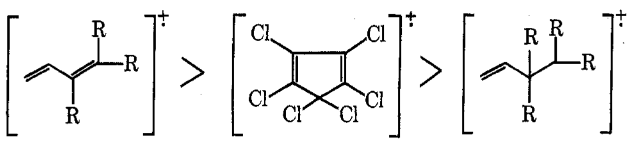
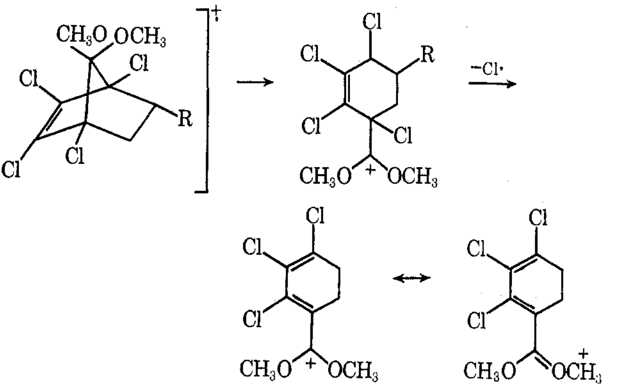


Compound XI is capable of generating an ionized conjugated diolefin in this reaction, but it fails to produce such an ion in high abundance. This is probably due to the existence of a competing reaction which is mentioned in the next section.

Ions Formed by the Elimination of Chlorine and Hydrogen Chloride.—All of the compounds eject various combinations of chlorine and hydrogen chloride on electron impact, but only compound XI produces such ions which represent more than 9% of Σ_{31}. In the spectrum of this compound, the ion formed by the loss of a chlorine atom is the most abundant ion and the sum of the abundance of the M − Cl, M − HCl, and M − Cl − HCl ions represent 23.6% of Σ_{31}. It is apparent that special mechanisms are operative in this system, such as the following.



Experimental Section

General.—The olefins were obtained from Chemical Samples Co. or Phillips Petroleum Co. in high purity. Hexachlorocyclopentadiene was obtained from the Aldrich Chemical Co. and used without further purification. All boiling points and melting points are uncorrected. Molecular weight values were obtained from the mass spectra and are corrected for the presence of isotopic species. Nmr spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. The mass spectra were obtained on a Consolidated Electrodynamics Corp. 21-110 high-resolution mass spectrometer at 70 eV. Samples were introduced through a heated inlet system at 200° into an ion source which was also maintained at 200°.

1,2,4,4-Tetrachlorocyclopentadiene-1,3.—This compound was prepared according to the procedure described by Donish[10] and was obtained in 39% yield, mp 62–63° (lit.[10] mp 61°).

1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene.—The procedure of McBee[11] was employed to obtain this product in 89% yield, mp 27° (lit.[11] mp 27–28°).

Diels–Alder Adducts of Hexachlorocyclopentadiene, 1,2,3,4-Tetrachlorocyclopentadiene-1,3, and 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadine.—The chlorinated norbornenes were prepared by heating equivalent amounts of chlorinated cyclopentadiene and the appropriate olefin in a sealed glass tube for 18 hr at 95°. The yields and analyses are listed in Table I. No peaks produced by impurities could be detected in the mass spectra. The nmr spectra indicated that reaction occurs excessively between the chlorinated diene and the least hindered double bond of the acyclic olefin and that no double bond isomerization occurs.

Registry No.—I, 15584-72-2; *trans*-II, 28861-40-7; III, 28861-43-0; *cis*-IV, 28861-37-2; *trans*-V, 28861-35-0; *cis*-V, 28861-36-1; *cis*-VI, 28861-44-1; *trans*-VII, 29005-85-4; VIII, 29005-86-5; IX, 29005-87-6; *trans*-X, 29005-88-7; *trans*-XI, 29005-89-8.

(10) A. A. Donish, M. Silverman, and Y. A. Tajima, *J. Amer. Chem. Soc.*, **76**, 6144 (1954).

(11) E. T. McBee, D. L. Crain, R. D. Crain, L. R. Beloholv, and H. P. Braendlin, *ibid.*, **84**, 3557 (1962).

Electronic Effects in E2 Reactions. III. Base-Induced Eliminations of Some Phenyl 2-Pentyl Sulfones[1]

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Products of elimination have been determined for reaction of a series of 2-pentyl aryl sulfones with sodium ethylene glycolate in refluxing ethylene glycol and potassium *tert*-butoxide in refluxing pyridine. Compounds studied were *p*-nitrophenyl, *p*-bromophenyl, phenyl, *p*-methylphenyl, *p*-methoxyphenyl, 2,4,6-trimethylphenyl, and *p*-dimethylaminophenyl 2-pentyl sulfones. With a single exception (*p*-NO_2 sulfone in ethylene glycol) the proportion of 1-pentene from the base-induced eliminations was constant within the estimated limits of experimental error. In both media the ratio of *trans*- to *cis*-2-pentene from the mesityl sulfone was significantly different from that from the other sulfones. Several compounds failed to undergo base-induced elimination under these conditions. The *p*-bromophenyl sulfone was converted to *p*-hydroxyphenyl 2-pentyl sulfone in ethylene glycol and was recovered unchanged from the pyridine medium. The *p*-nitrophenyl sulfone yielded no volatile products in pyridine. The *p*-dimethylaminophenyl sulfone underwent elimination in the absence of base in both media. The results are discussed.

In recent years, the concept of a continuous spectrum of transition states for E2 reactions, differing in the extent to which the $C_\beta H$ and $C_\alpha X$ bonds are broken in the transition state, has found widespread acceptance.[2] The model has been used to account for a wide variety of structural and environmental influences on the rates and products of E2 reactions. The proposal[3] that the direction of elimination can be strongly influenced by steric factors has met with less general acceptance,

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[1] (a) Abstracted from the Ph.D. Thesis of R. E. Miller, Jr., Carnegie-Mellon University, June 1967. (b) Parts I and II of this series: A. K. Colter and R. D. Johnson, *J. Amer. Chem. Soc.*, **84**, 3289 (1962); A. K. Colter and D. R. McKelvey, *Can. J. Chem.*, **43**, 1282 (1965).

[2] Recent reviews: (a) W. H. Saunders, Jr., in "The Chemistry of the Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, Chapter 2; (b) D. V. Banthorpe in "Studies on Chemical Structure and Reactivity," J. H. Ridd, Ed., Wiley, New York, N. Y., 1966, Chapter 3; (c) J. F. Bunnett, *Surv. Progr. Chem.*, **5**, 53 (1969).

[3] H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, **78**, 2203 (1956).

especially with regard to the importance of the steric requirements of the leaving group.[4,5]

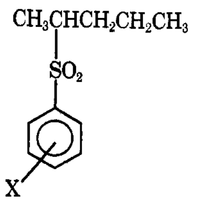
In this and previous work we have attempted to assess the importance and nature of electronic influences imposed by the leaving group in determining the products of elimination. Our approach has been to examine the products of elimination from a series of compounds differing only in a substituent in the meta or para position of a benzene ring in the leaving group. In such systems the steric requirements of the leaving group in the transition state should be constant except for small differences due to differences in solvation[6] and extent of bond fission. In earlier studies[1b] we examined the olefin mixtures from E2 reactions of a series of arenesulfonates of 2-pentanol and 2-methyl-3-pentanol. In both of these studies the composition of the olefin mixture varied in a fairly regular way with changes in the electronic nature of the leaving group, with the proportion of the more stable olefin (2-pentene and 2-methyl-2-pentene, respectively) increasing, for the most part, with increasing electron withdrawal. We interpreted these results to mean that the increasing ease of heterolysis of the C–O bond leads to a shift toward the E1-like extreme with an accompanying increase in the double bond character in the transition state.

The model of the E2 transition state elaborated by Bunnett[2c,7] does not lead to a clear-cut prediction of the effect of substitution in an arenesulfonate leaving group on the direction of elimination. Thus, it is stated[7] that a change to a leaving group of greater electron-attracting character should result in a shift toward the E1cb-like extreme while a shift toward a better leaving group should cause a shift toward the E1-like extreme.

Both of the previous studies[8] have dealt with compounds which yield predominant amounts of the more highly substituted olefin (Saytzeff pattern) under the more usual elimination conditions, presumably through transition states in the synchronous or E1-like regions. We therefore felt that it was worthwhile extending these studies to eliminations yielding predominantly the less alkylated olefin (Hofmann pattern), presumably[7] *via* transition states closer to the E1cb-like extreme. We chose for this study a series of 2-pentyl phenyl sulfones (**1**–**7**). Although the study was intended to be mainly an investigation of an electronic influences on orientation, 2-pentyl mesityl sulfone **7** was also examined.

Results

Synthesis of Sulfones.—The 2-pentyl phenyl sulfones **1**–**7** were synthesized by oxidation of the corresponding sulfide, obtained by reaction of the appropriate benzenethiol with 2-pentyl *p*-toluenesulfonate. The sulfones were characterized by elemental analysis and nmr and infrared spectroscopy. The infrared spectra all showed strong absorption in the regions 1280–1300 and 1120–1140 cm^{-1}, characteristic of the sulfone function.[9]



1, X = *p*-N$(CH_3)_2$
2, X = *p*-OCH_3
3, X = *p*-CH_3
4, unsubstituted
5, X = *p*-Br
6, X = *p*-NO_2
7, X = 2,4,6-$(CH_3)_3$

Product Studies.—Any suitable reaction medium must be one which will induce elimination without bringing about isomerization of the olefinic products before they can be isolated. Previous studies of sulfone eliminations[4c,10–13] indicated that quite vigorous conditions would be required.

In view of the results of Hofmann, *et al.*, several attempts were made to induce elimination using *tert*-BuOK in DMSO or DMSO–*tert*-butyl alcohol mixtures. In the present work, however, no conditions were found which would yield elimination without isomerization. Reaction of the *p*-methoxyphenyl sulfone **2** in 0.2 *M* *tert*-BuOK–DMSO at 100° for 7.75 hr, followed by work-up of the reaction medium (see Experimental Section), led to recovery of *p*-hydroxyphenyl 2-pentyl sulfone in 39% yield. The rate of demethylation is therefore at least comparable to the rate of elimination under these conditions, making any estimate of the products of elimination from **2** very difficult. Basic cleavage of alkyl aryl ethers is a well-documented reaction.[14] In this case the reaction is presumably facilitated by the electron-withdrawing *p*-2-pentylsulfonyl group.

After completion of this work Bartsch and Bunnett[4c] reported a 14% yield of hexenes from 2-hexyl phenyl sulfone after 40 min in 0.5 *M* *tert*-BuOK–DMSO at 50.8° using a nitrogen bubbler and reported also that no isomerization of the hexenes occurs under these conditions.

Five of the seven sulfones were found to yield analyzable quantities of olefin in 6–8 hr using 0.4 *M* sodium ethylene glycolate (EGONa) in refluxing (bp 195–200°) ethylene glycol (EGOH). A control experiment using pure 1-pentene showed no detectable isomerization under these conditions. In all cases volatile products were collected as formed in a Dry Ice trap and analyzed by gas liquid chromatography (glc). The results of the EGONa–EGOH eliminations are summarized in Table I. With the *p*-dimethylaminophenyl, mesityl, *p*-

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[4] The following authors have presented explanations based on steric influences to account for trends in the direction of elimination: (a) I. N. Feit and W. H. Saunders, Jr., *Chem. Commun.*, 610 (1967); D. L. Griffiths and D. L. Meges, *ibid.*, **90**, (1968); (c) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 1376, 1382 (1969); (d) R. A. Bartsh, *J. Org. Chem.*, **35**, 1334 (1970).

[5] The following authors have proposed steric explanations to account for other experimental observations: (a) D. H. Froemsdorf, W. Dowd, and K. E. Leimer, *J. Amer. Chem. Soc.*, **88**, 2345 (1966); (b) D. S. Bailey and W. H. Saunders, Jr., *Chem. Commun.*, 1598 (1968); (c) ref 4c; (d) I. N. Feit and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **92**, 1630 (1970).

[6] H. C. Brown and R. L. Klimisch, *ibid.*, **88**, 1425 (1966).

[7] J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, **1**, 225 (1962).

[8] For a similar study of E2 reactions of alkyl arenesulfonates, see C. H. Snyder and A. R. Soto, *Tetrahedron Lett.*, 3261 (1965).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1058, p 360.

[10] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 3127 (1928); 2338 (1929); 705 (1930).

[11] H. C. Brown and O. H. Wheeler, *J. Amer. Chem. Soc.*, **78**, 2199 (1956).

[12] (a) J. E. Hofmann, T. J. Wallace, P. A. Argabright, and A. Schriesheim, *Chem. Ind.* (*London*), 1243 (1963); (b) T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *J. Amer. Chem. Soc.*, **85**, 2739 (1963); (c) J. E. Hofmann, T. J. Wallace, and A. Schriesheim, *ibid.*, **86**, 1561 (1964).

[13] J. F. Bunnett and E. Baciocchi, *Proc. Chem. Soc.*, 238 (1963); *J. Org. Chem.*, **32**, 11 (1967).

[14] (a) G. I. Feutril and R. N. Mirrington, *Tetrahedron Lett.*, 1327 (1970) and references cited; (b) R. L. Burwell, *Chem. Rev.*, **54**, 615 (1954).

TABLE I

PRODUCTS OF ELIMINATION REACTIONS OF SUBSTITUTED PHENYL 2-PENTYL SULFONES IN REFLUXING ETHYLENE GLYCOL[a,b]

Phenyl substituent	Base[c]	1-Pentene, %	*trans*-2-Pentene, %	*cis*-2-Pentene, %
p-N(CH$_3$)$_2$	EGONa[d]	52.6	32.2	15.2
	EGONa	54.5	30.9	14.6
	None	50.6	33.7	15.7
	Quinoline	52.6	32.8	14.6
2,4,6-(CH$_3$)$_3$	EGONa	78.4	14.8	6.8
	EGONa	79.6	14.0	6.8
	EGONa	77.9	14.7	7.4
p-CH$_3$	EGONa	78.2	12.5	9.3
	EGONa	74.4	14.6	11.0
	EGONa	74.2	14.7	11.1
	EGONa	80.8	11.3	7.9
None	EGONa	75.8	14.1	10.1
	EGONa	76.3	13.6	10.1
	EGONa[e]	74.9	14.0	11.0
p-NO$_2$	EGONa	65.4	20.9	13.7
		59.8	25.1	15.1

[a] Gc analyses of individual mixtures considered accurate to *ca.* ±0.5% or better. [b] Concentration of sulfone, 0.2 *M*. [c] Concentration of base, 0.4 *M*, except where otherwise noted. [d] Sodium ethylene glycolate. [e] 0.8 *M*.

methylphenyl, and phenyl sulfones, **1**, **7**, **3**, and **4**, respectively, dilution of the reaction mixture with water, followed by ether extraction, yielded only unreacted sulfone, and there was no evidence for any reaction other than elimination. With the sulfones **7**, **3**, and **4** reaction occurred to the extent of roughly 2–4% per hour, based on the quantity of recovered sulfone, while the dimethylaminophenyl sulfone **1** reacted about three to six times more rapidly. The behavior of the *p*-nitrophenyl sulfone **6** was abnormal in several respects: no unreacted sulfone was recovered after 6 hr, the yield of olefins was small, and there were several unidentified volatile products formed along with the pentenes. The principal unidentified product was tentatively identified as *n*-pentane, based on glc retention times. It is clear that reactions other than base-induced elimination occur with the *p*-nitrophenyl sulfone, but we have no evidence bearing on the mechanism of formation of the pentenes. Because of the unusual reactivity of the *p*-dimethylaminophenyl sulfone **1** and the unusual composition of its elimination product, the possibility of a unimolecular elimination was examined. Surprisingly, it was found that **1** underwent elimination in refluxing EGOH, with or without added quinoline, at approximately the same rate as in the presence of alkoxide base. The olefin compositions (Table I) together with the approximate rates of reaction indicate that this sulfone undergoes elimination primarily by a mechanism not involving base, even in the presence of alkoxide. A similar control with the phenyl sulfone **4** yielded no olefin after 6.5 hr.

Reaction of *p*-bromophenyl 2-pentyl sulfone (**5**) under the usual conditions in EGONa–EGOH gave no detectable olefin after 7 hr. Dilution of the reaction mixture with water, acidification, and extraction with ether afforded a 72% yield of *p*-hydroxyphenyl 2-pentyl sulfone. This product is apparently the result of a nucleophilic displacement of bromide by EGO$^-$ followed by basic ether cleavage as observed with the *p*-methoxyphenyl sulfone **2** in *tert*-BuOK–DMSO. In view of these results, elimination of **2** was not attempted in EGONa–EGOH.

The second medium investigated was 0.3 *M* *tert*-BuOK in refluxing (bp 113–115°) pyridine. Five of the seven sulfones afforded good yields of olefins after 6–7 hr. Again, with the exception of sulfone **6**, only unreacted sulfone could be isolated from the reaction mixture and there was no evidence for any reaction other than elimination. A control experiment with 1-pentene showed rapid liberation of the olefins with about 1% isomerization. Volatile products were again collected continuously and analyzed by glc. The results of the *tert*-BuOK–pyridine eliminations are summarized in Table II.

TABLE II

PRODUCTS OF ELIMINATION REACTIONS OF SUBSTITUTED PHENYL 2-PENTYL SULFONES IN REFLUXING PYRIDINE[a,b]

Phenyl substituent	Base[c]	1-Pentene, %	*trans*-2-Pentene, %	*cis*-2-Pentene, %
p-N(CH$_3$)$_2$	*tert*-BuOK[d]	79.1	14.0	6.9
	none	52.5	33.9	13.6
p-OCH$_3$	*tert*-BuOK	96.4	1.8	1.8
		96.3	2.0	1.7
2,4,6-(CH$_3$)$_3$	*tert*-BuOK	96.1	1.6	2.4
	tert-BuOK	95.9	1.6	2.5
p-CH$_3$	*tert*-BuOK	95.9	2.0	2.1
	tert-BuOK	95.9	2.4	1.7
None	*tert*-BuOK	95.1	2.8	2.1
	tert-BuOK	95.7	2.1	2.2

[a] Gc analyses of individual mixtures considered accurate to *ca.* ±0.5% or better. [b] Concentration of sulfone, 0.2 *M*. [c] Concenration of base, 0.3 *M*. [d] Potassium *tert*-butoxide.

While the *p*-methoxyphenyl sulfone **2** reacted normally in the refluxing pyridine medium, the *p*-bromo- and *p*-nitrophenyl sulfones **5** and **6** failed to yield any volatile products after 7 hr. The *p*-bromophenyl sulfone was recovered unchanged after this period, while the *p*-nitrophenyl sulfone was converted to unidentified dark material(s). A possible reason for the failure of **5** and **6** to eliminate under these conditions is considered below.

The dimethylaminophenyl sulfone **1** again underwent elimination in the absence of alkoxide base yielding substantial amounts of olefin in 6.5 hr. In this case the reaction in the absence of alkoxide is noticeably slower than that in the presence of alkoxide and the two product mixtures (Table II) differ substantially. Nevertheless, there is no question that a portion of the product in the presence of *tert*-BuOK is due to a mechanism not involving alkoxide. Similar control experiments with **2**, **3**, and **4** gave no detectable volatile products after 6.5 hr.

Finally, since little was known about the properties of *tert*-BuOK–pyridine as an elimination medium, elimination of 2-pentyl *p*-toluenesulfonate was carried out using conditions identical with those for the sulfone eliminations giving 66.4% 1-pentene, 23.5% *trans*-2-pentene, and 10.1% *cis*-2-pentene.

TABLE III

SUMMARY OF PRODUCTS OF BASE-INDUCED ELIMINATIONS[a]

Phenyl substituent	No. of runs	1-Pentene,[b] %	*trans*-2-Pentene,[c] %	*cis*-2-Pentene,[c] %	Trans/cis,[d] %
EGONa in Refluxing EGOH					
2,4,6-$(CH_3)_3$	3	78.5 ± 0.5	14.5 ± 0.3	7.0 ± 0.3	2.1 ± 0.1
p-CH_3	4	76.9 ± 2.6	13.3 ± 1.4	9.8 ± 1.2	1.4 ± 0.1
None	3	75.7 ± 0.5	13.9 ± 0.2	10.4 ± 0.4	1.3 ± 0.1
p-NO_2	2	62.6 ± 2.8	23.0 ± 2.1	14.4 ± 0.7	1.6 ± 0.1
tert-BuOK in Refluxing Pyridine					
p-OCH_3	2	96.4 ± 0.0	1.9 ± 0.1	1.7 ± 0.1	1.1 ± 0.1
2,4,6-$(CH_3)_3$	2	96.0 ± 0.1	1.6 ± 0.0	2.4 ± 0.1	0.66 ± 0.02
p-CH_3	2	95.9 ± 0.0	2.2 ± 0.2	1.9 ± 0.2	1.2 ± 0.2
None	2	95.4 ± 0.3	2.5 ± 0.4	2.1 ± 0.1	1.2 ± 0.2

[a] Averages of values listed in Tables I and II with average deviations. [b] Estimated uncertainties ±2–3% in EGOH, ±0.5% in pyridine. [c] Estimated uncertainties ±1–2% in EGOH, 0.2–0.4% in pyridine. [d] Averages and average deviations of cis/trans ratios calculated separately for each run.

Discussion

A summary of the products of the base-induced elimination is presented in Table III. For reasons not entirely understood, the reproducibility of duplicate runs in EGONa–EGOH is considerably poorer than we have obtained in previous work on arenesulfonate eliminations[1b] or in the *tert*-BuOK–pyridine eliminations. We have established *via* a control experiment using a pentene mixture that olefin fractionation is not responsible for the spread in results. We have established also (see above) that no detectable olefin isomerization occurs under the reaction conditions. It seems doubtful that the poorer temperature control achieved by the use of a refluxing solvent could lead to significant variation.

Comparison of the two base–solvent systems investigated in this work reveals a much closer adherence to the Hofmann pattern in the *tert*-BuOK–pyridine medium. This is expected either on the basis of the electronic theory[2c] (the stronger base should result in a transition state closer to the E1cb extreme and hence a greater proportion of 1-pentene) or the steric theory[15] (the proportion of 1-pentene should increase with increasing steric requirements of the base). In view of the large temperature difference, further discussion of the differences between the two reaction media does not seem warranted.

With the single exception of sulfone **6** in EGONa–EGOH the proportion of 1-pentene is independent of the phenyl substituent. Since the behavior of the *p*-nitrophenyl sulfone was abnormal in several respects (above), it does not seem safe to assume that the olefin mixture arises *via* the same mechanism as in the other cases. If the principal influence of a phenyl substituent on positional orientation is through the leaving-group inductive effect, then the products of the sulfone eliminations should be more sensitive to such substitution than the products of sulfonate elimination. If, however, the main influence is through changes in the extent of C–S (or C–O) bond fission in the transition state,[1b] then the absence of any observable effect in the sulfone eliminations is understandable. Both the strongly electron-withdrawing nature of sulfone groups and their relatively poor leaving-group properties lead to the expectation[2c,7] of a transition state near the E1cb-like extreme with very little C–S bond breaking. In line with this expectation is the strong preference for Hofmann elimination. If the extent of C–S bond fission is very small, differences in C–S bond fission between the different phenyl sulfones are also necessarily small.

It is interesting that, in spite of the invariance of the proportion of 1-pentene with leaving-group substitution, the ratio of *trans*- to *cis*-2-pentene from the mesityl sulfone **7** is out of line in both media. Particularly noteworthy is the observation that in *tert*-BuOK–pyridine the trans/cis ratio is less than 1 for the mesityl sulfone alone. Preferential formation of the less stable of a pair of geometric isomers in base-induced elimination has been reported by several groups.[4a,c,5a,d,16–18] Closely related to the present work is the observation by Bartsch and Bunnett[4c] of preferential formation of *cis*-2-hexene (over *trans*-2-hexene) from 2-hexyl phenyl sulfone in *tert*-BuOK–*tert*-BuOH and *tert*-BuOK–DMSO. In explaining this phenomenon, Brown,[18] Froemsdorf,[5a] Saunders,[5d] Bunnett,[4c] and their coworkers have ascribed an important role to the steric requirements of the leaving group. Sicher[19] and Saunders[20] have emphasized the importance of the competition between syn and anti elimination pathways in determining trans/cis ratios, and Sicher[19] has argued that steric effects *alone* cannot account for the trends in trans/cis ratios in cases where syn and anti elimination occur in competition. The present results indicate quite conclusively that trans/cis ratios can be influenced by the steric requirements of the leaving group. We have no information on the stereochemistry of the eliminations studied in this work. However, a syn mechanism for the sulfone eliminations is *a priori* not unreasonable, especially in *tert*-BuOK–pyridine, in view of the poor leaving-group, strong base, and poor ion-solvating medium.[5b,21]

The breadth of this study was severely limited by the failure of several of the sulfones to undergo base-induced elimination under the conditions investigated. Some

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[15] H. C. Brown, I. Moritani, and Y. Okamoto, *J. Amer. Chem. Soc.*, **78**, 2193 (1956).

[16] A. C. Cope, N. A. LeBel, H. Lee, and W. R. Moore, *ibid.*, **91**, 1376 (1969).

[17] (a) J. Zavada and J. Sicher, *Proc. Chem. Soc.*, **96** (1963); (b) J. Zavada and J. Sicher, *Collect. Czech. Chem. Commun.*, **30**, 438 (1965).

[18] H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, **87**, 5517 (1965).

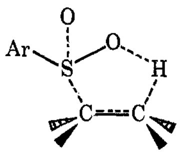
[19] J. Sicher, J. Zavada, and M. Pankova, *Chem. Commun.*, 1147 (1968).

[20] I. N. Feit and W. H. Saunders, *J. Amer. Chem. Soc.*, **92**, 5615 (1970).

[21] J. Sicher and J. Zavada, *Collect. Czech. Chem. Commun.*, **33**, 1278 (1968).

further comment on the various kinds of "abnormal" behavior is appropriate. The behavior of the *p*-methoxyphenyl sulfone **2** in *tert*-BuOK–DMSO and the *p*-bromophenyl sulfone **5** in EGONa–EGOH have been considered earlier.

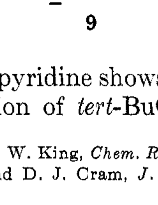
The facile elimination of the *p*-dimethylaminophenyl sulfone **1** in the absence of base was unexpected. The most reasonable kind of mechanism would appear to be a unimolecular cis elimination involving a cyclic transition state **8** analogous to that generally accepted for amine oxide and sulfoxide pyrolyses.[22,23] To our knowledge, pyrolytic elimination of sulfones has not been reported previously. Pyrolysis of simple alkyl sulfones occurs only at much higher temperatures than those studied in this work to yield sulfur dioxide together with products derived from the alkyl free radicals.[24] In view of the greater basicity of sulfoxides than sulfones,[25] it is tempting to attribute the abnormal behavior of the *p*-dimethylaminophenyl sulfone to the electron-supplying character of the dimethylamino group. If this is the case, however, it is difficult to understand the relative stability of the conjugate base of *p*-hydroxyphenyl 2-pentyl sulfone, formed in the reaction of **5** in EGONa–EGOH. Further investigations of this reaction, particularly its stereochemistry, are planned.



8

A possible side reaction in the case of the *p*-nitrophenyl sulfone **6** in either medium is a one-electron transfer from alkoxide or from the conjugate base of the sulfone to the sulfone to yield a radical anion. This reaction would be analogous to that proposed for *p*-nitrocumyl chloride with various nucleophiles.[26] The radical anion derived from **6** would then presumably cleave to form the *p*-nitrophenylsulfinate anion plus the 2-pentyl free radical. The latter could then produce *n*-pentane *via* hydrogen atom abstraction from solvent in EGOH.

The failure of the *p*-bromophenyl sulfone **5** to react in *tert*-BuOK–pyridine could be due to complete conversion to its conjugate base **9**. A solution of the unsubstituted sulfone **4** in pyridine shows no absorption below *ca.* 290 mμ. Addition of *tert*-BuOK results in a new band, λ_{max} 307 mμ, which we believe to be due to the conjugate base. No quantitative measurements of acidity were carried out.



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Experimental Section[27]

Starting Materials.—Commercial 2-pentanol (Matheson Coleman and Bell, practical) was purified by fractional distillation through a 4-ft column packed with stainless steel helices. Analysis by glc using a UCON Polar[28] column showed no detectable impurities. 2-Pentyl *p*-toluenesulfonate was prepared from pure 2-pentanol and *p*-toluenesulfonyl chloride as previously described.[1b] *p*-Methoxybenzenesulfonyl chloride was prepared by the method of Morgan and Cretcher[29] and had mp 39–40° (lit.[29] 41–42°). Mesitylenesulfonyl chloride was prepared as described by Wang and Cohen,[30] mp 54–56° (lit.[30] 56–57°). *p*-*N*,*N*-Dimethylaminophenyl thiocyanate was prepared by the method of Brewster and Schroeder,[31] mp 72–74° (lit.[31] 73–74°). *p*-Methoxybenzenethiol, *p*-bromobenzenethiol, and 2,4,6-trimethylbenzenethiol were prepared from the corresponding sulfonyl chloride by reduction with zinc dust and sulfuric acid.[32] *p*-Methoxybenzenethiol[33] was obtained in 73% yield as a yellow oil. *p*-Bromobenzenethiol was obtained in 73% yield as white plates from acetone–water, mp 74.5–75.5° (lit.[34] 75°). 2,4,6-Trimethylbenzenethiol[30] was obtained in 94% yield as a colorless oil. Commercial benzenethiol (Pitt-Consol) and *p*-methylbenzenethiol (Eastman Kodak) were used without further purification. *p*-*N*,*N*-Dimethylaminothiophenol was obtained as a yellow liquid from *N*,*N*-dimethylaminophenyl thiocyanate following the procedure of Banfield.[35] *p*-Nitrobenzenethiol was prepared from *p*-nitrochlorobenzene, sulfur, and sodium sulfide by the method of Waldren and Reid,[36] mp 77–78° (lit.[36] 77°).

Preparation of Phenyl 2-Pentyl Sulfides.—All of the sulfides were prepared in the same manner. Preparation of *p*-methylphenyl 2-pentyl sulfide is typical. A 42.3-g (0.341 mol) quantity of *p*-methylbenzenethiol, 82.6 g (0.341 mol) of 2-pentyl *p*-toluenesulfonate, and 13.7 g (0.342 mol) of NaOH dissolved in the minimum amount of 95% ethanol was refluxed for 48 hr. The solution was then concentrated by evaporation of the ethanol under vacuum and then diluted with water until an oil separated. The mixture was then extracted with ether, and the ether extract was washed with aqueous sodium carbonate and water and dried over $MgSO_4$. Filtration, followed by evaporation at reduced pressure, yielded 47.3 g (72%) of yellow oil. All of the sulfides were oils and all could be vacuum distilled except for the *p*-nitrophenyl and dimethylaminophenyl sulfides. The yields were *p*-dimethylamino, 78%; *p*-methoxy, 77%; unsubstituted, 71%; *p*-bromo, 95%; *p*-nitro, 74%; 2,4,6-trimethyl, 62%. Except for the *p*-methoxy-, *p*-methyl-, and *p*-bromophenyl sulfides (below), these compounds were directly oxidized to the corresponding sulfone without complete characterization. Except for the phenyl 2-pentyl sulfone,[37] all were previously unknown. *Anal.* Calcd for *p*-methylphenyl 2-pentyl sulfide, $C_{12}H_{18}S$: C, 74.16; H, 9.33; S, 16.50. Found: C, 74.14; H, 9.15; S, 16.45. *Anal.* Calcd for *p*-methoxyphenyl 2-pentyl sulfide, $C_{12}H_{18}OS$: C, 68.52; H, 8.63; S, 15.25. Found: C, 68.71; H, 8.58; S, 15.73. *Anal.* Calcd for *p*-bromophenyl 2-pentyl sulfide, $C_{11}H_{15}BrS$: C, 50.96; H, 5.85. Found: C, 50.70; H, 5.51.

Preparation of Phenyl 2-Pentyl Sulfones.—All of the sulfones were prepared in the same manner. The preparation of 2,4,6-trimethylphenyl 2-pentyl sulfone is typical. A 17.2-g (0.068 mol) quantity of sulfide was dissolved in acetic acid and 24 ml (0.18 mol) of 30% hydrogen peroxide added. Sufficient acetic

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acid was then added to make the solution homogeneous. The solution was heated on the steam bath overnight and then diluted with water until an oil separated out. The mixture was then extracted with ether, the ether extract was washed with dilute aqueous NaOH and water, dried over $MgSO_4$, and filtered, and the ether was removed under vacuum. The residue solidified on standing. Two crystallizations from Skellysolve B gave 12.2 g (62%) of white crystals, mp 84–86°. The other sulfones were prepared in the same way except that only 2 equiv of hydrogen peroxide were used in the oxidation of the *p*-dimethylaminophenyl sulfide. The *p*-nitrophenyl sulfone had mp 44–46°. The other sulfones were oils and all but the *p*-dimethylamino sulfone could be vacuum distilled. The yields were *p*-dimethylamino, 18%; *p*-methoxy, 49%; *p*-methyl, 49%; unsubstituted, 52%; *p*-bromo, 84%; *p*-nitro, 66%. The sulfones were characterized by elemental analyses and nmr and ir spectra.

***p*-*N*,*N*-Dimethylaminophenyl 2-Pentyl Sulfone.** *Anal.* Calcd for $C_{13}H_{21}NO_2S$: C, 61.14; H, 8.29; N, 5.49. Found: C, 61.43; H, 8.32; N, 5.69. Ir (neat) 1285, 1124 cm^{-1} (SO_2).

***p*-Methoxyphenyl 2-Pentyl Sulfone.** *Anal.* Calcd for $C_{12}H_{18}O_3S$: C, 59.47; H, 7.49. Found: C, 59.43; H, 7.63. Ir (neat) 1302, 1282, 1133 cm^{-1} (SO_2).

***p*-Methylphenyl 2-Pentyl Sulfone.** *Anal.* Calcd for $C_{12}H_{18}O_2S$: C, 63.68; H, 8.02. Found: C, 63.33; H, 8.22. Ir (neat) 1289, 1136 cm^{-1} (SO_2).

Phenyl 2-Pentyl Sulfone. *Anal.* Calcd for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60; S, 15.10. Found: C, 62.43; H, 7.66; S, 15.25. Ir (neat) 1294, 1139 cm^{-1} (SO_2).

***p*-Bromophenyl 2-Pentyl Sulfone.** *Anal.* Calcd for $C_{11}H_{15}BrO_2S$: C, 45.36; H, 5.19; S, 11.01. Found: C, 45.48; H, 5.17; S, 11.12. Ir (neat) 1300, 1142 cm^{-1} (SO_2).

***p*-Nitrophenyl 2-Pentyl Sulfone.** *Anal.* Calcd for $C_{11}H_{15}NO_4S$: C, 51.34; H, 5.87; N, 5.54. Found: C, 51.58; H, 5.98; N, 5.11. Ir (neat) 1290, 1138 cm^{-1} (SO_2).

2,4,6-Trimethylphenyl 2-Pentyl Sulfone. *Anal.* Calcd for $C_{14}H_{22}O_2S$: C, 66.10; H, 8.77; S, 12.61. Found: C, 66.30; H, 8.70; S, 12.53. Ir (CCl_4) 1320, 1136 cm^{-1} (SO_2).

Reaction Media.—Commercial ethylene glycol (Fisher, purified) was dried by reaction with sodium, followed by fractionation under reduced pressure. A weighed amount of sodium was then dissolved with stirring under a nitrogen atmosphere to give a solution 0.4 *M* in base.

Commercial pyridine (Baker, analyzed) was dried by refluxing over sodium hydroxide and then distilling. Sufficient potassium *tert*-butoxide (MSA Research Corp.) was dissolved to give a 0.3 *M* solution.

Product Studies.—A measured amount of base solution was heated nearly to boiling, and sulfone was added to 0.2 *M*. The solution was then refluxed in a flask fitted to an 18-in. distilling column fitted with a Dry Ice–acetone condenser and receiver. In this manner the olefins were distilled from the refluxing reaction medium on formation. The olefins were analyzed by glc using a 50-ft column of 20% dimethylsulfolane[38] on 60–80 mesh Chromosorb P. The peak areas were measured with a planimeter. No correction was made for differences in thermal response of the olefins. The individual peaks were identified by comparison with authentic samples.

Products of Reaction of *p*-Methoxyphenyl 2-Pentyl Sulfone in *tert*-BuOK–DMSO and *p*-Bromophenyl 2-Pentyl Sulfone in EGONa–EGOH.—A 200-ml volume of a solution of 0.175 *M* *p*-methoxyphenyl 2-pentyl sulfone (8.47 g) and 0.2 *M* *tert*-BuOK in DMSO was heated at 101° for 7.75 hr. The solution was diluted with water and extracted with ether, and the ether evaporated to yield a small amount of unidentified black liquid. The aqueous layer was acidified and extracted with ether, and the extracts were washed with water and the ether evaporated to yield 3.57 g of a brown oil. Purification of 0.65 g of this material by chromatography on alumina led to 0.60 g whose nmr ($CDCl_3$) τ showed an A_2X_2 multiplet, 4 aromatic protons, centered at 2.56, $\delta_{A-X} \approx 0.67$ ppm, $J_{A-X} = 8.4$ Hz, 6.90 (m, 1), 8.0–9.3 (m, typical of 2-pentyl group, 10). A small amount (0.5 g) of the brown oil was refluxed with an excess of methyl iodide in aqueous ethanol, diluted with water, and extracted with ether, and the ether evaporated to yield a yellow liquid which was vacuum distilled. The ir and nmr spectra of this material were identical with those of *p*-methoxyphenyl 2-pentyl sulfone.

A 200-ml volume of a solution of 0.200 *M* *p*-bromophenyl 2-pentyl sulfone (11.64 g) and 0.415 *M* EGONa in EGOH was refluxed for 7.5 hr (temperature *ca.* 197°). Work-up as described above led to 5.5 g (72%) of *p*-hydroxyphenyl 2-pentyl sulfone, identified by its nmr spectrum.

Control Experiments.—A 1-ml quantity of pure (glc) 1-pentene was dissolved in 100 ml of 0.389 *M* EGONa in EGOH. The solution was then subjected to the normal reaction procedure. The distillate showed no detectable isomerization and distillation of the pentene from the reaction mixture was complete. A similar control using 0.3 *M* *tert*-BuOK in pyridine gave a distillate which analyzed for 98.8% 1-pentene, 0.2% *trans*-2-pentene, and 1.0% *cis*-2-pentene.

A solution of 8.5 g (0.033 mol) of *p*-*N*,*N*-dimethylaminophenyl 2-pentyl sulfone and 8.6 g (0.067 mol) of quinoline in 165 ml of EGOH was refluxed for 3 hr, after which time the reaction was complete. The olefinic product consisted of 52.6% 1-pentene, 32.8% *trans*-2-pentene, and 14.6% *cis*-2-pentene. A solution of 8.48 g (0.04 mol) of phenyl 2-pentyl sulfone and 5.16 g (0.04 mol) of quinoline in 100 ml of EGOH was refluxed for 6.5 hr. No detectable volatile products were produced.

A solution of 5.91 g (0.0232 mol) of *p*-*N*,*N*-dimethylaminophenyl 2-pentyl sulfone in 110 ml of pyridine was refluxed for 6.5 hr yielding a mixture of olefins analyzing for 52.5% 1-pentene, 33.9% *trans*-2-pentene, and 13.6% *cis*-2-pentene. Similar controls in refluxing pyridine were carried out with phenyl, *p*-methoxyphenyl, and *p*-methylphenyl 2-pentyl sulfones. In none of these cases were any detectable volatile products produced.

Registry No.—**1**, 29182-76-1; **2**, 29182-77-2; **3**, 29182-78-3; **4**, 29182-79-4; **5**, 29182-80-7; **6**, 29182-81-8; **7**, 29182-82-9; *p*-methylphenyl 2-pentyl sulfide, 29182-83-0; *p*-methoxyphenyl 2-pentyl sulfide, 29182-84-1; *p*-bromophenyl 2-pentyl sulfide, 29182-85-2.

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