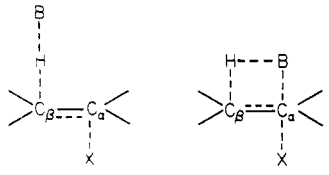
Table I. Product Distribution in the Solvolysis of 2-Bromo-3,3-dimethylbutane (1, 2.47×10^{-2} M) in Methanol at 70.1 °C with 0.0458 M 2,6-Lutidine Present

time, days	yield, % 4	6	5	2	3	sum of GC product yields, %	extent of reaction by titration, %
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**.



8 **9**

Bunnett and Eck[2] 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 neopentylic 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 neopentylic 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 neopentylic 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 Benzenethiosulfinates. A Search for Neighboring-Group Participation in Acid-Catalyzed Decomposition of Thiosulfinates

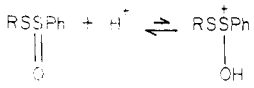
Larry G. Faehl and John L. Kice*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

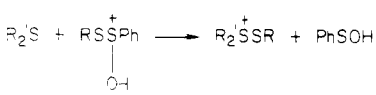
Received January 11, 1980

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

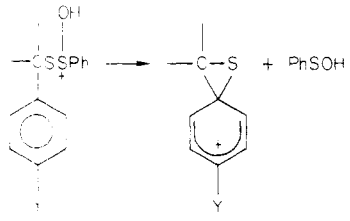
0022-3263/80/1945-2507$01.00/0



1



step nucleophilic attack of the sulfide on the dicoordinate sulfur of the protonated thiosulfinate (eq 1b).[1,2] We were curious whether the nucleophilic "push" for cleavage of the S–S bond normally provided by the alkyl sulfide could ever be provided instead by a neighboring aryl group (eq 2).



To explore this question, we have studied the acid-catalyzed decomposition of two 1-aryl-1-methylethyl benzenethiosulfinates (**1a**, R = Me_2CPh; **1b**, R = $Me_2CC_6H_4OCH_3$-*p*). These particular thiosulfinates were selected because previous work[2] with the *tert*-butyl ester has shown that attack by an external nucleophile on the dicoordinate sulfur of such a tertiary thiosulfinate should be markedly hindered. This should optimize the possibility that neighboring aryl group participation can compete kinetically with attack of an alkyl sulfide on the protonated thiosulfinate.

Thiosulfinates **1a** and **1b** were synthesized by reacting the corresponding 2-aryl-2-propanethiols with benzenesulfinyl chloride, and their structures were confirmed by the usual techniques (see Experimental Section). Their experimental first-order rates of decomposition (k_1) in acetic acid–1% water containing 0.05–0.20 M H_2SO_4 and varying amounts of *n*-butyl sulfide are shown in Table I.

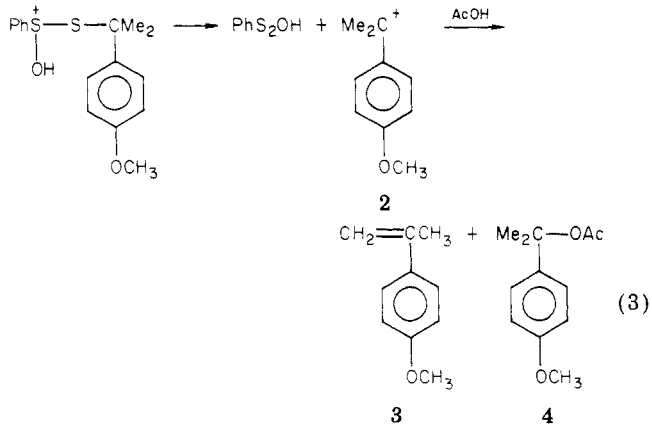
When neighboring aryl group participation (eq 2), rather than nucleophilic attack by the alkyl sulfide (eq 1b), is kinetically dominant, k_1 should be independent of alkyl sulfide concentration. The fact that the rate of decomposition of **1a** is proportional to [*n*-Bu_2S] shows that for **1a** neighboring-group participation by the phenyl group is unable to compete effectively with attack of *n*-Bu_2S on protonated **1a**. The acid-catalyzed decomposition of **1a** thus proceeds by the same type of mechanism involving nucleophilic attack of sulfide on protonated thiosulfinate (eq 1b, R = Me_2CPh) as for the phenyl[1] to *tert*-butyl[2] esters. The rate constant, $k_d = k_1/[R_2S]$, for **1a** is about the same under a given set of conditions as that for the *tert*-butyl ester[2] and much smaller than the rate constant for the phenyl ester.[1] This shows that the 1-phenyl-1-methylethyl group in **1a** sterically hinders nucleophilic attack by the sulfide on the dicoordinate sulfur of **1a** to essentially the same degree as the *tert*-butyl group in *t*-BuSS(O)Ph.

The rate of decomposition of **1b**, while dependent on strong-acid concentration, is, however, independent of [*n*-Bu_2S], showing that when *p*-anisyl is the neighboring aryl group unimolecular decomposition of the protonated thiosulfinate has now become faster than attack of the sulfide on the same species.

Table I. Rates of Decomposition of 1-Aryl-1-Methylethyl Benzenethiosulfinates in Acetic Acid–1% H_2O at 25 °C

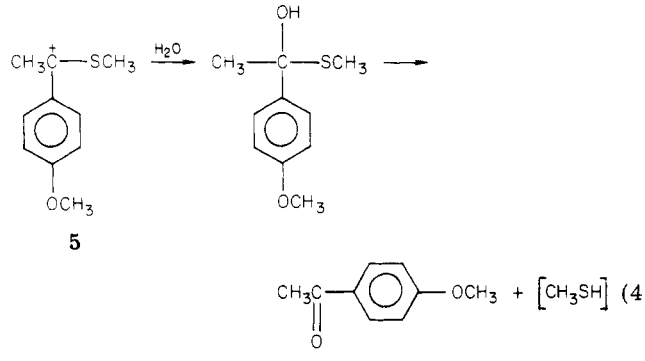
thiosulfinate (concn, M)	$[H_2SO_4]$, M	[*n*-Bu_2S], M	10^3k_1, s^{-1}
1a (1.0×10^{-4})	0.20	0.010	3.8
		0.005	2.0
	0.10	0.010	1.2
1b (1.0×10^{-4})	0.20	0.00	21.3
	0.10	0.00	9.8
		0.010	9.9
	0.05	0.00	4.4

To establish that this unimolecular decomposition represents anchimeric assistance to the cleavage of the S–S bond in protonated **1b**, one must rule out the alternative of rate-determining heterolysis of the C–S bond (eq 3).



Were carbocation **2** being formed, this should lead to sizable amounts of alkene **3** and/or acetate **4** in the reaction products. The products of the acid-catalyzed decomposition of **1b** are a complex mixture but contain almost no **3** or **4**. For this reason we believe that unimolecular decomposition of protonated **1b** does indeed involve cleavage of the S–S bond and *not* the alternative shown in eq 3.

One major product of the decomposition of **1b** that was identified was *p*-methoxyacetophenone (0.38 mmol/mmol of **1b**). The simplest way to explain the formation of this ketone is from carbocation **5** via the path shown in eq 4.

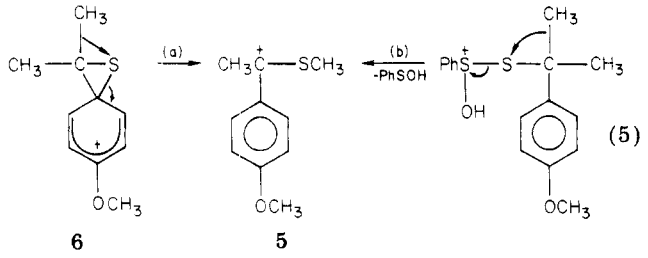


If **5** is an intermediate, this requires either that bridged ion **6** formed by *p*-anisyl group participation (eq 2, Y = OMe) must be prone to rearrange to **5** (eq 5a) or, alternatively, that the unimolecular dissociation of protonated **1b** takes place, not as in eq 2, but rather by methyl migration, as shown in eq 5b.

Thus, while this work shows that the presence of a *p*-anisyl group in **1b** (but *not* of a phenyl group in **1a**) is enough to allow unimolecular decomposition of the pro-

(1) (a) Kice, J. L.; Venier, C. G.; Heasley, L. *J. Am. Chem. Soc.* **1967**, *89*, 3557. (b) Kice, J. L.; Large, G. B. *J. Org. Chem.* **1968**, *33*, 1940. (c) Kice, J. L.; Venier, C. G.; Large, G. B.; Heasley, L. *J. Am. Chem. Soc.* **1969**, *91*, 2028.

(2) Ju, T.-L.; Kice, J. L.; Venier, C. G. *J. Org. Chem.* **1979**, *44*, 610.



6 5 (5)

tonated thiosulfinate to replace the usual bimolecular path involving the alkyl sulfide, it is possible that the *p*-anisyl promotes the dissociation of protonated **1b** by stabilizing the positive charge that would develop on the carbon adjacent to the dicoordinate sulfur concomitant with migration of a methyl group, rather than by bridging, as in eq 2.

Experimental Section

1-Methyl-1-phenylethyl Benzenethiosulfinate (1a). Thionyl chloride (5.0 g, 0.042 mol) was slowly added with stirring to a solution of 2-phenyl-2-propanol (5.0 g, 0.037 mol) (Aldrich) in 10 mL of dry ether at 0 °C. After 2 h at room temperature, the solvent and excess thionyl chloride were removed under reduced pressure. The residue was added with stirring to thiourea (2.8 g, 0.037 mol) dissolved in the minimum amount of absolute ethanol, and the mixture was refluxed for 2 h. Sodium hydroxide (4.0 g), dissolved in a minimum amount of water, was added, and the solution was refluxed for an additional 2 h. The reaction mixture was poured into water and extracted with ether, the extracts were washed (H_2O) and dried ($MgSO_4$), and the ether was removed under reduced pressure. Distillation gave 4.6 g, bp 52–56 °C (1 mmHg), shown by ^1H NMR to be a mixture of 84% 2-phenyl-2-propanethiol [δ 1.8 (s, 6 H), 2.2 (s, 1 H), 7.4 (m, 5 H)] and 16% 2-phenyl-2-propanol [δ 1.51 (s, 6 H), 2.1 (br s, 1 H), 7.4 (m, 5 H)], the methyl singlets being used to determine the relative amounts of thiol and alcohol present. This mixture (4.6 g) of thiol and alcohol and pyridine (2.4 g) in 50 mL of anhydrous ether was added slowly at room temperature over 2 h to a stirred solution of freshly prepared benzenesulfinyl chloride[3] (4.8 g, 0.03 mol) in 50 mL of ether. The precipitate of pyridine hydrochloride was removed, the filtrate was washed (1 N sulfuric acid, 5% sodium bicarbonate, and water) and dried (Na_2SO_4), and the ether was removed. Thiosulfinate **1a**, mp 43–45 °C, was isolated (1.6 g, 20%) by crystallization from hexane at −78 °C: IR 1080 cm^{-1} (s, S=O); ^1H NMR ($CDCl_3$) δ 2.00 (s, 3 H) and 2.18 (s, 3 H), diastereotopic methyl groups in **1a**, 7.6 (m, 10 H, Ar H). Anal. Calcd for $C_{15}H_{16}O_2S$: C, 65.20; H, 5.85; S, 23.17. Found: C, 65.10; H, 6.06; S, 23.07.

1-(*p*-Anisyl)-1-methylethyl Benzenethiosulfinate (1b). *p*-Methoxyacetophenone (Aldrich) (10 g, 0.066 mol) was added to an equimolar amount of methylmagnesium iodide in ether, and the reaction mixture was worked up in the usual fashion, giving 8.0 g (73%) of crude 2-(*p*-anisyl)-2-propanol: NMR ($CDCl_3$) δ 1.51 (s, 6 H), 2.7 (br s, 1 H), 3.76 (s, 3 H), 7.15 (AA'BB' m, 4 H). Since attempted distillation of the crude alcohol gave olefin and tar, it was used without further purification.

To 3.0 g of 2-(*p*-anisyl)-2-propanol dissolved in 20 mL of glacial acetic acid was added 3 drops of concentrated sulfuric acid. The bright purple solution was warmed slightly and shielded from light, and hydrogen sulfide was passed through it for 45 min. The solution was poured into water and extracted with ether. The ether extracts were washed (5% sodium bicarbonate and water) and dried ($MgSO_4$), and the ether was removed under reduced pressure, yielding 2-(*p*-anisyl)-2-propanethiol (2.6 g, 79%): NMR ($CDCl_3$) δ 1.81 (s, 6 H), 2.2 (s, 1 H), 3.85 (s, 3 H), 6.8–7.7 (AA'BB' m, 4 H). Since the thiol loses H_2S and decomposes on attempted distillation, it was used without further purification. The infrared spectrum showed no alcohol was present as an impurity.

2-(*p*-Anisyl)-2-propanethiol (2.6 g) was reacted with benzenesulfinyl chloride (2.3 g) and the reaction mixture worked up in the same fashion as in the synthesis of **1a**. Low-temperature crystallization from hexane gave **1b** (0.60 g, 14%): mp 54–57 °C; NMR ($CDCl_3$) δ 1.97 (s, 3 H), 2.13 (s, 3 H), 3.81 (s, 3 H), 6.8–7.7 (m, 9 H); IR ($CHCl_3$) 3000, 1610, 1510, 1460, 1445, 1390, 1370, 1300, 1200 (s), 1080–1030 cm^{-1} (s, S=O). Anal. Calcd for $C_{16}H_{18}O_2S_2$: C, 62.73; H, 5.92. Found: C, 62.90; H, 6.05.

Kinetic Study of Decomposition of 1a and 1b. Solutions of **1a** and **1b** in acetic acid–1% H_2O alone show no change in UV absorption over a period of several days. Acetic acid–1% water (3.5 mL) containing the desired amounts of sulfuric acid and *n*-butyl sulfide was placed in a thermostated cell and 35 μL of a 0.01 M solution of either **1a** or **1b** in acetic acid–1% H_2O was added to follow the kinetics of the acid-catalyzed decompositions. The change in optical density with time at a suitable wavelength (268 nm for **1a**, 257 nm for **1b**) was then monitored. With **1b** the initial change in absorbance associated with the decomposition of **1b** was followed by a small further change in absorbance; this was slow enough and small enough, however, that there was no difficulty in determining the "infinity time" absorbance associated with the decomposition of **1b** itself.

Decomposition Products of 1b. Thiosulfinate **1b** (2.1 g, 6.9 mmol) was dissolved in 75 mL of acetic acid–1% water, sulfuric acid was added to make the solution 0.10 M in H_2SO_4, and the solution was allowed to stand at room temperature for 1 h. It was poured into water (225 mL) and extracted with ether. The ether extracts were washed (10% sodium carbonate and water) and dried ($MgSO_4$), and the ether was removed. The residue (2.0 g) was chromatographed on silica gel with successively hexane, carbon tetrachloride, and acetone (and mixtures of same) as eluants. The first fraction consisted of diphenyl disulfide (40 mg). This was followed by a minute amount (~20 mg) of 2-(*p*-methoxyphenyl)propene (**3**). A large amount of material (1.5 g) was eluted by 1:2 hexane–CCl_4 containing 5% acetone. One component of this material was shown to be *p*-methoxyacetophenone, identical in all respects with a known sample. The total amount of this ketone in the several fractions (0.40 g, 2.67 mmol) was estimated by NMR from the intensity of the δ 2.46 singlet for the $CH_3C(O)$ group. The remaining components of the mixture could not be satisfactorily separated and were not identified, although it was established from infrared and NMR examination that no significant amount of acetate **4** was present. The NMR also indicated that *p*-anisyl and phenyl groups were present in the different components in a ratio of 2:1.

Acknowledgment. Support of this research by the Robert A. Welch Foundation (Grant D-650) is gratefully acknowledged.

Registry No. **1a**, 73396-84-6; **1b**, 73396-85-7; 2-phenyl-2-propanol, 617-94-7; 2-phenyl-2-propanethiol, 16325-88-5; benzenesulfinyl chloride, 4972-29-6; *p*-methoxyacetophenone, 100-06-1; 2-(*p*-anisyl)-2-propanol, 7428-99-1; 2-(*p*-anisyl)-2-propanethiol, 73396-86-8.

(3) Pawlowski, N. E. Ph.D. Thesis, Oregon State University, 1965.

Evidence for a Hydroxyl Directing Effect in Dichlorocarbene Addition to 2-Cycloalkenols

Robert H. Ellison

General Electric Corporate Research and Development Center, Schenectady, New York 12301

Received November 30, 1979

Introduction

The influence of hydroxyl groups on the stereochemical outcome of Simmons–Smith cyclopropanation[1] and epoxidation[2,3] of 2-cycloalkenols is well-documented. Complexation of the incoming reagent to the hydroxyl oxygen

(1) C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Am. Chem. Soc.*, **91**, 6892 (1969).
(2) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957).
(3) T. Itoh, K. Jitsukawa, K. Kaneda, and S. Teranishi, *J. Am. Chem. Soc.*, **101**, 159 (1979).

0022-3263/80/1945-2509$01.00/0