(53) This would imply that the push does not obey a simple Brønsted relationship.
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Tetraoxysulfuranes from Phenols. Synthesis and the Dehydration of Alcohols[1]

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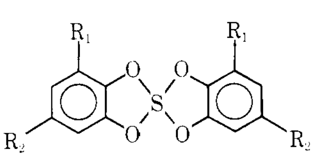
Abstract: Lithium salts of phenols react with SF_4 to form tetraoxysulfuranes. Reaction of **1** with alcohols bearing β-hydrogen atoms leads to olefins by what appears to be a cyclic elimination mechanism from a sulfurane generated by ligand exchange with the alcohol. Borneol and isoborneol give rearrangement products. The products from methanol are guaiacol, dimethyl ether, and dimethyl sulfite in addition to catechol and *o*-phenylene sulfite.

Introduction

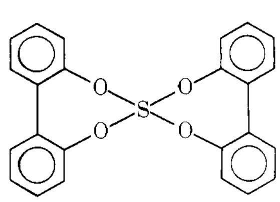
Since the isolation of SCl_4[3] and SF_4[4] there has been a continued interest in the generation of stable sulfuranes functionalized with ligands other than halogens[5] and in studies of their structure-reactivity relationships and their stereochemical dynamics. Extensive examples of the chemical reactivity of a number of oxysulfuranes have been reported.[6] A suggestion of the extension of the concept of pseudorotation developed for pentacoordinate phosphorus compounds to tetracoordinate sulfur(IV)[7] stimulated a number of workers[8-14] to look for examples of this phenomenon in the sulfuranes. In this report we describe a general synthesis of tetraoxysulfuranes of phenols, some reactions of catechol spirosulfurane **1** with alcohols, and an NMR spectrum of **1** which requires that pseudorotation be occurring in this sulfurane.

Results and Discussion

The reaction of sulfur tetrafluoride with lithium salts of phenols provides a general route to stable symmetrical tetraoxysulfuranes. For example, tetraoxysulfurane **1** is formed by addition of a premeasured quantity of sulfur tetrafluoride to the lithium salt of catechol in scrupulously dry ether at −78 °C under a rigorously dry and oxygen-free nitrogen atmosphere. After removal of excess sulfur tetrafluoride by the nitrogen stream, the inorganic salt is removed by room temperature filtration in a glovebag filled with dry, oxygen-free nitrogen, and the sulfurane is isolated by crystallization at −78 °C. The method is of general utility, and we have also obtained sulfuranes **2**, **3**, and **4** in good yield.



1, $R_1 = R_2 = H$
2, $R_1 = Me$; $R_2 = H$
3, $R_1 = R_2 = t$-Bu



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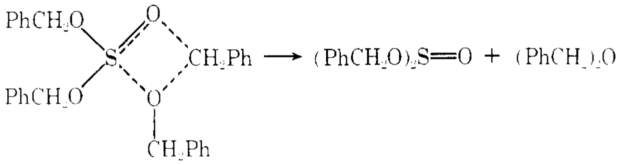
The nature of the intermediates in the reaction of the lithium salts with sulfur tetrafluoride is not clear; however, catechol itself does not react with SF_4 suggesting the importance of the nucleophilicity of the oxygen in the reaction or a coordination of the lithium atom with the departing fluorine atoms. When the lithium salt of benzyl alcohol was allowed to react with sulfur tetrafluoride under the same conditions, the isolated products were dibenzyl sulfite and dibenzyl ether, presumably arising from collapse of an intermediate sulfurane. This could occur by an electrocyclic mechanism through **5** as previously postulated for the formation of ethers from dialkoxysulfuranes.[6b,15]



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The tetraoxysulfuranes reported here are exceptionally susceptible to hydrolysis, as has been observed by others.[16]

The molecular ion of **1** occurs at *m/e* 248.017 (calcd 248.016), and the 60-MHz spectrum shows a single aromatic proton peak. At 220 MHz this peak is resolved into an AA′BB′ pattern centered at 6.95 ppm downfield from internal Me_4Si. The AA′BB′ patterns for *o*-phenylene sulfite and catechol, compounds which are always isolated together with the sulfurane, occur at 7.14 and 6.82 ppm, respectively. The 220-MHz NMR is inconsistent with all alternative covalent nontetracoordinate sulfur compounds of the correct molecular weight and further requires a structure in which all chemically identical protons are magnetically equivalent or one in which structural interconversions make these protons magnetically equivalent on a time average.

All tetracovalent sulfur(IV) compounds for which structures have been determined have been shown to possess a trigonal bipyramidal geometry about sulfur.[11a,b,12,17] Assuming that tetraaryloxysulfuranes are trigonal bipyramidal, rapid conformational averaging is required in order to account for the AA′BB′ coupling pattern. In the absence of such averaging, an ABCD pattern would be expected as a result of inherent differences between apical and equatorial positions.[18]

The 220-MHz NMR spectrum of sulfurane **2** at 18 °C shows aromatic absorption centered about 6.82 ppm downfield from Me_4Si and a methyl singlet at 2.25 ppm well separated from the methyl peaks of the 3-methylcatechol, 2.20 ppm, and 3-methyl-*o*-phenylene sulfite, 2.34 ppm, which occur with and cannot readily be separated from the sulfurane. The temper-

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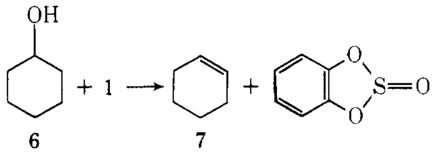
Table I. Products of the Reactions of Sulfurane **1** with Alcohols in $CDCl_3$

alcohol	products	% yield[a]
cyclohexanol	cyclohexene	100
2-methylcyclohexanol (28% cis, 72% trans)	1-methylcyclohexene	50
	3-methylcyclohexene	50
3-methylcyclohexanol (78% cis, 22% trans)	3-methylcyclohexene	50
	4-methylcyclohexene	50
4-*tert*-butylcyclohexanol (68% trans, 32% cis)	4-*tert*-butylcyclohexene	32[b]
	o-hydroxyphenyl-*cis*-4-*tert*-butylcyclohexyl sulfite	13[b]
	o-hydroxyphenyl-*trans*-4-*tert*-butylcyclohexyl sulfite	58[b]
methanol	dimethyl ether	52
	dimethyl sulfite	29
	guaiacol	15
pinacol	pinacolone	100
benzopinacol	benzopinacolone	100
isoborneol	camphene	91
	tricyclene	9
borneol	camphene	100[b]

[a] Yields were measured by NMR using the aromatic protons as an internal integration standard. [b] Yield based on alcohol consumed.

ature dependence of the ^{1}H and ^{13}C spectra of **3** has been investigated in detail.[19]

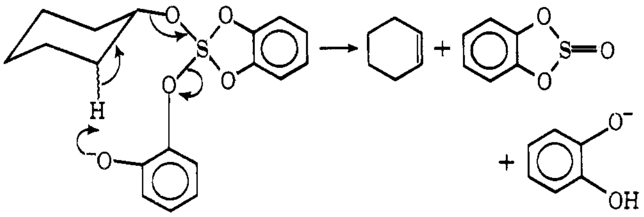
Reactions with Alcohols. Following a course which has been previously observed in several cases,[6b,c,15] sulfurane **1** reacts with alcohols having β protons to form olefins within minutes at room temperature (Table I). Thus cyclohexene (**7**) was formed quantitatively from cyclohexanol (**6**). The *o*-phenylene sulfite observed as a byproduct was demonstrated to be incapable of effecting the dehydrations, and additionally the olefins were stable to isomerization under the reaction conditions.



Substituted cyclohexanols were used to study the stereoselectivity of the elimination. A mixture of 2-methylcyclohexanols containing 72% trans isomer provided a 1:1 mixture of 1- and 3-methylcyclohexenes. The same mixture was obtained from *trans*-2-methylcyclohexanol. When the reaction was run with an excess of 2-methylcyclohexanol, the isomeric composition of the recovered alcohol was identical within experimental error with that of the starting alcohol. A similar result was obtained with both 3-methylcyclohexanol and 4-*tert*-butylcyclohexanol.

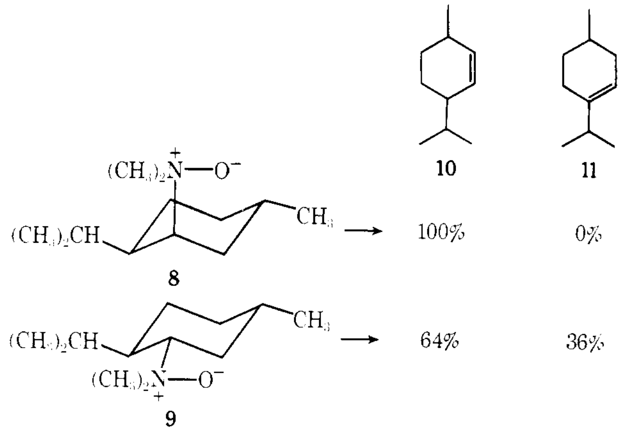
The reaction stereoselectivity does not seem compatible with either an E1 or E2 elimination mechanism. For the E1 elimination one would expect predominantly the most stable olefin, 1-methylcyclohexene. For a pure E2 trans elimination the product ratios should be different for the two starting materials recognizing that a trans coplanar elimination to provide 1-methylcyclohexene from the trans isomer is impossible. In fact, dehydration of 1-methylcyclohexanol by 85% phosphoric acid gives 85% of 1-methylcyclohexene.[20] Dehydration of *cis*- and *trans*-2-*tert*-butylcyclohexanol by 85% phosphoric acid provides exclusively 1-*tert*-butylcyclohexene and a 60:40 mixture of the 1 and 3 isomers, respectively.[21] The trans diaxial elimination of *trans*- and *cis*-2-methylcyclohexanol in the gas phase at 220 °C over alumina provides respectively the 3- and 1-methylcyclohexenes as the major products in accord with stereochemical predictions for the E2 path.[22]

A third possibility for an elimination mechanism is a cyclic one similar to that shown below for cyclohexanol.



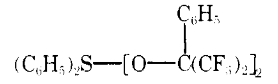
In such a transformation it is clear that the transition state might also include a proton associated with one of the sulfurane oxygen atoms. The sulfurane function attached to the cyclohexane ring is clearly a bulky group, and would be expected to occupy the equatorial position exclusively, thus influencing the direction of elimination in some cases. It is interesting that pyrolysis of *trans*-2-methylcyclohexyl acetate provides a 55:44 mixture of 1- and 3-methylcyclohexene.[23] The cis isomer, on the other hand, yields a 6:94 mixture. Although the reaction in this case appears to be an example of cyclic elimination, deuterium scrambling experiments led the authors to favor a transition state involving hydrogen participation as a neighboring group in the elimination.

In the pyrolysis of amine oxides **8** and **9** elimination of *N*,*N*-dimethylhydroxylamine proceeds intramolecularly exclusively cis through a five-membered transition state.[24] Thus dimethylneomenthylamine oxide (**8**), with only one cis hydrogen available, yields only 2-menthene **10** whereas the dimethylmenthylamine oxide **9**, with two cis hydrogens available, yields both 2- and 3-menthene **11** (major and minor, respectively).



Excluding from consideration the surprisingly low temperature at which olefin formation using sulfurane takes place, a concerted cis elimination pathway cannot be excluded on stereochemical grounds. The bulky sulfurane moiety in the intermediate will adopt the equatorial position in both the cis and trans isomers. This, in turn, may lead to a six-membered cyclic transition state in which cis and trans isomers may eliminate H-2 and H-6 with similar ease in a cis fashion.

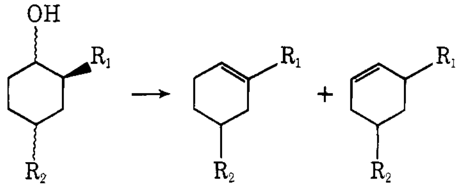
It is interesting to contrast the stereochemical course of the elimination reaction of the 2-methylcyclohexanols effected by **1** with the trans elimination reported by Arhart and Martin[6b] using the sulfurane **12**. The two sulfuranes **1** and **12** seem to be complementary mild reagents for effecting stereochemically controlled eliminations of alcohols, but further studies with **1** are necessary to establish generality.



$$(C_6H_5)_2S—[O—C(C_6H_5)(CF_3)_2]_2$$

12

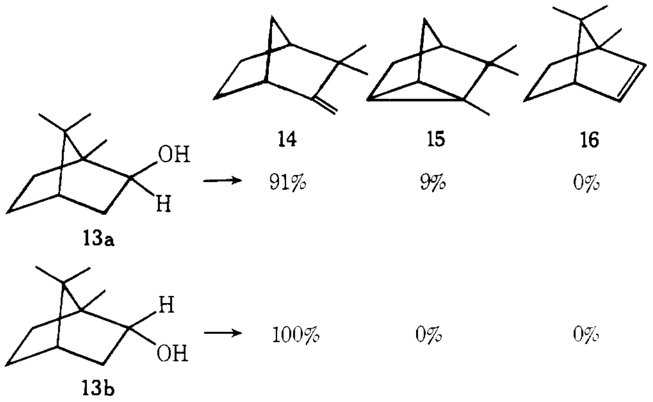
Table II. Comparison of Product Compositions for Dehydration of 2-Substituted Cyclohexanols

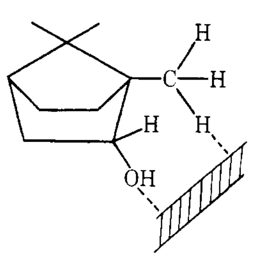


alcohol	R_1	R_2	conditions	1-R_1, %	3-R_1, %	ref
trans	Me	H	alumina, 220 °C		major	22
cis	Me	H	alumina, 220 °C	major		22
trans	*t*-Bu	H	85% phosphoric acid	60	40	21
cis	*t*-Bu	H	85% phosphoric acid	100		20
trans[a]	Me	H		55	44	23
cis[a]	Me	H		6	94	23

[a] As the acetate.

The products observed from the dehydration of isoborneol (**13a**) by sulfurane **1** in $CDCl_3$ are camphene (91%) and tricyclene (9%). The reaction is complete in 30 min and no bornylene (**16**) was observed in the product mixture. Borneol (**17**) reacts much slower with sulfurane **1**, and product formation is incomplete after 19 h. The only observed product was camphene. No bornylene or tricyclene was observed. The fact that no tricyclene was detected from the reaction with borneol indicates that these two isomeric alcohols do not pass through the same intermediate. Alternatively, an additional pathway may be open to isoborneol by which tricyclene is formed. In contrast, the gas-phase pyrolysis of isobornyl chloride gives 25% bornylene and 75% rearranged camphene and tricyclene.[25] Dehydration of borneol over alumina at high temperatures (289 °C), on the other hand, yielded 87.5% camphene and 12.5% tricyclene, and isoborneol gave 95.2% camphene and 4.3% tricyclene.[26] A concerted mechanism via **17** was proposed, wherein an acidic site on the catalyst attracts the hydroxyl group from the alcohol, while the basic site of the catalyst removes the proton.



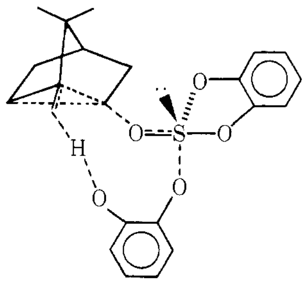


17

A large ratio of bornylene to rearranged product was obtained in the thermal decomposition of bornyl and isobornyl acetates.[27] Bornylene is the normal product of cis elimination,[28] and assistance from C-1 and C-6 in the transition state is invoked to explain the occurrence of the rearrangement products along with cis elimination. Predominance of norbornene formed by exo-cis elimination was reported for the elimination under E2 conditions from *exo*-2-norbornyl tosylate[29] and bromide.[30]

Rearrangement products **14** and **15** are usually associated with a carbonium ion intermediate. Thus formation of **14** and **15** in the dehydration of isoborneol **13a** could have been attributed to formation of a free carbonium ion intermediate. However, predominance of camphene over tricyclene (91:9, respectively) suggests that any carbonium ion formed may not be a free one. The exclusive formation of camphene from borneol (**13b**) in the reaction with sulfurane **1** tends to exclude a free carbonium ion intermediate in the dehydration of the endo epimer.

By analogy to the mechanism proposed in the alumina-catalyzed dehydration of borneol[25] to which our results are closely related, a concerted pathway is proposed with a transition state similar to **18**.

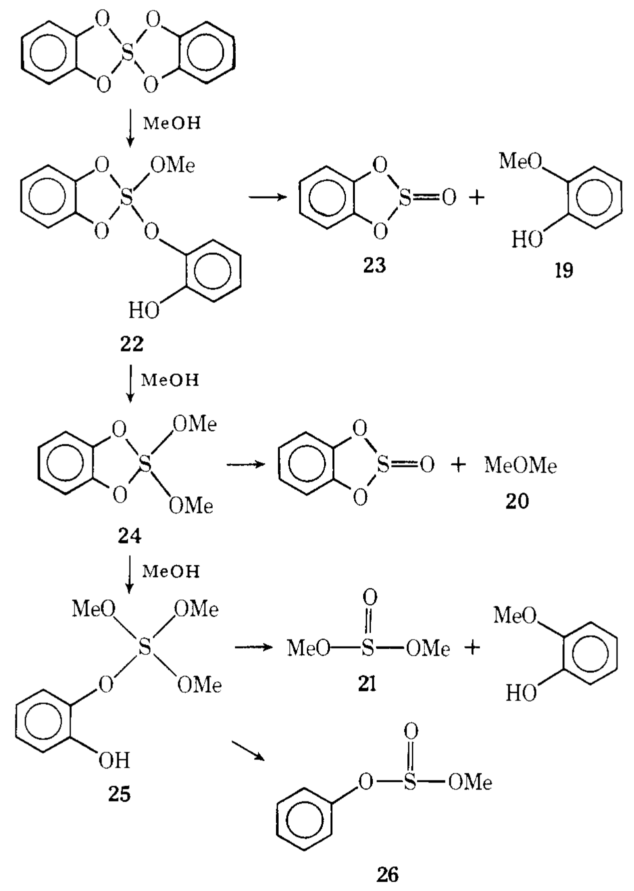


18

It is interesting to contrast the reaction of **1** with borneol and isoborneol to that observed by Arhart and Martin for **12**.[6b] The latter authors observed 61% camphene, 17% tricyclene, and 22% bornylene from borneol and a mixture of camphene (59%) and tricyclene (41%) from isoborneol. It is clear that the eliminations in this system caused by the sulfuranes show a strong dependence upon the nature of the sulfurane, but further work is necessary to explain the differences.

The reaction of methanol with sulfurane **1** afforded three methanol-containing products, guaiacol (**19**), dimethyl ether (**20**), and dimethyl sulfite (**21**), in addition to catechol and *o*-phenylene sulfite (**22**). The reaction is complete within seconds at room temperature. Several pathways may be proposed in order to explain formation of ethers and sulfites in this reaction including collapse of any member of a series of sulfurane intermediates; nucleophilic attack by alcohols on sulfonium salt or sulfurane intermediates; or collapse of a sulfurane may occur by a concerted electrocylic reaction with one molecule

Scheme I



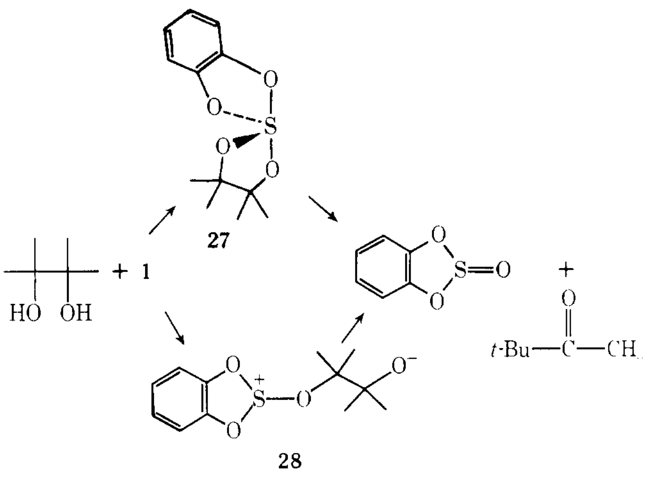
of ether and one molecule of sulfite being formed from a given sulfurane. Since several sulfuranes may be formed, several possibilities for coupled ether and sulfite formation exist (Scheme I).

The degree of ligand exchange into the sulfurane can be partially inferred from the products. In order to account for the observed products via sulfurane intermediates, at least one catechol ligand position must be exchanged for a methanol to form intermediate **23** and consequently allow formation of guaiacol. At least two ligand positions must exchange in order to allow formation of dimethyl ether. Although these exchanges do not necessarily involve one catechol, this formalism has been adopted in Scheme I to simplify it. At least three ligand positions must be exchanged to allow generation of dimethyl sulfite and formation of dimethyl sulfite from sulfurane **24** can be ruled out because the epoxide of catechol would be formed.

Formation of dimethyl ether **19** and dimethyl sulfite **21** could in principle occur partly via path IV from intermediate **26** as well as from **24** and **25.** There is, however, no compelling evidence that requires formation of **26** as a precursor.

An alternative to collapse of a series of sulfurane intermediates as a mechanism of ether formation is a nucleophilic attack of alcohols on a series of sulfonium ion intermediates. Thus, an ether will be formed each time a methoxide anion displaces an oxygen from an aromatic or a methoxyl carbon with a sulfite being generated simultaneously. Rapid exchange of methoxyl groups on the sulfonium ions would have to occur to account for the observed rate; however, exchange of alcohols on sulfonium salts is not a fast reaction. Johnson and Phillips[31] observed only 4.2% exchange in 1 h at 70 °C when dibenzylethoxysulfonium tetrafluoroborate was dissolved in radioactive ethanol. In addition, no evidence for the existence of a stable sulfonium salt form was found in the ^{13}C studies of **1** or **2.**[19]

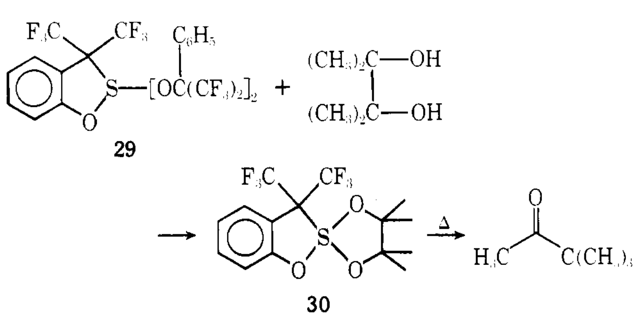
Scheme II



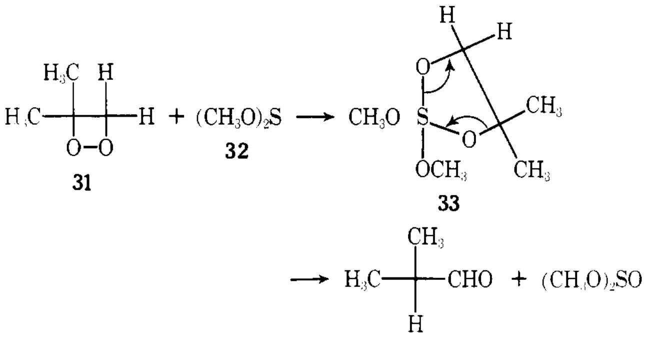
Thus, collapse of a series of sulfurane intermediates, as depicted schematically in Scheme I, is presently favored as a single mechanism, capable of accounting for all the observed results. Formation of dimethyl sulfite by methanolysis of mixed sulfite **26** can be ruled out since this reaction was independently shown to require 3 h at 60 °C to reach approximately 90% completion, whereas the methanol reaction with sulfurane **1** is over within seconds.

A stereochemical requirement for the ether-sulfite formation is suggested by the examination of the disproportionation of intermediate **22.** Since the five-membered ring spans one apical and one equatorial position,[19] guaiacole formation by an electrocyclic mechanism from **22** must involve reaction of one apical and one equatorial ligand.

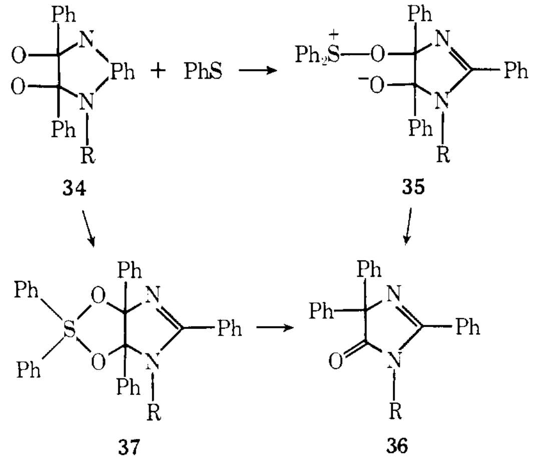
Pinacol and benzopinacol react with sulfurane **1** to produce pinacolone and benzopinacolone. Neither catechol nor *o*-phenylene sulfite catalyzed the rearrangement. The reaction with pinacol, most conveniently followed by NMR spectroscopy, reached completion over 4 h with the single methyl peak of pinacol gradually changing into the two singlets of pinacolone. The possibility of intermediacy of tetramethylethylene oxide in the rearrangement under discussion was ruled out since it proved to be unreactive under the conditions employed. The mechanism for the transformation (Scheme II) may involve either a sulfurane (**27**) or sulfonium salt (**28**). Although **12** was observed to react with pinacol to form the epoxide,[32a] the sulfurane **29** was reported to react with pinacol to form a new sulfurane, **30**, which decomposed at high temperature to provide pinacolone.[32b] Thus there is in this case also a structurally dependent diversity in the reactions of sulfuranes with alcohols.



In a reaction analogous to that for pinacolone formation, Denney and co-workers observed the formation of sulfurane **32** as an intermediate in the conversion of dioxetane **31** to isobutyraldehyde by sulfoxylate **33.**[33] Finally, it is interesting to note the analogous class of rearrangements encountered by Wasserman and Saito[34] upon addition of diphenyl sulfide to 1,2-dioxetanes. The transformation **34** → **36** bears a remarkable resemblance to the rearrangement of benzopinacol to



benzopinacolone. Zwitterionic intermediate **35**, which contains an alkoxysulfonium moiety, was proposed as the intermediate leading to the rearranged **36**. However, sulfurane **37** as an alternative might also be readily envisaged.



Experimental Section

General. Proton magnetic resonance spectra were recorded on Varian Associates A-60 and HR 220 spectrometers equipped with variable temperature controllers. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane as internal standard. Temperatures in variable-temperature experiments were determined by using a precalibrated curve which relates methanol peak separation to temperature. The methanol sample tube was considered to have reached thermal equilibrium when two successive readings 10 min apart showed no change in peak separation. Vapor phase chromatography was performed on a Varian Aerograph 200 chromatograph. Infrared spectra were recorded on a Perkin-Elmer 521 grating infrared spectrophotometer. Mass spectra were obtained on an Hitachi Perkin-Elmer RMU-6E mass spectrometer with ionizing potential of 70 eV unless otherwise stated. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Chloroform-*d* was dried by passage through a column of neutral alumina. Ether was dried by distillation from lithium aluminum hydride and then stored over sodium. Pyridine was distilled from barium oxide and stored over potassium hydroxide. Sulfur tetrafluoride was purchased from Matheson Gas Products. All other chemicals were obtained from Aldrich Chemical Co. Prepurified nitrogen was passed through Oxisorb (Analabs) to provide simultaneous oxygen scavenging and moisture removal.

Bis(*o*-phenylene)tetraoxysulfurane. Catechol (2.20 g, 0.02 mol) and lithium hydride (0.35 g, 0.044 mol) were mixed at ambient temperature in a 200-mL flask under a constant stream of dry, prepurified nitrogen. After 30 min 100 mL of anhydrous ether was added to the stirred mixture. When effervescence subsided (15-20 min), the reaction flask was surrounded by a dry ice-acetone bath and sulfur tetrafluoride, previously condensed into a calibrated trap and measured volumetrically (0.57 mL, 0.01 mol) at its boiling point, was carried into the reaction flask by the nitrogen stream. The exiting nitrogen stream was passed through a dry ice-acetone condenser, dry ice-acetone trap, and aqueous potassium hydroxide trap to prevent SF_4 escape to the atmosphere. The reaction flask was kept in a dry ice-acetone bath for 4 h, with stirring, after which it was allowed to warm to room temperature. Stirring under a nitrogen stream was continued overnight (16 h) during which time about 20 mL of the ether evaporated. Filtration of inorganic salts under inert atmosphere in a glovebag and crystallization from ether at −78 °C afforded 1.7-2.0 g (70-80%) of bis(*o*-phenylene)tetraoxysulfurane in the form of a colorless powder: mp 175 °C dec; ν_{max} (Nujol) 1478 (s), 1362 (m), 1275 (m), 1258 (s), 1235 (s), 1220 (s), 1094 (m), 812 (s), 740 (s) cm^{-1}; δ_{CDCl_3} (60 MHz) 6.95 (s) ppm.

At 220 MHz a tight AA′BB′ pattern, centered at 6.95 ppm, is observed. The mass spectrum gives a molecular ion at *m/e* 248.017 (calcd, 248.016).

3,3′-Dimethylbis(*o*-phenylene)tetraoxysulfurane was synthesized in 50% yield from sulfur tetrafluoride and 3-methylcatechol by the procedure described above: mp 113-114 °C dec; ν_{max} (CCl_4) 1480 (m), 1460 (s), 1360 (m), 1260 (s), 1245 (s), 1170 (m), 1075 (m), 1025 (m), 950 (m), 850 (m) cm^{-1}; δ_{CDCl_3} (220 MHz) 2.27 (s, 3 H, CH_3), 6.82 (m, 3 H) ppm. The mass spectrum shows a molecular ion at *m/e* 276, ionizing voltage 25 eV.

Bis(*o*,*o*-biphenyl)tetraoxysulfurane was synthesized in 53% yield from sulfur tetrafluoride and *o*,*o*-biphenol by the procedure described above: mp 71-73 °C; ν_{max} (CCl_4) 1500 (m), 1470 (s), 1435 (s), 1250 (s), 1235 (s), 1185 (s), 1090 (s), 900 (m), 875 (s), 860 (s), 825 (s) cm^{-1}. The 220-MHz NMR spectrum shows a symmetrical multiplet (between δ_{CDCl_3} 7.54 and 7.27 ppm) which is centered at approximately 7.40 ppm. The mass spectrum (25 eV) shows a molecular ion at *m/e* 400 (calcd, 400).

3,3′,5,5′-Tetra-*tert*-butylbis(*o*-phenylene)tetraoxysulfurane was synthesized in 46% yield from sulfur tetrafluoride and 3,5-di-*tert*-butylcatechol by the procedure described above: mp 148-150 °C; ν_{max} (CCl_4) 1478 (s), 1410 (s), 1360 (s), 1260 (m), 1225 (m), 990 (m), 970 (s), 855 (m), 835 (s) cm^{-1}; δ_{CDCl_3} (220 MHz) 1.25 (s, 36 H), 6.89 (s, 4 H) ppm. Unreacted dilithium salt of 3,5-di-*tert*-butylcatechol is observed at 1.07 (s, 9 H) 1.25 (s, 9 H), 6.79 (broad s, 1 H), and 6.93 (broad s, 1 H) ppm. The signal at 1.25 ppm belonging to the sulfurane is not resolved upon cooling the sample down to −60 °C. The mass spectrum shows a molecular ion (25 eV) at *m/e* 536 (calcd, 536).

Reaction of Sulfur Tetrafluoride with the Lithium Salt of Benzyl Alcohol. Benzyl alcohol (4.33 g, 0.04 mol) dissolved in 100 mL of anhydrous ether was added to lithium hydride (0.40 g, 0.044 mol) with stirring, under a constant stream of dried nitrogen. Stirring was continued until no more effervescence of hydrogen was observed, at which time the reaction vessel was cooled to −78 °C and sulfur tetrafluoride, premeasured volumetrically in a calibrated trap (0.57 mL, 1.08 g, 0.01 mol), was distilled into the reaction flask. Stirring at −78 °C was continued for an additional 4 h. The reaction mixture was then allowed to warm to room temperature, with stirring continued overnight (16 h). Solids were filtered under inert atmosphere in a drybox. Ether was evaporated under dry nitrogen. The mixture was dissolved in $CDCl_3$ and analyzed by NMR: δ_{CDCl_3} (60 MHz) 5.01 (AB, J = 11.5 Hz), 4.90 (AB, J = 11.5 Hz) (dibenzyl sulfite, 46%) and 4.50 (s) (dibenzyl ether, 40%), 3.90 (unknown 9%). Using a short-path distillation apparatus, dibenzyl ether was isolated from the product mixture: bp 90 °C (0.1 Torr); δ_{CDCl_3} (60 MHz) 4.50 (s, 2 H) and 7.32 (s, 5 H) ppm.

***o*-Phenylene sulfite** was synthesized by the method of Carius[35] and distilled: bp 40 °C (1.5 Torr); NMR (220 MHz) δ_{CDCl_3} 7.14 ppm (AA′BB′).

***o*-Phenylene sulfate** was synthesized by the reaction of catechol with sulfuryl chloride[35] in 11% yield: mp 35 °C (lit.[36] 34-35 °C); ν_{max} (KBr) 1550, 1480, 1230, 1210, 750, and 680 cm^{-1}; NMR (220 MHz) δ_{CDCl_3} 7.20 ppm.

3-Methyl-*o*-phenylene sulfite was synthesized using the general method of Carius.[35]

To 3-methylcatechol (2.48 g, 0.02 mol) and pyridine (3.16 g, 0.04 mol) in 40 mL of anhydrous ether was added 2.50 g (0.021 mol) of thionyl chloride dissolved in 20 mL of anhydrous ether dropwise over a period of 30 min, with stirring and exclusion of moisture. After the mixture was stirred for an additional 2 h, solid pyridinium hydrochloride was filtered out under a dry atmosphere, ether was distilled off, and the residue was distilled under reduced pressure, using a short-path distillation apparatus. The 3-methyl-*o*-phenylene sulfite was collected at 51 °C (0.3 Torr): δ_{CDCl_3} (220 MHz) 2.33 (s, 3 H) 6.99 (m, 3 H) ppm; ν_{max} (neat) 1460 (s), 1322 (m), 1230 (s), 1170 (m), 1072 (m), 1032 (m), 950 (m), 840 (s), 760 (s) cm^{-1}. The mass spectrum shows a molecular ion at *m/e* 170.

Anal. Calcd for $C_7H_6O_3S$: C, 49.40; H, 3.55; S, 18.84. Found: C, 49.32; H, 3.44; S, 18.78.

Dibenzyl sulfite was synthesized in 78% yield from thionyl chloride and benzyl alcohol (dried by distillation from calcium oxide) by the procedure described above: bp 147–149 °C (0.25 Torr); ν_{max} (neat) 1495 (m), 1450 (m), 1260 (s), 945 (s), 900 (s), 835 (m) cm^{-1}; δ_{CDCl_3} (60 MHz) 5.01 (AB, J = 11.5 Hz), 4.90 (AB, J = 11.5 Hz). The mass spectrum showed a molecular ion at m/e 262.

Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38; S, 12.22. Found: C, 64.37; H, 5.17; S, 11.98.

Dehydration Procedure and Product Analysis. The dehydration reactions with bis-*o*-phenylenetetraoxysulfurane were carried out in an NMR tube. In general, a known amount of sulfurane was dissolved in approximately 0.5 mL of dry $CDCl_3$, and added to a known amount of the alcohol at room temperature, under a nitrogen atmosphere in a drybox. The yields were determined by NMR using the aromatic protons as an internal standard. All NMR peaks outside the aromatic proton region were identified by 60- and 220-MHz NMR using authentic samples to enhance the product peaks. In cases where NMR was used to identify the products, integration accounted for 100 ± 5% of materials present.

Reaction of Sulfurane 1 with Cyclohexanol. An excess of sulfurane **1** (ca. 0.50 mmol) dissolved in 0.5 mL of $CDCl_3$ was added to cyclohexanol (0.043 g, 0.427 mmol) in an NMR tube under inert atmosphere. The tube was shaken vigorously and the NMR spectrum was taken. Cyclohexene was formed within minutes.

Reaction of Excess Sulfurane 1 with 3-Methylcyclohexanol. Sulfurane **1** (ca. 0.57 mmol dissolved in 2.5 mL of $CDCl_3$) was added to ca. 0.55 mmol of 3-methylcyclohexanol. The composition of the alcohol was shown by integration of the NMR peaks at 3.48 and 4.20 ppm to be 78% cis and 22% trans. The reaction gave 50% of 3-methylcyclohexene (2-peak multiplet at 5.63 ppm, C=CH) and 50% of 4-methylcyclohexene (broad singlet at 5.69 ppm, C=CH) by NMR integration. A control reaction with *o*-phenylene sulfite in place of sulfurane did not yield cyclohexenes within 24 h. Reaction conditions did not isomerize 1-, 3-, and 4-methylcyclohexene.

Reaction of Sulfurane 1 with 4-*tert*-butylcyclohexanol. Sulfurane **1** (0.176 g, 1.63 mmol) with 4-*tert*-butylcyclohexanol (0.332 g, 2.13 mmol) (68% trans, 32% cis, as determined by NMR) was allowed to react for 1 h at room temperature. A 220-MHz NMR spectrum indicated 4-*tert*-butylcyclohexene (32%), *o*-hydroxyphenyl-*trans*-4-*tert*-butylcyclohexyl sulfite (58%), and *o*-hydroxyphenyl-*cis*-4-*tert*-butylcyclohexyl sulfite (13%) based upon unreacted alcohol. The unreacted alcohol was present in a 70:30 trans:cis ratio.

In a preparative reaction, sulfurane **1** (2.00 g, 8 mmol) in 25 mL of anhydrous ether was added with stirring at room temperature to 4-*tert*-butylcyclohexanol (1.65 g, 10 mmol) and the reaction mixture was stirred for 3 h. The reaction mixture was then washed with 3 × 25 mL of 10% aqueous sodium bicarbonate and 3 × 25 mL of water, dried over magnesium sulfate, and concentrated under vacuum. The residual brown oil was distilled under reduced pressure providing 0.4 g (38%) of 4-*tert*-butylcyclohexene, bp 28–29 °C (1.5 Torr).

Reaction of *o*-Phenylene Sulfite with 4-*tert*-Butylcyclohexanol. *o*-Phenylene sulfite (0.5248 g, 3.36 mmol) was added to 4-*tert*-butylcyclohexanol (0.1560 g, 1.0 mmol, 32:68 ratio of cis:trans) with vigorous mixing. A 60-MHz NMR spectrum ($CDCl_3$) taken after 30 min shows the disappearance of starting alcohol (cis and trans isomer peaks at 4.02 and 3.50 ppm, respectively) and the appearance of new peaks at 5.21 (multiplet, *o*-hydroxyphenyl-*cis*-4-*tert*-butylcyclohexyl sulfite) and 4.82 ppm (multiplet, *o*-hydroxyphenyl-*trans*-4-*tert*-butylcyclohexyl sulfite). The ratio of cis:trans sulfite was 31:69. No change in the NMR spectrum was observed after the reaction was allowed to proceed for an additional 24 h. No 4-*tert*-butylcyclohexene was observed to form.

Reaction of Sulfurane 1 with Methanol. Methanol (0.079 g, 2.47 mmol) dissolved in 0.5 mL of $CDCl_3$ was added in one portion to sulfurane **1** (0.1300 g, 0.424 mmol) in an NMR tube. The tube was shaken vigorously to effect solution, and the NMR spectrum was taken within 5 min. The methyl region of the NMR spectrum showed four peaks at 3.31, 3.45, 3.60, and 3.83 ppm. Addition of a second portion of sulfurane **1** (0.098 g, 0.355 mmol) resulted in the disappearance of the 3.45-ppm peak (methanol) which reappeared immediately upon addition of methanol. Slight warming (40–50 °C) for short periods of time (3–5 min at a time) resulted in the evolution of a colorless gas with simultaneous decrease in the intensity of the peak at 3.31 ppm. The intensity of this peak was increased upon addition of dimethyl ether. Heating the solution at 65 °C for 3 h resulted in a change of the relative intensities of the peaks at 3.83 and 3.60 ppm. Addition of dimethyl sulfite to the solution caused the increase in the intensity of the peak at 3.60 ppm, and addition of guaiacol increased the intensity of the peak at 3.83 ppm. TLC (Baker-flex silica gel 1B-F) with ethyl acetate-cyclohexane (1:9), on a separate batch prepared similarly, revealed a spot that has the same R_f (0.37) as guaiacol. Reextraction of this spot into ether, evaporation of the ether, and injection of the liquid into a gas chromatograph ($^1/_4$ in. × 2 ft OV -17, 10% Chromosorb P 60/80) gave a peak with the same retention time and molecular weight (mass spectrum) as guaiacol.

Yields were calculated from a second experiment employing equimolar quantities of sulfurane and methanol. The product ratios observed were dimethyl ether: dimethyl sulfite:guaiacol 52:39:30.

Reaction of Benzopinacol with Sulfurane 1. Sulfurane **1** (1.450 g, 5.85 mmol) in 25 mL of anhydrous ether was added to benzopinacol (0.430 g, 123 mmol) and the reaction solution was stirred at room temperature for 24 h after which the ether was evaporated, and the residue (1.90 g) was chromatographed on 60 g of silica gel 60 (finer than 230 mesh, Brinkmann) using the dry column technique. Elution with hexane–ethyl acetate (9:1) gave 0.35 g of benzopinacolone (82%), mp 180–181 °C. The IR spectrum is identical with that of authentic benzopinacolone. The control reaction with *o*-phenylene sulfite in place of sulfurane **1** did not yield a carbonyl-containing compound within 24 h.

Reaction of Sulfurane 1 with Pinacol. Sulfurane **1** (0.0658 g, 0.668 mmol) dissolved in 0.5 mL of $CDCl_3$ was added to pinacol (0.0390 g, 0.333 mmol) in an NMR tube. The reaction was followed by NMR and the only product formed was pinacolone. The reaction was not affected by either catechol or *o*-phenylene sulfite.

Reaction of Sulfurane 1 with Isoborneol. Sulfurane **1** (0.1480 g, 0.597 mmol) was added at room temperature to isoborneol (0.0460 g, 0.298 mmol) under inert atmosphere. Products were identified by comparison to 220-MHz spectra of authentic samples, and assayed by integration. The reaction, which was complete within 30 min, gave 9% tricyclene and 91% camphene. Camphene: NMR ($CDCl_3$) 1.02 and 1.04 (s, 6 H, $C(CH_3)_2$), 1.89 (m, 1 H, $CHC(CH_3)_2$), 2.66 (m, 1 H, CHC=C), and 4.50 and 4.72 (two s, 2 H, $C{=}CH_2$) ppm. Tricyclene: NMR ($CDCl_3$) 0.82 (s, 6 H, $C(CH_3)_2$) and 1.02 (s, 3 H, bridgehead CH_3) ppm. No bornylene was detected. The control reaction with *o*-phenylene sulfite in place of sulfurane **1** did not yield dehydration products.

Reaction of Sulfurane 1 with Borneol. Excess sulfurane **1** (0.1670 g, 0.673 mmol) dissolved in $CDCl_3$ was added to borneol (0.0520 g, 0.336 mmol). The reaction was slow, requiring >20 h for completion. The only observed product was camphene. No tricyclene or bornylene could be observed.

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Solvation as the Cause for Slower Rates of Cyanide and Thiol Anion Catalyzed Proton Abstraction from Carbon Compared to Oxy Anions of the Same Basicity

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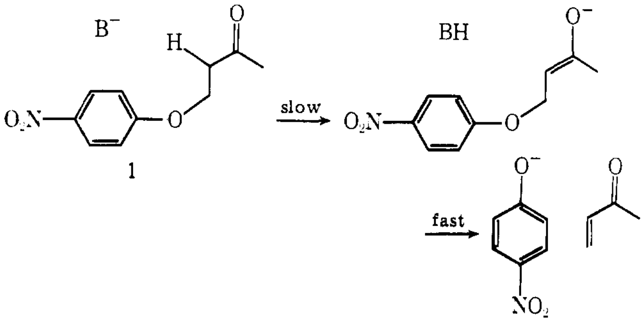
Abstract: Rate constants have been measured for the elimination of 4-nitrophenol from **1** at 25°C in aqueous solution with μ = 1.0 using cyanide ion and thiol anions (pK_a range 2.68–10.35) as catalysts. The Brønsted plot for the rate-determining proton transfer from carbon has a value of 0.59 and shows that thiol anions are much slower than moderately basic oxy anions of equivalent pK_a. Thus, even though the equilibrium constants for proton abstraction from carbon are equivalent for $HOCH_2CH_2S^-$ and phenoxide ion, the rate constant for phenoxide is approximately 30 times greater. The cyanide ion catalyzed proton abstraction, an unusual example of proton transfer between carbon atoms, exhibits a rate constant that fits on the thiol anion Brønsted line rather than the oxy anion line. These results are consistent with a previously proposed explanation for the curvature of the oxy anion Brønsted plot. The solvation effect which enhances the rate of oxy anion catalyzed proton abstraction is predicted to be absent for thiol anions and cyanide ion and is therefore consistent with the results of this study.

Introduction

The compound 4-(4-nitrophenoxy)-2-butanone (**1**) exhibits general base catalyzed decomposition in aqueous solution to yield *p*-nitrophenol and methyl vinyl ketone.[1] The reaction involves rate-determining proton abstraction from carbon with no E2 component and **1** is therefore a very convenient substrate for the spectrophotometric study of the enolization process. It has been previously demonstrated that the Brønsted plot for the reaction of a wide variety of oxy anion catalysts with **1** is curved, as shown in Figure 1.



We suggested that this rapid change in slope was not due to a "Hammond postulate" type of change in transition state structure in which the β value can be directly translated into the degree of bond formation in the transition state. Rather, it was argued that an effect due to solvation was responsible for the observed behavior. As shown in Figure 2, the energy required for desolvation of an oxy anion increases with increasing basicity and tends to make the transition state more solvated. Opposing this tendency is the fact that the solvent molecules would then be left in an entropically unfavorable position. This solvation effect increases the rate of proton abstraction for moderately basic oxy anions from carbon because the favorable stabilization of the partial negative charge in the transition state is not completely offset by the unfavorable effect of leaving the solvent molecules in position.[1]

If this interpretation is correct, then it should be possible to predict the behavior of bases of the same charge type but having different solvation properties. Thiol anions are less well solvated than correspondingly basic oxy anions[2] and thiols hydrogen bond much less readily than do oxygen analogues.[3] Therefore, as is shown in Figure 2, the desolvated corner of the energy diagram is lower for thiols than for comparably basic oxy anions whereas the solvated corner is higher. It seemed reasonable to expect, therefore, that thiol anions would be slower than correspondingly basic oxy anions in abstracting a proton from carbon and that the dramatic curvature observed in the Brønsted plot for oxy anions would not be present for thiol anions.

Only limited data exist for the rates of proton abstraction from carbon by thiol anions. The rates of proton abstraction from acetylacetone by several thiol anions having a pK_a range of less than two units have been reported.[4] These data suggest that thiol anions are less effective than oxy anions of the same

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