Table II. Secondary Deuterium Isotope Effects[a] in the Ene Reaction of 3-Phenylpropene and Diethyl Mesoxalate (1) at 180 ± 0.05 °C

position of deuteration in 3-phenylpropene	f[b]	R_{A_f}[b]	R_{A_0}[b]	$[(k_H/k_D)\alpha]/D$	av $(k_H/k_D)\alpha$
C_2 (1 D)	0.837	2.3521		0.951	0.957 ± 0.006
C_2 (2 D)	0.829	2.3557		0.964	
C_1 (2 D)	0.852	1.2237		$(0.9017)^{1/2} = 0.950$	0.950 ± 0.001
C_1 (2 D)	0.897	1.2100	(0.9050)	$(0.9050)^{1/2} = 0.951$	
C_2 (1 D)	0.00		2.3099		
C_1 (2 D)	0.00		1.1818		

[a] Kinetic procedure: The respective mono- and dideuterated allylbenzenes[17] were added together with protioallylbenzene to obtain a ca. 50:50 mixture. A Pyrex reaction tube was charged with this mixture and the equivalent amount of diethyl mesoxalate and solvent as described in the procedure of Table I. After sealing of the tubes and immersion in the thermostat, an appropriate interval of reaction time was allowed (as previously determined) to effect the desired degree of completion. The vials were then rapidly cooled and opened. The contents were poured into water and extracted with pentane. The neutral extracts were combined, dried over $MgSO_4$, and carefully concentrated. The residue was checked on a precision GLC instrument for degree of conversion relative to an internal standard. The remainder of the solution was preparative gas chromatographed on a 0.25 in. × 4 ft, 10% SE-30 column, condensing the allylbenzene fraction in a dry capillary at −78 °C. Analysis of the appropriate mass ratios was performed by the MS technique previously described,[10] using the required correction factors also discussed in these references. [b] Computations: The values of k_H/k_D were calculated with the aid of the equation, $1/(k_H/k_D) = \{[\ln (R_{A_f}/R_{A_0})]/[\ln [(1-f)(1+R_{A_0})/(1+R_{A_f})] + 1\}$, where R_{A_0} is the ratio of heavy to light isotope MW at $t = 0$ and R_{A_f} is the heavy to light ratio after an f fraction of reaction is completed.

plex of the ene and enophile was formed in low concentrations prior to the rate-determining H transfer, a situation which is still in accord with the kinetics. To probe for the intervention of a CT complex along the pathway to product, rather than some rapidly reversible, colored, side-reaction product (as could be the case in the carbonyl cyanide ene reaction[14] cited[5] above), we devised a secondary D isotope effect test. The results listed in Table II show that inverse secondary D isotope effects of almost identical magnitude exist at both ends of the double bond. They comprise the most definitive evidence for a symmetrically structured intermediate lying close to the major TS of this ene reaction.

Furthermore, in previously studied cases of an allylic H-abstraction TS, where a bridged radical complex has been implicated,[17] as well as in a variety of bridged intermediates shown to be formed in the course of addition reactions of the double bond,[18] the inverse secondary D isotope effects are found to be different at both ends of the double bond. This has been interpreted[18] as descriptive of the dissymmetry of the three-membered-ring, π-type complex. By contrast a (2 + 2) cyclic complex possessing a symmetrical interaction structure might be deduced here from the very symmetry of the inverse secondary isotope effect results.

A second feature of the highly electrophilic heteroenophile that greatly beneficiates this ene reaction process stems from the presence of an n electron pair. The participation of such properly oriented, unshared electrons of a member atom of the complex is what brings about the angular H abstraction in the course of exchanging roles with a bonding electron pair in the pseudopericyclic[19] TS. A fruitful analogy is to the superenophilic reagents ArN=S=X (for example, where Ar = tosyl and X = O) of Kresze and co-workers.[20] Evidence has been presented to support the proposal that a super-ene reaction involves a bent TS of nonlinear H transfer arising from a four-membered complex of the reactants in which the unshared pair on nitrogen becomes the agent of H abstraction in the "pseudopericyclic" process.[21] A somewhat analogous picture of the course of the ene reaction between mesoxalic esters and allylic olefins, illustrated in Figure 2, is regarded as completely in accord with the results being reported here.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-79 11110. We also acknowledge with gratitude valuable discussions and suggestions received from Professor G. Kresze and Dr. H. Munsterer of the Org. Chem. Institute of the Technical University of Munich during the tenure of an Alexander von Humboldt Senior U.S. Scientist Award to one of us (H.K.).

Registry No. Diethyl mesoxalate, 609-09-6; allylbenzene, 300-57-2; deuterium, 7782-39-0.

(17) See 16a as well as Kwart, H.; Brechbiel, M. W.; Miles, W.; Kwart, L. D., submitted for publication.
(18) Wilkens, C. L.; Regulski, T. W. *J. Am. Chem. Soc.* **1972**, *94*, 6016 and other references cited therein.
(19) (a) Ross, J. A.; Seiders, R. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 4325. (b) Bushweller, C. H.; Ross, J. A.; Lemal, D. M. *Ibid.* **1977**, *99*, 629. For further examples see ref 16 and 21.
(20) Bussas, R.; Kresze, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 732, 737 and references cited therein.
(21) Munsterer, H.; Kresze, G.; Brechbiel, M. W.; Kwart, H. *J. Org. Chem.*, **1982**, *47*, 2677.

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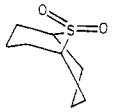
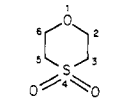
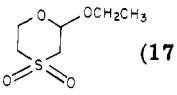
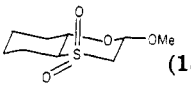
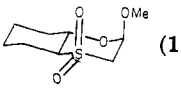
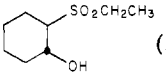
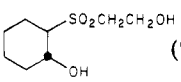
Sulfur-33 Nuclear Magnetic Resonance Spectroscopy of Simple Sulfones. Alkyl-Substituent-Induced Chemical Shift Effects

Summary: The ^{33}S NMR chemical shifts of a series of symmetrical dialkyl and diaryl sulfones as well as some cyclic sulfones have been measured and the magnitude of the β-methyl substituent effect has been determined. The ^{33}S nuclei of diaryl sulfones are more shielded than the dialkyl sulfones and diastereoisomeric sulfones are distinguishable.

0022-3263/82/1947-3355$01.25/0

Table I. ^{33}S NMR Chemical Shifts and Signal Widths ($W_{1/2}$) for Simple Alkyl and Aryl Sulfones[a]

sulfone	$\delta_{^{33}S}$ (±1 ppm)	$W_{1/2}$, Hz
$CH_3SO_2CH_3$ (1)	320 (332,[b] 321[c])	~50 (275,[b] 50[c])
$CH_3CH_2SO_2CH_2CH_3$ (2)	334	70
$(CH_3)_2CHSO_2CH(CH_3)_2$ (3)	351	160
$(CH_3)_3CSO_2C(CH_3)_3$ (4)	366	160
$CH_3CH_2CH_2SO_2CH_2CH_2CH_3$ (5)	333 (335)[c]	180 (130)[c]
$CH_3(CH_2)_3SO_2(CH_2)_3CH_3$ (6)	336	180
$C_6H_5SO_2C_6H_5$ (7)	312 (305)[c]	120 (130)[c]
$(p\text{-}CH_3C_6H_4)_2SO_2$ (8)	311	140
$(p\text{-}HOC_6H_4)_2SO_2$ (9)	313	
$(C_6H_5CH_2)_2SO_2$ (10)	330	120
 (12)	322	50
 (13)	370 (370)[c]	50 (50)[c]
 (14)	361 (360)[c]	50 (50)[c]
 (15)	325	190
 (16[d])	315	100
 (17)	315	100
 (18α)	323	200
 (18β)	313	200
 (19)	340 ($CHCl_3$, 4.64)[e]	320
	340 ($(CH_3)_2C{=}O$, 20.7)[e]	130
	343 (CH_3OH; 32.6)[e]	250
	340 ($(CH_3)_2S{=}O$, 46.6)[e]	600
 (20)	340 ($CHCl_3$, 4.64)[e]	1000
	338 ($(CH_3)_2C{=}O$, 20.7)[e]	150
	337 (CH_3OH, 32.6)[e]	200-250

[a] All ^{33}S NMR spectra were obtained on the Bruker WM-250 NMR spectrometer at 19.196 MHz (ca. 22-25 °C) as 20-45 w/w % chloroform solutions (unless otherwise indicated), using carbon disulfide as external reference. [b] Trifluoroacetic acid solvent. [c] Dimethyl sulfoxide solvent. See Faure, R.; Vincent, E. J.; Ruiz, J. M.; Lena, L. *Org. Magn. Reson.* 1981, *15*, 401-403. [d] ^{33}S shift data was obtained at +50 °C. [e] Dielectric constants.

Sir: Our interest in developing an analytical NMR technique for rapid and accurate analyses of sulfur in organosulfur constituents of coal and petroleum extracts (e.g., condensed thiophenes,[1] alkyl- and aryl sulfides,[2,3] disulfides,[4] etc.) has led to a ^{33}S NMR spectral investigation of a series of simple sulfones. The ^{33}S isotope has a spin I of 3/2 and a natural abundance of 0.76%. The ^{33}S nucleus also possesses an electric quadrupole moment and the electric field gradients at the nucleus lead to short relaxation times, thus affording broad resonance lines and low resolution. However, short relaxation times allow for rapid pulse repetition in FT experiments and this improves substantially the signal-to-noise (S/N) ratio.[5]

The widths of the ^{33}S signals in sulfides may vary from 0.5 to 9 kHz and preclude accurate measurement of chemical shifts resulting from structural and electronic effects within classes of sulfides (e.g., aryl vs. alkyl). However, the "apparent" *electronic symmetrization* resulting from conversion of a sulfenyl to a sulfonyl group (i.e., $-S- \rightarrow -SO_2-$) serves to reduce the width at half-height ($W_{1/2}$) of the ^{33}S absorption sufficiently to allow useful experimental distinction between similar ^{33}S nuclei.

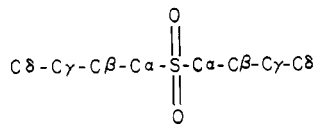
Two reports have appeared which present ^{33}S NMR shifts for a very limited number of organosulfur compounds.[7,8] Here, we report our preliminary findings on the potential significance of substituent-induced chemical shift (SCS) effect and the utility of ^{33}S NMR as a useful technique for distinguishing between dialkyl and diaryl sulfones.[9]

The naturally abundant ^{33}S NMR chemical shifts for both cyclic and acyclic aliphatic sulfones reported herein appear in the range of δ 300 to 370 downfield of external carbon disulfide (CS_2; naturally abundant ^{33}S).[9]

In the acyclic, aliphatic sulfones, a systematic, symmetrical replacement of the hydrogens attached to the α-

(1) Paulson, R. F. *Prepr., Div. Fuel Chem., Am. Chem. Soc.* **1975**, *20*, 183-97.
(2) Attar, A.; Dupuis, F. In "Coal Structure"; Advances in Chemistry Series; Gorbaty, M. L., Ouchi, K., Ed.; American Chemical Society: Washington, DC, 1981; Adv. Chem. Ser. No. 192, Chapter 168 pp 239-56.
(3) Attar, A. "Analytical Methods for Coal and Coal Products"; Karr, C., Jr., Ed.; Academic Press: New York, 1979; Vol. 3, Chapter 56, pp 585-624.
(4) Peet, N. J.; Simeon, S. R.; Stott, J. B. *Fuel* **1969**, *48*, 259-65.
(5) Harris, R. K. "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Ed.; Academic Press: New York, 1978; Chapter 1, pp 1-9.
(6) Wehrli, F. W. In "Annual Reports on NMR Spectroscopy"; Mooney, E. F., Ed.; Academic Press: New York, 1979; Vol. 9.
(7) Retcofsky, H. L.; Friedel, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 6579.
(8) Faure, R.; Vincent, E. J.; Ruiz, J. M.; Lena, L. *Org. Magn. Reson.* **1981**, *15*, 401-03.
(9) All of the sulfones employed in this investigation have been prepared by previously reported procedures or are commercially available, and the physical properties (IR, ^1H NMR, melting point, and boiling point) of recrystallized or distilled samples are consistent with those reported for authentic materials. The ^{33}S NMR spectra were obtained as chloroform solutions unless otherwise indicated, using a Bruker WM-250 NMR spectrometer. The ^{33}S NMR spectra were obtained at 19.196 MHz with a spectral width of 50 kHz, an acquisition time of 1.28-10.24 ms, a pulse width of 75 μs (45°), and data points 128-1024 with a 600-μs delay between the pulse and acquisition time to eliminate acoustic ringing. The sample was placed in a 15-mm NMR tube as a solution and occupied a volume approximately 15 mm (o.d.) × 3 cm. The temperature is ambient unless otherwise indicated and the number of transients required for adequate signal presentation ranged from 50 000 to 6 000 000 (8 min to 15 h). Carbon disulfide was employed as external reference (δ = 0.00), and all of the reported signals are downfield of CS_2.

carbons by methyl groups causes a downfield shift of the ^{33}S nucleus. Comparisons of the ^{33}S NMR chemical shifts



for dimethyl sulfone (1; δ 320), diethyl sulfone (2; δ 334), diisopropyl sulfone (3; δ 351), and di-*tert*-butyl sulfone (4; δ 366) illustrate the effect of a Cα-methyl substitution on the ^{33}S chemical shift. This "β methyl effect" (β_{Me} effect) is nearly additive within the limits of our experimental error, averaging 7–8 ppm/Me, and mirrors a trend in the ^{13}C NMR chemical shifts of the carbonyl carbons for an analogous series of dialkyl ketones[10] (with exception of di-*tert*-butyl ketone).[11] The β_{Me} effect on the carbonyl carbon calculated for a series of dialkyl ketones is also deshielding, but the magnitude (~2.0–2.5 ppm/Me) is less than the average β_{Me} effect (~7–8 ppm/Me) for the dialkyl sulfones.[12]

As the alkyl chain increases in length, the ^{33}S chemical shifts are essentially invariant (Table I) indicating that alkyl substitution resulting in chain lengthening beyond the Cβ carbon exerts a minimal influence on the shift of the ^{33}S nucleus. This observation supports the premise that beyond Cβ, the influence of a methylene (or methyl) group on the sulfonyl ^{33}S nucleus is likely to be transferred through the sulfonyl oxygens rather than through the bonds. Thus, steric and electronic perturbations on the ^{33}S nucleus caused by alkyl substituents *outside* the γ anti/gauche conformations involving Cβ and the SO_2 oxygens are not expected to be of major influence.

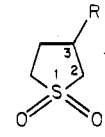
The three diaryl sulfones (7, 8, and 9) examined here have ^{33}S shifts 7–9 ppm to higher field than sulfone 1, perhaps implying that the aryl groups exert a slight shielding effect on the ^{33}S nucleus. While this may be the case, the para substituents (OH and Me) do not reinforce the shielding component as might be anticipated from the magnitude of the Hammett σ (–0.17 and –0.37) and σ^+ (–0.31 and –0.92) values for Me and OH, respectively.[13] When the phenyl groups are isolated from the sulfonyl sulfur by methylene groups [e.g., dibenzyl sulfone (10)], the ^{33}S chemical shift falls in the region for dialkyl sulfones.

The ^{33}S chemical shift of divinyl sulfone (11; in Me_2SO-d_6)[8] is 32 ppm to higher field than that for sulfone 2 in chloroform solvent. While this result might imply substantial (2p–3d)π or (2p–3p)π interactions between the olefinic group and the sulfonyl sulfur to account for the shielding,[8] the ^{17}O NMR chemical shifts for sulfone 2 (δ 140) and sulfone 11 (δ 141 ppm) are not strongly supportive of interactions involving the vinyl group and the S=O bond.[14]

The ^{33}S chemical shifts for the cyclic sulfones extend over a slightly wider shift range (δ 315–370), reflecting both gross structural variations and substitution patterns. For example, the ^{33}S NMR shift for thiane 1,1-dioxide (12) is 48 ppm more shielded than thiolane 1,1-dioxide (13; Table I). However, 3-thiolene 1,1-dioxide (14) is shielded by 9 ppm over the saturated analogue 13. 9-Thiabicyclo-[3.3.1]nonane *S,S*-dioxide (15)[15] exhibits a ^{33}S chemical shift (δ 325) close to that for sulfone 12. The two additional Cβ methylene groups would be expected to deshield the sulfonyl sulfur but having both sulfonyl oxygens γ gauche to the ring methylenes may *shield* the ^{33}S nucleus and effectively diminish the magnitude of the β effect.[16]

The ^{33}S nucleus in 1,4-oxathiane 4,4-dioxide (16) is shielded by 7 ppm compared to thiane sulfone 12. The ring geometries of these two sulfones are quite similar and it is not clear whether small conformational changes are responsible for the shift difference or whether the γ gauche oxygen interacts directly with the sulfonyl sulfur to affect the ^{33}S chemical shift. Substitution of an "equatorial" ethoxy group at C2 (γ anti oxygen) in the 1,4-oxathiane 4,4-dioxide skeleton (i.e., 17) has essentially no effect on the ^{33}S chemical shift. The conformational free energy of the ethoxyl[20] (methoxyl)[21] group in sulfone 17 is approximately 1.3 kcal/mol (tetrachloromethane solvent, 40 °C), favoring the equatorial conformation (i.e., 89% equatorial).

The bicyclic sulfones, α- and β-2-methoxy-*trans*-hexahydrobenzoxathiane 4,4-dioxides (18α, 18β),[21] provide a firm indicator that the ^{33}S chemical shift differences between diastereoisomers are not only discernible but may also be extremely valuable in stereochemical assignments. In this particular case, 18β with the axial OMe group exhibited a ^{33}S chemical shift at δ 313, which is 10 ppm more shielded than the sulfonyl sulfur in 18α (δ 323) with the equatorial OMe group. This shift difference between 18β and 18α can be attributed to electronic and steric interactions between the 1,3-synaxial oxygens. Faure et al.[8] have shown that substitution of a hydrogen at C3 with R (= Me, NH_2, and OH) in 13 where the R group is "nearly" synaxial to one of the sulfonyl oxygens also induces a 5–9-ppm upfield shift of the ^{33}S nucleus relative to the parent thiolane sulfone 13.



When sulfone 1 is dissolved in trifluoroacetic acid (TFA; 9×10^{-2} M), the ^{33}S resonance is shifted downfield by 12 ppm compared to its chemical shift in chloroform solvent. Strong hydrogen bonding by TFA to the sulfonyl oxygens could result in the development of partial positive charge on both the oxygen(s) and sulfur of the sulfonyl group and cause a deshielding effect. The ^{33}S NMR chemical shifts of ethyl *trans*-2-hydroxycyclohexyl sulfone (19) and 2-hydroxyethyl *trans*-2-hydroxycyclohexyl sulfone (20) vary only slightly in solvents of different dielectric constants (ϵ) and hydrogen bonding capabilities. However, with both

(10) The ^{13}C NMR chemical shifts (ppm) for the analogous carbonyl carbons are as follows: $(CH_3)_2C{=}O$, 205.1; $(CH_3CH_2)_2C{=}O$, 209.3; $[(CH_3)_2CH]_2C{=}O$, 215.6; $[(CH_3)_3C]_2C{=}O$, 215.8 (in carbon disulfide solution).[11]

(11) Jackman, L. M.; Kelly, D. P. *J. Chem. Soc. B* **1970**, 102–10.

(12) It is apparent that the ^{33}S nucleus in sulfone 4 and the ^{13}C nucleus in di-*tert*-butyl ketone do not respond in the same manner to quarternization of the α-carbon. This may be more related to the hybridization of the atom in question. For example, the ^{13}C shift of the carbinol carbon of the corresponding secondary alcohols (R_2CHOH) gives a "near" linear downfield shift with increased alkyl branching.[11]

(13) Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323.

(14) Dyer, J. C.; Harris, D. L.; Evans, S. A., Jr. *J. Org. Chem.* **1982**, in press.

(15) We thank our colleagues, Paul J. Kropp and Robert L. McKee of this Department, for samples of sulfone 15 and sulfone 9, respectively.

(16) It has been argued in ^{13}C NMR that in some cases the decreasing β-substituent effects in hydrocarbons can be adequately interpreted in terms of increased synclinal interactions.[17] In light of proposals by Stothers[18] and more recently Gorenstein,[19] the prediction has been made that bond angle widening caused by severe steric perturbations within a molecular fragment (particularly, for conformations involving synclinal interactions) will result in increased shielding of the atom(s) involved.[18,19]

(17) Beierbeck, H.; Saunders, J. K. *Can. J. Chem.* **1975**, *53*, 1307.

(18) Stothers, J. B.; Tann, C. T. *Can. J. Chem.* **1976**, *54*, 917.

(19) Gorenstein, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 2254.

(20) Unpublished results with Robert E. Williams, Jr., The University of North Carolina.

(21) Lee, D.; Keifer, J. C.; Rooney, R. P.; Garner, T. B.; Evans, S. A., Jr. *J. Org. Chem.* **1979**, *44*, 2580.

19 and 20, the $W_{1/2}$ of the ^{33}S absorption responds to changes in the solvent environment. The band width is directly related to the correlation time, which can be factorized into the components: molecular size, solution viscosity, and symmetry.[5] On the basis of the solvent dependence of $W_{1/2}$ for both 19 and 20, it appears that the rotational motions of these sulfones are more restricted in chloroform and dimethyl sulfoxide solvents than in acetone and methanol, which is probably related to the magnitude and degree of intra- and intermolecular hydrogen bonding. Comparisons of the $W_{1/2}$ for sulfones 1–6 illustrates the relationship between molecular size and correlation times for simple dialkyl sulfones.

Acknowledgment is made to the Department of Energy (Contract DE-A505-80ER10641) and the University of North Carolina for support of this research. The Bruker WM-250 NMR spectrometer was purchased from a grant from the National Science Foundation (CHE-79-12130). We are grateful to Dr. Clifford Venier of Iowa State University for his suggestions and valuable input. We are grateful to Professors Robert L. McKee and Paul J. Kropp for homogeneous samples of sulfones.

Registry No. 1, 67-71-0; 2, 597-35-3; 3, 595-50-6; 4, 1886-75-5; 5, 598-03-8; 6, 598-04-9; 7, 127-63-9; 8, 599-66-6; 9, 80-09-1; 10, 620-32-6; 12, 4988-33-4; 13, 126-33-0; 14, 77-79-2; 15, 6522-45-8; 16, 107-61-9; 17, 82338-32-7; 18α, 70332-86-4; 18β, 70355-05-4; 19, 82338-33-8; 20, 82338-34-9; ^{33}S, 14257-58-0.

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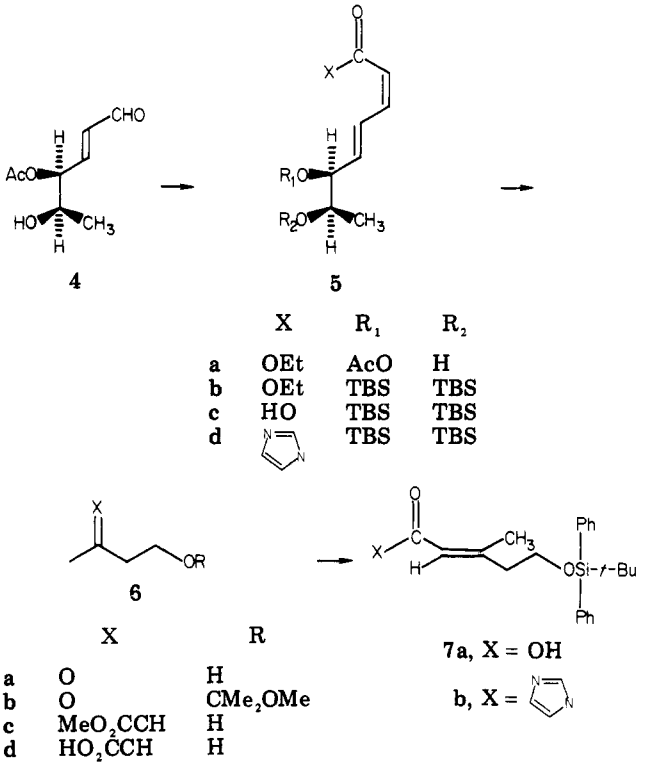
Synthesis of Trichoverrin B and Its Conversion to Verrucarin J

Summary: Anguidine (**3b**) was converted to verrucarol (**3a**), which in turn was selectively acylated to yield trichoverrin B (**2**). Trichoverrin B reacts with pyridinium dichromate in dimethylformamide, via a novel oxidative ring closure, to give verrucarin J (**11a**) in 50% yield.

Sir: Recently the isolation and characterization of the trichothecenes trichoverrins A (**1**) and B (**2**) from *Myrothecium verrucaria* was reported.[1] These compounds contain all the functionality characteristic of the macrocyclic roridins[2] and baccharins[3] except that the macrocyclic ring is broken. We now report the synthesis from verrucarol (**3a**) of trichoverrin B (**2**) and its conversion into verrucarin J (**11a**) via a novel oxidative ring closure. Since the total synthesis of verrucarol (**3a**) has recently been reported,[4] this work constitutes a formal total synthesis of these two trichothecenes. While this work was in progress, other procedures for acylating verrucarol were reported from the laboratories of Still[5] and White;[6] previous work by Tamm[7] in this area must also be noted.

Scheme I



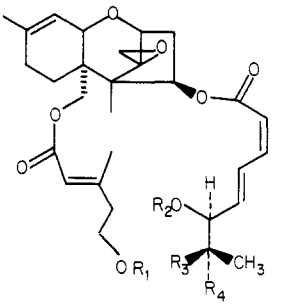
4 5

	X	R_1	R_2
a	OEt	AcO	H
b	OEt	TBS	TBS
c	HO	TBS	TBS
d		TBS	TBS

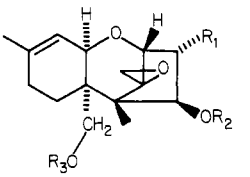
6

	X	R
a	O	H
b	O	CMe_2OMe
c	MeO_2CCH	H
d	HO_2CCH	H

7a, X = OH
b, X =



	R_1	R_2	R_3	R_4
1	H	H	H	OH
2	H	H	OH	H
10	DPS	TBS	TBSO	H



3a, $R_1 = R_2 = R_3 = H$
b, $R_1 = OH$; $R_2 = R_3 = Ac$
c, $R_1 = OC(=S)OPh$; $R_2 = R_3 = Ac$
d, $R_1 = H$; $R_2 = R_3 = Ac$
e, $R_1 = R_2 = H$; $R_3 = Ac$

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