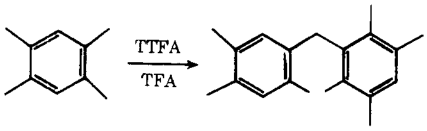
electrophile with the aromatic substrate; and (c) oxidative aromatization of the intermediate thus produced by TTFA. Formation of arene radical cations in the reactions of certain alkyl benzenes with TTFA in TFA has been demonstrated by Elson and Kochi,[18] while formation of small amounts of biaryls during electrophilic aromatic thallation using TTFA and other thallium(III) salts has been noted on several occasions.[19] Moreover, treatment of durene with TTFA in TFA gives the heptamethyldiphenylmethane 7 (~15% yield), which is also one of the products formed by electrochemical oxidation of durene, a process known to proceed via the radical cation.[20] An important consequence of the radical cation mechanism is that the oxidation potential of an aromatic substrate should be one of the major factors governing the particular reaction course which will be followed when that aromatic substrate is treated with TTFA, i.e., electrophilic aromatic thallation or oxidative coupling. Studies to establish this point and to define more rigorously the scope and limitations of this new biaryl synthesis are currently in progress.



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(12) Conversion data are based on the amount of starting material which is recovered, while yield data are based on the amount of starting material which is consumed. Starting material was recovered from all but three of the reactions; in the other cases use of excess TTFA did result in complete oxidation of the starting materials but led to substantially lower yields of biaryls. This is due to competitive reactions in which the starting material and product are oxidized by TTFA to highly colored, polymeric materials.
(13) The following procedure for the preparation of 2,2′-dibromo-4,4′,5,5′-tetramethoxybiphenyl illustrates the general experimental method. 4-Bromoveratrole (4.34 g, 0.02 mol) was added in one portion to a solution of TTFA (5.50 g, 0.01 mol) in TFA (25 ml) at room temperature. The solution immediately turned deep red in color and became warm, and a colorless solid precipitated within a few minutes. The mixture was stirred for 10 min then poured into water and the resulting mixture extracted with chloroform. The chloroform solution was passed through a short column of basic alumina using petroleum ether (bp 40–60 °C)/chloroform (1:1) as eluent to remove highly colored polymeric materials. Evaporation of the eluent under reduced pressure followed by crystallization of the residual solid thus obtained from petroleum ether (bp 100–120 °C)/toluene gave 3.48 g of pure 2,2′-dibromo-4,4′,5,5′-tetramethoxybiphenyl as colorless needles, mp 159–160 °C [lit..mp 160 °C: W. Baker, J. W. Barton, J. F. W. McOmie, R. J. Penneck, and M. L. Watts, *J. Chem. Soc.*, 3986 (1961)]. Concentration of the mother liquors gave 0.35 g (8% recovery) of 4-bromoveratrole. The yield of biaryl based on 92% conversion of the starting material is 88%.
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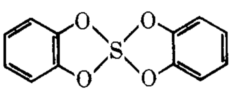
Sulfuranes. The Use of Tetraoxysulfuranes in the Formation of Olefins and Ethers from Alcohols

Summary: Phenylene orthosulfite synthesized from SF_4 and the dilithium salt of catechol reacts with alcohols to form olefins probably by means of a cyclic elimination route.

Sir: Interest in alkoxysulfuranes has been stimulated by reports of their utility as dehydrating reagents.[1-6] The dialkoxysulfurane $[C_6H_5C(CF_3)_2O]_2S(C_6H_5)_2$ reacts with primary alcohols to form unsymmetrical ethers of the type $C_6H_5C(CF_3)_2OR$ and with secondary alcohols to form olefins preferentially by trans coplanar elimination.[1]

We report results indicating that considerable control over the stereochemistry of elimination and the products formed from primary alcohols may be possible by a judicious choice of the sulfurane reagent.

Tetraoxysulfurane 1 reacts rapidly with cyclohexanol in $CDCl_3$ solution at room temperature to provide cyclohexene.



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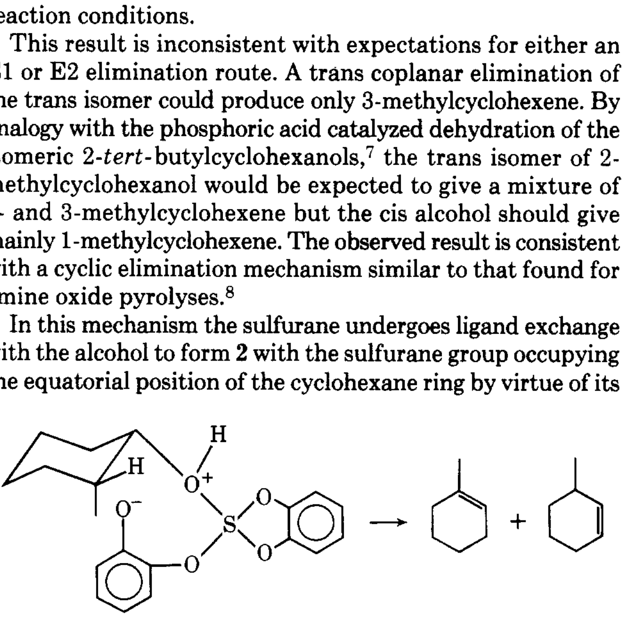
Both the cis and trans isomers of 2-methylcyclohexanol provide a 1:1 mixture of 1-methyl- and 3-methylcyclohexene together with *o*-phenylene sulfite. The sulfite is incapable of effecting the dehydration, and the olefins are stable under the reaction conditions.

This result is inconsistent with expectations for either an E1 or E2 elimination route. A trans coplanar elimination of the trans isomer could produce only 3-methylcyclohexene. By analogy with the phosphoric acid catalyzed dehydration of the isomeric 2-*tert*-butylcyclohexanols,[7] the trans isomer of 2-methylcyclohexanol would be expected to give a mixture of 1- and 3-methylcyclohexene but the cis alcohol should give mainly 1-methylcyclohexene. The observed result is consistent with a cyclic elimination mechanism similar to that found for amine oxide pyrolyses.[8]

In this mechanism the sulfurane undergoes ligand exchange with the alcohol to form 2 with the sulfurane group occupying the equatorial position of the cyclohexane ring by virtue of its



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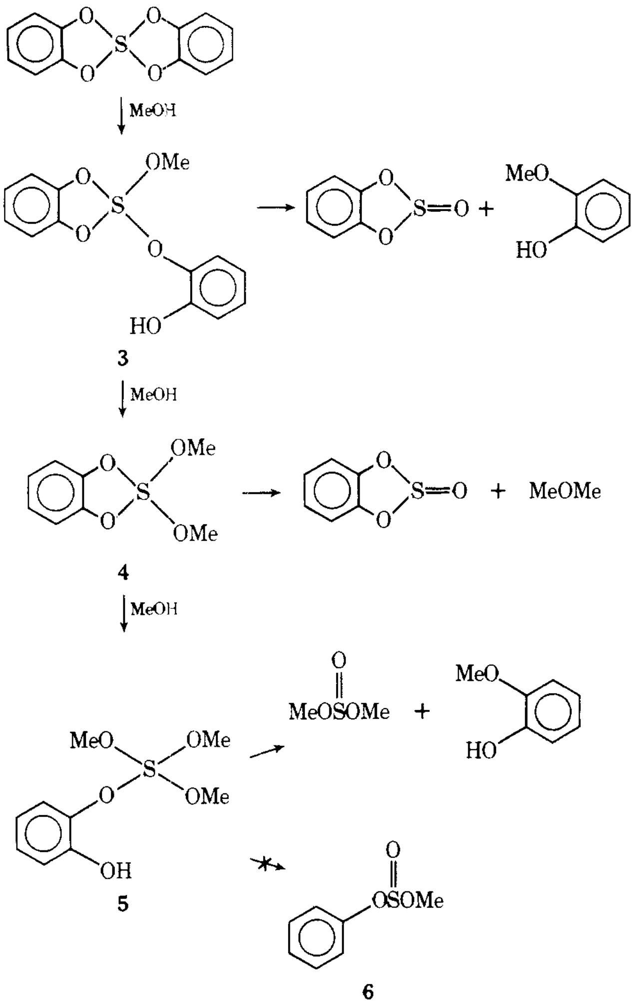
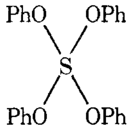
bulk. Elimination then proceeds by a cyclic process initiated by the phenolic oxygen.

Scheme I



The reaction of tetraoxysulfurane 1 with methanol provided a set of products (Scheme I), explicable by internal coupling reactions of sulfuranes generated by successive ligand exchange. Thus methanol reacts with an equimolar quantity of sulfurane 1 in $CDCl_3$ solution within seconds at room temperature to form guaiacol, dimethyl ether, and dimethyl sulfite in a 30:26:20 ratio in addition to *o*-phenylene sulfite and the normal sulfurane hydrolysis product, catechol. A possible sequence is presented in Scheme I for ether formation but others including methanol and catechol attack on intermediate sulfuranes or sulfonium salts are not presently excluded by our data. Mixed sulfite **6** was not observed, and it cannot be a precursor of dimethyl sulfite by methanol attack because this reaction was shown independently to require 3 h at 60 °C to reach 90% completion. The inclusion of **3**, **4**, and **5** in the ligand coupling scheme is necessary because the ratio of guaiacol to dimethyl sulfite is significantly different from unity which it would be if ligand combination of **3** were excluded. Although we have no compelling evidence, it is possible that tetramethoxysulfurane is also an intermediate. Under similar conditions, Arhart and Martin[3] observed only a mixed ether from the reaction of methanol with their dialkoxydiphenylsulfurane. Thus, it appears that tetraoxysulfuranes have lifetimes commensurate with more extensive ligand exchange than do the dioxysulfuranes. Tetraoxysulfurane 1 is formed by addition of a premeasured quantity of sulfur tetrafluoride to the lithium salt of catechol in scrupulously dry ether at $-78\ ^\circ C$ 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 glove bag filled with dry, oxygen-free nitrogen and the sulfurane is isolated by crystallization at $-78\ ^\circ C$. The method is of general utility and we have also obtained sulfuranes **7–10** in good yield.[9] All the sulfuranes are exceptionally sensitive to moisture, decomposing to sulfite and the phenol. However, all are stable for several days at room temperature in the absence of moisture, and at $-5\ ^\circ C$ they have half-lives of several weeks.



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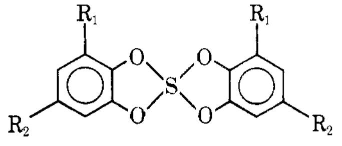
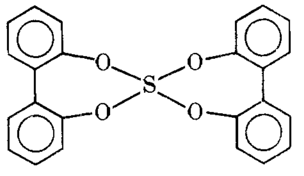


1, $R_1 = R_2 = H$
8, $R_1 = Me$; $R_2 = H$
9, $R_1 = R_2 = t$-Bu



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Sulfurane 1 shows a molecular ion at m/e 248.017 (calcd 248.016). The NMR spectrum at 220 MHz in $CDCl_3$ consists of a tight AA′BB′ pattern, 6.95 ppm downfield from TMS, downfield of the AA′BB′ pattern for catechol at 6.82 ppm but upfield of the singlet at 7.20 ppm for phenylene sulfate, and the tight AA′BB′ pattern at 7.14 ppm for phenylene sulfite, respectively. At 60 MHz the sulfurane pattern is a sharp singlet. The 220-MHz NMR pattern is inconsistent with all alternative covalent nontetracoordinate sulfur compounds of the same molecular weight, and the position of the resonances relative to those of sulfite and sulfate suggests that the sulfur atom is less effective at electron withdrawal, as expected. Structures of the analogous sulfuranes **7–10** were assigned on the basis of the m/e of the molecular ion and the NMR spectra.

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