Tf. Mixtures of various olefins and the complex **1** in varying relative amounts were dissolved in the acetic-d_4 acid containing a trace of TMS, and nmr spectra of these solutions were recorded. The mole ratio of Cu(I) to olefin was determined by comparison of appropriate integrated peak areas using the absorption due to benzene as an internal standard for estimation of CuOTf.

Elemental microanalysis was performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Analysis for copper(I) was performed by oxidation of a solution of ferric chloride and back titration with standard ceric solution. Melting points were measured in sealed capillary tubes. Nuclear magnetic resonance spectra were obtained on a Varian HA-100 or A-60 spectrometer. The spectrum of isolated complexes were obtained in dilute solution of acetone-d_6. Infrared spectra were recorded on a Perkin-Elmer 137G spectrometer. Molecular weights were measured with a Mechrolab 301A vapor pressure osmometer at 37°. Ultraviolet spectra were recorded with a Cary 14 spectrophotometer.

All reactions were conducted under a blanket of dry nitrogen. Benzene was freshly distilled from sodium benzophenone ketyl. Pentane was purified by stirring for 12 hr with concentrated sulfuric acid, then with 0.5 M potassium permanganate in 3 M sulfuric acid for 12 hr. It was washed successively with water and aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate and finally with phosphorus pentoxide. It was fractionally distilled under nitrogen. All other solvents were reagent grade materials used without further purification.

Complexes were prepared in vessels sealed with an air tight rubber septum cap, and separated from the mother liquor by filtration through a sintered glass disk with the aid of a positive pressure of nitrogen. After washing, the complexes were dried under a stream of dry nitrogen in the same apparatus.

Acknowledgment. We wish to thank the National Science Foundation for generous financial assistance.

Insensitivity to Steric Hindrance of E2 Olefin-Forming Elimination Induced by Halide Ions in Aprotic Solvents[1]

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Contribution from the University of California, Santa Cruz, California 95060.

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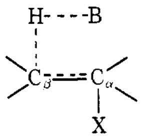
Abstract: In olefin-forming elimination induced by chloride ion in acetone solution, cyclohexyl tosylate reacts only 12 times faster than 2,2-dimethylcyclohexyl tosylate. In the latter substrate, access to C_α is hindered by the methyl groups. The fact that they retard elimination by only one power of ten shows that, in the transition state, chloride ion does not interact with C_α in fashion geometrically similar to an SN2 transition state. This is further evidence against the putative "E2C" mechanism of elimination.

In 1956 it was discovered that halide ions in acetone solution[2] and mercaptide ions in alcoholic solvents[3] are surprisingly effective at bringing about olefin-forming elimination from secondary and tertiary alkyl halides and arenesulfonates. Noting that these rather weakly basic reagents are strong nucleophiles toward carbon, Winstein proposed transition states in which the base (nucleophile) interacts covalently with the α carbon of the substrate.[2] In most of his later publications on this subject,[4-6] he was joined by Parker, and Parker has been the chief advocate of these views since Winstein's death.

The general idea of Winstein and Parker is that E2 reactions occur *via* transition states which represent various points in a spectrum between an "E2H" extreme (**1**) and an "E2C" extreme (**2**). They suggest that seldom is a real reaction adequately represented by either **1** or **2**; rather, most transition states have partial association of the base (nucleophile) with both H_β and C_α, as in **3**, a larger degree of association with H_β implying less with C_α, and *vice versa*. Reactions induced by *tert*-butoxide ion are considered to lie close to the "E2H" extreme, and those induced by bromide ion to have a great deal of "E2C" character.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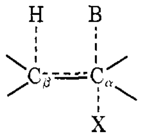
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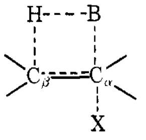
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Parker's descriptions of the proposed "E2C" transition states vary in their implications as to the nature of interaction of base (nucleophile) with C_α. For example, he said in 1971:[7] "The E2C transition state... has a rigorous stereochemical requirement that is reminiscent of that for the transition state of SN2 substitution. Thus the base, B:, and leaving group, X, at sp^2-hybridized C_α are colinear and at opposite corners of a trigonal bipyramid, anti to each other." Also, in 1968,[8] some rate correlations were taken to "...support the concept of an E2C-like transition state, having much the same type of bonding and charge distribution between Y, C_α, and X, as is present in the concurrent SN2 transition state." These statements depict the "E2C" and SN2 transition states as very similar insofar as the interaction of base (nucleophile) and C_α are concerned.

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

(2) S. Winstein, D. Darwish, and N. J. Holness, *J. Amer. Chem. Soc.*, 78, 2915 (1956).

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

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

(5) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 115 (1970).

(6) (a) G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, **93**, 4735 (1971); (b) A. J. Parker, M. Ruane, D. A. Palmer, and S. Winstein, *ibid.*, **94**, 2228 (1972); G. Biale, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, **94**, 2235 (1972); (c) P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *ibid.*, **94**, 2240 (1972); (d) P. Beltrame, A. Ceccon, and S. Winstein, *ibid.*, **94**, 2315 (1972).

(7) A. J. Parker, *Chem. Technol.*, 297 (1971).

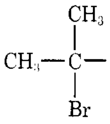
(8) D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5183 (1968).

On the other hand, he stated in 1969:[9] "E2C-like reactions will always have a looser C_α–Y bond in the transition state than will the SN2 reactions of the same reactants." And in 1970:[5] "...the transition state for a type of E2 reaction, which we have classified as E2C-like, is not the same as that for an SN2 reaction."

The question toward which our work is directed is whether, in these reactions, there is bonding between the base (nucleophile) and C_α with geometrical characteristics substantially similar to those of an SN2 transition state. We hold that if the energetic consequences of such bonding are to be substantially the same in substitution and elimination transition states, their geometries, especially the C_α–Y bond lengths, must be very similar. Conversely, if the geometrical characteristics are quite different, the energetic consequences of the purported interaction must be quite different.

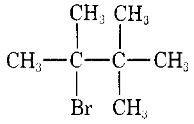
It has long been recognized that SN2 reactions are sensitive to steric hindrance of the "neopentylic" type, which is present when C_β is fully substituted by alkyl groups. Neopentyl bromide reacts 240,000-fold slower than ethyl bromide with sodium ethoxide in ethanol[10] and 160,000-fold slower with chloride ion in dimethylformamide.[11] If eliminations induced by chloride ion in acetone occur *via* "E2C" transition states in which the Y–C_α interaction is similar to that in an SN2 transition state, they should be subject to steric hindrance of similar magnitude.

In applying this experimental criterion, we first examined the olefin-forming elimination reactions of *tert*-butyl bromide (**4**) and 2-bromo-2,3,3-trimethylbutane (**5**) with chloride ion in acetone and in dioxane solutions.[12] Both are tertiary alkyl bromides, and the latter is neopentylic as well. In either solvent, elimination from the more hindered substrate **5** is actually *faster*, about twice as fast.[13] Solvolysis of **5** is also faster in either solvent, about tenfold, doubtless due to steric compressions in **5** which are partially relieved in the solvolysis transition state. After correction of the rate of elimination from **5** for presumed steric acceleration of similar magnitude, and for a statistical factor, the introduction of massive steric hindrance in changing from **4** to **5** was reckoned to have retarded elimination by a factor of about 4. It was concluded that had the base interacted with C_α in a fashion similar to an SN2 transition state, the rate ought to have been reduced by several powers of ten.[12]



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

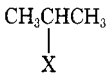
4



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

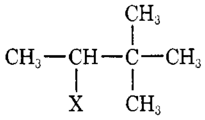
5

Cook and Parker[9] responded with the not unreasonable argument that neopentylic steric hindrance should have less effect on SN2 reaction at a tertiary than at a primary carbon atom. In support of this position, they reported rates of SN2 reactions with chloride ion in acetone of two *secondary* alkyl bromides, isopropyl bromide (**6a**) and neopentylically hindered 2-bromo-3,3-dimethylbutane (**7a**), of which the former was only 500-fold more reactive. A nearly identical difference in SN2 rates with the same reagent has been reported for the corresponding *p*-toluenesulfonate esters, **6b** and **7b**.[6a] However, neither report states how the SN2 reaction of **7a** or **7b** was recognized as such. Cook and Parker[9] estimated the SN2 rate of reaction of **5** with azide ion in acetone to be less than that of **4** by only a factor of 3; the estimate is based entirely on a 3.5% difference in titers and is admittedly uncertain.



$\underset{X}{CH_3CHCH_3}$

6a, X = Br
b, X = OTs

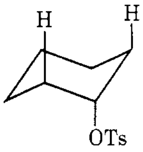


$CH_3-\underset{X}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

7a, X = Br
b, X = OTs

We consider their report concerning SN2 rates of tertiary bromides **4** and **5** to be too uncertain to be accepted but tentatively accept the data concerning the **6a**–**7a** and **6b**–**7b** pairs, despite the incompleteness of the published reports. It is noteworthy, however, that the SN2 reactivity of **6a** with thioethoxide ion in methanol is at least 28,000 times greater than of its neopentylically hindered analog, **7a**.[15] From these indications, it appears that neopentylic steric hindrance retards SN2 reactions at secondary carbon by three or four powers of ten.

With these considerations in mind, we undertook to compare a pair of secondary alkyl substrates, one rather unhindered, the other heavily hindered, in their reactions with chloride ion in acetone. The two chosen are cyclohexyl tosylate (**8**) and its 2,2-dimethyl derivative (**9**).



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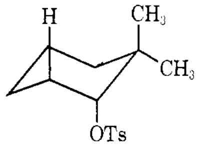

9

Results

Our rate measurements for reactions of **8** and **9** with tetrabutylammonium chloride in acetone, and for solvolysis in acetone, are summarized in Table I. Cyclohexyl tosylate (**8**) solvolyzes about twice faster than does its 2,2-dimethyl derivative (**9**).

The product from reaction of chloride ion with **9** is entirely 3,3-dimethylcyclohexene, which represents normal β-elimination without any complication of carbon skeleton rearrangement. As reported earlier by Parker, *et al.*,[4] the main product from cyclohexyl tosylate is cyclohexene and a minor product is cyclohexyl chloride. From infinity acid–base titration values, they estimated 72.3% of cyclohexene to be formed at

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[9] D. Cook and A. J. Parker, *Tetrahedron Lett.*, 4901 (1969).

[10] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 552.

[11] D. Cook and A. J. Parker, *J. Chem. Soc. B*, 142 (1968).

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

[13] In Tables III and IV of the present paper, which appear only in the microfilm edition of this journal, the kinetic data of Eck and Bunnett[12] are tabulated.[14]

[14] Tables III and IV will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-0000. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[15] J. F. Bunnett and D. L. Eck, *J. Amer. Chem. Soc.*, **95**, 1900 (1973).

Table I. Reactions of Cyclohexyl Tosylate (**8**) and 2,2-Dimethylcyclohexyl Tosylate (**9**) in Acetone, with and without Tetrabutylammonium Chloride,[a] at 69.9°

Substrate	$[Bu_4N^+Cl^-]$, M	10^5k_ψ,[b] sec^{-1}	F_E[c]	10^4k_E, M^{-1} sec^{-1}	10^4k_S, M^{-1} sec^{-1}
8	Nil	0.017			
	0.064	20.5	0.79	25.2	6.7
	0.130	42.9	0.79	26.0	6.9
9	Nil	0.0089			
	0.130	2.88	1.00	2.21	
	0.193	4.08	1.00	2.12	
	0.260	5.59	1.00	2.15	

[a] 2,6-Lutidine (*ca.* 0.03–0.05 M) present in all runs. [b] k_ψ is the pseudo-first-order rate coefficient. [c] F_E is the fractional yield of olefin.

75°; by the same method, we find 79% of cyclohexene in the products formed at 69.9°.

From the pseudo-first-order rate coefficients, k_ψ, and from the product composition from **8**, second-order rate constants for elimination, k_E (and, from **8**, for substitution), were reckoned, as displayed in Table I. From cyclohexyl tosylate (**8**), our value for k_E at 69.9° is about half that reported by Parker, *et al.*,[4] for 75°, and our value for k_S at 69.9° is about one-third of theirs at 75°, these relationships are not unreasonable in view of the 5° difference in temperature.

The result of principal interest is that the average k_E for cyclohexyl tosylate (**8**), namely 25.6×10^{-4} M^{-1} sec^{-1}, is only 11.9 times greater than the average k_E for 2,2-dimethylcyclohexyl tosylate (**9**), which is 2.16×10^{-4} M^{-1} sec^{-1}. Inasmuch as **8** has twice as many β hydrogens as does **9**, the 11.9-fold rate supremacy must be divided by a statistical factor of 2, reducing it to a 5.9-fold supremacy.

Reactions in Methanol. We hoped to study the reactions of **8** and **9** with $NaOCH_3$ and $NaSC_2H_5$ in methanol, especially to see what effect the introduction of two methyl groups in the 2 position of **8** would have on the rate of olefin-forming elimination with the mercaptide reagent. Some preliminary measurements toward that end are reported in Table II. Reactions of **9** with $NaOCH_3$ were only slightly faster than solvolysis. One run with $NaSC_2H_5$ suggested an appreciable augmentation of rate. On the whole, this system was reminiscent of the reactions of 2-chloro-2,3,3-trimethylbutane with these bases in methanol,[16] which afforded kinetic data subject to some ambiguities of interpretation. We therefore discontinued study of the reactions of **8** and **9** in methanol.

Table II. Reactions of Cyclohexyl Tosylate (**8**) and 2,2-Dimethylcyclohexyl Tosylate (**9**) in Methanol and 50% Methanol–50% Dioxane, at 69.9°

Substrate	Solvent	Other solute	10^5k_ψ, sec^{-1}
8	Methanol	2,6-Lutidine[a]	6.29[b]
	50% Methanol–50% dioxane	2,6-Lutidine[a]	0.57
9	Methanol	2,6-Lutidine[a]	5.87
		$NaOCH_3$, 0.0597 M	7.82
	50% Methanol–50% dioxane	$NaOCH_3$, 0.0597 M	0.85
		$NaSC_2H_5$, 0.0597 M[c]	2.1

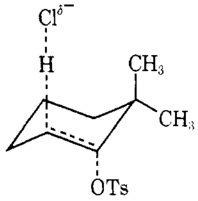
[a] *Ca.* 0.03–0.05 M. [b] From data of W. Hückel and H. D. Sauerland, *Justus Liebigs Ann. Chem.*, **592,** 190 (1955), at 30 and 50°, k_ψ at 69.9° is reckoned to be 4.86×10^{-5} sec^{-1}. [c] C_2H_5SH, 0.03 M, also present.

It is noteworthy that methanolysis of **8** is only 7% faster than of **9**. This suggests that, in this solvent, solvolysis of both substrates occurs mainly by a carbonium ion mechanism.

Discussion

Data in Table I show that cyclohexyl tosylate undergoes olefin-forming elimination with chloride ion in acetone solution 12 times faster than does its 2,2-dimethyl derivative, **9**. After statistical correction, the rate supremacy of the less hindered substrate is reduced to a factor of 6.

A further correction of conformational origin should perhaps be applied. If these elimination reactions involve anti-periplanar transition states, such as **10** (from **9**), the tosylate group is necessarily axial. Whatever the detailed character of the transition state, it seems a fair first approximation that any energetic disadvantage to having the tosylate group axial is much the same whether the substrate was **8** or **9**. Any conformational energy effects on reactivity should therefore be sought in the initial states. Free energy differences between the axial and equatorial conformers of 4-substituted-1,1-dimethylcyclohexanes are much the same as in the corresponding monosubstituted cyclohexanes.[17] However, in a 2-substituted-1,1-dimethylcyclohexane, there are two gauche interactions between the 2 substituent and methyl groups in the equatorial conformer and only one in the axial conformer. Therefore, the conformation with axial tosyloxy group should be more favored for **9** than for **8**. The free energy difference between the two conformers of **9** has not been measured and is difficult to estimate. However, an upper limit can be put on any rate advantage of conformational origin that might accrue to **9**. That limit is governed by the free energy difference between the axial and equatorial conformers of **8**, which is 0.5 kcal/mol.[18] It follows that the maximum conformational kinetic advantage that **9** might enjoy at 69.9° is a factor of 2.1 in rate. The fully corrected rate supremacy of **8** over **9** is therefore estimated to lie between 6- and 12-fold.



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Whether corrected or not, the rate data show that the two methyl groups of **9** retard elimination by about one power of ten, very much less than the deceleration by three powers of ten that would be expected if attainment of the transition state required that the chloride ion approach C_α in fashion substantially similar to an S$_N$2 displacement.

On the other hand, the modest deceleration caused by introduction of the two methyl groups is intelligible

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(16) J. F. Bunnett and D. L. Eck, *J. Org. Chem.*, **36,** 897 (1971).

(17) G. Ransbotyn, R. Ottinger, J. Reisse, and G. Chiurdoglu, *Tetrahedron Lett.*, 2535 (1968); G. E. Hawkes and J. H. P. Utley, *Chem. Commun.*, 1033 (1969).

(18) J. A. Hirsch, *Top. Stereochem.*, **1,** 215 (1967).

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 S_N2 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 S_N2 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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Received July 13, 1972

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).