in terms of the conventional E2 mechanism, with transition state **10**. A 6- to 12-fold retardation is plausibly attributed to 1,3-diaxial interaction between a methyl group and the chloride ion attacking β hydrogen.

Data listed by Cook and Parker[9] concerning the reactivity of **6a** and **7a** with chloride ion in acetone in the elimination mode are of similar character. Whereas the neopentylic steric hindrance in **7a** reduces SN2 reactivity by 250- or 500-fold (their table and text disagree), it reduces elimination rate by less than tenfold, if at all.

Neither the present data nor those previously published concerning **4** and **5** prove the absence of *any* interaction of chloride ion with C_α in the E2 transition state. They do show, however, that whatever interaction there may be is geometrically different from that in an SN2 transition state. If the interactions are geometrically different, they must differ in chemical character and in their energetic consequences. The good correlations of log k_S with log k_E reported by Parker, Ruane, Biale, and Winstein[4] and by Lloyd and Parker[8] therefore cannot be taken as evidence that in the two transition states the interaction of the base (nucleophile) with C_α is "much the same."

In these circumstances, we see little if any basis for asserting that there is covalent interaction between the base (nucleophile) and C_α in the transition states for olefin-forming elimination induced by halide ions in acetone. The "C" in "E2C" lacks justification. On the other hand, we are in substantial agreement with Parker in respect to some other conclusions he has drawn about these transition states.[19-22] Both Bunnett and Baciocchi[21] and Lloyd and Parker[20] have concluded, for instance, that they have a large degree of carbon–carbon double bond character, that they have little electrical charge on either C_α or C_β, and that they involve a large degree of scission of the bond between C_α and the nucleofugic group departing from it. However, it is still unclear why a transition state with these characteristics is chosen by these reactions.

Experimental Section

2,2-Dimethylcyclohexyl *p*-Toluenesulfonate (9). To a slurry of 12 g (0.5 mol) of sodium hydride in dry 1,2-dimethoxyethane was added dropwise 2-methylcyclohexanone (63 g). The mixture was stirred overnight at 40°, and then methyl iodide (90 g) was added. The crude dimethylcyclohexanone mixture was isolated by standard means, and 2,2-dimethylcyclohexanone was isolated by the method of Meinwald and Ouderkirk.[23] The latter was reduced to 2,2-dimethylcyclohexanol with $NaBH_4$ in water.[24] The alcohol was converted to **9** by treatment with *p*-toluenesulfonyl chloride in dry pyridine. **9** was obtained as colorless needles (from pentane), mp 57–58.5° (lit.[25] mp 55°). *Anal.*[26] Calcd for $C_{15}H_{22}O_3S$: C, 63.79; H, 7.85. Found: C, 63.81, 63.65; H, 7.88, 7.82.

Rate Measurements. Runs were conducted, as described by Bunnett and Baciocchi,[21] by the ampoule technique. The initial substrate concentration was about 0.02 *M*. Concentrations listed in the tables have been corrected for solvent expansion. Infinity NaOH titers from reaction of **8** with tetrabutylammonium chloride in acetone were less than expected for complete reaction in the elimination mode; the shortfall was attributed to substitution, after Parker, *et al.*[4]

In Tables III and IV, the second-order rate constants (k_E) listed were derived from the k_ψ values and reagent concentrations by linear regression analysis.

Product from Reaction of 9 with Tetrabutylammonium Chloride. One gram of **9** was allowed to react in 50 ml of 0.24 *M* Bu_4NCl in acetone at 69.9°; the cooled product mixture was poured onto 1 ml of CCl_4, water was added, and the CCl_4 layer was separated, washed with sodium bisulfite solution, and dried over anhydrous Na_2SO_4. The pmr spectrum was as expected for 3,3-dimethylcyclohexene, the chief point of interest being a strong singlet at δ 1.16. Examination of this solution by glpc revealed peaks only for the solvent and one solute component.

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[19] We note in passing that Lloyd and Parker[20] mistakenly represented Bunnett and Baciocchi[21] and Bunnett[22] as advocating paenecarbonium transition states (with substantial carbonium character at C_α) for eliminations induced by chloride ion in acetone.

[20] D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5029 (1970).

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

[22] J. F. Bunnett, *Surv. Progr. Chem.*, **5**, 53 (1969).

[23] J. Meinwald and J. T. Ouderkirk, *J. Amer. Chem. Soc.*, **82**, 480 (1960).

[24] H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

[25] W. Hückel and S. K. Gupté, *Justus Liebigs Ann. Chem.*, **685**, 112 (1965).

[26] Analysis by Micro-Tech Laboratories, Inc., Skokie, Ill.

Insensitivity to Steric Hindrance of E2 Olefin-Forming Elimination Induced by Mercaptide Ions in Methanol[1]

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Abstract: 2-Bromo-3,3-dimethylbutane, in which C_α is shielded from nucleophilic attack by the adjacent *tert*-butyl group, undergoes elimination induced by methanolic methoxide or thioethoxide ion more rapidly (after statistical correction) than does isopropyl bromide. The olefin formed is, in either case, 3,3-dimethyl-1-butene. The fact that neopentylic steric hindrance does not impede elimination induced by the mercaptide reagent requires rejection of the "E2C" mechanism proposed by other workers. The fact that unrearranged olefin is formed is incompatible with a conceivable ion pair mechanism.

Despite their lower basicity, mercaptide ions are more effective than alkoxide ions in bringing about olefin-forming elimination from tertiary alkyl halides in alcoholic solvents. This has been observed in the cases of thiophenoxide ion *vs.* ethoxide ion reacting with *tert*-butyl chloride in ethanol,[2,3] and of

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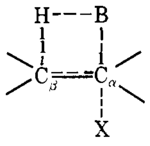
[1] Financial support by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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

[3] D. J. McLennan, *J. Chem. Soc. B*, 709 (1966).

thioethoxide ion *vs.* methoxide ion reacting with benzyldimethylcarbinyl chloride in methanol.[4] In these examples, the mercaptide reagent is about 10 times more reactive than the alkoxide. In reactions with secondary alkyl halides, the superiority of the mercaptide ion is less pronounced; thiophenoxide ion effects elimination from cyclohexyl bromide only 1.6 times as fast as does ethoxide ion, both in ethanol solution, and thiophenoxide is slightly less reactive than ethoxide in converting cyclohexyl chloride to cyclohexane.[5]

It has been suggested that the remarkable effectiveness of mercaptide ions is functionally related to their high nucleophilicity toward carbon, and indeed that the mercaptide ion interacts nucleophilically with C_α of the substrate, as well as with H_β, in the elimination transition state. This idea was originally proposed as a "merged" substitution–elimination mechanism,[6] but more recently it has been recast in the form of the "E2C" mechanism, for which transition states such as **1** have been proposed.[7] The proponents of the "E2C" hypothesis consider that alkoxide ions, in contrast, attack principally at β hydrogen; transition states such as **2** are sketched for these so-called "E2H" reactions.[7] Transition states such as **2** have, of course, been visualized for E2 reactions for many years.[8]



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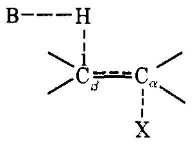

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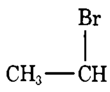
The "E2C" mechanism was also proposed for elimination reactions induced by halide ions in acetone solution. However, it has been shown that chloride ion-induced eliminations from tertiary alkyl halides and secondary alkyl tosylates are but slightly affected by the introduction of massive, neopentylic steric hindrance about C_α.[9,10]

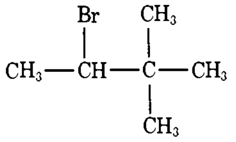
We now apply the same test to eliminations induced by thioethoxide ion in methanol and to comparison reactions induced by methoxide ion. Because tertiary alkyl halides solvolyze rather rapidly in methanol and because the kinetics of their reactions with CH_3O^- and $C_2H_5S^-$ are not susceptible to straightforward interpretation,[11] we now confine our attention to secondary alkyl bromides. The substrates studied are isopropyl bromide (**3**) and 2-bromo-3,3-dimethylbutane (**4**). The former has the minimum steric hindrance possible in a secondary alkyl bromide, while C_α in the latter is neopentylic and massively hindered.

A further advantage in the choice of **4** is that the corresponding carbonium ion **6** is prone to rearrange, as in eq 1.[12] The occurrence of elimination *via* that ion or an ion pair would therefore be manifest in the formation of olefins of rearranged carbon skeleton.



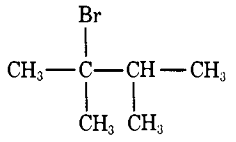
$$\mathrm{CH_3-\overset{Br}{CH}-CH_3}$$

3



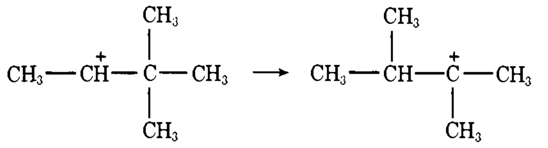
$$\mathrm{CH_3-\overset{Br}{CH}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3}$$

4



$$\mathrm{CH_3-\underset{CH_3}{\overset{Br}{C}}-\underset{CH_3}{CH}-CH_3}$$

5

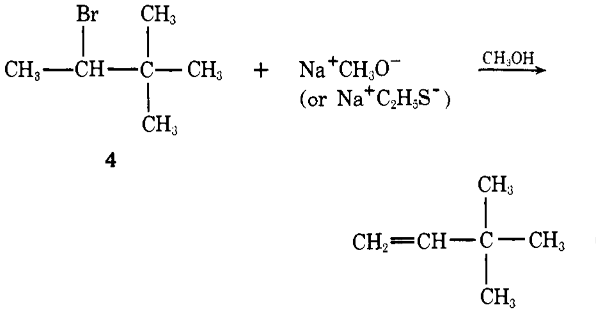


$$\mathrm{CH_3-\overset{+}{C}H-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{CH}-\underset{CH_3}{\overset{+}{C}}-CH_3} \qquad (1)$$

6 **7**

Results

Synthesis of **4** presented some difficulty. Treatment of the corresponding alcohol with PBr_3 afforded exclusively the rearranged bromide, **5**. Such rearrangement would be expected of any process going *via* the 3,3-dimethyl-2-butyl cation **6**, because of the facility of its rearrangement to the more stable tertiary cation, **7**.[12] However, reaction of 3,3-dimethyl-2-butanol with triphenylphosphine and bromine in dimethylformamide solvent[13,14] yielded **4** in substantial amount, although contaminated by **5**. The contaminant was removed by selective solvolysis; being a tertiary halide, **5** solvolyzes much faster than **4**.



$$\mathrm{CH_3-\overset{Br}{CH}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3} + \begin{matrix}\mathrm{Na^+CH_3O^-}\\ \mathrm{(or\ Na^+C_2H_5S^-)}\end{matrix} \xrightarrow{\mathrm{CH_3OH}} \mathrm{CH_2{=}CH-\underset{CH_3}{\overset{CH_3}{C}}-CH_3} \qquad (2)$$

4 **8**

Kinetic data pertaining to the reactions of **4** with $NaOCH_3$ and with $NaSC_2H_5$ in methanol (eq 2) are set forth in Table I. Reactions were run under conditions conducive to pseudo-first-order kinetics. The pseudo-first-order rate coefficients, k_ψ, are linearly related to $NaOCH_3$ or $NaSC_2H_5$ concentration; the plots are not shown. The slopes of those plots, as reckoned by linear regression analysis, constitute second-order rate constants for reactions of **4** with the two bases; these are tabulated as k_E. It will be noted that k_E for reaction with the mercaptide reagent is 1.7 times greater than with methoxide ion. Also noteworthy is that k_ψ values for reaction with either base are much greater than for solvolysis.

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

(5) D. J. McLennan, *J. Chem. Soc. B*, 705 (1966).

(6) E. L. Eliel and R. S. Ro, *Tetrahedron*, 2, 353 (1958); E. L. Eliel and R. G. Haber, *J. Amer. Chem. Soc.*, **81**, 1249 (1959).

(7) (a) D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5183 (1968); (b) D. Cook, A. J. Parker, and R. Ruane, *ibid.*, 5715 (1968); (c) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 115 (1970); (d) A. J. Parker, *Chem. Technol.*, 297 (1971).

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(9) D. Eck and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 3099 (1969).

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(13) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *ibid.*, **86**, 964 (1964).

(14) R. A. Bartsch and J. F. Bunnett, *ibid.*, **90**, 408 (1968).

Table I. Kinetics of Reactions of 2-Bromo-3,3-dimethylbutane (**4**) with $NaOCH_3$ and $NaSC_2H_5$ in Methanol at 69.9°

Reagent	[Reagent], *M*	$[C_2H_5SH]$, *M*	10^5k_ψ, sec^{-1}	10^5k_E, M^{-1} sec^{-1}
None[a]			0.036	
$NaOCH_3$	0.200		0.398	
	0.400		0.726	
	0.600		1.06	
	0.800		1.44	1.74
$NaSC_2H_5$	0.200	0.100	0.59	
	0.400	0.200	1.17	
	0.600	0.300	1.68	
	0.800	0.400	2.40	2.91

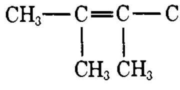
[a] Solvolysis run; 2,6-lutidine, 0.04 *M*, present to neutralize HBr formed.

Table II. Products of Reactions of 2-Bromo-3,3-dimethylbutane (**4**) with $NaOCH_3$ and $NaSC_2H_5$ in Methanol at 70.4°

Reagent	[Reagent], *M*	Per cent of olefin		
		8	**9**	**10**
None[a]		Trace	83.2	16.8
$NaOCH_3$	0.200	91.7	4.4	3.2
	0.400	93.8	3.6	1.2
	0.600	95.4	1.9	1.2
	0.800	96.9	0.8	0.4
$NaSC_2H_5$[b]	0.193	91.1	6.0	2.3
	0.372	95.2	2.6	0.7
	0.540	96.5	1.5	0.8
	0.697	96.9	1.4	0.4

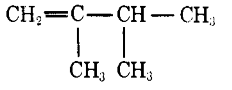
[a] 2,6-Lutidine was present. [b] C_2H_5SH was present, at half the concentration of C_2H_5SNa.

Product composition data are listed in Table II. Solvolysis gives almost entirely 2,3-dimethyl-2-butene (**9**) and 2,3-dimethyl-1-butene (**10**) which have a rearranged carbon skeleton indicating initial formation of carbonium ion **6**, followed by rearrangement to **7** (eq 1) and then proton release to form **9** or **10**. On the other hand, the olefin formed from reaction of **4** with either $NaOCH_3$ or $NaSC_2H_5$ in methanol is mainly 3,3-dimethyl-1-butene (**8**). The small amounts of **9** and **10** produced in the latter reactions are entirely accounted for by the small component of solvolysis indicated by the rate data of Table I. Thus, reaction with the alkoxide or mercaptide ion occurs without rearrangement, according to eq 2. No trace of ether or thioether substitution product could be found from the $NaOCH_3$ or $NaSC_2H_5$ reactions.



$CH_3—\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}—CH_3$

9



$CH_2=\underset{CH_3}{\underset{|}{C}}—\underset{CH_3}{\underset{|}{CH}}—CH_3$

10

Rate and product data for reactions of isopropyl bromide (**3**) with $NaOCH_3$ and $NaSC_2H_5$ are displayed in Table III. Reaction with methoxide ion occurs slightly more than half in the elimination mode, to give propylene, and slightly less than half by substitution to give methyl isopropyl ether. The measured k_ψ values were split into elimination and substitution components according to the product data. Division of the latter by $NaOCH_3$ concentration afforded the second-order k_E and k_S values tabulated.

Reaction of isopropyl bromide with thioethoxide ion occurs overwhelmingly in the substitution mode. Efforts to determine the amount of propylene formed were only marginally rewarding. However, they do suffice to place an upper limit on the fraction of elimination which occurred, and thus on the k_E value. The k_E listed in Table III represents that upper limit.

Discussion

The kinetic data of Tables I and III enable two kinds of comparisons of rate ratios to be made. The comparisons are less exact than we would wish, owing to the fact that we were able to measure k_E for the reaction of isopropyl bromide with thioethoxide ion only as an upper limit. Nevertheless, important qualitative relationships are clear.

First, the thioethoxide/methoxide rate ratio is 1.7 for reactions with hindered substrate **4** but less than 0.55 for reaction with isopropyl bromide. To understate the matter, this comparison provides no indication that thioethoxide ion-induced elimination from the hindered substrate is retarded, relative to methoxide ion-induced elimination, by neopentylic steric hindrance about C_α.

The thioethoxide/methoxide rate ratio of 1.7 with **4** is rather similar to the thiophenoxide/ethoxide ratio of 1.6 observed by McLennan[5] for elimination from cyclohexyl bromide in ethanol.

Second, the reactivity of isopropyl bromide (in the elimination mode) relative to that of **4** is 1.37 with methoxide ion and less than 0.45 with thioethoxide ion. After statistical correction, these ratios are 0.68 and <0.22, respectively. The hindered substrate is more reactive than the unhindered with both reagents.

In contrast, S_N2 substitution with either reagent is prominent with isopropyl bromide but undetectable with hindered substrate **4**. The k_S values for the (hypothetical) substitution reactions with **4** are estimated as not more than 1% of the k_E values listed in Table I. Accordingly, **4** is estimated to be less reactive than **3** in the substitution mode by at least 1300-fold with methoxide ion and at least 28,000-fold with thioethoxide ion. It is evident that neopentylic steric hindrance severely impedes nucleophilic attack on C_α of **4**.

Our data provide no indication whatsoever that thioethoxide ion-induced elimination is retarded by neopentylic steric hindrance about C_α as would be expected if a transition state such as **1** were involved.

We have now investigated the effect of massive, neopentylic steric hindrance about C_α in three systems for which the "E2C" mechanism has been advocated. These involve tertiary alkyl bromides reacting with chloride ion in acetone or dioxane,[9] secondary alkyl tosylates reacting with chloride ion in acetone,[10] and secondary alkyl bromides reacting with thioethoxide ion in methanol (this work). Although the "E2C" mechanism, if significantly similar to the S_N2 mechanism, would predict great sensitivity to steric hindrance about C_α, little or no sensitivity to steric hindrance can be observed.

We conclude that the transition states of these elimination reactions do not involve covalent interaction of the base with C_α in fashion geometrically similar to that in S_N2 transition states. Dissimilarity in geometry implies dissimilarity in energetic consequences. The interpretation placed by Parker, *et al.*,[7,15] on the linear

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(15) A. J. Parker, M. Ruane, D. A. Palmer, and S. Winstein, *ibid.*, **94**, 2228 (1972); P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *ibid.*, **94**, 2240 (1972).

Table III. Reactions of Isopropyl Bromide (3) with $NaOCH_3$ and $NaSC_2H_5$ in Methanol at 69.9°

Reagent	[Reagent], M	$[C_2H_5SH]$, M	10^3k_ψ, sec^{-1}	F_E[a]	10^4k_E, $M^{-1}\ sec^{-1}$	10^4k_S, $M^{-1}\ sec^{-1}$
$NaOCH_3$	0.300		0.137	0.514	2.34	2.22
	0.600		0.281	0.518	2.42	2.26
$NaSC_2H_5$	0.200	0.100	1.72	0.015, 0.004	1.3[b]	84.6
	0.600	0.300	5.25	0.009, 0.006		86.7

[a] Fraction of propylene in product mixture. [b] Upper limit, reckoned from F_E 0.015.

correlations sometimes observed between substitution and elimination rates[16] is thus refuted.

Insofar as reaction mechanisms can be defined, they are defined not by direct proof, but by the rejection of possibilities which are found to be incompatible with experimental evidence. The present data, together with those from companion studies, not only require rejection of the "E2C" mechanism, but constitute strong evidence against another possibility, namely, that these elimination reactions occur *via* ion-pair intermediates. The possibility of an ion-pair mechanism has long been visualized, and arguments against it in respect to one tertiary halide system have been stated elsewhere.[17] The ion-pair mechanism elimination has recently been advocated, at least for some reactions, by two research groups.[18] Were it at play in the reactions of **4** with $NaOCH_3$ or $NaSC_2H_5$ in methanol, substantial rearrangement of carbonium ion **6** to **7** would occur within the ion pair,[12,19] and the product would consist substantially of olefins **9** and **10**. The fact, discussed above, that the small fractions of **9** and **10** in the product mixtures from the $NaOCH_3$ and $NaSC_2H_5$ reactions (Table II) are accounted for, within experimental error, by the minor solvolysis component shows that these reactions do not occur *via* ion pair intermediates.

That hindered substrate **4** actually undergoes faster elimination (after statistical correction) than isopropyl bromide with either $NaOCH_3$ or $NaSC_2H_5$ calls for comment. Probably there is some steric acceleration due to partial release, in the transition state, of steric compressions in the ground state of **4** between the bromine atom and the methyls of the *tert*-butyl group. The fact that the enhanced reactivity of **4** is especially pronounced in its reaction with thioethoxide ion is perhaps to be attributed to favorable London dispersion interactions between the high polarizability mercaptide ion and the additional methyl groups of **4** in the transition state.[20]

Finally, let us ask what *is* the mechanism of the mercaptide-induced elimination, inasmuch as both the "E2C" and the ion-pair mechanisms have been found untenable? We see no grounds for abandoning the general E2 mechanism as it has been recognized for years.[8,17] The question of why mercaptide ions are so effective, despite their low basicity, remains an interesting one. Ideas on this question have been expressed elsewhere,[17,21] and we refer the interested reader to those discussions.

Experimental Section

2-Bromo-3,3-dimethylbutane (4). To a solution of 10.2 g (0.1 mol) of 3,3-dimethyl-2-butanol[22] and 28.0 g (0.17 mol) of triphenylphosphine in 100 ml of dry dimethylformamide was added bromine until an orange color persisted.[13,14] The solution was stirred for 3 hr and then distilled at 16 Torr until the temperature reached 100°; the distillate was collected in a receiver cooled by solid carbon dioxide. Water (100 ml) was added to the distillate. The organic phase was separated and dissolved in 50 ml of 80% methanol to which $NaHCO_3$ had been added. The mixture was allowed to set overnight, more water was added, and the organic phase was dried and distilled at 200 Torr, all material boiling below 125° being collected. The distillate was injected in portions into a Hewlett-Packard 776 preparative gas chromatograph with an SE-30 silicone rubber column, and the desired fraction of **4** was collected as a colorless liquid: yield 1.54 g (9.3%); nmr (in CCl_4) δ 1.07 (s, 9 H), 1.62–1.70 (d, 3 H), 3.85–4.19 (q, 1 H). *Anal.* Calcd for $C_6H_{13}Br$: Br, 48.46. Found: Br, 48.57.

3,3-Dimethyl-2-butyl Methyl Ether. To a suspension of 2.4 g of sodium hydride in 100 ml of dimethyl sulfoxide was added 10.2 g of 3,3-dimethyl-2-butanol.[22] The mixture was stirred several hours and then 14.2 g of CH_3I was added dropwise. After the mixture had been stirred overnight, 200 ml of water was added. The organic layer was separated, washed with water, dried over anhydrous Na_2SO_4, and distilled at atmospheric pressure. The desired ether was obtained as the fraction boiling at 97–98°: yield 5.85 g (51%); nmr (neat) δ 0.94 (s, 9 H), 1.01–1.10 (d, 3, H), 2.73–3.21 (q, 1 H), 3.33 (s, 3 H).

Dimethylbutenes. 3,3-Dimethyl-1-butene (**8**) was obtained from Aldrich Chemical Co., and its structure was verified by nmr analysis.[23] A mixture of 2,3-dimethyl-2-butene (**9**) and 2,3-dimethyl-1-butene (**10**) was obtained by warming a mixture of 20.4 g of 3,3-dimethyl-2-butanol with 100 ml of 85% phosphoric acid and collecting the distillate until the temperature of the distilling vapors reached 65°. The distillate was washed with water, dried over anhydrous Na_2SO_4, and injected in portions onto a Hewlett-Packard Model 776 preparative gas chromatograph with an SE-30 silicone rubber column operated at 40°. The first fraction collected was **10**: nmr (in CCl_4) δ 0.98–1.08 (d, 6 H), 1.67–1.73 (t, 3 H), 1.93–2.60 (m, 1 H), 4.67 (m, 2 H). The second was **9**: nmr (in CCl_4) δ 1.61 (s, 12 H). The yields were 12 and 43%, respectively.

Product Analysis for Reactions of 4 with $NaOCH_3$ or $NaSC_2H_5$. The technique previously described[11] was used, except that the methanol solutions were extracted with heptane prior to analysis and glpc column was operated at ambient temperature.

Product Analysis for Reactions of Isopropyl Bromide (3) with $NaOCH_3$ or $NaSC_2H_5$. In these runs, **3** was 0.1 *M* and the reagent concentration was as shown in Table III. Reaction solutions (10 ml) were sealed in ampoules and kept for 10 half-lives at 69.9°. The ampoules were cooled with solid carbon dioxide and opened, and the contents were poured into 2 ml of cold CH_2Cl_2 (for $NaSC_2H_5$ runs) or CCl_4 (for $NaOCH_3$ runs). Ice-chilled water (10 ml) was added, followed immediately by bromine (dropwise) until a faint orange color persisted. The two phases were separated, and the organic phase was washed with chilled water and dried over anhydrous Na_2SO_4 in a vial capped with a septum. The ratio of 1,2-dibromopropane to methyl isopropyl ether or ethyl isopropyl sulfide was determined by glpc on a 305-cm long column, 6.3 mm in diameter, packed with 5% SE-30 on Chromosorb P and operated at 82°. Methyl isopropyl ether was found to be stable to the conditions of extraction and bromine addition, but ethyl isopropyl sulfide was

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(16) Good linear correlations are obtained between some sets of data, but not between other sets of apparently equal relevance.[15]

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converted to 1,2-dibromopropane to a small extent (less than 1%). The poor precision in the olefin analyses from the $NaSC_2H_5$ runs evident in Table III is believed due to this complication; the values listed are uncorrected.

Rate measurements were conducted as previously described.[11] The substrate concentration was 0.02-0.04 *M*. All concentrations listed in the tables have been corrected for thermal expansion of the solvent.

Free Radical Elimination Reactions. Reaction of Phenyl Radicals with Phenyl Amyl Sulfides

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Abstract: The reactions of phenyl radicals with the β hydrogens of *tert*-butyl, phenyl *tert*-butyl, and phenyl amyl sulfides initiate an elimination reaction. The reactivity profile, I:II:III::1:8.5:43, for phenyl radical with hydrogens β to sulfur is obtained from the observed yields of olefins formed from four phenyl amyl sulfides. Competition of *tert*-butyl sulfide against carbon tetrachloride for phenyl radicals gives $k_H/k_{Cl} = 0.26$. Both results show the reactivities of the β hydrogens of sulfides toward phenyl radicals to be the same as those of alkanes. These results indicate a simple, unassisted hydrogen abstraction and are inconsistent with significant bridging by sulfur or double bond character in the transition state for hydrogen abstraction. The elimination reaction, therefore, is described by a simple two-step process involving a β-thioalkyl radical intermediate.

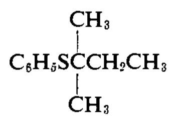
The preceding paper[2] described a free radical elimination reaction initiated by attack by phenyl radicals on the β hydrogens of *tert*-butyl and phenyl *tert*-butyl sulfides.

$$C_6H_5\cdot + (CH_3)_3CSR \longrightarrow C_6H_6 + CH_2{=}C(CH_3)_2 + RS$$

Hydrogen abstraction product and olefin are formed in equivalent yields; intermediate radicals from the sulfides, if present, must therefore fragment more rapidly than they are scavenged by other radicals in the reaction mixture. Other data[3,4] indicated that the β hydrogens of *tert*-butyl sulfide are appreciably more reactive than comparable primary hydrogens in alkanes. Several mechanisms for the elimination reaction were discussed; the combination of stoichiometric elimination and enhanced reactivity of *tert*-butyl sulfide seemed best accommodated by a concerted EH2 mechanism. The present work makes use of competitive elimination reactions to study the relative reactivities of the β hydrogens in several *tert*-butyl and amyl sulfides. In addition, the primary β hydrogens of *tert*-butyl sulfide are pitted against carbon tetrachloride for phenyl radicals. In contrast to previous results, both competitions show that the reactivities of these hydrogens β to sulfur to phenyl radicals are the same as the reactivities of hydrogens β to carbon.

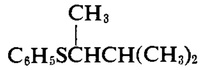
Results and Discussion

Four phenyl amyl sulfides (A–D) were prepared and allowed to react with phenyl radicals generated by the thermal decomposition of phenylazotriphenylmethane (PAT) at 77°. The sulfides were used as solvents and the reaction mixtures were carefully deoxygenated. The reaction of phenyl radical with phenyl *tert*-amyl sulfide (A) provides an intramolecular competition between primary and secondary β-hydrogen abstraction to give 2-methylbutene-1 and 2-methylbutene-2, respectively. Since the previous work[2] established a 1:1 correspondence of H abstraction to olefin, the statistically corrected ratio of the yields of olefins gives the relative reactivities of the β hydrogens. Phenyl *sec*-isoamyl sulfide (B) provides primary/tertiary competition to give 3-methylbutene-1 and 2-methylbutene-2. Mixtures of phenyl isoamyl (C) and phenyl *act*-amyl sulfide (D) as substrates for phenyl radical give 3-methylbutene-1 and 2-methylbutene-1, respectively, and the relative reactivity of secondary to tertiary β hydrogens. In the latter experiments, the ratio of sulfides, C/D, was varied. The reactivity ratio was calculated from the appropriate expression for competitive reactions, k_{sec}/k_{tert} = [3-methylbutene1][D]/2·[2-methylbutene-1][C].



$$C_6H_5S\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_3$$

A

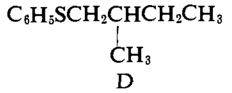


$$C_6H_5S\overset{CH_3}{C}HCH(CH_3)_2$$

B

$C_6H_5SCH_2CH_2CH(CH_3)_2$

C



$$C_6H_5SCH_2\underset{CH_3}{C}HCH_2CH_3$$

D

All of these sulfides, A–D, are also susceptible to attack at α, γ, and δ hydrogens to give radicals whose fate is unknown. These side reactions affect the absolute yields of olefins (mol of olefin/mol of PAT) as well as the benzene/olefin ratio. They should not, however, perturb the relative yields of olefins which form the basis of the reactivity comparisons. The olefins and benzene were identified by mass spectral

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