

$R = 0.045$ and $R_w = 0.051$ for the 966 observed reflections. The final difference map has no peaks greater than $\pm 0.2 \text{ e } \text{Å}^{-3}$.

Extraction of *Heterocoma albida*. Aerial parts of *Heterocoma albida* DC (4 kg) were collected by Dr. de Freitas Leitão Filho in Serra do Caraca, Minas Gerais, Brazil, in December 1978, extracted with CHCl_3 , and worked up in the usual manner.²³ The crude gum (80 g) was chromatographed over 600 g of silica gel, 400-mL fractions being collected as follows: fractions 1-8, hexane; 9-16 hexane-EtOAc (50:1); 17-46, hexane-EtOAc (20:1). Subsequent fractions contained progressively more EtOAc. Fractions 198-209 were EtOAc; subsequent fractions were EtOAc-EtOH mixtures. The only identifiable material was obtained from

fractions 32-33 (98 mg), which showed one spot on TLC and were combined. Purification by PLC (hexane-EtOAc) gave 49 mg of eremanthin.

Registry No. 1, 37936-58-6; 2a, 63569-75-5; 3a, 63599-46-2; 5a, 58030-93-6; 5b, 69883-96-1; 8, 73396-46-0; β -sitosterol, 83-45-4.

Supplementary Material Available: Table I, atomic parameters for 2a; Table II, anisotropic thermal parameters for 2a; Table III, bond lengths in 2a; Table IV, bond angles in 2a (3 pages). Ordering information is given on any current masthead page.

Notes

Methanolysis of 2-Bromo-3,3-dimethylbutane and Its Reaction with Ethanethiolate Ion in Methanol¹

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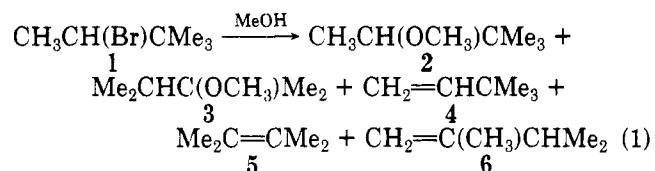
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Received November 19, 1979

We have recently had occasion to repeat some experiments reported in 1973 by Bunnett and Eck.² In some cases our observations differ substantially from those reported earlier, enough to affect significantly the conclusions drawn from the work. In other cases we confirm earlier reports.

Results

From solvolysis of 2-bromo-3,3-dimethylbutane (1) in methanol in the presence of 2,6-lutidine (eq 1), we obtained

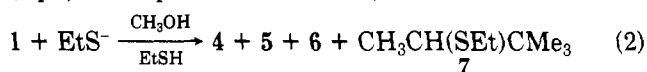


much (41.3%) rearranged ether 3 and a little (4.4%) of unrearranged ether 2, as well as substantial amounts of rearranged olefins 5 (27.8%) and 6 (25.0%) and a mere 1.5% of olefin 4 with an unrearranged skeleton. These figures are normalized to total 100%; the measured product proportions (Table I) in samples taken at various times during the solvolysis reaction showed little variation, although it may be noted that 6 exceeded 5 in early samples while 5 exceeded 6 later on. Bunnett and Eck reported only the olefin products, as 83.2% 5, 16.8% 6, and a mere trace of 4.² Our experience differs from that reported earlier both in our observation of ether products and in the relative amounts of 5 and 6 found.

We also repeated the determination of the products of reaction of 1 with ca. 0.8 M methanolic NaOCH_3 . Our product composition, 92.1% 4, 1.4% 5, 0.8% 6, 0.5% 2, and 0.9% 3, is very similar to that reported by Bunnett and

Eck.² Likewise our evaluation of the pseudo-first-order rate constant for the reaction of 1 with 0.80 M NaOCH_3 in methanol at 69.9 °C as $1.33 \times 10^{-5} \text{ s}^{-1}$ is close to their value of $1.44 \times 10^{-5} \text{ s}^{-1}$.

Bunnett and Eck² reported the reaction of 1 with methanolic sodium ethanethiolate containing also ethanethiol to form mainly olefin 4, very small amounts of olefins 5 and 6, and no ether or thioether product. In contrast, we find ethyl 3,3-dimethyl-2-butyl sulfide (7) to be the predominant product (46%), accompanied by olefins 4, 5, and 6 in proportions somewhat as given earlier (eq 2; see Experimental Section).



Our determinations of the pseudo-first-order rate constant for reaction of 1 with 0.756 M $\text{EtS}^- \text{Na}^+$ and 0.378 M EtSH in methanol at 70.0 °C gave a value, $2.07 \times 10^{-5} \text{ s}^{-1}$, close to the $2.40 \times 10^{-5} \text{ s}^{-1}$ with 0.800 M $\text{EtS}^- \text{Na}^+$ and 0.400 M EtSH published earlier.²

We have confirmed the report of Bunnett and Eck³ that the reaction of the tertiary alkyl bromide 2-bromo-2,3,3-trimethylbutane with methanolic sodium ethanethiolate furnishes no thioether product.

Of interest is the method we used for the preparation of 1, namely, the $\text{S}_{\text{N}}2$ reaction of 3,3-dimethyl-2-butyl benzenesulfonate with tetrabutylammonium bromide in dry acetone. We obtained 1 in 62% yield (by GLC) or 41% yield (isolated), accompanied by olefins. This represents preparative employment of earlier kinetic/product observations of other workers;⁴ our estimate of 62% substitution is similar to their estimates regarding reactions of other 3,3-dimethyl-2-butyl arenesulfonates.

Discussion

Our observation that the reaction of 1 with methanolic $\text{EtS}^- \text{Na}^+$ gives nearly equal amounts of substitution product 7 and olefin 4 is significant with regard to the mechanism of the elimination component of this reaction. It has been proposed⁵ that eliminations induced by thiolate ions occur by the "E2C" mechanism in which the base attacks simultaneously the carbon (usually designated C_α) from which the nucleofugal group is to depart and a hy-

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

(4) Biale, G.; Cook, D.; Lloyd, D. J.; Parker, A. J.; Stevens, I. D. R.; Takahashi, J.; Winstein, S. *J. Am. Chem. Soc.* 1971, 93, 4735.

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

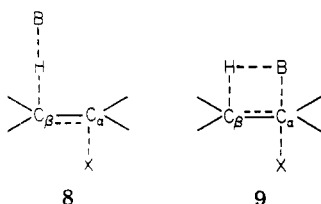
(1) Research supported in part by the National Science Foundation.

(2) Bunnett, J. F.; Eck, D. L. *J. Am. Chem. Soc.* 1973, 95, 1900.

Table I. Product Distribution in the Solvolysis of 2-Bromo-3,3-dimethylbutane ($1, 2.47 \times 10^{-2}$ M) in Methanol at 70.1 °C with 0.0458 M 2,6-Lutidine Present

time, days	yield, %					sum of GC product yields, %	extent of reaction by titration, %
	4	6	5	2	3		
3.8	0.3	4.0	2.6	0.6	5.6	13.1	14.0
11	0.7	8.8	6.9	1.2	10.7	28.3	29.1
22	0.8	14.7	12.3	2.2	21.1	51.1	56.5
46	1.1	19.1	21.2	3.3	31.5	76.2	80.9

drogen atom on the adjacent C_β . Whereas the usual E2 mechanism involves a transition state which we may sketch as 8, the "E2C" transition state is depicted as 9.



Bunnett and Eck² argued against the "E2C" mechanism for the elimination component of reaction 2 on grounds that the approach of a nucleophile to C_α in 9, if close enough to be energetically significant, should suffer steric hindrance somewhat comparable to that experienced by S_N2 substitution at a neopentyl site such as in 1. In support of their argument, they compared the (apparent) changes in ethanethiolate-induced elimination and substitution rates with change of the substrate from 2-bromopropane to 1. With 2-bromopropane, only substitution was observable and at most a maximum elimination rate could be estimated, whereas with 1 it seemed that only elimination occurred. It was estimated that the change from 2-bromopropane to 1 depressed the substitution rate by at least 28 000-fold but the elimination rate by not more than 2.2-fold.

These estimated changes in reactivity must now be revised. The corrected depression in substitution rate is 675-fold and in elimination rate less than 4.4-fold.⁶ Certainly the depression of rate of EtS^- -induced substitution at the secondary site in 1 caused by the introduction of neopentyl steric hindrance is less than indicated by early measurements of the rates of reactions of ethyl and neopentyl bromides with sodium ethoxide.⁷ It is similar to the 500-fold difference between the rates of reactions of 3,3-dimethyl-2-butyl and isopropyl tosylates with bromide ion in acetone.⁴ The reason perhaps lies in factors suggested by Cook and Parker.⁸ Whether the fact that neopentyl steric hindrance affects the substitution rate at least 150-fold more than it does the elimination rate serves to disqualify transition state 9 is to some extent a matter of personal taste because the dotted line in 9 between B and C_α is ill-defined.

What can be said is that the transition state for substitution in 1, vs. 2-bromopropane as a point of reference, is less favored in Gibbs free energy by 4.4 kcal mol⁻¹ whereas the elimination transition state is less favored, if at all, by less than 1.0 kcal mol⁻¹. It seems clear that if the elimination reaction occurs by a transition state of type 9, the B--- C_α bond must be significantly longer than in the S_N2 transition state.⁹

(6) This figure is based on the assumption that the measured yield of 7 from reaction 2 is accurate and that the measured olefin yields were low because of volatility losses.

(7) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969; p 552.

(8) Cook, D.; Parker, A. J. *Tetrahedron Lett.* 1969, 4901.

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

Experimental Section

2-Bromo-3,3-dimethylbutane. 3,3-Dimethyl-2-butyl benzenesulfonate (12 g), prepared according to standard procedures from the corresponding alcohol, was combined with 19 g of tetrabutylammonium bromide (Eastman Kodak, recrystallized from ethyl acetate) in 100 mL of dry acetone (distilled twice from anhydrous $CaCO_3$) in the presence of 8 g of 2,6-lutidine. The reaction mixture was kept at 70 °C in sealed ampules for 5 days, then poured into 150 mL of water, and extracted twice with diethyl ether. The organic phase was washed once with 0.5 N HCl and twice with water and dried over $MgSO_4$. The solvent was removed at atmospheric pressure and the product (3.4 g, 41%) isolated by distillation under mild vacuum. The material used for kinetic experiments was further purified by preparative GLC on an Aerograph Model 204 apparatus by using a 180 × 0.6 cm column of 10% UC-W98 on Chromosorb W/AW. The NMR spectrum matched that reported by Bunnett and Eck;² mass spectrum (70 eV) m/e M (164, 166) absent, 151, 149, 109, 107, 85, 69, 57, 41.

From the reaction of 1 with 0.756 M $EtSNa$ and 0.378 M $EtSH$ in methanol at 70 °C, we obtained 37.4% of 4, 2.5% of 5, 0.7% of 6, and 46.3% of 7 (by GLC analysis).

Rate measurements were conducted as previously described,³ except that diethyl ether was used as the extraction solvent instead of hexane.

Product Analysis. Aliquots (5 mL or 2 mL) withdrawn from the constant temperature bath at measured times were poured into 20 mL (10 mL) of ice-cold water and extracted with 20 mL (10 mL) of *p*-xylene plus a known aliquot of a standard solution of cyclohexene (internal standard) in *p*-xylene. The solutions were analyzed on a Hewlett-Packard Model 5750 GLC instrument with a 300-cm column of 5% Bentone 34, 5% SE-54 on Chromosorb P/AW. For $NaSC_2H_5$ runs, olefins were determined as described above, except that the organic phase was washed with 0.5 N NaOH and water. Analysis of the substitution product was handled separately: samples were extracted with diethyl ether and analyzed on a 180-cm column of 10% UC-W98 80-100 WAW DMCS vs. *m*-methylanisole as internal standard. Ethyl 3,3-dimethyl-2-butyl sulfide was isolated by preparative GLC from the product mixture and identified by the match of its NMR spectrum with that reported by Paquer and Vialle;¹⁰ mass spectrum (70 eV) m/e 146 (M), 89, 85, 61, 57.

Registry No. 1, 26356-06-9; 2, 25246-75-7; 3, 26356-10-5; 4, 558-37-2; 5, 563-79-1; 6, 563-78-0; 7, 38372-67-7; 3,3-dimethyl-2-butyl benzenesulfonate, 73323-97-4; $EtSNa$, 811-51-8.

(10) Paquer, D.; Vialle, J. C. R. *Hebd. Seances Acad. Sci., Ser. C* 1972, 275, 589.

Acid-Catalyzed Decomposition of 1-Aryl-1-methylethyl Benzenethiosulfonates. A Search for Neighboring-Group Participation in Acid-Catalyzed Decomposition of Thiosulfonates

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Received January 11, 1980

The facile decompositions of alkyl or aryl benzenethiosulfonates (1) that occur in acid media in the presence of small amounts of added alkyl sulfides have as their key