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Registry No.—**1**, 428-76-2; **1** potassium salt, 33249-12-6; **1** morpholine salt, 31322-96-1; **1** diethylamine salt, 40906-76-1; **1** *N*-methylaniline salt, 40906-77-2; **1** piperidine salt, 31323-01-0; **1** guanidine salt, 31322-97-1; **2**, 29214-37-7; **3**, 29214-34-4; **4**, 31253-33-5; **4** triethylamine salt, 40906-78-3; **4** potassium salt, 40906-79-4; **5**, 40906-80-7; **6**, 40906-81-8; **7**, 40906-82-9; **8**, 40906-83-0; **9**, 40906-84-1; **10**, 40906-85-2; **11**, 30354-36-0; **11** potassium salt, 40906-86-3; **12**, 29214-36-6; **13**, 31139-48-7; **14**, 30354-37-1; **15**, 29269-32-7; **16**, 30354-38-2; **16** sodium salt, 30354-42-8; **16** potassium salt, 30354-43-9; **17**, 29214-39-9; **17** potassium salt, 40906-87-4; **18**, 31322-84-6; **21**, 40906-88-5; **22**, 40906-89-6; **23**, 40906-90-9; **25**, 40906-91-0; **27**, 30354-40-6; **28**, 30416-82-1; **29**, 30354-41-7; **30a**, 40906-92-1; **30b**, 25466-54-0; methylmagnesium chloride, 676-58-4; trifluoromethanesulfonyl fluoride, 335-05-7; nonafluorobutanesulfonyl fluoride, 375-72-4; methylmagnesium bromide, 75-16-1; heptadecafluorooctanesulfonyl fluoride, 307-35-7; ethylmagnesium bromide, 925-90-6; benzylmagnesium chloride, 6921-34-2; allyl bromide, 106-95-6; benzyl chloride, 100-44-7; ethylene oxide, 75-21-8; bromine, 7726-95-6; chlorine, 7782-50-5; 4-chlorobutene-1, 927-73-1; 3-butenoic acid, 625-38-7; octene-1, 111-66-0; toluene, 108-88-3; benzyl bromide, 100-39-0; benzal bromide, 618-32-6.

Mechanisms of Elimination Reactions. XIX. Rates and Product Proportions in the Reactions of 2-Methyl-2-butyl Halides with Thiolate Ions[1]

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Rates of reaction of 2-chloro-2-methylbutane with various thiolates have been determined in ethyl, isopropyl, and *tert*-butyl alcohols. The proportions of 2-methyl-1-butene and 2-methyl-2-butene in the products have been determined under the same conditions. Some experiments have also been done with 2-iodo- and 2-bromo-2-methylbutane, and with alkoxide, phenoxide, and phenylselenoxide bases. The elimination is faster with the sulfur than with the oxygen bases. The Brønsted β values for the reaction of substituted thiophenoxides with 2-methyl-2-butyl chloride run 0.13 to 0.16, reflecting a low sensitivity of rate to pK_b. The orientation also is little affected by changes in the basicity or steric requirements of the thiolates, showing a strong preference for the Saytzev-rule product in all cases. The nature of the transition state for elimination is discussed in the light of these results.

A problem of long standing in discussions of the effect of the nature of the base on rates and product proportions in eliminations is that the base is usually the conjugate base of the solvent. A change in base thus entails a change in solvent as well. If the base is changed without changing the solvent, the possibility remains that conjugate base of the solvent, in equilibrium with the added base, will be the actual reactant. Only when the added base is much weaker than the conjugate base of the solvent is this problem minimized.

Because thiolates are much weaker bases than the corresponding alkoxides or phenoxides, and because thiolates are reported to react more rapidly than alkoxides with tertiary alkyl halides,[3,4] we chose the reaction of thiolates with 2-methyl-2-butyl halides in alcoholic media as a means of studying steric and electronic effects of the base on rates and product proportions in eliminations from 2-methyl-2-butyl halides. Observed rate constants are recorded in Table I. To the rate constants used in the Brønsted correlations (see below), a small correction for accompanying solvolysis was applied where necessary.[5] The corrected values are given in Table II. The proportions of 2-methyl-1-butene in the olefinic products were determined by glpc and are recorded in Table III. No correction for solvolysis is necessary. The solvolysis gives primarily substitution product, and control experiments showed that the olefin composition is not affected by changing the thiolate concentration.

The low sensitivity of the relative yields of 2-methyl-1-butene and 2-methyl-2-butene (Table III) to the nature of the thiolate indicates a rather loose transition state, in which the base has not interacted strongly enough with the substrate for differences in base strength to have an appreciable effect. Particularly striking is the apparent absence of any steric effect along the series *n*-BuSH, *sec*-BuSH, *t*-BuSH. Although few other examples of variation of base without concomitant variation of solvent are known, it is certainly not true that orientation is generally insensitive to the nature of the base under such circumstances. The phenoxide gives substantially more 1-ene than the thiophenoxide (Table III), and substituted phenoxides with 2-butyl tosylate give a decrease in 1-ene with decreasing basicity of the phenoxide.[6] A slight trend in the same direction is noted with the substituted thiophenoxides in the present work, but the variation is barely outside experimental error.

There is somewhat more variation of product proportions with change of solvent and leaving group. While results in ethyl and isopropyl alcohols are similar, there is a marked increase in 1-ene and decrease in rate in *tert*-butyl alcohol. Perhaps the base is less hydrogen bonded, and therefore stronger, in *tert*-butyl than in

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TABLE I

OBSERVED RATE CONSTANTS FOR REACTIONS OF 2-CHLORO-2-METHYLBUTANE[a]

Registry no.	Base	Temp, °C	$k_2 \times 10^5$, l. mol^{-1} sec^{-1}, in EtOH	*i*-PrOH	*t*-BuOH
26385-25-1	*n*-BuSK	35.2	7.55 ± 0.23		2.49 ± 0.12
	n-BuSK	55.2	74.1 ± 0.8	62.4 ± 0.9	11.9 ± 0.0
40973-65-7	*sec*-BuSK	55.2	71.5 ± 1.7		
10577-48-7	*t*-BuSK	55.2	64.4 ± 1.5		
3111-52-2	C_6H_5SK	35.2	5.97 ± 0.28	5.26 ± 0.09	
	C_6H_5SK	55.2	60.4 ± 0.5	40.6 ± 0.03	
31367-69-8	*p*-MeC_6H_4SK	55.2	64.3 ± 1.5	47.1 ± 1.0	11.9 ± 0.3
40645-42-9	*p*-ClC_6H_4SK	55.2	41.8 ± 2.3	28.0 ± 0.1	8.83 ± 0.08
40973-68-0	*m*-ClC_6H_4SK	55.2	38.5 ± 0.2		
40973-69-1	*p*-BrC_6H_4SK	55.2			8.34 ± 0.09
40973-70-4	*p*-$MeCOC_6H_4SK$	55.2	26.4 ± 0.4	19.8 ± 1.6	
	ROK	35.2	0.619 ± 0.027	0.239 ± 0.014	
	ROK	55.2	9.80 ± 0.05		0.57 ± 0.10
1192-96-7	*p*-MeC_6H_4OK	55.2	13.0 ± 0.70		0.51 ± 0.10
40973-72-6	C_6H_5SeK	55.2	89.0		
	Solvolysis	55.2	0.826 ± 0.027	0.173 ± 0.012	
	Solvolysis	60.5	1.35	0.272	
	n-BuSK	35.2			248[b]
	n-BuSK	35.2			2070[c]

[a] Each figure is the average of two to five runs, with indicated average deviation. The figure is for a single run where no deviation is listed. [b] For 2-bromo-2-methylbutane. [c] For 2-iodo-2-methylbutane.

TABLE II

RATE CONSTANTS FOR REACTIONS OF 2-CHLORO-2-METHYLBUTANE AT 55.2°, CORRECTED FOR SOLVOLYSIS[a]

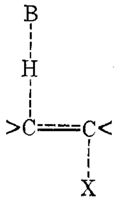
Base	$k_2 \times 10^5$, l. mol^{-1} sec^{-1}, in EtOH	*i*-PrOH	*t*-BuOH
p-MeC_6H_4SK	60.0	46.2	11.9
C_6H_5SK	56.5	39.7	
p-ClC_6H_4SK	37.3	27.1	8.83
m-ClC_6H_4SK	33.9		
p-BrC_6H_4SK			8.34
p-$MeCOC_6H_4SK$	21.9	18.9	

[a] Corrected by the method of McLennan: D. J. McLennan, *J. Chem. Soc. B*, 705 (1966).

ethyl or isopropyl alcohol. While this might explain the change in orientation, it is difficult to see why a stronger base would react at a slower rate. The decrease in rate may indicate conversion of the base to a less reactive, ion-paired form in *tert*-butyl alcohol. In contrast to the present results, 2-phenylethyl halides react faster in *tert*-butyl alcohol.[7,8] Different blends of solvent and base properties must be involved in the two cases. The Hughes–Ingold qualitative theory of solvent effects would predict a faster reaction in a less polar solvent,[9,10] again in contrast to the present results.

The decrease in per cent 1-ene along the series Cl > Br > I is indicative of increasing double-bond character of the transition state with increasing leaving-group ability of the halogen, as noted before with oxygen bases.[11,12] This leaving-group effect, and the other orientation data we have discussed above, are all consistent with the variable transition state theory of the E2 reaction.[13–15] In the framework of this theory, the transition state would be one with a great deal of double-bond character, and loose bonds between the leaving group and the α carbon, the β hydrogen, and the β carbon, and the β hydrogen and the base.

More recently, a different form of the variable transition state theory has been suggested, in which it is considered that the transition state ranges from E2H (**1**) to E2C (**3**).[16–21] Eliminations promoted by halide ions in acetone and by thiolate ions in alcohol are proposed to have transition states near the E2C end of the spectrum.



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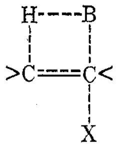

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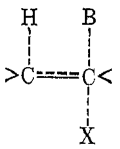

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The thiolate-promoted eliminations fit well into either the conventional variable transition state theory or the E2H–E2C theory, for both can accommodate a loose transition state with high double-bond character. An E2C-like transition state, with its interaction between

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TABLE III

OLEFIN COMPOSITIONS FOR ELIMINATIONS FROM 2-CHLORO-2-METHYLBUTANE

Base	Temp, °C	% 1-ene[a] in		
		EtOH	*i*-PrOH	*t*-BuOH
n-BuSK	35.2	25.0 ± 0.7		27.7 ± 0.3
	55	25.5 ± 1.0	26.2 ± 0.5	31.2
	85	30		33.7 ± 0.4
sec-BuSK	55	26.9 ± 0.5		
t-BuSK	35	24.6		28.3 ± 0.5
	55	27.9 ± 0.6		31.2
	85	30		34.2 ± 0.6
p-MeC_6H_4SK	55	28.9 ± 0.5	28.5 ± 0.5	33.4 ± 0.5
	85	32.0	32.4 ± 1.0	37.5 ± 1.0
	110		34.0 ± 0.5	
C_6H_5SK[d]	35	29.0 ± 0.4		30.0 ± 0.2
	55	29.4 ± 0.2	28.5 ± 0.5	32.2 ± 0.3
	85	31.4 ± 0.3		
	110	33.7 ± 0.7		
p-ClC_6H_4SK	55	27.2 ± 0.2	27.2 ± 0.5	30.8 ± 0.4
	85	30.6 ± 0.3		36.6 ± 2.0
p-$MeCOC_6H_4SK$	55	27.0 ± 0.5	26.5 ± 0.5	
C_6H_5OK[e]	55			45.0
	85	39		
C_6H_5SeK	55	27.4		
	85	29.0		
n-BuSK	55			25.6[b]
	35			20.8[c]
t-BuSK	55			25.7[b]
	85			27.5[b]
	35			20.7[c]

[a] Out of total olefin (2-methyl-1-butene + 2-methyl-2-butene). Deviations are average deviations from the average of two to six runs. The figure is for a single run where no deviation is listed. [b] For 2-bromo-2-methylbutane. [c] For 2-iodo-2-methylbutane. [d] W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Amer. Chem. Soc.*, **87**, 3401 (1965), gives 32% 1-ene at reflux and G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 4735 (1971), gives 29.5% at 50° in ethanol. R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **90**, 408 (1968), also report 26% 1-ene from 2-bromo-2-methylbutane in ethanol. [e] Part of the reaction with "C_6H_5OK" may involve the conjugate base of the solvent. While a 10% excess of phenol was used to suppress solvent ionization, the conjugate base of the solvent may be sufficiently reactive to compete even in very small concentration.

the base and the α carbon, affords a reasonable explanation of the high effectiveness of the weakly basic but strongly nucleophilic thiolates relative to the much more strongly basic alkoxide. Otherwise, there is nothing in the present results that compels either the acceptance or rejection of the E2C mechanism for the reaction of tertiary alkyl halides with thiolates.

More recently, it has been suggested that E2C reactions and other second-order eliminations from readily ionizable substrates may occur *via* attack of base on an ion pair derived from the substrate.[22,23] It seems difficult to reconcile such a mechanism with the dependence of orientation on leaving group, which is qualitatively the same as that observed for the reaction of alkoxides with secondary halides,[11,12] a reaction which is almost certainly E2. That the anion in an ion pair would have much effect at all on the susceptibility of the various β hydrogens of the cation to attack by base, let alone the same effect as in E2 reactions, appears *a priori* improbable. Evidence on whether the leaving group affects orientation in E1 reactions would be relevant to the ion-pair hypothesis, for many examples of the E1 reaction doubtless involve attack of solvent or counterion on a β hydrogen of the cation in an ion pair. A recent study has shown that the proportion of 2-pentene (out of total pentenes) from ethanolysis of 2-pentyl derivatives remains constant at 94% for the leaving groups Br, SMe_2Br, SMe_2I, and NMe_3I, though there is a curious decrease to 87% for SMe_2ClO_4.[24] Except for the last substrate, which differs from the others in having a totally nonnucleophilic anion, the data support the belief that the leaving group should have little or no effect on orientation in E1 reactions. In the ion-pair mechanism, where the more reactive alkoxide or thiolate ion is supposed to attack the ion pair, even less discrimination would be expected. While the evidence is not sufficiently comprehensive for a definitive conclusion, we consider it improbable that our reactions occur *via* the ion-pair mechanism.

The insensitivity of the rates to the structure and strength of the thiolate bases confirms our conclusion that the base is only weakly bound to the β hydrogen in the transition state. The low Brønsted β values (Table IV), along with the value of 0.17 for *tert*-butyl chloride at 45° reported by McLennan,[4] give a more quantitative expression to this insensitivity. We do not wish to make too much of the β values, for those in isopropyl and *tert*-butyl alcohols utilize p*K*'s measured in ethanol, and recent work has cast doubt on the general validity of β as a measure of the extent of proton transfer in the transition state.[25-28] We still feel that our β values at least represent proton transfers that are substantially

TABLE IV

BRØNSTED COEFFICIENTS AND RELATIVE RATES WITH SULFUR AND OXYGEN BASES IN ELIMINATIONS FROM 2-CHLORO-2-METHYLBUTANE

Solvent	Temp, °C	β[a]	$k_{n\text{-BuS}^-}/k_{\text{RO}^-}$	$k_{\text{PhS}^-}/k_{p\text{-MeC}_6\text{H}_4}$
EtOH	55.2	0.19	5	5
i-PrOH	55.2	0.16		
t-BuOH	55.2	0.13	21	23
t-BuOH	35.2		6[d]	
t-BuOH	35.2		10[b,d]	
t-BuOH	35.2		20[c,d]	

[a] From the slope of a least squares plot of log *k* (Table II) *vs.* pK_a's for the substituted thiophenols in 95% ethanol at 20°: G. Schwartzenbach and E. Rudin, *Helv. Chim. Acta.* **22,** 360 (1939). [b] For 2-bromo-2-methylbutane. [c] For 2-iodo-2-methylbutane. [d] Rates with *tert*-butoxide ion from H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, **76**, 455 (1954), and R. L. Klimisch, Ph. D. Thesis, Purdue University, 1965.

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less than half complete in the transition states, for three main reasons.

First, Marcus points out that β should be a reliable measure of the extent of proton transfer if the "intrinsic barrier" (the activation energy when the free-energy differences is zero) remains nearly constant.[29] This condition is usually fulfilled when the structural variation is in oxygen or nitrogen bases, and presumably also in sulfur bases. Second, Murdoch's strictures should not apply to our reactions, which are of high activation energy[30] and unlikely to involve kinetically significant hydrogen-bonded complexes between substrate and base. Finally, England and McLennan[5,31] report substantially larger β values for the reactions of thiophenoxides with cyclohexane derivatives (0.27–0.58) and 2,2-di(*p*-chlorophenyl)-1,1,1-trichloroethane (0.77). These figures increase just as one would expect the extent of proton transfer in the transition state to increase, strongly suggesting that the much lower values with the tertiary halides indicate a low extent of proton transfer.

Experimental Section

Thiols.—All alkyl and aryl thiols except *p*-acetylthiophenol and *m*-chlorothiophenol were commercially available and were purified by standard procedures. The properties of the purified thiols agreed satisfactorily with literature values.

***p*-Acetylthiophenol** was prepared essentially in the manner described by Riesz and Frankfurter.[32] Distillation of the product at *ca.* 100° (1 mm) gave material of mp 27–29° (lit.[33] mp 27–28.5°).

***m*-Chlorothiophenol** was prepared essentially in the manner described by Campaigne and Osborn.[34] The product had bp 75° (0.3 mm), $n^{25}\mathrm{D}$ 1.5835 (lit.[35] $n^{25}\mathrm{D}$ 1.5830).

2-Chloro-2-methylbutane was Eastman White Label grade which was washed with water, dried over magnesium sulfate, and distilled at reduced pressure. Analysis by glpc on a 15 ft × 0.25 in. column of didecyl phthalate on Chromosorb P showed only 0.3% olefin. The material had bp 85°, $n^{25}\mathrm{D}$ 1.4038 (lit.[11,36] bp 84.3–85°, $n^{20}\mathrm{D}$ 1.4036).

2-Bromo-2-methylbutane.—2-Methyl-2-butanol (100 ml) was added slowly to 150 ml of 48% hydrobromic acid with stirring. The alkyl bromide was separated from the aqueous layer, washed with 5% sodium carbonate and water, and dried over magnesium sulfate. Analysis by glpc, using the same procedures as with 2-chloro-2-methylbutane, showed no detectable olefin. The material had $n^{20}\mathrm{D}$ 1.4425 (lit.[37] $n^{20}\mathrm{D}$ 1.4421).

2-Iodo-2-methylbutane.—To 50 ml of 2-methyl-2-butanol was added dropwise with stirring (magnetic stirrer) 250 g of 48% hydriodic acid. After two layers developed, the top layer was separated, washed with 5% sodium carbonate and water, and dried over magnesium sulfate. Final purification was by bulb-to-bulb distillation under reduced pressure, and the unstable product was used immediately. Analysis by glpc, using the same procedure as with 2-chloro-2-methylbutane, showed no detectable olefin. The material had $n^{20}\mathrm{D}$ 1.4940 (lit.[32] $n^{20}\mathrm{D}$ 1.4946).

Solvents.—Ethanol was distilled twice under dry nitrogen from magnesium following Lund and Bjerrum.[38] Isopropyl and *tert*-butyl alcohols were distilled twice from calcium hydride.[39]

Kinetic Procedures.—Sufficient aryl or alkyl thiol was weighed into a nitrogen-flushed 100-ml volumetric flask to provide, when filled to the mark with a standardized solution of potassium alkoxide in the corresponding alcohol, a *ca.* 0.2 *M* solution of thiolate containing 10% of unreacted thiol. The solution was brought to temperature, transferred to the reaction vessel equipped with a rubber septum for withdrawal of aliquots, and equilibrated again. Then 1.0 ml (*ca.* 0.87 g) of 2-chloro-2-methylbutane (to give a *ca.* 0.08 *M* solution) was injected from a calibrated 1.0-ml syringe and the solution was mixed rapidly. Aliquots (5 ml) were withdrawn with a calibrated syringe, quenched in cold absolute ethanol, and titrated with standardized hydrochloric acid in ethanol to a bromcresol green end point.[5] Rate constants were calculated from the usual equation for second-order reactions with unequal initial concentrations.

When the base used was selenophenoxide, the procedure was the same except that titration was to a methyl orange end point. When the base was *p*-acetyl- or *m*-chlorothiophenoxide, sharper end points resulted when the reaction was quenched in ethanol containing excess standard acid and back-titrated to the bromcresol green end point with standard ethoxide in ethanol. As a control, these two variants on the usual technique were tried with thiophenoxide. All three techniques gave rate constants within experimental error of each other. The hydrochloric acid in ethanol was standardized weekly with sodium carbonate to a methyl orange end point in water. The ethoxide in ethanol used for back-titration was standardized with potassium acid phthalate to a phenolphthalein end point in water.

The solvolysis reactions of the tertiary halides in ethanol and 2-propanol were measured over the first 20–30% of reaction by quenching the aliquots in cold absolute ethanol and titration to the bromcresol green end point with ethoxide in ethanol.

Observed rate constants are recorded in Table I.

Corrected Rate Constants and Brønsted Coefficients.—The observed rate constants were corrected for solvolysis following McLennan.[5] No other correction was made for nonquantitative olefin formation, as all of the 5–10% of substitution product arises from the first-order reaction. The corrected rate constants are given in Table II. Brønsted coefficients were calculated from these corrected rate constants by the method of least squares, using the pK_a values of the thiophenols in 95% ethanol reported by Schwartzenbach and Rudin.[40] These form the most complete series available. No pK_a's in the higher alcohols are available.

Olefin Proportions.—Solutions of the thiolate with 10% excess thiol were prepared and standardized as in the kinetic runs. The appropriate amount of alkyl halide was weighed into a 10-ml volumetric flask and the flask was filled to the mark with the thiolate solution. The contents was transferred immediately to a stainless-steel reaction tube with a gas-tight seal[41] and the reaction was allowed to run to completion. The reaction mixture was then analyzed directly on an Aerograph A-90-P2 gas chromatograph with thermal conductivity detector, using either a 20 ft × 0.25 in. column of 20% adiponitrile on Chromosorb P-AW, 60–80 mesh, or a 15 ft × 0.25 in. column of 20% didecyl phthalate on Chromosorb P, both columns being operated at 30°. Usual concentrations were alkyl halide, 0.08 *M*, and base, 0.2, 0.5, or 1.0 *M*. Results are recorded in Table III.

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Registry No.—C_6H_5OK, 100-67-4; 2-chloro-2-methylbutane, 594-36-5; 2-bromo-2-methylbutane, 507-36-8; 2-iodo-2-methylbutane, 594-38-7.

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