(28) (a) J. F. Bunnett in "Investigation of Rates and Mechanisms of Reactions", Part I, 3rd ed, E. S. Lewis, Ed., Wiley, New York, 1974, p 138; (b) *ibid.*, p 404.

(29) Cf. N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *J. Am. Chem. Soc.*, **89**, 725 (1967).

(30) We are persuaded by the nomenclature proposals of Olah[31] and abandon the previously proposed *paenecarbonium* for *paenecarbenium*.

(31) G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973).

(32) R. A. More O'Ferrall, *J. Chem. Soc. B*, 274 (1970).

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

(34) J. P. Danehy and C. J. Noel, *J. Am. Chem. Soc.*, **82**, 2511 (1960).

(35) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **82**, 795 (1960).

(36) J. E. Bartmess and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **99**, 4163 (1977).

(37) Cf. R. F. Hudson, *Chimia (Aarau)*, **16**, 173 (1962).

(38) D. J. McLennan, *Tetrahedron*, **31**, 2999 (1975).

(39) P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2240 (1972).

(40) D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5183 (1968).

(41) W. N. Olmstead and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 4219 (1977).

(42) G. Bartoli and P. E. Todesco, *Acc. Chem. Res.*, **10**, 125 (1977).

(43) G. Bartoli, L. Di Nunno, and P. E. Todesco, *Tetrahedron Lett.*, 2369 (1968).

(44) R. A. Bartsch, G. M. Pruss, B. A. Bushaw, and K. E. Wiegers, *J. Am. Chem. Soc.*, **95**, 3405 (1973).

(45) W. Fischer and C. A. Grob, *Tetrahedron Lett.*, 3547 (1975); *Helv. Chim. Acta*, in press; C. A. Grob, B. Schmitz, A. Sutter, and A. H. Weber, *Tetrahedron Lett.*, 3551 (1975).

(46) A more elaborate model would include a solvent-separated ion pair intermediate, but we see no need to invoke such a model for present purposes.

(47) F. G. Bordwell and G. A. Pagani, *J. Am. Chem. Soc.*, **97**, 118 (1975).

(48) W. H. Saunders, Jr., *Acc. Chem. Res.*, **9**, 19 (1976).

(49) A reviewer has suggested also the possibility of an electron-transfer mechanism for thiolate ion induced elimination, as follows: $RS^- + R'Cl \rightarrow [RS\cdot + R'Cl^-\cdot] \rightarrow [RS\cdot + Cl^- + R'\cdot] \rightarrow RS^- + R'^+ \rightarrow RSH +$ olefin. We think this unlikely. Presumably it would operate best with the substrate having the greatest electron affinity, which would be with **5f** among those in the present study. But **5f** is the substrate with which the EtS^-/MeO^- reactivity ratio is lowest.

Could Ionization Potentials of Free Radicals Serve as Alkyl Inductive Substituent Constants?

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Four sets of heterolytic bond dissociation energies, eight sets of gas-phase ionization potentials of compounds having unshared electron pairs, five sets of activation energies of S_N2 reactions, one set of activation energies for alkaline hydrolysis of alkyl acetates, one set of activation energies for hydrogen abstraction by bromine atoms, and four sets of activation energies for gas phase unimolecular reactions, have been correlated with ionization potentials of alkyl free radicals, IP(R)'s. It has been shown that IP(R)'s can be treated as additive alkyl inductive substituent constants. For example, correlation $IP(R_1R_2C{=}O) = 0.148\Sigma IP(R_i) + 6.697$ ($r = 0.981$) covers (almost) all the available ionization data for a total of 19 aldehydes and ketones with eight different alkyl groups (plus hydrogen). Charton's steric constants υ_{OX} and $\upsilon_{NX_1X_2}$ are related to IP(R)'s as follows: $1/\upsilon_{OX} = 0.851IP(R) - 5.113$ ($r = 0.993$) and $\upsilon_{NX_1X_2} = -0.3455\Sigma IP(X_i) + 7.195$ ($X = R$, $r = 0.999$, eq 17). Equation 17 has been used to calculate 27 unavailable values of $\upsilon_{NX_1X_2}$. An attempt was made to rationalize most of the observed correlations.

Since the electron has been viewed as a "chemical entity",[1] it appears reasonable to wonder whether it could be considered as a substituent as well. Indeed, the presence of an odd electron in an organic chemical structure appears to impart to this structure properties, other than magnetic ones, that are markedly different from those of the parent molecule which has all its electrons paired. To limit this discussion to neutral radicals, the best, perhaps, known example that can be cited is the acidity of the radical $R_1R_2\dot{C}{-}OH$ and of the alcohol $R_1R_2CH{-}OH$ from which the radical derives. The pK_a values of these species can differ by 5–10 pK_a units, depending on the kind of R's. For example, although the alcohols ethyl, isopropyl, benzyl, and benzhydryl all have $pK_a = 18$,[2] the corresponding radicals, $CH_3\dot{C}HOH$, $(CH_3)_2\dot{C}OH$, $Ph\dot{C}HOH$, and $Ph_2\dot{C}OH$, differ significantly in their acidities,[3] i.e., 11.6, 12.2, 8.4, and 9.2, respectively. The structure-dependent pK_a values can be taken as the manifestation of the odd electron's ability to amplify the different contributions of R_1 and R_2 to the ionization of OH, in these radicals.

As a further example, one can compare bond dissociation energies, a molecular parameter widely used to rationalize reactivity,[4] with some other thermochemical data, such as gas phase ionization potentials. Namely, the bond dissociation energies for the series R–Br, D(R–Br), for R = CH_3, Et, *i*-Pr, and *t*-Bu, are respectively[5] 70, 68, 68, and 67 kcal/mol. The first gas phase ionization potentials[6] of the corresponding bromides, IP(R–Br), are respectively[7] 242.7, 236.0, 232.0, and 227.5 kcal/mol. We can see that the range of the structural effect, from CH_3Br to *t*-BuBr, in D(R–Br)'s is 3 kcal/mol only, as compared to 15.2 kcal/mol in IP(R–Br)'s. Again, it becomes apparent that in the case of the process where an odd electron species is involved, the effect of the alkyl substituent has been amplified to an extent which obviously depends on its structure. Even more pronounced is the difference between the range of the structural effects of D(R–Br)'s and of the ionization potentials of free radicals R·, IP(R)'s. Ionization potentials of free radicals are defined as the enthalpy change for reaction 1, and it is given by eq 2.

$$R\cdot \rightarrow R^+ + e^- \tag{1}$$

$$IP(R) = \Delta H_f(R^+) - \Delta H_f(R\cdot) \tag{2}$$

The IP(R)'s of CH_3, Et, *i*-Pr, and *t*-Bu are[7] 226.8, 193.2, 174.0, and 159.7 kcal/mol, respectively. In this case the range of the structural effect of 3 kcal/mol in D(R–Br)'s is compared to 67.1 kcal/mol in IP(R)'s. In the latter example the effect of the odd electron is dramatic.

The first gas phase ionization potential of a series R–X, where X is any group having unshared electron pairs or π electrons, and R = CH_3, Et, *n*-Pr, *n*-Bu, *i*-Bu, *i*-Pr, *s*-Bu, and *t*-Bu, shows a systematic decrease from R = CH_3 to R = *t*-Bu. In Table I is given the difference between the IP(CH_3-X) and IP(t-Bu-X) in kcal/mol and it is designated as range of the structural effect, RSE. It can be seen that RSE depends on X and it is maximal for X = odd electron.

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