(m, 10 H, ArH); ^{13}C NMR δ 31.1 (C-3), 36.5 (C-3a*), 45.9 (C-4*), 54.4 and 55.3 (CH_3O), 72.4 and 72.6 ($ArCH_2$), 80.9 (C-5*), 82.6 (C-6a*), 82.7 (C-6*), 104.8 ($CH(OMe)_2$), 127.8, 127.95, 127.99, 128.4, 128.5, 137.6, 138.1, 177.7 (COOR lactone); IR (neat) 1755, 1215, 775 cm^{-1}; $[\alpha]^{20}_D = -34.34°$ (c 0.82, $CHCl_3$); GC/CIMS (CH_4) m/z 441 ($M + C_2H_5$)$^+$, 381 ($MH - CH_3OH$)$^+$; HRMS calcd for $C_{24}H_{32}NO_6$ ($M + NH_4$)$^+$ 430.2230, found 430.2233.

[3a*S*-(4*S*,5*R*,6*S*,6a*R*)]-5,6-Diacetoxyhexahydro-4-(dimethoxymethyl)-2*H*-cyclopenta[*β*]furan-2-one (40). A solution of bicyclic compound **22** (33 mg, 0.115 mM) and CSA (12 mg) in MeOH (3 mL) was stirred at 40 °C under argon until all of the starting material and the intermediate lactone **39** had been consumed. Addition of triethylamine and evaporation of the solvents gave the crude diol which was dissolved in EtOAc and treated with (dimethylamino)pyridine (cat.) and Ac_2O (excess) at room temperature. An ice-cooled solution of $NaHCO_3$ was added, and the aqueous phase was extracted with EtOAc. Drying and evaporation of the organic solvent followed by filtration through silica gel afforded lactone **40** (32 mg, 88%) as a colorless oil: ^1H NMR δ 2.04 (s, 3 H, CH_3CO_2R), 2.09 (s, 3 H, CH_3CO_2R), 2.59 (dd, $J_{3,3'}$ = 18.9, $J_{3,3a}$ = 10.9, 1 H, H-3), 2.69 (ddd, $J_{4,3a}$ = 9.6, $J_{4,5}$ = 7.5, $J_{4,H}$ = 5.4, 1 H, H-4), 2.95 (dd, $J_{3',3}$ = 18.9, $J_{3',3a}$ = 4.3, 1 H, H-3'), 3.23 (m, 1 H, H-3a), 3.39 (s, 3 H, CH_3O), 3.41 (s, 3 H, CH_3O), 4.40 (d, $J_{H,4}$ = 5.4, 1 H, $CH(OMe)_2$), 4.79 (dd, $J_{6a,3a}$ = 8.0, $J_{6a,6}$ = 1.9, 1 H H-6a), 5.3-5.4 (m, 2 H, H-5, H-6); ^{13}C NMR δ 20.69, 20.73, 30.2 (CH_2CO_2R), 35.2, 45.7, 55.6 and 55.8 (OCH_3), 72.5, 75.1, 84.0, 104.8 ($CH(OMe)_2$), 169.3 and 169.7 (CH_3CO_2R), 176.4 (CO_2R lactone); IR (neat) 1790, 1750 cm^{-1}; $[\alpha]^{18}_D = -32.0°$ (c 1.5, $CHCl_3$); GC/CIMS (NH_3/CH_4) m/z 334 (($M + NH_4$)$^+$, 100), 317 (MH^+, 2).

Formation of Functionalized Cyclohexanes. Ethyl 6-(Benzoyloxy)-3,4-bis(benzyloxy)-5-hydroxy-2-[2-(1,3-dithianyl)]cyclohex-1-ylacetate (44b). Stock solutions of boron trifluoride etherate (0.07 mL) in dry CH_2Cl_2 (0.93 mL) and 1,3-propanedithiol (0.06 mL) in dry CH_2Cl_2 (0.94 mL) were prepared. To a solution of benzoate **25b** (25.1 mg, 0.0376 mmol) in dry CH_2Cl_2 (1 mL) at -15 °C (ice-salt bath) was added 1,3-propanedithiol stock solution (0.1 mL, 0.05 mmol) and boron-trifluoride etherate stock solution (0.1 mL, 0.05 mmol). The resulting solution was stirred at -15 °C for 1 h; TLC (20% EtOAc-PE) showed the appearance of a spot with higher R_f. Another aliquot (0.1 mL) of each stock solution was added to the reaction mixture, and after an additional 15 min, no change was observed by TLC. The reaction contents were warmed to 0 °C and stirred for 30 min. TLC showed the apparance of a spot with lower R_f. The reaction mixture was diluted with EtOAc (30 mL) and washed in succession with saturated aqueous sodium bicarbonate (25 mL) and brine (25 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. Flash chromatography (10% → 30% EtOAc-PE) of the residue afforded **44a** (14.9 mg, 62%): ^1H NMR δ 1.25 (t, J = 7.1, 3 H, CH_2CH_3), 1.81-1.97 (m, 1 H, $SCH_2CH_2CH_2S$), 2.04-2.16 (m, 1 H, $SCH_2CH_2CH_2S$), 2.58-2.99 (m, 7 H, SCHS, H-2', H-2a, $SCH_2CH_2CH_2S$), 3.22-3.66 (m, 1 H, H-2b), 3.82 (dd, $J_{3',4'}$ = 8.0, $J_{4',5'}$ = 3.5, 1 H, H-4'), 4.05-4.25 (m, 4 H, H-3', H-5', CH_2CH_3), 4.66 (ABq, J = 11.3, $\Delta\delta$ = 0.11, 2 H, $ArCH_2$), 4.77 (d, $J_{H,2'}$ = 5.7, 1 H, SCHS), 4.94 (ABq, J = 10.4, $\Delta\delta$ = 0.08, $ArCH_2$), 5.45 (t, $J_{5',6'} = J_{6',1'}$ = 3.7, 1 H, H-6'), 7.23-7.48 (m, 12 H, ArH), 7.53-7.64 (m, 1 H, ArH), 7.94-8.00 (m, 2 H, ArH); IR (neat) 3475, 1725 cm^{-1}; $[\alpha]^{20}_D = +6.4°$ (c 1.49, $CHCl_3$); GC/CIMS (NH_3/CH_4) m/z 654 ($M + NH_4$)$^+$; HRMS calcd for $C_{35}H_{40}NO_7S_2$ ($M + NH_4$)$^+$ 654.2559, found 654.2530. A small sample of **44a** was acetylated to give **44b** (Ac_2O/EtOAc/cat. DMAP): ^1H NMR δ 1.28 (t, J = 7.1, 3 H, CH_2CH_3), 1.80-1.97 (m, 1 H, $SCH_2CH_2CH_2S$), 2.06-2.17 (m, 1 H, $SCH_2CH_2CH_2S$), 2.20 (s, 3 H, CH_3CO_2), 2.67-2.98 (m, 7 H, H-2', H-1', H-2a, $SCH_2CH_2CH_2S$), 3.38-3.45 (m, 1 H, H-2b), 3.90 (dd, $J_{3',4'}$ = 8.8, $J_{4',5'}$ = 3.7, 1 H, H-4'), 4.01 (dd, $J_{2',3'}$ = 10.6, $J_{3',4'}$ = 8.8, 1 H, H-3'), 4.12-4.25 (m, 2 H, CH_2CH_3), 4.61 (ABq, J = 10.9, $\Delta\delta$ = 0.16, 2 H, $ArCH_2$), 4.81 (d, $J_{H,2'}$ = 5.4, 1 H, SCHS), 4.96 (ABq, J = 10.2, $\Delta\delta$ = 0.19, 2 H, $ArCH_2$), 5.30 (dd, $J_{4',5'} \approx J_{5'6'} \approx$ 3, 1 H, H-5'), 5.55 (dd, $J_{5',6'} \approx J_{6',1'} \approx$ 3, 1 H, H-6'), 7.23-7.48 (m, 12 H, ArH), 7.53-7.61 (m, 1, ArH), 7.90-7.96 (m, 2 H, ArH); IR (neat) 1745, 1725 cm^{-1}; GC/CIMS (NH_3/CH_4) m/z 696 ($M + NH_4$)$^+$; HRMS calcd for $C_{37}H_{46}NO_8S_2$ ($M + NH_4$)$^+$ 696.2665, found 696.2648.

Ethyl 3,5-Diacetoxy-6-(benzoyloxy)-4-(benzyloxy)-2-[2-(1,3-dithianyl)]cyclohex-1-ylacetate (45). The bicyclic benzoate **32b** (15.1 mg, 0.0293 mmol) was ring opened to give a diol which was acetylated directly to give the diacetate **45** (12.3 mg, 66%), following the method described for the preparation of **44b**: ^1H NMR δ 1.23 (t, J = 7.1, 3 H, CH_3CH_2O), 1.73-1.93 (m, 1 H, $SCH_2CH_2CH_2S$), 1.98-2.20 (m, 1 H, $SCH_2CH_2CH_2S$), 2.12 (s, 6 H, CH_3CO_2), 2.61-3.01 (m, 7 H, H-2', H-2a, $SCH_2CH_2CH_2S$, H-1'), 3.17 (dd, $J_{2a,2b}$ = 15.8, $J_{1',2b}$ = 5.4, 1 H, H-2b), 3.74 (dd, $J_{3',4'}$ = 8.4, $J_{4',5'}$ = 3.5, 1 H, H-4'), 4.05-4.19 (m, 2 H, CH_3CH_2O), 4.39 (d, $J_{2',H}$ = 5.8, 1 H, SCHS), 4.55 (ABq, J = 12.2, $\Delta\delta$ = 0.07, 2 H, $ArCH_2$), 5.29-5.37 (m, 1 H, H-6'), 5.49 (dd, $J_{4',5'} \cong J_{5',6'} \cong$ 4, 1 H, H-5'), 5.55 (dd, $J_{2',3'} \cong J_{3',4'} \cong$ 9, 1 H, H-3'), 7.22-7.33 (br s, 5 H, ArH), 7.41-7.50 (m, 2 H, ArH), 7.56-7.63 (m, 1 H, ArH), 7.91-7.97 (m, 2 H, ArH); IR (neat) 1730 cm^{-1}; $[\alpha]^{20}_D = +6.0°$ (c 1.23, $CHCl_3$); GC/CIMS (NH_3/CH_4) m/z 648 ($M + NH_4$)$^+$; HRMS calcd for $C_{32}H_{42}O_9NS_2$ ($M + NH_4$)$^+$ 648.2301, found 648.2285.

A New Way toward *Z* α,β Unsaturated Esters: A Pyrethroid Application

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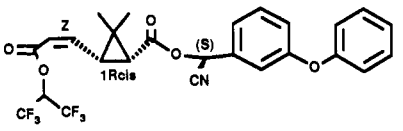
Use of the stereospecific condensation of β carbalkoxysulfones with aldehydes, followed by the stereospecific reduction of the afforded sulfonyl acrylate with sodium dithionite allows us to propose this method as a new way to prepare *Z* α,β unsaturated esters. Steric hindrance seems to be the reason for the selectivity of the reduction and the mechanism was proved, by X-ray of an intermediate, to be a cis Michael addition of HSO_2^-, followed by an anti elimination of SO_2 and the sulfinate group. This method discovered in the pyrethroid series for the synthesis of acrinathrin 1 could have general application.

Introduction

RU 38702 (acrinathrin) 1 is a new miticide/insecticide recently introduced on the market. It belongs to the Roussel family of norpyrethrates characterized by their *Z* α,β unsaturated ester group. This geometry is the only one which gives good biological activity.[1] While searching for an industrial synthesis of this compound, we were in-

(1) Tessier, J.; Tèche, A.; Demoute, J. P. *Proceedings of the 5th IUPAC International Congress of Pesticide Chemistry*; Miyamoto, J., Kearney, P. C., Eds.; Pergamon Press: 1982.

0022-3263/92/1957-0584$03.00/0



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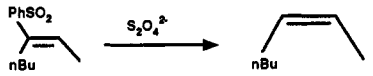
terested in the creation of such a geometry. A few methods exist toward this goal.[2] However, none of them were universal, easy, and cheap, and there was, evidently, a need for some improvement. The work of Julia et al.[3] prompted us to apply this concept in our case, all the more interesting since the starting material for such a reduction seemed to be easily accessible. We describe here a new route to α,β unsaturated esters and comment on some stereochemical conclusions from our work.

Results and Discussion

Julia et al. described a stereospecific reduction of *E* vinylic sulfones with sodium dithionite leading to the *Z* olefin. Julia explained his results by a Michael-type ad-



dition of dithionite to the double bond followed by elimination of sulfur dioxide and phenyl sulfinate. We decided to use the same methodology in order to prepare *Z* α,β unsaturated esters. A vinyl sulfonyl acrylate is obviously a good Michael acceptor, and the same dual elimination could be applied. We needed an aldehyde/acid to build the skeleton of acrinathrin; for this we used *cis*-caronaldehyde **2** (1*R*,3*S*), a key optically pure synthon in our pyrethroid chemistry[4] (see Scheme I).

Preparation of the Starting Sulfones. The starting sulfones with the desired *E* geometry were easily prepared by condensation of α-sulfonyl α-carbalkoxy carbanions with the aldehyde **2** giving a lactone which reacts as the *E* acid, leading after esterification to the *E* sulfonyl acrylate **5**. The first step of the condensation of carbalkoxysulfones, sulfoxides, or sulfides with aldehydes is an equilibrium[5] and the yields are not as good as expected (see Table I). We did not investigate this problem further but did consider its stereochemical aspects. It is claimed[6] that such a reaction gives *Z* or *E* products depending on the steric requirements of the CO_2R and SO_2R' groups but this assumption is based only on the vinylic proton shift in both cases. Treatment of *cis*-caronaldehyde **2** by *tert*-butyl-2-(phenylsulfonyl)acetate (**3c**) (pyrrolidine/THF/rt) gave the lactone **4c** which after esterification lead to the sulfones **5**. The condensation of *tert*-butyl-2-(phenylsulfenyl)-acetate (**6a**) with *cis*-caronaldehyde **2** gave a sulfide acid **7a** which after esterification and oxidation (*m*-CPBA) led to isomeric sulfones **9**. In the same way the sulfoxide afforded after esterification a compound which was reduced (NaI, TMSCl, CH_3CN) to the *E* sulfide. We noticed that when we oxidized (2 equiv of *m*-CPBA) the sulfide acid **7a**, we obtained the lactone **4c** which gave the sulfones **5** by esterification (see Scheme I). So, the formation of the lactone **4** allows the synthesis of pure *E* sulfonyl acrylates. At that point we had in hand a stereospecific synthesis of either *Z* or *E* sulfonyl acrylates. Vinylic proton shifts alone are not sufficient to assign the stereochemistry of such trisubstituted double bonds, especially in our case where the proton is subjected to the anisotropy of the carbonyl and the sulfonyl groups. In the sulfides, the vinylic proton shifts are 7.66 ppm (*Z*) and 6.75 ppm (*E*) but in the sulfone pair the shifts are 7.91 (*Z*) and 7.97 ppm (*E*). ^{13}C NMR on the *Z* sulfide **8a** ($^3J_{C-H}$ = 5.5 Hz), the *Z* sulfone **9a** ($^3J_{C-H}$ = 7 Hz), and the *E* sulfones **5a** ($^3J_{C-H}$ = 11.5 Hz) and **5b** ($^3J_{C-H}$ = 11.5 Hz) allowed us to confirm these assignments.[7] The sulfoxides obtained by condensation of β-carbalkoxy sulfoxides with the aldehyde **2** and esterification were found to have the same stereochemistry as the sulfones.

When R = R' = *t*-Bu, the condensation with *cis*-caronaldehyde **2** gave a 66% yield of the lactone **4f**. The esterification of this lactone (DCC, DMAP, CH_2Cl_2) with (1*S*)-1-cyano-1-(3-phenoxyphenyl)methanol (SPC) (74%) or 3-phenoxybenzyl alcohol (MPB) (67%) gave the corresponding esters **5b** or **5c**.

The condensation of some of these sulfones with other aldehydes (2-methylpropanal, benzaldehyde, *n*-heptanal) gave the same kind of results especially concerning the stereochemistry (see the end of this paper).

Stereospecific Reduction. The reduction of the pure *E* sulfones in a phase-transfer catalytic process as in the Julia paper ($Na_2S_2O_4$, $NaHCO_3$, cyclohexane/water, PTC agent, 80 °C) worked quite well, but aromatic sulfones did not give sufficient stereospecificity and we obtained mostly the *E* ester. We decided to prepare many other starting

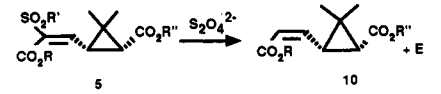


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Table I. Condensation of Sulfones or Sulfides with *cis*-Caronaldehyde 2

ester	R	R'	yield % 4	yield % 7
3a	Me	Ph	55	
3b	Et	Ph	64	
3c	*t*-Bu	Ph	66	
3d	$CH(CF_3)_2$	Ph	33	
3e	*t*-Bu	4-NO_2Ph	60	
3f	*t*-Bu	*t*-Bu	66	
6a	*t*-Bu	Ph		69
6b	*t*-Bu	4-MeOPh		71

Table II. Reductive Elimination of Compounds 5

entry	R	R'	R''	*Z*/*E* ratio	yield (%)
1	Et	Ph	CH_3	33/66	70
2	*t*-Bu	Ph	CH_3	60/40	71
3	*t*-Bu	Ph	MPB[a]	70/30	80
4	*t*-Bu	4-NO_2Ph	CH_3	E[b]	nd
5	*t*-Bu	4-MeOPh	CH_3	74/26	70
6	*t*-Bu	4-NH_2Ph	CH_3	71/29	66
7	*t*-Bu	4-NMe_2Ph	CH_3	65/35	nd
8	*t*-Bu	CH_3	CH_3	14/86	45
9	*t*-Bu	4-MeOPh	MPB	78/22	65
10	*t*-Bu	2-MeOPh	MPB	85/15	60
11	*t*-Bu	*t*-Bu	SPC	95/5	60
12	*t*-Bu	*t*-Bu	MPB	95/5	70

[a] MPB = 3-phenoxybenzyl group. SPC = (1*S*)-1-cyano-1-(3-phenoxyphenyl)methyl group. [b] Dithionite reduces nitro group to amino group: at the beginning, only *E* isomer was formed, then, owing to reduction of the nitro group, *Z* isomer appeared.

(2) See for example: (a) Favorskii reaction: Rappe, C.; Adestrõm, R. *Acta Chem. Scand.* **1965**, *19*, 383. (b) Trifluoroethyl phosphonate: Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, 4405. (c) Cyclic phosphonate: Breuer, E.; Bannet, D. M. *Tetrahedron* **1978**, *34*, 997. (d) Carbohydrates: Valverde, S. et al. *Tetrahedron* **1987**, *43*, 1895. (e) Alkyne hydrogenation: Heathcock, C. H. et al. *Org. Synth.* **1986**, *64*, 108.

(3) Julia, M.; Lauron, H.; Stacino, J. P.; Verpeaux, J. N. *Tetrahedron* **1986**, *42*, 2475 and references cited therein.

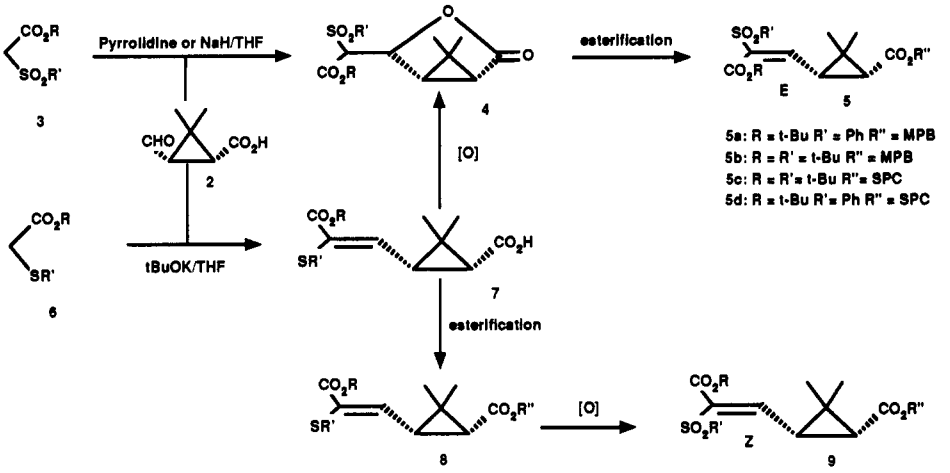
(4) Tessier, J. *Chem. Ind.* **1984**, 199.

(5) (a) Tanikaga, R.; Tamura, T.; Nozaki, Y.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1984**, 87. (b) Tanikaga, R.; Kanya, N.; Fogi, A. *Chem. Lett.* **1985**, 1583.

(6) Harper, D. A. R.; Steetson, B. *Synthesis* **1980**, 806.

(7) Gregory, B.; Hinz, W.; Jones, R. A.; Sepuvelda-Arques, J. *J. Chem. Res., Synop.* **1984**, 311; *J. Chem. Res., Miniprint* **1984**, 2801.

Scheme I. Stereoselective Synthesis of *Z* and *E* Sulfonyl Acrylates



sulfone esters to study the electronic and the steric factors which influence the stereochemistry of the reduction. The following different effects were noticed:

With the aromatic sulfones, the electronic effect of substituents is important: the less electron-withdrawing character of the substituent, the more *Z* proportion was produced (Table II, entries 4 and 5).

The steric effect seems to be more important: in the vinylic ester moiety, the *Z*/*E* ratio is totally reversed from Et to *t*-Bu (33/66 to 60/40) (entries 1 and 2). In the sulfone moiety, the same effect occurred and the *t*-Bu group gave us the best results (compare for example entries 3, 9, 10, 12).

If the sulfoxides gave, in some cases, slightly more *Z* isomer, the yields were poor. The phenyl sulfide gave only double-bond reduction as in the case of α,β unsaturated ketones.[8]

The use of NaSH instead of dithionite in an homogenous methanolic medium gave only the *E* isomer in 80% yield.

Many other experiments involving changes in the solvent, temperature, or the source of HSO_2^-,[9] did not lead to better yields or higher *Z*/*E* ratios but lead to a homogeneous medium.

Finally, the conditions were as follows: 2 equiv of $Na_2S_2O_4$ in 2 equiv of $NaHCO_3$ (2 equiv of Aliquat 336; cyclohexane/water (1/1); 1 h, 80 °C) (PTC) or (MeOH/THF/H_2O (2/1/1); 60 °C, 3 h) (homogeneous).

With both conditions, we obtained an 80% yield with the ester **5a** and 70% yield with the ester **5b**.

Mechanism. All these data prompt us to propose the following mechanism in accordance with Julia's scheme.

Primary: dismutation of $S_2O_4^{2-}$ to HSO_2^-.

Secondary: Michael-type cis addition of HSO_2^- to the double bond.

Tertiary: Anti reductive elimination of SO_2 and RSO_2^-.

The Michael addition could be supported in our case by some examples[10] and by the fact that hydrosulfide ion, a poor reductive species but a good nucleophile, gave reduction of sulfonyl acrylate. Concomitant β elimination of sulfinate and another group has, also, already been described.[11]

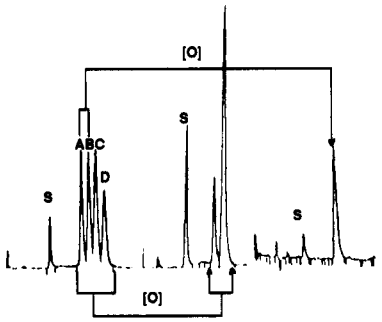


Figure 1. HPLC trace of sulfinates and sulfonates (silica gel, heptane/AcOEt (8/2)). S is the sulfone **5b** formed by decomposition on the column.

In order to support this mechanism, we carried out further reactions with **5b** (R = R' = *t*-Bu and R" = MPB):

We verified that the *Z* reduced ester did not isomerize in the reaction medium and that the *Z* starting sulfones gave the *E* esters on reduction.

When the reaction was monitored by TLC we observed two steps; the starting material disappeared within 0.25 h at rt to give a $R_f = 0$ spot; within 1 h at reflux or 24 h at rt the reduced ester spots appeared (*Z*/*E* ratio = 95/5) and increased as the reaction went to completion.

In the homogeneous medium, we have been able to quench the intermediate by methylation with diazomethane and then to isolate the methylated compound **11** by fast preparative chromatography despite its instability. In fact, the HPLC trace of the isolated derivative showed four peaks (A, B, C, D) (see Figure 1) and the spectra of the mixture were in good agreement with a sulfinate–sulfone intermediate. Of the eight theoretically possible diastereoisomers only four were found; the oxidation of which gave two HPLC peaks corresponding to the sulfonates (Figure 1). The A,B pair gave only one sulfonate peak by oxidation; that is to say A and B have the same stereochemistry on the carbons but a different one on the sulfinate sulfur atom. Unfortunately, the sulfonates did not crystallize and we had to separate the four sulfinates. B and D crystallized, and B allowed us to carry out an X-ray determination[12] (see Figure 2). Since B is 1*R*,3*S* on the cyclopropane, it is 1'*R*,2'*R* on the asymmetric car-

(8) Louis-Andrê, O.; Gelbard, G. *Tetrahedron Lett.* **1985**, 831.

(9) For a review on sodium dithionite see: Louis-Andrê, O.; Gelbard, G. *Bull. Soc. Chim. Fr.* **1986**, 565.

(10) (a) Beck, G.; Günther, D. *Chem. Ber.* **1973**, *106*, 2758. (b) Posner, G. H.; Mallamo, J. P.; Mivra, K. *J. Am. Chem. Soc.* **1981**, *103*, 2886.

(11) (a) Ochiai, M.; Ukita, J.; Fujita, E. *Chem. Lett.* **1983**, 1457. (b) Seechler, H. *Tetrahedron Lett.* **1984**, 1219. (c) Ono, N. et al. *Tetrahedron Lett.* **1978**, 763.

(12) $C_{29}H_{42}O_9S_2$, space group $P2_1P2_1P2_1$, a = 11.992 Å, b = 6.68 Å, c = 42.039 Å; full description will be published elsewhere. We thank Prof. BAERT from Lille University (France) for performing the X-ray determination.

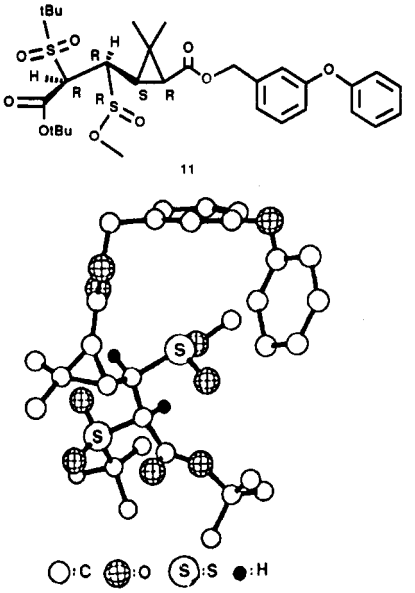
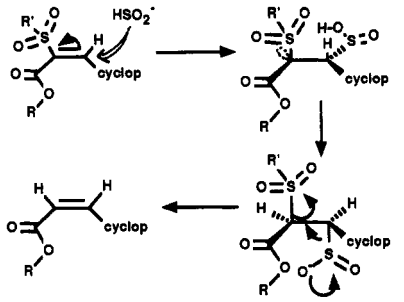


Figure 2. X-ray of the reduction intermediate (computer-generated image; only the two important hydrogens are represented for clarity).

Scheme II. Mechanism of the Reduction

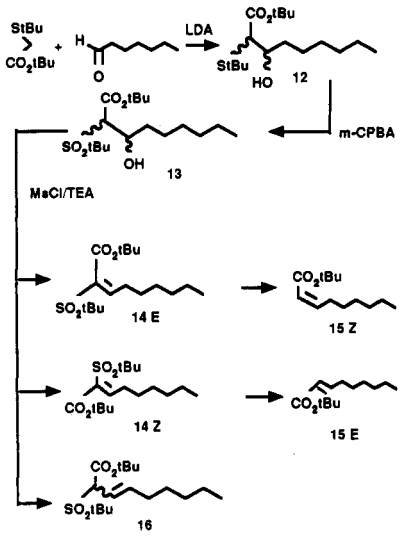


bons resulting from addition and *R* on the sulfur atom. So it was derived from a cis addition of SO_2^{2-} and H^+ on the double bond. This is in accordance with the mechanism shown in Scheme II.

The intermediate carbanion formed by addition has to be protonated on the same face as the addition to give the *RR* or *SS* compound. Corey has done some work[13] on the protonation of α-sulfonyl carbanions and found that the orbital pair is bisecting the oxygen pair of the sulfonyl group and so the protonation takes place on this face; he concluded that it is only the rotation of the C–S bond which determines the geometry of the protonation. In our case the carbanion is α to a sulfonyl and an ester group. Two explanations can account for our results: either we have a direct proton transfer from the sulfinic acid function to the carbon independently of the orientation of the sulfonyl oxygen atoms or any proton can attack the anion and so the HSO_2^- ion has to approach the double bond on the face determined by the sulfonyl oxygen atoms. When we look at the X-ray-derived structure, we see that sulfonyl oxygen atoms are anti to the sulfinic sulfur atom and so the proton comes from the sulfinic function. If the anion is not short lived and if the groups are not bulky enough, it could be inverted and by the same direct proton transfer give the *E* isomer. The steric factor seems to be the most important reason for good selectivity.

(13) Corey, E. J.; Lowry, T. H. *Tetrahedron Lett.* **1965**, 801, 803. See also: Bernardi F.; *Organic Sulfur Chemistry*; Elsevier: New York, 1985.
(14) Camps, F. et al. *J. Org. Chem.* **1982**, *47*, 5402.

Scheme III. Condensation with Heptanal and Reduction



Scope. In order to investigate the versatility of this methodology, we worked with some other aldehydes and especially with heptanal. The condensation of the di-*tert*-butyl sulfono ester with heptanal seemed to be totally reversible and we had to condense the sulfenyl ester to obtain after dehydratation and oxidation a mixture of conjugate **14** (20%) and deconjugate **16** (80%) compounds. The two isomers (**14***Z* and **14***E*) of the conjugate structure were separated and each of them were submitted to dithionite reduction and gave stereospecifically the esters **15** (Scheme III) showing that this method is not limited to cyclopropyl aldehyde.

Conclusion

We have been able to prepare the *Z* α,β unsaturated ester function of acrinathrin by a two-step stereoselective methodology including dithionite reduction of an (*E*)-vinylsulfonyl acrylate. This new route to *Z* α,β unsaturated ester seems to be versatile but some problems remain. If the aldehyde is not easily enolizable, and if steric hindrance in the sulfonyl acrylate does not give deconjugation, this new methodology could be a good way of preparing *Z* α,β unsaturated esters. It seems that it may be possible to use activating groups other than sulfone and also Michael donors other than dithionite provided that they could give reductive elimination.

Experimental Section

General. Unless otherwise noted, materials and solvents were obtained from commercial suppliers (upper grade) and used without purification. Melting points are done on an automatic Mettler FP62 system, ^1H NMR spectra were recorded at 60 MHz (unless otherwise noted) in $CDCl_3$ as solvent and TMS as internal standard; chemical shifts are expressed in ppm and coupling constants in Hz. IR spectra were recorded in $CHCl_3$ solution. Preparative chromatography were usually conducted on 100 parts of 9385 Merck silica gel. DCC = dicyclohexylcarbodiimide; DMAP = 4-(dimethylamino)pyridine; *m*-CPBA = 3-chloroperoxybenzoic acid.

***tert*-Butyl 2-(*tert*-Butylthio)acetate (6f).** To a stirred solution of 9 g (0.1 mol) of *tert*-butylthiol in 100 mL of THF under N_2 at 10 °C was added in 15 min 11.2 g (0.1 mol) of *t*-BuOK and then a solution of 19.5 g (0.1 mol) of *tert*-butyl bromoacetate in 50 mL of THF. After 1 h of further stirring at rt, 75 mL of brine was added and the organic layer was separated. Evaporation under vacuum gave 20 g (98%) of an oil which was further used as such. ^1H NMR: δ 1.31 (s, S-*t*-Bu); 1.45 (s, O-*t*-Bu); 3.14 (s, CH_2).

***tert*-Butyl 2-(Phenylsulfenyl)acetate (6a).** As above, yield = 95%. ^{1}H NMR: δ 1.42 (s, *t*-Bu); 3.58 (s, CH_2); 7.38 (m, Ar). IR: 1734 cm^{-1} (CO ester).

***tert*-Butyl 2-(*tert*-Butylsulfonyl)acetate (3f).** To a stirred solution of 20 g (0.098 mol) of crude sulfide **6f** in 300 mL of methanol at 0 °C was added a solution of 92 g (0.29 mol) of Oxone ($KHSO_5$, $KHSO_4$, K_2SO_4) in 400 mL of water. After overnight stirring at rt, methanol was evaporated under vacuum and the aqueous phase was extracted with methylene chloride. The organic layer, after drying, was evaporated to give 21.5 g (91%) of sulfone. Mp: 70 °C. ^{1}H NMR: δ 2.22 (s, *t*-Bu); 2.3 (s, *t*-Bu); 5.82 (s, CH_2). Anal. Calcd for $C_{10}H_{20}O_4S$: C, 50.82; H, 8.53; S, 13.57. Found: C, 50.7; H, 8.5; S, 13.5.

***tert*-Butyl 2-(Phenylsulfonyl)acetate (3c).** To a stirred solution of 11.5 g (0.042 mol) of sulfide **6a** in 500 mL of methylene chloride was added stepwise 21.6 g (0.1 mol) of commercial *m*-CPBA. After overnight stirring at rt, 14.8 g of dry KF[11] was added to complex *m*-chlorobenzoic acid. After stirring, filtration, and evaporation, chromatography (hexane/AcOEt (7/3)) gave 11.28 g (88%) of an oil. ^{1}H NMR: δ 1.73 (s, *t*-Bu); 4.05 (s, CH_2); 7.61 (m, Ar); 7.96 (m, H *o*-SO_2). IR: 1730 (CO ester); 1330 cm^{-1} (SO_2).

(1*R*,1α,3α)-6,6-Dimethyl-4-[2-*tert*-butoxy-2-oxo-1-(*tert*-butylsulfonyl)ethyl]-3-oxabicyclo[3.1.0]hexan-2-one (4f). To a stirred solution of 15.8 g (0.067 mol) of sulfone **3f** in 160 mL of THF at rt under N_2, 3.2 g of NaH (50% in oil) was added stepwise. After $^1/_2$ h at rt, the voluminous precipitate formed was dissolved by addition of 10 mL of DMF. After a further 15 min, 9.5 g of aldehyde **2** was added and the mixture was stirred *4 days at rt*. A 150-mL portion of saturated NaH_2PO_4 solution was added, and the product was extracted with ethyl acetate. After drying and evaporation under vacuum, the crude lactone was chromatographed with hexane/AcOEt (1% AcOH) as eluent to afford 14.4 g (60%) of pure lactone. ^{1}H NMR: δ 1.22 (s, Me *gem*), 1.5 (s, *t*-Bu), 2 (m, H_1), 2.5 (m, H_3), 4.35 (m, CH), 4.85 (m, CH). IR: 1770 (CO lactone), 1738 (CO ester), 1311 cm^{-1} (SO_2). MS: *m/z* 360 (M^+), 345, 248.

(1*R*,1α,3α)-6,6-Dimethyl-4-[2-*tert*-butoxy-2-oxo-1-(phenylsulfonyl)ethyl]-3-oxabicyclo[3.1.0]hexan-2-one (4c). To a stirred solution of 11.28 g (0.044 mol) of sulfone **3c** and 6.25 g (0.044 mol) of aldehyde **2** in 50 mL of THF was added 0.22 mL of pyrrolidine. After overnight stirring, evaporation followed by chromatography (hexane/AcOEt (1/1)) gave 11 g (65%) of lactone. ^{1}H NMR: δ (2 diastereoisomers) 1.2–1.23 (s, Me *gem*); 1.3–1.4 (s, *t*-Bu); 2.01 (m, H_1); 2.55 (m, H_3); 4.25 (m, CHS); 4.92 (m, CHO); 7.82 (m, Ar). IR: 1774 (CO lactone); 1734 (CO ester); 1330 cm^{-1} (SO_2).

[1*R*,1α,3α(*Z*)]-2,2-Dimethyl-3-[3-*tert*-butoxy-3-oxo-2-(phenylsulfenyl)-1-propenyl]cyclopropanecarboxylic Acid (7a). To a stirred solution of 13.46 g (60 mmol) of sulfide **6a** and 8.53 g (60 mmol) of aldehyde **2** in 120 mL THF at −50 °C was added in 45 min a solution of 13.46 g (120 mmol) of *t*-BuOK in 90 mL of THF. After 1 h at −50 °C, the reaction was hydrolyzed at −20 °C with saturated NaH_2PO_4 and then the medium was stirred 10 min at rt to dehydrate the intermediate alcohol. After extraction with AcOEt and drying, evaporation under vacuum and chromatography (hexane/AcOEt (1/1)) gave 14.4 g (69%) of the acid. ^{1}H NMR: δ 1.23 (s, Me); 1.4 (s, Me); 1.32 (s, *t*-Bu); 1.9 (m, H_1); 2.62 (m, H_3); 7.28 (m, Ar); 7.68 (m, H vinylic).

[1*R*,1α(*S),3α(*E*)]-1-Cyano-1-(3-phenoxyphenyl)methyl 2,2-Dimethyl-3-[3-*tert*-butoxy-2-(*tert*-butylsulfonyl)-3-oxo-1-propenyl]cyclopropanecarboxylate (5c).** To a stirred solution of 3 g (8.32 mmol) of lactone **4f** and 1.87 g (8.32 mmol) of (1*S*)-1-cyano-1-(3-phenoxyphenyl)methanol in 25 mL of methylene chloride at 10 °C was added a solution of 1.72 g (8.32 mmol) of dicyclohexylcarbodiimide and 50 mg of DMAP in 50 mL of CH_2Cl_2. After 18 h at rt, filtration, evaporation, and chromatography (hexane/diisopropyl ether (6/4)) gave 3.5 g (74%) of ester. Mp: 102 °C. ^{1}H NMR: δ 1.3 (s, Me); 1.4 (s, *t*-Bu); 1.57 (s, *t*-Bu); 2.32 (m, H_1, H_3); 6.33 (s, CHCN); 7.24 (m, Ar and vinylic proton). IR: 1743 (CO); 1304 cm^{-1} (SO_2). MS: *m/z* 567 (M^+). Anal. Calcd for $C_{31}H_{37}NO_7S$: C, 65.59; H, 6.57; N, 2.47; S, 5.65. Found: C, 65.6; H, 6.7; N, 2.4; S, 5.6.

[1*R*,1α,3α(*E*)]-(3-Phenoxyphenyl)methyl 2,2-Dimethyl-3-[3-*tert*-butoxy-2-(*tert*-butylsulfonyl)-3-oxo-1-propenyl]cyclopropanecarboxylate (5b). As above, yield = 67%. Mp: 72 °C. ^{1}H NMR: δ 1.27 (s, Me); 1.33 (s, Me); 1.37 (s, *t*-Bu); 1.64 (s, *t*-Bu); 2.22 (m, H_1, H_3); 5.04 (s, CH_2); 7.1 (m, Ar, vinylic proton). ^{13}C NMR (75 MHz): δ 14.3, 23.3, 28, 28.4, 30.7, 32.5, 35, 61.4, 66, 83.6, 118.3, 118.4, 118.9, 122.8, 123.4, 129.7, 129.9, 134.4, 137.7, 150.6, 156.7, 157.4, 162.1 (d, $^3J_{C-H}$ = 11.5 Hz), 169.3. IR: 1723 cm^{-1} (CO). MS: *m/z* 542 (M^+).

[1*R*,1α(*S),3α(*E*)]-1-Cyano-1-(3-phenoxyphenyl)methyl 2,2-Dimethyl-3-[3-*tert*-butoxy-2-(phenylsulfonyl)-3-oxo-1-propenyl]cyclopropanecarboxylate (5d).** As above, yield = 76%, oil. ^{1}H NMR (300 MHz): δ 1.32 (s, Me); 1.39 (s, Me); 1.36 (s, *t*-Bu); 2.2 (d, *J* = 8.5, H_1); 2.94 (dd, *J* = 8.5 and 10.5, H_3); 6.39 (s, H-CN); 7.92 (dd, vinylic H); 7.88 (dd, H ortho SO_2); 7.3 (m, Ar). ^{13}C NMR (75 MHz): δ 14.8, 27.9, 28.2, 32.4, 32.7, 35.3, 62.7, 83.9, 115.8, 117.6, 119.4, 120.2, 122.2, 124.2, 128.1, 128.8, 130.7, 133, 133.3, 137.1, 140.5, 151, 156.2, 158.3, 160.7 (d, $^3J_{C-H}$ = 11.5), 168.1. IR: 1742 (CO); 1712 (CO); 1318 cm^{-1} (SO_2).

[1*R*,1α,3α(*Z*)]-(3-Phenoxyphenyl)methyl 2,2-Dimethyl-3-[3-*tert*-butoxy-2-(phenylsulfenyl)-3-oxo-1-propenyl]cyclopropanecarboxylate (8a). To a stirred solution of 1.64 g (4.7 mmol) of acid **7a** and 0.94 g (4.7 mmol) of *m*-phenoxybenzyl alcohol in 15 mL of CH_2Cl_2 at rt was added a solution of 0.97 g of DCC and 30 mg of DMAP in 20 mL of CH_2Cl_2. After stirring overnight, filtration, evaporation, and chromatography (hexane/AcO(Et (95/5)) gave 2 g (80%) of an oil. ^{1}H NMR: δ 1.22 (s, Me); 1.35 (s, Me); 1.32 (s, *t*-Bu); 2.01 (m, H_1); 2.58 (m, H_3); 5.13 (s, CH_2); 7.25 (m, Ar); 7.69 (d, vinylic proton). MS: *m/z* 530 (M^+). Anal. Calcd for $C_{32}H_{34}O_5S$: C, 72.43; H, 6.46; S, 6.04. Found: C, 72.1; H, 6.4; S, 5.8.

[1*R*,1α,3α(*Z*)]-(3-Phenoxyphenyl)methyl 2,2-Dimethyl-3-[3-*tert*-butoxy-2-(phenylsulfonyl)-3-oxo-1-propenyl]cyclopropanecarboxylate (9a). To a stirred solution of 0.1 g of the sulfide in 5 mL of CH_2Cl_2 at 0 °C was added 80 mg of *m*-CPBA. After stirring for 5 h at rt, evaporation and chromatography (hexane/AcOEt (9/1)) gave 0.1 g (95%) of a colorless oil. ^{1}H NMR (300 MHz): δ 1.33 (s, *t*-Bu); 1.35 (s, Me); 1.37 (s, Me); 2.26 (d, *J* = 8.5 H_1); 3.46 (dd, *J* = 8.5 and 10.5 H_3); 5.09 (ABsyst, CH_2O); 7.91 (d, vinylic proton); 7.93 (dd, H, *o*-SO_2); 7.27 (m, Ar). ^{13}C NMR (75 MHz): δ 15, 27.8, 28.5, 31.1, 32.3, 36.2, 66.1, 83.2, 118.3, 118.4, 119.4, 122.7, 123.5, 127.5, 128.7, 129.8, 129.9, 133.1, 135.7, 137.2, 141.7, 153.1, 156.8, 157.6, 161.1 (d, $^3J_{C-H}$ = 7), 169.7.

General Procedure for Reductive Elimination. [1*R*,1α,3α(*X*)]-(3-Phenoxyphenyl)methyl 2,2-Dimethyl-3-(3-*tert*-butoxy-3-oxo-1-propenyl)cyclopropanecarboxylate (10a). In a homogeneous medium. To a stirred solution of 3 g of sulfone **5b** in 110 mL of a THF/MeOH/H_2O (2/1/1) mixture was added during $^1/_2$ h a solution of 1.34 g (7.7 mmol) of sodium dithionite in 30 mL of water. After 1 h of stirring at rt (disappearance of the sm), the solution was heated for $3^1/_2$ h at 60 °C to carry out the elimination. After evaporation under vacuum, extraction with AcOEt, drying, and concentration, chromatography (hexane/AcOEt (9/1)) gave 1.52 g of the *Z* isomer and 80 mg of the *E* (*Z*/*E* = 95/5, *Z* + *E* yield = 69%).

In a phase-transfer system. To a stirred solution of 0.32 g of sulfone **5b** (0.6 mmol) and 1.2 mmol of Aliquat 336 in 3 mL of cyclohexane was added 3 mL of water, 0.21 g (1.2 mmol) of sodium dithionite, and 0.126 g (1.5 mmol) of sodium bicarbonate. The mixture was heated under reflux for $1^1/_4$ h and decanted. Extraction with CH_2Cl_2, drying, concentration, and chromatography gave 157 mg of the *Z* isomer and 13 mg of the *E* (*Z*/*E* = 92/8, *Z* + *E* yield = 68%).

Z isomer: ^{1}H NMR (300 MHz): δ 1.2 (s, Me); 1.32 (s, Me); 1.52 (s, *t*-Bu); 1.83 (m, H_1); 3.29 (m, H_3); 5.13 (s, CH_2); 5.85 (d, *J* = 12 Hz, H α CO); 6.58 (d, H β CO); 7.26 (m, Ar). IR: 1720 (CO), 1702 (CO), 1632 cm^{-1} (double bond). *E* isomer: ^{1}H NMR (300 MHz): δ 1.22 (s, Me); 1.34 (s, Me); 1.5 (s, *t*-Bu); 1.89 (m, H_1, H_3); 5.13 (s, CH_2); 5.93 (d, *J* = 16 Hz, H α CO); 7.22 (H β CO and Ar). IR: 1725, 1702 (CO), 1642 cm^{-1} (double bond).

Isolation of Intermediate Adducts. [1*R*,1α,3α]-(3-Phenoxyphenyl)methyl 2,2-Dimethyl-3-[1-(methoxysulfinyl)-2-(*tert*-butylsulfonyl)-3-*tert*-butoxy-3-oxo-1-propyl]cyclopropanecarboxylate (11). To a stirred solution of 3 g of sulfone **5b** in 55 mL of THF, 27 mL of MeOH, and 27 mL of water was added dropwise a solution of 1.34 g of sodium dithionite in 30 mL of water. After 1 h at rt, the starting material had disappeared. The reaction mixture was evaporated under vacuum at 25 °C. The resulting aqueous phase was cooled at 5 °C, acidified until

pH 1, then extracted twice with diethyl ether. After drying and concentration, the crude oil (3.4 g) was dissolved in 40 mL of CH_2Cl_2, cooled at 10 °C, and treated with 40 mL of an 0.3 M diazomethane/CH_2Cl_2 solution. After a further 15 min at rt, concentration and fast chromatography (20 min, 50 parts of silica gel, hexane/AcOEt (7/3)) gave 1 g of pure ester sulfinate. These esters gave by decomposition on silica gel the starting sulfone. By HPLC, we observed four peaks A, B, C, D. The preparative HPLC on a 100-mg scale allowed us to separate each of them in a pure state. Only B and D crystallized. ^{1}H NMR (250 MHz): A δ 1.31 (s, Me *gem*); 1.37 (s, Me *gem*); 1.49 (s, *t*-Bu); 1.50 (s, *t*-Bu); 1.7–1.9 (m, H_1, H_3); 3.67 (s, CH_3OS); 4.13 (dd, J = 1, 11 Hz); 5 (d, CHCO); 5.2 (AB, CH_2O); 6.9–7.4 (m, Ar); B δ 1.31 (s, Me *gem*); 1.35 (s, Me *gem*); 1.50 (s, *t*-Bu); 1.50 (s, *t*-Bu); 1.7–1.9 (m, H_1, H_3); 3.68 (s, CH_3OS); 4.29 (dd, J = 2.6, 11.5); 4.77 (d, CHCO); 5.07 (AB, CH_2O); 6.9–7.4 (m, Ar); C δ 1.23 (s, Me *gem*); 1.34 (s, Me *gem*); 1.41 (s, *t*-Bu); 1.49 (s, *t*-Bu); 1.9–2.2 (m, H_1, H_3); 3.80 (s, CH_3OS); 4.13 (dd, J = 1, 10.5); 5 (d, CHCO); 5.07 (AB, CH_2O); 6.9–7.4 (m, Ar); D δ 1.26 (s, Me *gem*); 1.33 (s, Me *gem*); 1.42 (s, *t*-Bu); 1.51 (s, *t*-Bu); 1.9–2.3 (m, H_1, H_3); 3.84 (s, CH_3OS); 4.19 (dd, J = 2.6, 11); 4.69 (d, CHCO); 5.08 (AB, CH_2O); 6.9–7.4 (m, Ar). CIMS (NH_3): m/z 640 ($M + NH_4^+$), 623 ($M + H^+$), 567, 542, 487, 349, 223, 183 for each of the four. IR: 1720–1735 (CO), 1312–1339 cm^{-1} (SO_2) for each of the four.

***tert*-Butyl 2-(*tert*-Butylthio)-3-hydroxynonanoate (12).** To a stirred solution of 5 mL of diisopropylamine (36 mmol) in 40 mL of dry THF was added at –60 °C 20 mL of a 1.6 M solution of *n*-BuLi in hexane (32 mmol). After 45 min at –60 °C was added a solution of 5.2 g of sulfide **6f** (25 mmol) in dry THF (40 mL). After 30 min at –30 °C, 4.2 g of commercial *n*-heptanal (31 mmol) in 20 mL of dry THF was added and the reaction mixture was allowed to warm to rt. The reaction medium was poured in 200 mL of saturated NaH_2PO_4 and extracted with isopropyl ether. After drying and evaporation of the organic phase, the crude alcohol was chromatographed on silica gel (hexane/AcOEt (9/1) as eluent) to afford 7.16 g (88%) of a mixture of isomers. Mp: 36 °C. ^{1}H NMR (250 MHz): δ 0.88 (t, CH_3); 1.17–1.75 (m, CH_2): 1.36 (s, *t*-Bu); 1.49 (s, *t*-Bu); 3.04 (s, OH); 3.08 (d, J = 8 Hz, CHS); 3.20 (d, J = 6, CHS); 3.67 (m, CHO); 3.76 (m, CHO). IR: 3598 (OH); 1718 (CO); 1368 cm^{-1} (Me).

***tert*-Butyl 2-[(*tert*-Butylsulfonyl)oxy]-3-hydroxynonanoate (13).** To a stirred solution of 0.5 g of sulfide **12** (16 mmol) in 2 mL of CH_2Cl_2 was added at 20 °C a solution f 0.88 g of commercial *m*-CPBA (4 mmol) in 13 mL of CH_2Cl_2. The white suspension was stirred 2 h at rt and poured in aqueous $NaHCO_3$ solution (0.4 g in 50 mL of water) and extracted with CH_2Cl_2 (3 × 25 mL). After drying and evaporation, the crude oil was chromatographed on silica gel to afford 0.37 g (67%) of a white solid. Mp: 58.5 °C. ^{1}H NMR (250 MHz): δ 0.88 (t, CH_3); 1.29–1.52 (m, CH_2); 1.46 (s, *t*-Bu); 1.49 (s, *t*-Bu); 3.70 (OH); 3.99 (d, J = 10 Hz, CHS); 4.39 (m, CHO). IR: 3550 (OH); 1728 (CO); 1369 (Me); 1298, 1109 cm^{-1} (SO_2).

tert*-Butyl 2-[(*tert*-Butylsulfonyl)oxy]-2-nonenoate (14).** To a stirred solution of 0.5 g of alcohol **13** (1.4 mmol) and 0.15 mL of methanesulfonyl chloride (1.94 mmol) in 5 mL of CH_2Cl_2 was added at 0 °C 0.4 mL of triethylamine (2.9 mmol). After 60 h at rt, the reaction medium was poured in saturated aqueous KH_2PO_4 solution and extracted with CH_2Cl_2. After drying and evaporation, the crude oil was chromatographed on silica gel (hexane/AcOEt (9/1)) to afford 0.18 g (38%) of a mixture of isomers and a large quantity of deconjugated sulfonyl product **16**. By careful chromatography on silica gel with hexane/isopropyl ether as eluent, the **14*Z and **14*E*** isomers were purely obtained. ^{1}H NMR (250 MHz): *Z* δ 0.89 (t, CH_3); 1.29 (m, CH_2); 1.41 (s, *t*-Bu); 1.53 (s, *t*-Bu); 2.75 (allylic CH_2); 7.37 (t, vinylic H); *E* δ 0.89 (t, CH_3); 1.29 (m, CH_2); 1.41 (s, *t*-Bu); 1.53 (s, *t*-Bu); 2.39 (allylic CH_2); 6.92 (t, vinylic H). ^{13}C NMR (75 MHz): *z* δ 14, 22.4, 23.7, 27.9–31.5, 62, 83.1, 132.5, 159.8, 162.3 (dt, $^1J_{C-H}$ = 6.5 Hz); *Z* δ 14.1, 22.4, 23.9, 27.9–31.5, 61.5, 83.7, 134.2, 153.2, 162.1 (dt, $^3J_{C-H}$ = 11 Hz); IR: 3550 (OH); 1728 (CO); 1369 (Me); 1298, 1109 cm^{-1} (SO_2).

tert*-Butyl 2-Nonenoate (15).** As for reduction of **5b** in PTC system. **14*Z gave **15*E*** in 25% yield. **14*E*** gave **15*Z*** in 16% yield (60–80% yield of deconjugated sulfonyl product **16**). ^{1}H NMR (250 MHz): *Z* δ 0.88 (t, CH_3); 1.2–1.45 (m, CH_2); 1.49 (s, *t*-Bu); 2.6 (m, allylic CH_2); 5.66 (dt, J = 1.5, 11 Hz, H α CO); 6.11 (dt, J = 7.5, 11 Hz, H β CO); *E* δ 0.88 (t, CH_3); 1.2–1.50 (m, CH_2); 1.48 (s, *t*-Bu); 2.16 (m, allylic CH_2); 5.74 (dt, J = 1.5, 15.5 Hz, H α CO); 6.86 (dt, J = 7, 15.5 Hz, H β CO). IR: *Z* 1708 (CO); 1639 (double bond *Z*), 1369 cm^{-1} (Me); *E* 1706 (CO); 1642 (double bond *E*), 1369 cm^{-1} (Me).

***tert*-Butyl 2-[(*tert*-Butylsulfonyl)oxy]-3-nonenoate (16).** Isolated from the above reduction. ^{1}H NMR (250 MHz): δ 0.88 (t, CH_3); 1.2–1.40 (m, CH_2); 1.45 (s, *t*-Bu); 1.50 (s, *t*-Bu); 2.14 (m, allylic CH_2); 4.55 (d, J = 9 Hz); 5.57 (dd, J = 9, 16 Hz); 5.81 (dt, J = 6, 16 Hz).

Acknowledgment. We thank Dr. D. Rowlands for giving a British touch to this manuscript.

Supplementary Material Available: ^{1}H NMR spectra of compounds **6a**, **6f**, **3c**, **4f**, **4c**, **7a**, **5b**, **9a**, **10a** (*Z* and *E*), **12–14**, **15** (*Z* and *E*), and **16** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

A Novel Entry to 4,7-Indoloquinones via the Fremy's Salt Oxidative Degradation of 4-Formyl-7-hydroxyindoles

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A novel synthetic approach toward 4-formyl-7-hydroxyindoles and 4,7-indoloquinones is described. Basically, two major operations need to be carried out, namely: (1) ozonization of the appropriately protected 4-amino-5-hydroxyindenes leading eventually to 4-formyl-7-hydroxyindoles and (2) Fremy's salt promoted oxidative degradation of the later compounds to the desired 4,7-indoloquinones. A formal synthesis of PDE I and PDE II has been achieved.

A common building block to mitosenes[1] and many naturally occurring quinones[2] such as isobatzellins,[3] kinamycins,[4] discorhabdin,[5] murrayaquinones,[6] etc. is the indoloquinone unit shown (Figure 1).

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