New Rearrangement Reactions of α-Phenylsulphinylacrylate Derivatives

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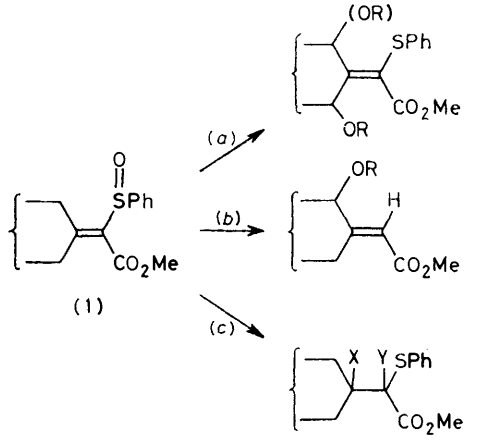
It is shown that α-phenylsulphinylacrylate derivatives undergo three modes of rearrangement reactions induced selectively by the agent used. On treatment with an acidic reagent (hot dioxan–dilute sulphuric acid or acetic anhydride) a vinylogous-type Pummerer rearrangement takes place to produce the γ-hydroxylated or -acetoxylated phenylthio-derivatives, while under basic condition (pyridine–water or –acetic anhydride) a sequential prototropic shift and allylic sulphoxide–sulphenate rearrangement occurs regioselectively to give the sulphur-free γ-hydroxy or -acetoxy acrylates. When a highly nucleophilic agent (acetyl chloride, trifluoroacetic anhydride, or thionyl chloride) is used, the αβ-difunctionalised α-phenylthio-ester derivatives are formed through the third mode of rearrangement, an additive-type Pummerer reaction.

THE transformation of sulphoxides into α-acetoxy sulphides, induced by hot acetic anhydride, is the well known Pummerer rearrangement,[1-3] although Parham and Edwards [2] reported that simple vinyl sulphoxides, such as 2-methyl-3-(phenylsulphinyl)but-2-ene and 1-(phenylsulphinyl)cyclohexene are stable to hot acetic anhydride. However, other types of rearrangement reactions involving the migration of a β-hydrogen or a sulphide group were recently reported for styryl sulphoxides [3,4] and β-aminovinyl sulphoxides.[5] Additional examples of unusual rearrangements were observed in the reaction of phenyl vinyl sulphoxide with dithioacetic acid,[6] and in the reaction of the cyclic vinyl sulphoxides, 1,4-thiazine 1-oxides.[7]

In this paper we describe three modes of rearrangement of the α-phenylsulphinylacrylate derivatives (1) (Scheme



SCHEME 1 The three rearrangements of α-phenylsulphinylacrylates (*a*) acidic reagents; (*b*) basic reagents; (*c*) highly nucleophilic reagents

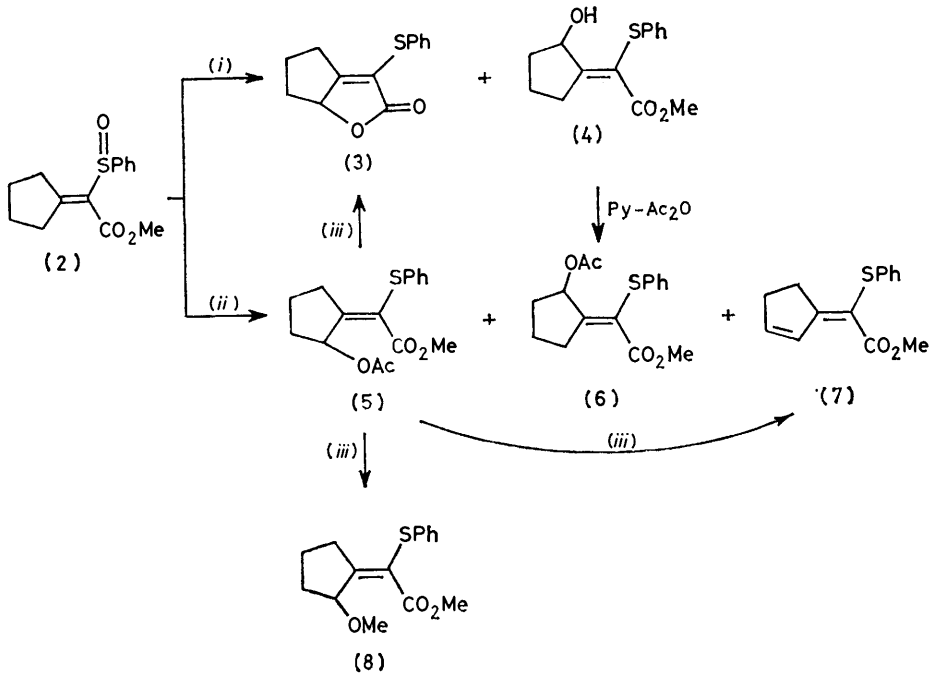
1): (*a*) the vinylogous Pummerer (acid-induced, weak nucleophile);[8] (*b*) the sequential prototropic shift and allylic sulphoxide–sulphenate rearrangement (base-induced, weak nucleophile);[8] and (*c*) the additive Pummerer (strong nucleophile).[9] These are additions to the numerous known vinyl sulphoxide reactions, and may also have wider synthetic applicability.

RESULTS AND DISCUSSION

The precursors, α-phenylthioacrylates, of compounds (1) were readily available from the reaction of the α-carbanion species of (phenylthio)acetic acid or its ester with ketones, followed by dehydration.[10] Among a number of derivatives (1), methyl α-(phenylsulphinyl)-cyclopentylidene acetate (2) was chosen as a typical derivative and examined in detail.

(*a*) *Vinylogous Pummerer Rearrangement.*—We examined first the reaction of compound (2) with acidic reagents (Scheme 2), and found that compound (2) underwent, on treatment with hot dilute sulphuric acid–dioxan or acetic anhydride, a novel rearrangement to produce γ-oxygen-functionalised products. Thus, reaction of (2) with dilute sulphuric acid–dioxan for 3 h at reflux gave the 3-(phenylthio)furanone (3) (53%) and the hydroxy-ester (4) (trace). The reaction of (2) with acetic anhydride at 75 °C for 3 h afforded two isomeric acetoxy-esters, (5) and (6), and the conjugated dienoic ester (7) in 50, 15, and 19% yields, respectively. When the reaction was conducted at reflux (7) was the sole product (42%). Treatment of the major acetoxy-ester (5) with perchloric acid in ether gave the furanone (3) (44%), the dienoic ester (7) (8%), and the methoxy-ester (8) (19%) (Scheme 2). This result, together with the predominant formation of the furanone (3) in the reaction of (2) with dilute sulphuric acid–dioxan, provides the evidence for the positions of the acetoxy group in compounds (5) and (6) and of the endocyclic double bond in (7) as indicated. In both reactions the phenylsulphinyl group in (2) was reduced to the phenylthio-group, and a hydroxy or acetoxy group was introduced at the allylic γ-position of (2); hence these reactions are formally regarded as a vinylogous Pummerer rearrangement.

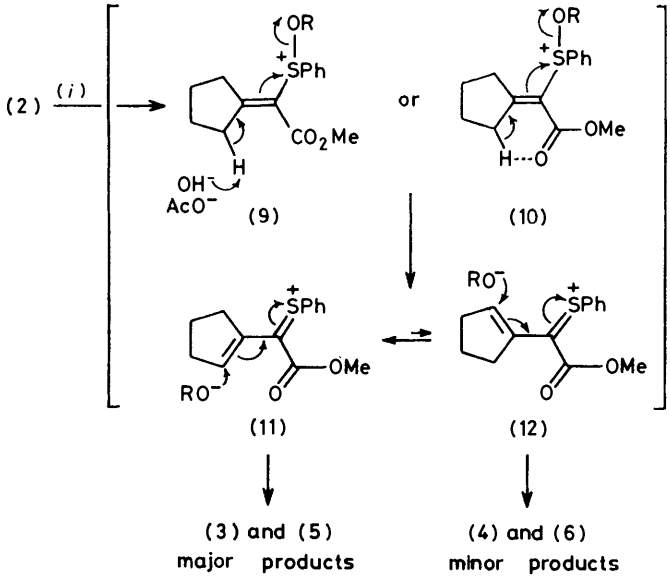
Thus, the formation of the products (3)—(6) could be accounted for by a reaction sequence including the vinylogous Pummerer-type intermediates (11) and (12), with concomitant lactonisation in the case of compound (3), as shown in Scheme 3. For easy deprotonation of the acylated precursor (9), in contrast to the observation by Parham and Edwards,[2] the ester group may play an important role, facilitating the deprotonation from the allylic carbon atom as depicted in (10). The preferential introduction of a hydroxy or acetoxy group *cis* to the ester group in the products is presumably attributable to the fact that the *transoid* intermediate (11) would be more favourable than the *cisoid* isomer (12). Although we have examined the reaction of compound (2) under



SCHEME 2 (*i*) H^+, dilute dioxan; (*ii*) Ac_2O; (*iii*) H^+

a variety of conditions (heating toluene-*p*-sulphonic acid–aqueous tetrahydrofuran; heating methanesulphonic acid–aqueous dioxan; perchloric acid in ether, room temperature) the yield of the furanone (3) could not be improved.

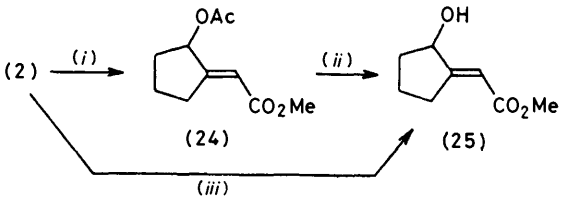
In the reaction of an asymmetric acrylate the introduction of a hydroxy group was not regioselective. Thus, an inseparable mixture of the two furanones (14) and (15) was obtained from the reaction of either (*E*)-(13) or (*Z*)-(13); the ratio (14) : (15) [*ca.* 2.2 : 1 from (*E*)-(13) and 1 : 1 from (*Z*)-(13)] was determined by n.m.r. comparison of the signals of the side-chain methylene in (14) and the olefinic methyl in (15). Similarly, other α-phenylsulphinylacrylates (16), (17), (18), and (19) gave on treatment with refluxing dilute sulphuric acid–dioxan the corresponding 3-(phenylthio)furanones (20) (10%), (21) (24%), (22) (21%), and (23) (27%), respectively (Scheme 4).



SCHEME 3 (*i*) H^+ or Ac^+

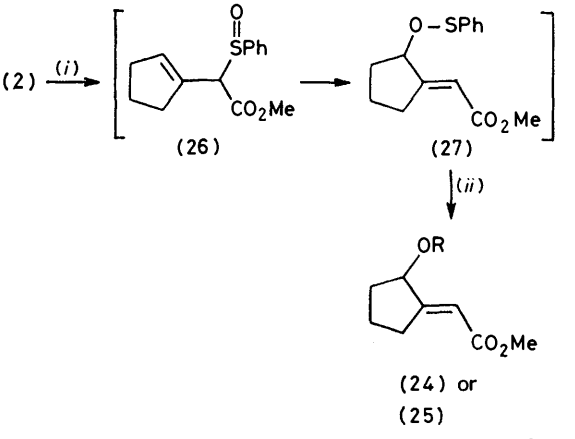
(*b*) *Sequential Prototropic Shift and Allylic Sulphoxide–Sulphenate Rearrangement.*—In one of the experiments to search for optimising the yield of the acetoxy-ester (5), the effect of pyridine [11] was examined, and we found that the presence of pyridine in the reaction of compound (2) with acetic anhydride affected markedly not only the reaction rate but also the rearrangement pathway. The reaction of compound (2) with acetic anhydride–pyridine proceeded smoothly and regioselectively even at room temperature, in contrast to the inertness of compound (2) at room temperature with acetic anhydride alone, to give the sulphur-free acetoxy-ester (24) as a single product in high yield. Treatment of the acetoxy-ester (24) with sodium methoxide in methanol afforded the hydroxy-ester (25) (91%), which confirms that the acetoxy-group in (24) is *trans* to the ester group (*E*-geometry). Furthermore, it was found that the hydroxy-ester (25) was obtained in 70% yield directly from compound (2) by treating with pyridine–water at room temperature or with pyridine alone followed by addition of water (Scheme 5). Thus, clearly, the presence of pyridine (base) is essential in this reaction. Moreover, the elimination of the sulphur-containing group and the introduction of an allylic acetoxy or hydroxy group during the reaction suggest that an allylic sulphoxide–sulphenate rearrangement reaction [12] might be involved; pyridine may act as both base and thiophile. Scheme 6 indicates the reaction pathway, which postulates the

pyridine-catalysed migration of the double bond to form the cyclo-olefin (26), assisted by the carbanion stabilising ester group, the rearrangement of (26) to the allylic sulphenate (27), and finally the cleavage of the sulphur–oxygen bond. In order to clarify the reaction sequence, and perhaps to detect the intermediates (26) and (27), the pyridine-catalysed rearrangement of (2) was followed by means of n.m.r. spectroscopy in [$^2H_5$]pyridine. The spectrum of (2) gradually changed on standing at room temperature (no change occurred in carbon tetrachloride or deuteriochloroform); new signals due to two protons appeared at δ 6.25 (m) and 4.25 (br t) and the relative intensities of these signals to that of the total methoxy-proton signal (3 H) reached 0.5 H each after 3 h and then 1 H each after 20 h, indicating that (2) had been completely transformed into an intermediate. From the chemical-shift values and the coupling patterns these new signals were assignable to the olefinic proton α to the



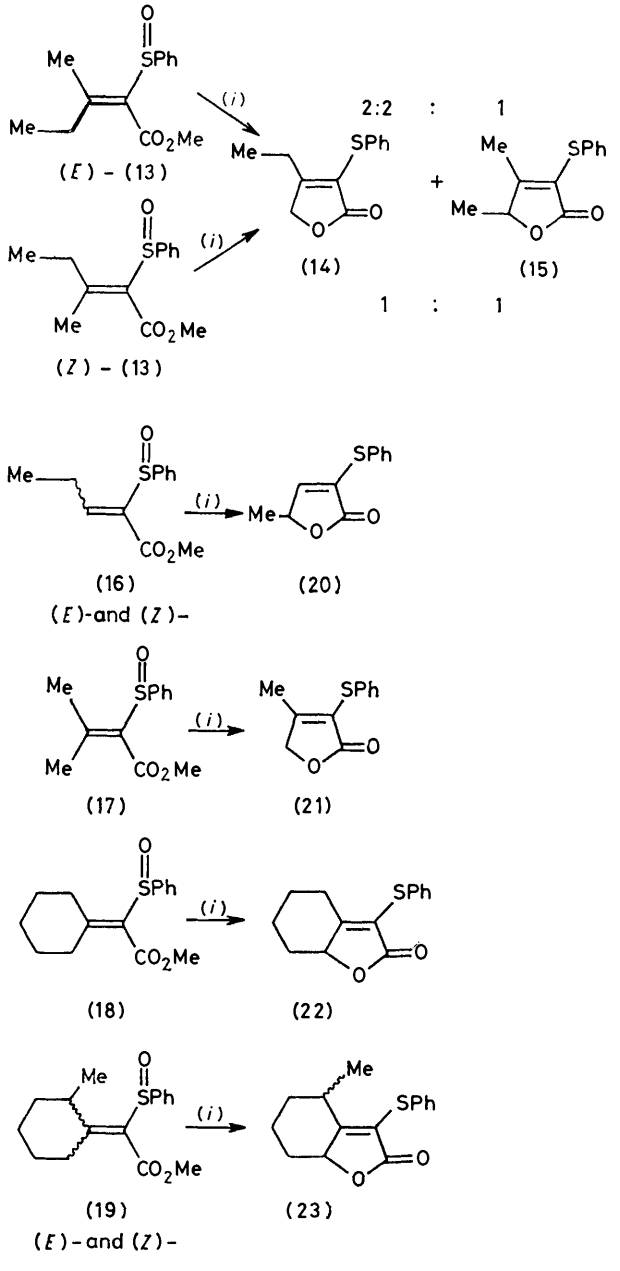
SCHEME 5 (*i*) Pyridine–Ac_2O; (*ii*) NaOMe–MeOH; (*iii*) pyridine–H_2O

ester group, and the allylic proton at the carbon atom bearing the sulphenyloxy-group in the intermediate (27), respectively. Addition of water to the solution, followed by work-up, gave the hydroxy-ester (25). Incorporation of deuterium in the hydroxy-ester (25) was observed when deuterium oxide was used. The n.m.r. spectrum of compound (25), isolated after deuterium oxide treatment (15 min in the n.m.r. tube), had an olefinic-proton signal corresponding to *ca.* 0.5 H; hence this substance is actually a *ca.* 1 : 1 mixture of (25) and deuteriated ([^{2}H]25) (Scheme 7). No deuterium incorporation was observed when the hydroxy-ester (25) was treated with pyridine–deuterium oxide.



SCHEME 6 (*i*) Pyridine; (*ii*) pyridine–Ac_2O or –H_2O

From these observations, the immediate conclusion which can be drawn is that deuterium incorporation is through the α-carbanion intermediate (28), formed reversibly from the intermediate (27), that there is a rapid equilibration [*via* (28)] between (27) and ([^{2}H]27), and that the hydrolysis step of the sulphenate group in (27) or ([^{2}H]27) is relatively slow. Additional proof for the existence of the carbanion species (28) and for the deuterium incorporation is furnished by the observation that the treatment of compound (2) with a mixture of pyridine–deuterium oxide gave the spectroscopically pure deuteriated hydroxy-ester ([^{2}H]25). The n.m.r.

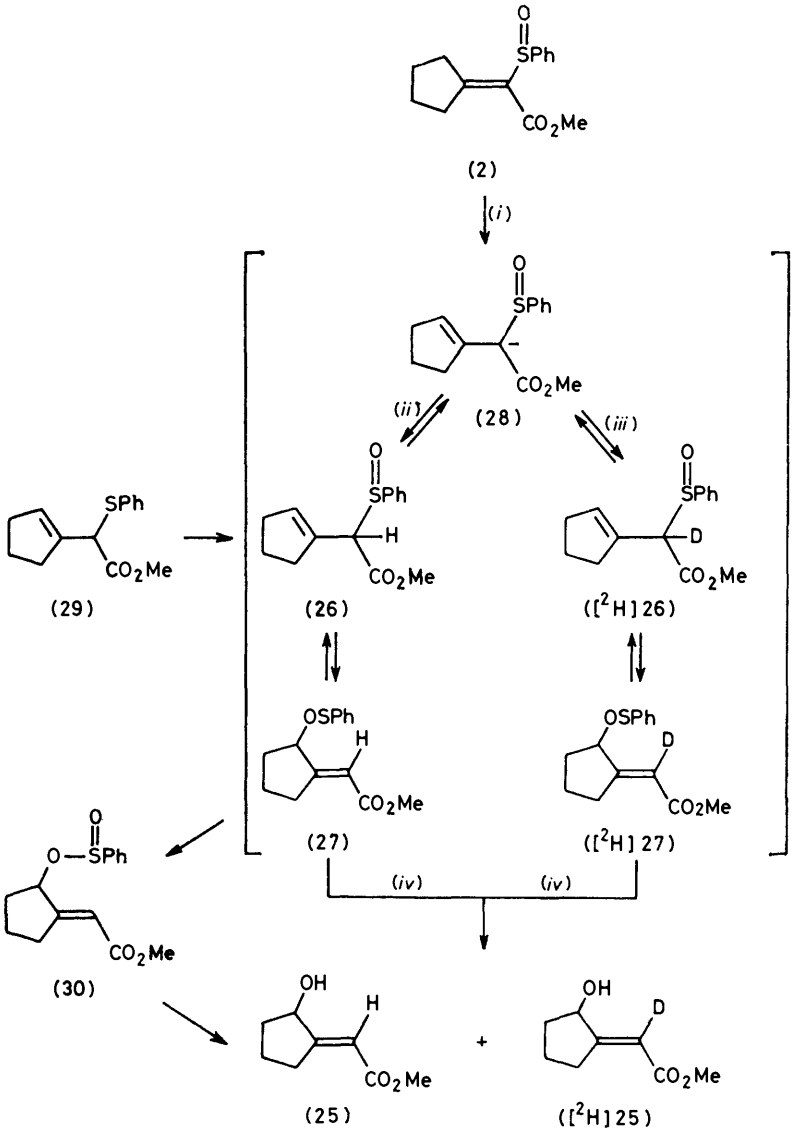


SCHEME 4 (*i*) H^+–dioxan, reflux

spectrum of ([^{2}H]25) showed no olefinic proton signal, but the signal at δ 4.41 (m) (exactly one proton) due to the proton at the γ-allylic carbon atom attached to the hydroxy group was observed. The latter finding clearly demonstrates that the process of double-bond migration between (2) (or its γ-carbanion species) and the α-carbanion (28) is irreversible; the α-carbanion in (28) would be effectively stabilised by two electron-withdrawing groups, ester and sulphoxide.

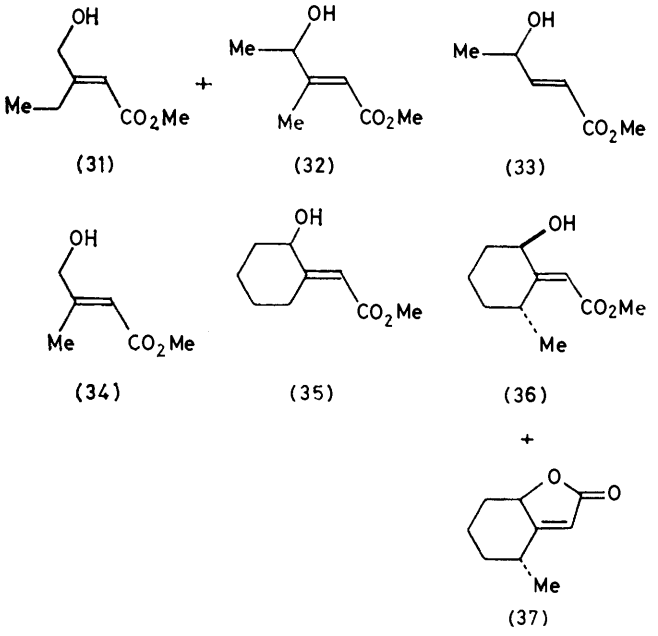
Furthermore, we have attempted to prepare the allylic sulphoxide (26) *via* an alternative route. Oxidation of the phenylthio-derivative (29) [10] with *m*-chloroperbenzoic acid afforded a mixture of products, which, without separation, was treated with pyridine–water to yield the hydroxy-ester (25) (23%) and a 1 : 1 mixture of two stereoisomers of the sulphinate derivative (30) (28%).[13] Compound (30) was identified by its n.m.r. spectrum, its stability to pyridine–water, and its smooth conversion to the hydroxy-ester (25) on treating with sodium methoxide in methanol; its formation provides additional evidence for the reaction sequence (26)→(27)→(25).

Other α-phenylsulphinylacrylates (13), (16), (17), (18), and (19) also underwent the rearrangement induced by pyridine–water under refluxing condition to give the corresponding hydroxy-esters: a mixture of (31) and (32) [inseparable; total 52% (*ca.* 5 : 1) from (*E*)-(13); total 51% (*ca.* 6 : 1) from (*Z*)-(13)], (33) (44%), (34) (64%), (35) (65%), and a mixture of (36) and (37) (separable; 37 and 42%), respectively. The ratio of the isomeric hydroxy-esters (31) and (32) was determined by comparison of the n.m.r. intensities of the ethyl-methylene in the isomer (31) and the olefinic methyl in the isomer (32). The predominant formation of the hydroxymethyl

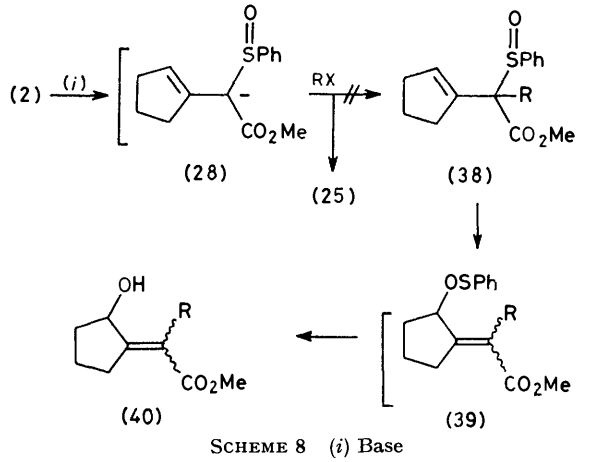


SCHEME 7 (*i*) [$^2H_5$]pyridine, 20 h; (*ii*) H^+; (*iii*) D^+; (*iv*) slow, D_2O for 15 min then isolation

ester (31) from both isomers of (13), and the exclusive introduction of the hydroxy group at the methylene position in compounds (36) and (37) [from a mixture of (*E*)- and (*Z*)-(19)], may be ascribed to the varying ease of deprotonation, in the order of $CH_3 > CH_2 \gg CH$. The stereochemistries of compounds (36) and (37) were assigned on the basis of the n.m.r. spectra.



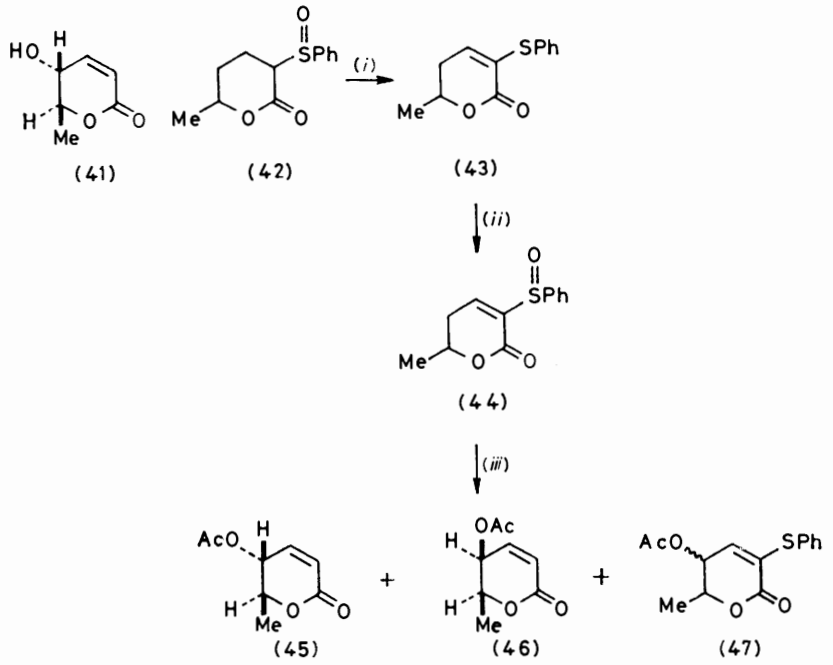
An attempt to extend this reaction was also examined. If the carbanion (28) has, in the presence of an appropriate base, sufficiently high nucleophilicity to react with alkyl halides, the difunctionalised product (40) would be formed in one step through a reaction sequence (28) ⟶ (39) (Scheme 8), *i.e.* an alkylative rearrangement. However, all the attempted experiments using methyl iodide as an alkylating agent under a variety of conditions [base (pyridine, triethylamine, lithium diisopropylamide, *etc.*), solvent, temperature] were unsuccessful, the hydroxy-ester (25) being the only isolable product.



SCHEME 8 (*i*) Base

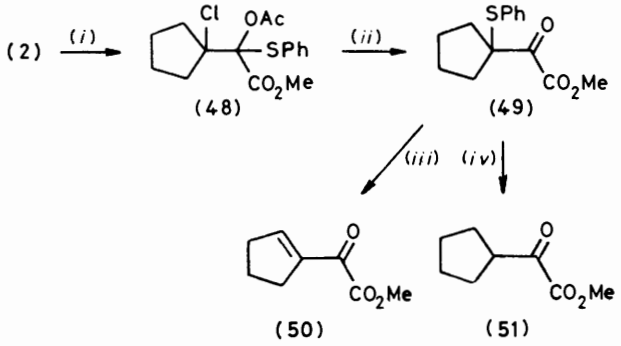
Osmundalactone (41), which is the aglycone of the fern glycoside osmundalin, isolated from *Osmunda japonica* Thunb. (akaboshi zenmai) and *O. regalis* var. *spectabilis* (Willd.) Gray,[14] has a γ-hydroxy-αβ-unsaturated lactone moiety and seems to be a synthetically suitable target for application of this rearrangement reaction. The easily accessible α-phenylsulphinyl lactone (42) [10] underwent smoothly, on treatment with trifluoroacetic anhydride,[15] the Pummerer rearrangement and the simultaneous elimination of trifluoroacetic acid [16] to give the (phenylthio)pyranone (43) in 71% yield, which was quantitatively converted into the corresponding sulphoxide (44) by oxidation with *m*-chloroperbenzoic acid. For convenience of isolation, the conversion of the compound (44) into the *O*-acetyl derivative of osmundalactone (41) was examined. Among the conditions employed, the best result was obtained when the reaction was performed in acetic anhydride–DBU–hot tetrahydrofuran. Thus, (±)-*O*-acetylosmundalactone (45), which was identified with an authentic sample derived from the natural osmundalactone (41), the stereoisomeric (46), and the phenylthiolactone (47) were isolated in 13, 7, and 8% yields, respectively (Scheme 9). The phenylthio-lactone (47) was clearly produced through the vinylogous Pummerer reaction. Hence, in an α-phenylsulphinyl-αβ-unsaturated lactone system such as (44), it was found that the sequential prototropic shift and allylic sulphoxide–sulphenate rearrangement was not a high yield reaction (and not affected sterically by a δ-substituent), and that, furthermore, the vinylogous Pummerer rearrangement took place competitively.

(*c*) *Additive Pummerer Rearrangement.*—In view of the quite interesting behaviour of compound (2) as described above, we also investigated the reactions of (2) with more powerful reagents, such as acetyl chloride, thionyl chloride, and trifluoroacetic anhydride. Treatment of compound (2) with acetyl chloride at 0 °C afforded the acetoxy-chloro-phenylthio-ester (48) in 90% yield, accompanied by small amounts of the dichloro-compound (see below) and the reduced product, methyl α-(phenylthio)cyclopentylidene acetate. The structure of compound (48), especially the positions of the acetoxy and chloro-groups, was rigorously confirmed by chemical means. Compound (48) rearranged further upon heating alone (distillation), or in solution in aqueous dioxan at 120 °C, to give a quantitative yield of the halogen-free β-phenylthio-glyoxylate (49), which was transformed into the unsaturated glyoxylate (50) by oxidation to the sulphoxide followed by dehydrosulphenylation, and into the saturated glyoxylate (51) by reductive desulphurisation with Raney nickel (Scheme 10). The latter compound (51) was identified with an authentic sample.[17] A reasonable pathway for the formation of the acetoxy-chloro-ester (48) from (2) is outlined in Scheme 11. The attack of a chloride ion on the β-carbon atom of the initially formed vinyl-acetoxy sulphonium salt (52) produced the Pummerer intermediate (53); addition of acetate ion to (53) gave the product (48); this is formally

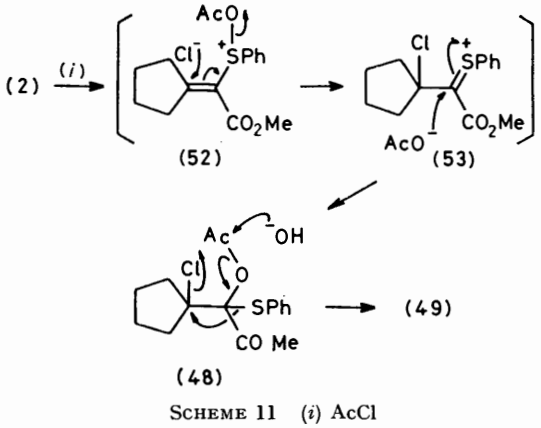


SCHEME 9 (*i*) $(CF_3CO)_2O$, 0 °C; (*ii*) [O]; (*iii*) Ac_2O–DBU–tetrahydrofuran, reflux

the additive Pummerer reaction, and is related to the rearrangement reactions of phenyl vinyl sulphoxide with dithioacetic acid [6] and of 1,4-thiazine 1-oxide derivatives with acetyl chloride.[7,18] The exclusive attack of chloride ion on the β-olefinic carbon atom of the sulphonium salt (52) is probably due to the high nucleophilic character of Cl^-, and is in contrast to the preferential abstraction of a γ-allylic hydrogen atom under the conditions suitable for the vinylogous Pummerer rearrangement of compound (2). Then, the transformation of the acetoxy-chloro-ester (48) to the β-phenylthio-glyoxylate (49) may take place by elimination of acetic acid and hydrogen chloride, or acetyl chloride, with concomitant migration of the phenylthio-group and ketonisation.

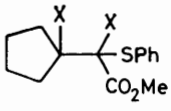


SCHEME 10 (*i*) AcCl; (*ii*) heat or dilute dioxan and heat (*iii*) *m*-chloroperbenzoic acid and heat; (*iv*) Raney nickel



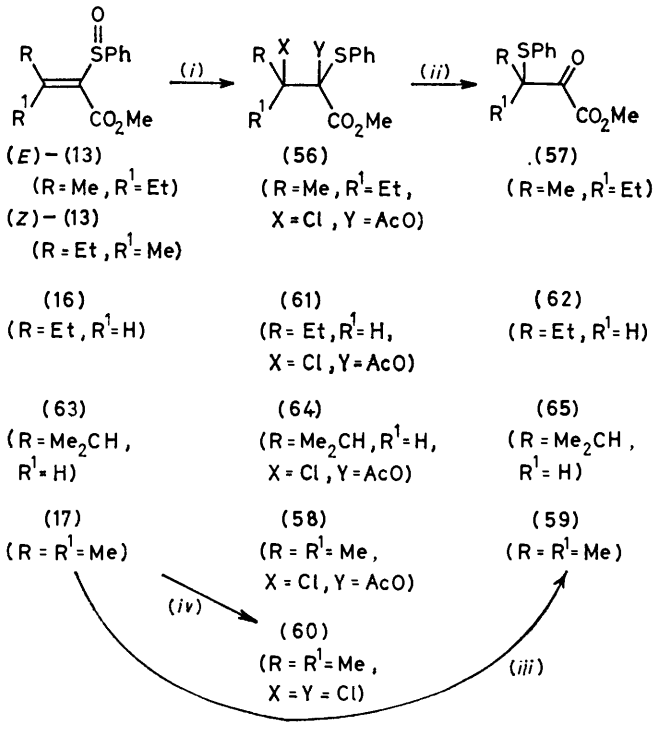
SCHEME 11 (*i*) AcCl

A similar rearrangement of compound (2) was also observed in the reaction with thionyl chloride or trifluoroacetic anhydride; the dichloro- and bis(trifluoroacetoxy)-(phenylthio)esters, (54) and (55), respectively, were obtained quantitatively. Compound (55) was also converted, upon treatment with hot dilute dioxan, into the glyoxylate (49) in quantitative yield, whereas compound (54) gave a low yield of the glyoxylate (49) (17%), along with other intractable products.



(54) : X = Cl
(55) : X = CF_3CO_2

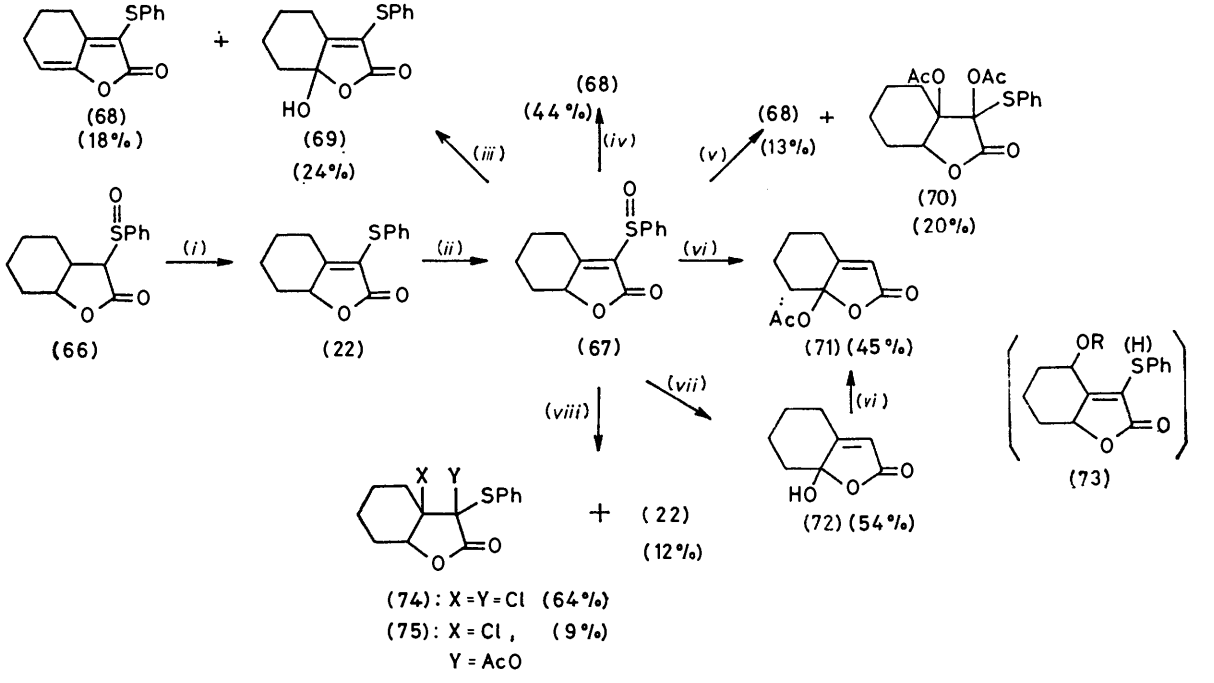
Additional examples of the additive Pummerer rearrangement are shown in Scheme 12. On treatment with acetyl chloride the phenylsulphinylacrylates (16) and (63), having a β-hydrogen atom, also underwent preferentially the additive Pummerer rearrangement to give the acetoxy-chloro-esters (61) and (64) in good yields, rather than the β-hydrogen-participating rearrangement to produce a chrolovinyl sulphide or β-ketosulphide, as observed in the reaction of styryl sulphoxides.[3,4]



SCHEME 12 (*i*) AcCl; (*ii*) dilute dioxan; (*iii*) $(CF_3CO)_2O$; (*iv*) $SOCl_2$

(*d*) *Reactions of Related Compounds.*—From a synthetic point of view, application of the above-mentioned reactions to fused α-phenylsulphinyl-αβ-unsaturated five-membered lactones would be of considerable interest, and we have selected compound (67) as a representative derivative and examined its reactions. Compound (67) was prepared by oxidation of the phenylthiobenzofuranone (22), which was synthesised from the known saturated derivative (66) [19] by treatment with trifluoroacetic anhydride.[16] The results of the reactions of (67) are summarised in Scheme 13, from which it is clear that in both the vinylogous Pummerer and sequential prototropic shift and allylic sulphoxide–sulphenate rearrangement reactions a hydroxy or acetoxy group was exclusively introduced at the carbon atom attached to the lactonic ethereal oxygen atom, giving rise to compounds (68), (69), (71), and (72), accompanied by the additive Pummerer rearrangement product (70) in the case of the reaction with acetic anhydride. The regioisomeric compounds (73) were not formed, probably due to the higher acidity of the hydrogen atom on the carbon atom attached to the lactonic ethereal oxygen atom. In the case of the additive Pummerer reaction with acetyl chloride, the dichloro-derivative (74) was predominantly produced; the minor acetoxy-chloro-derivative (75) was detected by the n.m.r. spectroscopy.

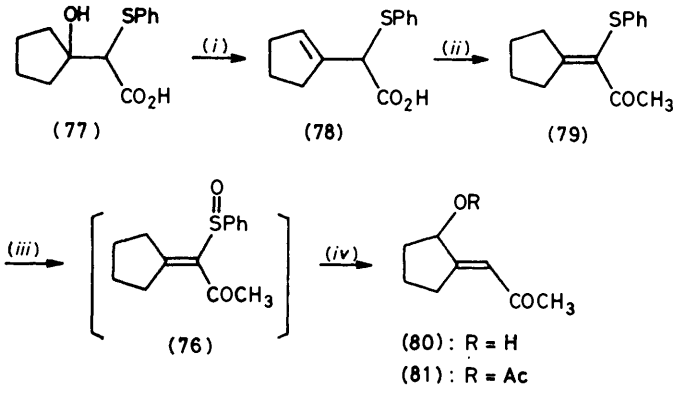
Finally, it is appropriate to compare the reactivity of the α-phenylsulphinyl-αβ-unsaturated ketone derivative (76) with that of the ester derivative (2). Synthesis of the precursory phenylthio-derivative (79) was accomplished *via* a reaction sequence starting from the hydroxy-acid (77) [10] as shown in Scheme 14. Unexpectedly, it was found that the vinyl-keto-sulphoxide (76) was fairly unstable, and was not isolable. The sequential prototropic shift and allylic sulphoxide–sulphenate rearrangement product (80) was the only identifiable product, obtained in 20% yield upon treating the crude



SCHEME 13 (*i*) $(CF_3CO)_2O$; (*ii*) [O]; (*iii*) H^+–dioxan, heat; (*iv*) Ac_2O–$MeSO_3H$; (*v*) Ac_2O; (*vi*) pyridine–Ac_2O; (*vii*) pyridine–H_2O; (*viii*) AcCl

oxidation product of the phenylthio-derivative (79) with pyridine–water, and identified as the acetate (81).

As is clear from the examples cited above the reactions of α-phenylsulphinylacrylates (1), together with the reactions of (phenylthio)acetic acid and its ester reported in the previous paper,[10] would be of considerable utility for the preparation of a wide variety of compounds starting from ketones.



SCHEME 14 (*i*) Toluene-*p*-sulphonic acid, benzene; (*ii*) $SOCl_2$ or $(COCl)_2$, then $LiMe_2Cu$; (*iii*) *m*-chloroperbenzoic acid; (*iv*) pyridine–H_2O

EXPERIMENTAL

Liquid products were usually purified by evaporative short-path distillation; oil-bath temperatures are recorded. I.r. spectra of solutions in carbon tetrachloride (unless otherwise indicated) were obtained with a Hitachi EPI-S2 or G2 spectrophotometer. N.m.r. spectra of solutions in carbon tetrachloride (unless otherwise indicated) were recorded with JEOL C-60 or PMX-60 (60 MHz), or PS-100 (100 MHz) instruments, with tetramethylsilane as internal standard; coupling constants are given in Hz. Microanalyses were carried out in the microanalytical laboratory of this Institute.

General Procedure for Preparation of α-Phenylsulphinylacrylates.—To a solution of the methyl α-phenylthioacrylate [10] in dichloromethane (*ca.* 10—15 ml per mmol of acrylate) was added a solution of *m*-chloroperbenzoic acid (1.02—1.10 equiv.) in dichloromethane (*ca.* 10 ml per mmol of the peracid) at 0 °C. The reaction mixture was stirred at 0 °C for 20—30 min, neutralised with 10% aqueous sodium hydroxide solution, and the water layer extracted with dichloromethane. The combined organic layers were washed with water and brine, dried, and evaporated to dryness. The residual crude α-phenylsulphinylacrylate was purified by chromatography on silica gel (eluant light petroleum–diethyl ether) and/or recrystallisation, but not by distillation.

Methyl cyclopentylidene-α-(phenylsulphinyl)acetate (2). *Compound* (2) (3.76 g, 67%) was obtained from methyl cyclopentylidene-α-(phenylthio)acetate (5.21 g); m.p. 41—43 °C [from light petroleum–diethyl ether (1 : 1)], $\nu_{max.}$ 1 715, 1 600, 1 430, 1 225, and 1 050 cm^{-1}; δ 1.40—2.00 (4 H, m), 2.30—3.35 (4 H, m), 3.56 (3 H, s), and 7.20—7.70 (5 H, m) (Found: C, 63.4; H, 6.1. $C_{14}H_{16}O_3S$ requires C, 63.6; H, 6.1%).

Methyl (E)- *and* (Z)-2-(*phenylsulphinyl*)*pent*-2-*enoate* (16). *Compound* (16) (0.47 g, 83%; the analytical sample was purified by preparative t.l.c.) was obtained from methyl (*E*)- and (*Z*)-2-(phenylthio)pent-2-enoate (0.53 g); $\nu_{max.}$ 1 715, 1 615, 1 435, 1 235, and 1 050 cm^{-1}; δ 1.12 and 1.17 (total 3 H, each t, *J* 7.0), 2.70 and 2.90 (total 2 H, each quintet, *J* 7.0), 3.62 (3 H, s), 6.97 and 7.18 (total 1 H, each t, *J* 7.0), and 7.00—8.00 (5 H, m) (Found: C, 60.6; H, 5.8. $C_{12}H_{14}O_3S$ requires C, 60.5; H, 5.9%).

Methyl β-*methyl*-α-(*phenylsulphinyl*)*crotonate* (17). *Compound* (17) (0.9 g, 71%) was obtained from methyl β-methyl-α-phenylthiocrotonate (1.2 g); m.p. 91—92 °C (from diethyl ether); $\nu_{max.}(CHCl_3)$ 1 720, 1 620, 1 445, 1 260, 1 205, and 1 040 cm^{-1}; $\delta(CDCl_3)$ 2.08 (3 H, s), 2.35 (3 H, s), 3.50 (3 H, s), and 7.35—7.75 (5 H, m) (Found: C, 60.4; H, 6.0. $C_{12}H_{14}O_3S$ requires C, 60.5; H, 5.9%).

Methyl cyclohexylidene-α-(phenylsulphinyl)acetate (18). *Compound* (18) (2.36 g, 82%; the analytical sample was purified by preparative t.l.c.) was obtained from methyl cyclohexylidene-α-(phenylthio)acetate (2.7 g); $\nu_{max.}$ 1 720, 1 615, 1 445, 1 210, and 1 051 cm^{-1}; δ 1.40—2.10 (6 H, m), 2.10—2.60 (2 H, m), 2.60—3.00 (2 H, m), 3.41 (3 H, s), and 7.20—7.65 (5 H, m) (Found: C, 64.8; H, 6.8. $C_{15}H_{18}O_3S$ requires C, 64.7; H, 6.5%).

Methyl (E)- *and* (Z)-(2-*methylcyclohexylidene*)-α-(*phenylsulphinyl*)*acetate* (19). *Compound* (19) (1.8 g, quantitative; the analytical sample was purified by preparative t.l.c.) was obtained from methyl (*E*)- and (*Z*)-(2-methylcyclohexylidene)-α-(phenylthio)acetate (1.66 g); $\nu_{max.}$ 1 720, 1 610, 1 215, and 1 050 cm^{-1}; δ 1.20 and 1.24 (total 3 H, each d, *J* 8.0), 0.90—2.50 (9 H, m), 3.40 and 3.46 (total 3 H, each s), and 7.10—7.50 (5 H, m) (Found: C, 65.6; H, 7.0. $C_{16}H_{20}O_3S$ requires C, 65.7; H, 6.9%).

Methyl (E)- *and* (Z)-4-*methyl*-2-(*phenylsulphinyl*)*pent*-2-*enoate* (63). *Compound* (63) (2.16 g, quantitative; the analytical sample was purified by preparative t.l.c.) was obtained from methyl (*E*)- and (*Z*)-4-methyl-2-(phenylthio)-pent-2-enoate (2.03 g); $\nu_{max.}$ 1 715, 1 615, 1 255, and 1 050 cm^{-1}; δ 0.98 (3 H, d, *J* 6.0), 1.14 (3 H, d, *J* 6.0), 3.33—4.17 (1 H, m), 3.57 (3 H, s), 6.97 (1 H, d, *J* 11.0), and 7.17—7.70 (5 H, m) (Found: C, 61.9; H, 6.4. $C_{13}H_{16}O_3S$ requires C, 62.0; H, 6.5%).

Vinylogous Pummerer Reaction of the α-Phenylsulphinylacrylate (2) *induced by Acetic Anhydride.*—A solution of the α-phenylsulphinylacrylate (2) (1.9 g) in acetic anhydride (5 ml) was heated at 75 °C for 3 h. Chopped ice and 30% sodium hydroxide solution were added and the resulting mixture was thoroughly extracted with ether. The combined extracts were washed with water and brine, and evaporated to dryness. Chromatography of the oil remaining (2.05 g) on silica gel [40 g, eluant light petroleum alone to light petroleum–diethyl ether (1 : 1)] gave *methyl* (E)-(*cyclopent*-2-*enylidene*)(*phenylthio*)*acetate* (7) (0.33 g, 18.7%), and *methyl* (Z)- (6) (0.31 g, 14.2%) and (E)-(2-*acetoxycyclopentylidene*)(*phenylthio*)*acetate* (5) (1.08 g, 50%). The dienoic-ester (7) polymerised during distillation; $\nu_{max.}$ 1 700, 1 580, 1 475, 1 435, and 1 235 cm^{-1}; δ 2.40—2.90 (3 H, m), 3.20 (1 H, m), 3.59 (3 H, s), 6.70 (1 H, m), and 6.80—7.50 (6 H, m) (Found: C, 68.6; H, 6.0. $C_{14}H_{14}O_2S$ requires C, 68.3; H, 5.7%).

The (*Z*)-acetoxy-ester (6) had m.p. 87—88 °C (crystallised on standing; washed with carbon tetrachloride); $\nu_{max.}$ 1 740, 1 715, 1 580, 1 435, 1 370, and 1 230 cm^{-1}; δ 1.50—2.30 (4 H, m), 1.82 (3 H, s), 2.30—3.08 (2 H, m), 3.50 (3 H, s), 5.80 (1 H, m), and 7.17 (5 H, s) (Found: C, 62.4; H, 6.2. $C_{16}H_{18}O_4S$ requires C, 62.7; H, 5.9%).

The (*E*)-acetoxy-ester (5) had m.p. 42—43 °C (crystallised on standing; washed with carbon tetrachloride); $\nu_{max.}$ 1 740,

1 720, 1 580, 1 430, 1 370, and 1 230 cm^{-1}; δ 1.40—2.30 (4 H, m), 1.92 (3 H, s), 2.30—2.81 (2 H, m), 3.48 (3 H, s), 5.91 (1 H, m), and 7.20 (5 H, s) (Found: C, 62.4; H, 5.9. $C_{16}H_{18}O_4S$ requires C, 62.7; H, 5.9%).

Saponification of the Major (E)-*Acetoxy-ester* (5).—A solution of the major (*E*)-acetoxy-ester (5) (0.39 g) in ether (10 ml) saturated with perchloric acid was stirred for 5 h at room temperature. The mixture was diluted with ether, washed with water and brine, and evaporated to dryness. Chromatography of the residue (0.3 g) [preparative t.l.c. on silica gel; eluant light petroleum–diethyl ether (5 : 2)] gave the *dienoic-ester* (7) (0.024 g, 7.7%), *methyl* (E)-(2-*methoxycyclopentylidene*)(*phenylthio*)*acetate* (8) (0.066 g, 19%), and 4,5,6,6a-*tetrahydro*-3-(*phenylthio*)*cyclopenta*[b]*furan*-2-*one* (3) (0.13 g, 44%). The methoxy-ester (8) had b.p. 100—130 °C at 1 mmHg; $\nu_{max.}$ 1 720, 1 580, 1 435, and 1 240 cm^{-1}; δ 1.30—2.25 (4 H, m), 2.25—3.00 (2 H, m), 3.22 (3 H, s), 3.50 (3 H, s), 4.75 (1 H, m), and 6.90—7.67 (5 H, m) (Found: C, 64.6; H, 6.3. $C_{15}H_{18}O_3S$ requires C, 64.7; H, 6.5%).

General Procedure for the Vinylogous Pummerer Reaction of the α-Phenylsulphinylacrylates induced by Dilute Sulphuric Acid–Dioxan.—A solution of the α-phenylsulphinylacrylate (*ca.* 1.0—2.4 mmol) in dioxan (*ca.* 4—10 ml) and 6N sulphuric acid (*ca.* 0.5—2 ml) was heated under reflux for 4—20 h. The reaction mixture was diluted with water and extracted with ether, chloroform, or dichloromethane. The combined extracts were washed with water and brine, and evaporated to dryness. The residual crude product was purified by preparative t.l.c. on silica gel (light petroleum–diethyl ether) and/or recrystallisation (or distillation).

4,5,6,6a-*Tetrahydro*-3-(*phenylthio*)*cyclopenta*[b]*furan*-2-*one* (3).—The 3-(*phenylthio*)*furanone* (3) (0.23 g, 53%) was obtained from the α-phenylsulphinylacrylate (2) (0.52 g); m.p. 95—96 °C [from diethyl ether–carbon tetrachloride (1 : 1)], $\nu_{max.}$($CHCl_3$) 1 780, 1 750, 1 640, 1 470, and 1 000 cm^{-1}; δ($CDCl_3$) 0.80—2.60 (6 H, m), 5.12 (1 H, dd, *J* 11.0 and 6.0), and 7.15—7.60 (5 H, m) (Found: C, 67.5; H, 5.4. $C_{13}H_{12}O_2S$ requires C, 67.2; H, 5.2%). In the scale-up experiment, a trace of *methyl* (Z)-(2-*hydroxycyclopentylidene*)(*phenylthio*)*acetate* (4) (oil), $\nu_{max.}$ 3 500, 1 715, and 1 240 cm^{-1}; δ 1.50—2.20 (4 H, m), 2.50—3.10 (3 H, m; 2 H by the addition of D_2O), 3.51 (3 H, s), 4.60—4.95 (1 H, m), and 7.20 (5 H, br s), was obtained by chromatographic separation, and acetylated by the usual manner (acetic anhydride–pyridine) to give the (Z)-*acetoxy-ester* (6).

4-*Ethyl*-3-(*phenylthio*)*furan*-2(5H)-*one* (14) *and* 4,5-*Dimethyl*-3-(*phenylthio*)*furan*-2(5H)-*one* (15).—An inseparable mixture of the two 3-(*phenylthio*)*furanones* (14) and (15) [0.17 g (2.2 : 1), 32% and 0.096 g (1 : 1), 33%] was obtained from the α-phenylsulphinylacrylate (13) [(*E*)-: 0.6 g and (*Z*)-: 0.34 g] and had b.p. 100—140 °C at 1 mmHg; $\nu_{max.}$ 1 775 (sh), 1 765, 1 625, 1 440, 1 145, 1 025, and 990 cm^{-1}; (14), δ 1.10 (3 H, t, *J* 7.0), 2.58 (2 H, q, *J* 7.0), and 4.70 (1 H, s); (15), δ 1.38 (3 H, d, *J* 7.0), 2.03 (3 H, s), 4.85 (1 H, q, *J* 7.0), and 7.15 (5 H, s) (Found: C, 65.4; H, 5.5. $C_{12}H_{12}O_2S$ requires C, 65.4; H, 5.5%).

5-*Methyl*-3-(*phenylthio*)*furan*-2(5H)-*one* (20).—The 3-(*phenylthio*)*furan*-2(5H)-*one* (20) (0.024 g, 10%) was obtained from the α-phenylsulphinylacrylate (16) (0.27 g) and identified by comparison with an authentic sample.[16]

4-*Methyl*-3-(*phenylthio*)*furan*-2(5H)-*one* (21).—The 3-(*phenylthio*)*furan*-2(5H)-*one* (21) (0.08 g, 24%) was obtained from the α-phenylsulphinylacrylate (17) (0.4 g); m.p. 50—51 °C (crystallised on standing, washed with carbon tetrachloride); $\nu_{max.}$ 1 785, 1 760, 1 635, and 1 020 cm^{-1}; δ 2.10 (3 H, br s), 4.69 (2 H, br s), and 7.10—7.50 (5 H, m) (Found: C, 64.1; H, 4.9. $C_{11}H_{10}O_2S$ requires C, 64.1; H, 4.9%).

5,6,7,7a-*Tetrahydro*-3-(*phenylthio*)*benzofuran*-2(4H)-*one* (22).—The 3-*phenylthiobenzofuranone* (22) (0.04 g, 21%) was obtained from the α-phenylsulphinylacrylate (18) (0.22 g); $\nu_{max.}$ 1 770, 1 630, and 995 cm^{-1}; δ 0.70—3.20 (8 H, m), 4.20—4.85 (1 H, m), 6.90—7.35 (5 H, m) (Found: C, 68.6; H, 5.8. $C_{14}H_{14}O_2S$ requires C, 68.3; H, 5.7%).

5,6,7,7a-*Tetrahydro*-4-*methyl*-3-(*phenylthio*)*benzofuran*-2(4H)-*one* (23).—The 3-*phenylthiobenzofuranone* (23) (0.075 g, 27%; a mixture of the stereoisomers) was obtained from the α-phenylsulphinylacrylate (19) (0.3 g); $\nu_{max.}$ 1 770, 1 630, and 1 000 cm^{-1}; δ 0.67—2.80 (7 H, m), 1.10 and 1.53 (total 3 H, each d, *J* 8.0), 4.48 and 4.78 (total 1 H, m), and 6.83—7.33 (5 H, m) (Found: C, 68.8; H, 6.6. $C_{15}H_{10}O_2S$ requires C, 69.2; H, 6.2%).

Sequential Prototropic Shift and Allylic Sulphoxide–Sulphenate Rearrangement Reaction of the α-Phenylsulphinyl acrylate (2) *induced by Pyridine–Acetic Anhydride.*—To a solution of the α-phenylsulphinylacrylate (2) (0.58 g) in acetic anhydride (3 ml) was added pyridine (1.5 ml). After being stirred at room temperature overnight, the reaction mixture was poured into chopped ice, acidified with ice-cold 6N sulphuric acid (indicator Congo Red), and extracted with ether. The combined extracts were washed with 30% aqueous sodium hydroxide solution, water, and brine, and evaporated to dryness. Chromatography of the residue [prepative t.l.c. on silica gel; light petroleum–diethyl ether (5 : 1)] gave *methyl* (E)-(2-*acetoxycyclopentylidene*)*acetate* (24) (0.36 g, 83%); b.p. 90—110 °C at 2 mmHg; $\nu_{max.}$ 1 740, 1 720, and 1 665 cm^{-1}; δ 1.40—2.40 (4 H, m), 2.02 (3 H, s), 2.65—3.10 (2 H, m), 3.68 (3 H, s), 5.53 (1 H, br, dd, *J* 7.5 and 5.0), and 5.90 (1 H, q, *J* 2.0) (Found: C, 60.6; H, 6.9. $C_{10}H_{14}O_4$ requires C, 60.6; H, 7.1%). A solution of the acetoxy-ester (24) (0.17 g) in anhydrous methanol containing a small amount of sodium methoxide was stirred at room temperature for 1 h. The mixture was poured into ice–water and thoroughly extracted with ether. The combined extracts were washed with water and brine, and evaporated to yield the *hydroxy-ester* (25) (0.12 g, 91%).

General Procedure for the Sequential Prototropic Shift and Allylic Sulphoxide–Sulphenate Rearrangement Reaction of the α-Phenylsulphinylacrylates induced by Pyridine–Water.—A solution of the α-phenylsulphinylacrylate (*ca.* 0.5—2 mmol) in pyridine (*ca.* 1—3 ml) and water (*ca.* 0.3—1.5 ml) was stirred at room temperature for 6 h in the case of (2) or heated under reflux for 0.6—3.5 h in other cases. The reaction mixture was diluted with ice–water, acidified with ice-cold 6N sulphuric acid, and extracted with ether. The combined extracts were washed with water and brine, and solvent evaporated off. The residual crude product was purified by preparative t.l.c. on silica gel (light petroleum–diethyl ether) and distillation (or recrystallisation).

Methyl (E)-(2-*Hydroxycyclopentylidene*)*acetate* (25).—The *hydroxy-ester* (25) (0.2 g, 70%) was obtained from the α-phenylsulphinylacrylate (2) (0.51 g); b.p. 90—120 °C at 2 mmHg; $\nu_{max.}$ 3 400, 1 715, and 1 660 cm^{-1}; δ 1.03—2.20 (4 H, m), 2.60—3.02 (2 H, m), 3.50 (1 H, OH), 3.65 (3 H, s), 4.41 (1 H, m), and 5.92 (1 H, q, *J* 2.0) (Found: C, 61.7; H, 8.0. $C_8H_{12}O_3$ requires C, 61.5; H, 7.8%).

When deuterium oxide instead of water was used, the α-deuterio-derivative ([^{2}H]25), δ 1.10—2.20 (4 H, m), 2.50—3.00 (2 H, m), 3.65 (3 H, s), 3.77 (1 H, OH), and 4.40 (1 H, m), was obtained.

Methyl (E)-3-(*Hydroxymethyl*)*pent*-2-*enoate* (31) *and Methyl* (E)-4-*Hydroxy*-3-*methylpent*-2-*enoate* (32).—The inseparable mixture of the two *hydroxy-esters* (31) and (32) [0.047 g (*ca.* 5 : 1), 52% and 0.045 g (*ca.* 6 : 1), 51%] was obtained from the α-phenylsulphinylacrylate (13) [(*E*)-: 0.153 g and (*Z*)-: 0.155 g]; b.p. 40—60 °C at 1 mmHg; $\nu_{max.}$ 3 400, 1 710, and 1 655 cm^{-1}; δ 1.07 (t, *J* 7.0), 1.28 (d, *J* 7.0), 2.05 (s with fine splitting), 2.50 (q, *J* 7.0), 3.27 (total 1 H, br s, OH), 3.63 (total 3 H, s), 4.07 (total 3 H, s, and m), and 5.80 (total 1 H, s) (Found: C, 58.1; H, 8.3 $C_7H_{12}O_3$ requires C, 58.3; H, 8.4%).

Methyl (E)-4-*Hydroxypent*-2-*enoate* (33).—The *hydroxy-ester* (33) (0.05 g, 44%) was obtained from the α-phenylsulphinylacrylate (16) (0.207 g); b.p. 35—45 °C at 1 mmHg; $\nu_{max.}$ 3 400, 1 715, and 1 655 cm^{-1}; δ 1.28 (3 H, d, *J* 7.0), 3.37 (1 H, br s, OH), 3.67 (3 H, s), 4.37 (1 H, m), 5.90 (1 H, dd, *J* 16.0 and 2.0), and 6.87 (1 H, dd, *J* 16.0 and 4.0) (Found: C, 55.6; H, 8.0. $C_6H_{10}O_3$ requires C, 55.4; H, 7.8%).

Methyl (E)-β-(*Hydroxymethyl*)*crotonate* (34).—The *hydroxy-ester* (34) (0.068 g, 64%) was obtained from the α-phenylsulphinylacrylate (17) (0.2 g); b.p. 30—50 °C at 1 mmHg; $\nu_{max.}$ 3 400, 1 715, and 1 655 cm^{-1}; δ 1.97 (3 H, finely split s), 3.58 (4 H, s, OH and OCH_3), 3.98 (2 H, s), and 5.80 (finely split s) (Found: C, 55.0; H. 7.8. $C_6H_{10}O_3$ requires C, 55.4; H, 7.8%).

Methyl (E)-(2-*Hydroxycyclohexylidene*)*acetate* (35).—The *hydroxy-ester* (35) (0.93 g, 65%) was obtained from the α-phenylsulphinylacrylate (18) (0.24 g); b.p. 75—85 °C at 1.5 mmHg; $\nu_{max.}$ 3 400, 1 715, and 1 655 cm^{-1}; δ 1.00—2.20 (8 H, m), 3.18 (1 H, br s, OH), 3.60 (3 H, s), 3.95 (1 H, m), and 5.80 (1 H, br s) (Found: C, 63.7; H, 8.5. $C_9H_{14}O_3$ requires C, 63.5; H, 8.3%).

Methyl (E)-(trans-2-*Hydroxy*-6-*methylcyclohexylidene*)-*acetate* (36) *and* 5,6,7,7a-*Tetrahydro*-4-*methylbenzofuran*-2(4H)-*one* (37).—The *hydroxy-ester* (36) (0.15 g, 37%) and the *furanone* (37) (0.14 g, 42%) were obtained from the α-phenylsulphinylacrylate (19) (0.64 g). Compound (36); b.p. 70—100 °C at 2 mmHg; $\nu_{max.}$ 3 450, 1 710, and 1 640 cm^{-1}; δ 1.10 (3 H, d, *J* 8.0), 1.20—2.22 (6 H, m), 3.08 (1 H, br s), 3.65 (3 H, s), 4.00—4.40 (2 H, m), and 5.90 (1 H, d, *J* 2.0) (Found: C, 65.0; H, 8.7. $C_{10}H_{16}O_3$ requires C, 65.2; H, 8.8%). Compound (37); m.p. 42—43 °C (from light petroleum); $\nu_{max.}$ 1 765, 1 750, and 1 640 cm^{-1}; δ 1.10 (3 H, d, *J* 8.0), 1.40—2.18 (5 H, m), 2.50 (1 H, m), 3.15 (1 H, m), 4.75 (1 H, ddd, *J* 11.0, 6.5, and 2.0), and 5.58 (1 H, d, *J* 2.0) (Found: C, 70.8; H, 8.2. $C_9H_{12}O_2$ requires C, 71.0; H, 8.0%).

Oxidation of Methyl (*Cyclopent*-1-*enyl*)(*phenylthio*)*acetate* (29) *and Subsequent Treatment with Pyridine–Water*.—To a solution of the α-(phenylthio)-ester (29) [10] (0.39 g) in dichloromethane (10 ml) was added a solution of *m*-chloroperbenzoic acid (0.39 g, 1.2 equiv.) in dichloromethane (10 ml) at 0 °C. The reaction mixture was stirred at room temperature for 30 min and worked up in the same manner as described earlier. The crude product was dissolved in pyridine (2 ml) and water (1 ml) and the resulting solution was stirred at room temperature for 17 h. Work-up in the same manner and chromatography of the crude material [preparative t.l.c. on silica gel; light petroleum–diethyl ether (1 : 1)] gave the *hydroxy-ester* (25) (0.05 g, 23%) and *methyl* (E)-(2-*phenylsulphinyloxycyclopentylidene*)*acetate* (30) (0.11 g, 28%; a mixture of the stereoisomers), in addition to the recovered starting ester (29) (0.05 g, 12%). Compound (30) could not be purified further by distillation (decomposed); $\nu_{max.}$($CHCl_3$) 1 710, 1 665, and 1 130 cm^{-1}; δ ($CDCl_3$) 1.10—2.30 (4 H, m), 2.50—3.00 (2 H, m), 3.69 and 3.71 (total 3 H, each s), 4.70—5.20 (1 H, m), 5.75 and 6.05 (total 1 H, each m), and 7.30—7.90 (5 H, m) (Found: C, 60.0; H, 5.7. $C_{14}H_{16}O_4S$ requires C, 60.0; H, 5.8%).

A solution of (30) (0.02 g) in methanol containing a catalytic amount of sodium methoxide was stirred at room temperature for 30 min. The reaction mixture was diluted with water and extracted with ether. The combined extracts were washed with water and brine, and solvent evaporated off. Chromatography of the crude product [preparative t.l.c. on silica gel; light petroleum–diethyl ether (1 : 1)] gave the *hydroxy-ester* (25) (0.005 g).

5,6-*Dihydro*-6-*methyl*-3-(*phenylthio*)*pyran*-2-*one* (43).—To a solution of δ-methyl-α-phenylsulphinyl-δ-valerolactone (42) [10] (2.15 g) in dichloromethane (30 ml) was added dropwise a solution of trifluoroacetic anhydride (1.9 ml, 1.5 equiv.) in dichloromethane (5 ml) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and evaporated under reduced pressure. The residue was dissolved in carbon tetrachloride, and the resulting solution was again evaporated under reduced pressure to remove trifluoroacetic anhydride and trifluoroacetic acid. The oil remaining (2.0 g) was chromatographed on silica gel [40 g, light petroleum–diethyl ether (4 : 1)] to yield the (*phenylthio*)*pyranone* (43) (1.43 g, 71%); b.p. 140—155 °C at 2 mmHg; $\nu_{max.}$ 1 720, 1 605, 1 225, 1 120, and 1 070 cm^{-1}; δ 1.37 (3 H, d, *J* 7.0), 2.31 (1 H, dd, *J* 10.0 and 5.0), 2.34 (1 H, dd, *J* 7.0 and 5.0), 4.56 (1 H, ddq, *J* 10.0, 7.0, and 7.0), 6.28 (1 H, t, *J* 5.0), and 7.10—7.80 (5 H, m) (Found: C, 65.4; H, 5.6. $C_{12}H_{12}O_2S$ requires C, 65.4; H, 5.5%).

5,6-*Dihydro*-5-*acetoxy*-6-*methylpyran*-2-*one* [(±)-O-*acetylosmundalactone*] (45), *the Stereoisomer* (46), *and* 5-*Acetoxy*-5,6-*dihydro*-6-*methyl*-3-(*phenylthio*)*pyran*-2-*one* (47).—To a solution of the (phenylthio)pyranone (43) (1.22 g) in dichloromethane (15 ml) was added dropwise a solution of *m*-chloroperbenzoic acid (1.06 g, 1.1 equiv.) in dichloromethane (20 ml) with ice–salt cooling, and the reaction mixture was stirred for 40 min. A dilute sodium hydrogencarbonate solution was added, and the water layer was extracted with dichloromethane. The combined organic layers were washed with water and brine, and solvent evaporated off to give 5,6-*dihydro*-6-*methyl*-3-(*phenylsulphinyl*)*pyran*-2-*one* (44) (1.39 g, quantitative); $\nu_{max.}$ ($CHCl_3$) 1 720, 1 085, 1 060, and 1 045 cm^{-1}; δ($CDCl_3$) 1.36 and 1.39 (total 3 H, each d, *J* 6.0), 2.00—2.80 (4 H, m), 4.00—4.90 (1 H, m), and 7.30—8.20 (6 H, m).

To a solution of the above pyranone (44) (0.72 g, 3.03 mmol) in tetrahydrofuran (80 ml) was added dropwise a solution of DBU (0.92 g, 6.06 mmol) in tetrahydrofuran (20 ml) and then a solution of acetic anhydride (0.62 g, 6.06 mmol) in tetrahydrofuran (20 ml) at room temperature. The reaction mixture was heated under reflux for 5 h. Ice–water and a dilute sodium hydrogencarbonate solution were added, and the resulting solution was thoroughly extracted with ether. The combined extracts were washed with water and brine, and evaporated to dryness. The residue (0.544 g) was chromatographed on silica gel [preparative t.l.c.; light petroleum–diethyl ether (1 : 3)] to give the *acetoxypyranone* (45) (0.067 g, 13%), the *stereoisomer* (46) (0.034 g, 7%), and a mixture of cis- and trans-*acetoxy*-(*phenylthio*)*pyranone* (47) (0.067 g, 8%): (45), b.p. 70—80 °C at 2 mmHg; $\nu_{max.}$($CHCl_3$) 1 750 (sh), 1 730, 1 630, 1 445, 1 385, 1 375, 1 345, 1 280, 1 160, 1 125, 1 115, 1 090, 1 053, 1 030, 970, 960, 920, 885, 848, 825, and 815 cm^{-1}; δ($CDCl_3$;

100 MHz) 1.43 (3 H, d, *J* 6.8), 2.15 (3 H, s), 4.60 (1 H, quintet, *J* 6.8), 5.29 (1 H, ddd, *J* 6.8, 3.3, and 1.4), 6.10 (1 H, dd, *J* 9.9 and 1.4), and 6.79 (1 H, dd, *J* 9.9 and 3.3) [these spectra are identical with those of the acetate of the natural osmundalactone (41)] (Found: C, 56.7; H, 5.7. $C_8H_{10}O_4$ requires C, 56.5; H, 5.9%). The stereoisomer (46); $\nu_{max.}$($CHCl_3$) 1 735, 1 720 (sh), 1 645, 1 630, 1 560, 1 445, 1 392, 1 375, 1 332, 1 305, 1 260, 1 190, 1 178, 1 140, 1 110, 1 065, 1 020, 985, 965, 930, 892, 855, and 828 cm^{-1}; δ($CDCl_3$; 100 MHz) 1.43 (3 H, d, *J* 6.7), 2.13 (3 H, s), 4.68 (1 H, dq, *J* 6.7 and 2.9), 5.19 (1 H, dd, *J* 5.8 and 2.9), 6.11 (1 H, d, *J* 9.7), and 6.95 (1 H, dd, *J* 9.7 and 5.8) (Found: C, 56.3; H, 6.3. $C_8H_{10}O_4$ requires C, 56.5; H, 5.9%).

One isomer of the acetoxy-phenylthiopyranone (47), still containing a small amount of impurities, was isolated by repeated preparative t.l.c. of the mixture, and the relative configuration of the methyl and acetoxy groups was assigned to be *cis* by comparison of the coupling constants with those of (46); δ($CDCl_3$) 1.40 (3 H, d, *J* 6.4), 2.06 (3 H, s), 4.69 (1 H, dq, *J* 6.4 and 2.6), 5.08 (1 H, dd, *J* 6.4 and 2.6), 6.00 (1 H, d, *J* 6.4), and 7.20—7.70 (5 H, m); $\nu_{max.}$($CHCl_3$) 1 735 (sh), 1 720, 1 640, 1 600, 1 440, 1 370, 1 160, and 1 080 cm^{-1}.

General Procedure for the Additive Pummerer Reaction of the α-Phenylsulphinylacrylates induced by Acetyl Chloride.—To a solution of the α-phenylsulphinylacrylate (*ca.* 0.5—2 mmol) in dichloromethane (*ca.* 2—5 ml) was added dropwise a solution of acetyl chloride (*ca.* 0.2—0.5 ml, 2.8—7 mmol) in dichloromethane (*ca.* 1—3 ml) at 0 °C. The reaction mixture was stirred at room temperature for 30 min, and then evaporated to dryness under reduced pressure without heating. The residual crude product was purified by preparative t.l.c. (light petroleum–diethyl ether). All the products were thermally unstable, and therefore elemental analyses were not obtained. As an example, the molecular weight of the representative derivative (48) was determined by mass spectroscopy.

Methyl α-Acetoxy-β-chloro-α-(phenylthio)cyclopentylacetate (48).—The *acetoxy-chloro-ester* (48) (0.5 g, 88%) was obtained from the α-phenylsulphinylacrylate (2) (0.41 g); $\nu_{max.}$ 1 770, 1 740, 1 250, and 1 210 cm^{-1}; δ 1.50—2.80 (8 H, m), 1.91 (3 H, s), 3.52 (3 H, s), and 7.10—7.80 (5 H, m) [*m/e* (M^+) 342 and 344 (taken on a Shimadzu LKB-9000 mass spectrometer). $C_{16}H_{19}O_4SCl$ requires *M*, 342 and 344].

Methyl α-Acetoxy-β-chloro-β-methyl-α-(phenylthio)valerate (56).—The *acetoxy-chloro-ester* (56) (0.22 g, 66%; and 0.2 g, 71%) was obtained from the α-phenylsulphinylacrylate (13) [(*E*)-: 0.25 g; and (*Z*)-: 0.22 g]; $\nu_{max.}$ 1 760 (sh), 1 740, 1 435, 1 365, 1 240, and 1 210 cm^{-1}; δ 1.12 (3 H, t, *J* 7.0), 1.72 (3 H, s), 1.88 (3 H, s), 2.04 (2 H, m), 3.58 (3 H, s), and 7.00—7.90 (5 H, m).

Methyl 2-Acetoxy-3-chloro-3-methyl-2-(phenylthio)butanoate (58).—The *acetoxy-chloro-ester* (58) (0.2 g, 67%) was obtained from the α-phenylsulphinylacrylate (17) (0.22 g); $\nu_{max.}$ 1 755 (sh), 1 740, 1 245, and 1 210 cm^{-1}; δ 1.80 (6 H, s), 1.86 (3 H, s), 3.57 (3 H, s), and 7.00—7.67 (5 H, m).

Methyl α-Acetoxy-β-chloro-α-(phenylthio)valerate (61).—The *acetoxy-chloro-ester* (61) (0.31 g, 70%; *ca.* 4 : 3 mixture of the stereoisomers) was obtained from the α-phenylsulphinylacrylate (16) (0.33 g); $\nu_{max.}$ 1 745, 1 440, 1 370, 1 220, and 1 210 cm^{-1}; δ 1.05 and 1.08 (total 3 H, each t, *J* 7.0), 1.30—3.00 (2 H, m), 2.00 and 2.06 (total 3 H, each s), 3.57 and 3.67 (total 3 H, each s), 4.07 and 4.10 (total 1 H, each t, *J* 11.0), and 7.16—7.77 (5 H, m).

Methyl α-Acetoxy-β-chloro-γ-methyl-α-(phenylthio)valerate (64).—The *acetoxy-chloro-ester* (64) (0.124 g, 64%; *ca.* 4 : 1 mixture of the stereoisomers) was obtained from the α-phenylsulphinylacrylate (63) (0.15 g); $\nu_{max.}$ 1 750 (br), 1 250, and 1 210 cm^{-1}; δ 0.93 and 1.08 (total 6 H, each d, *J* 7.0), 2.03 (3 H, s), 2.30—3.00 (1 H, m), 3.52 and 3.65 (total 3 H, each s), 4.00 and 4.20 (total 1 H, each d, *J* 2.0), and 7.10—7.70 (5 H, m).

Methyl α,β-Dichloro-α-(phenylthio)cyclopentylacetate (54).—To a solution of the α-phenylsulphinylacrylate (2) (0.1 g) in dichloromethane (3 ml) was added dropwise a solution of thionyl chloride (0.5 ml) in dichloromethane (2 ml) with ice–salt cooling. The reaction mixture was stirred at room temperature for 30 min. Ice–water was added, and the water layer was extracted with dichloromethane. The combined extracts were washed with water and brine, and evaporated to give the *dichloro-ester* (54) (0.12 g, 98%); b.p. 90—140 °C at 1 mmHg; $\nu_{max.}$ 1 740 and 1 435 cm^{-1}; δ 1.50—2.90 (8 H, m), 3.50 (3 H, s), and 7.00—7.70 (5 H, m) (Found: C, 53.1; H, 5.2; Cl, 21.7. $C_{14}H_{16}Cl_2O_2S$ requires C, 52.7; H, 5.1; Cl, 22.2%).

Methyl 2,3-Dichloro-3-methyl-2-(phenylthio)butanoate (60).—To a solution of the α-phenylsulphinylacrylate (17) (0.18 g) in dichloromethane (5 ml) was added dropwise a solution of thionyl chloride (0.5 ml) in dichloromethane (2 ml) at 0 °C, and the reaction mixture was stirred at room temperature for 30 min. Work-up in the same manner as described above gave the *dichloro-ester* (60) (0.23 g, quantitative); b.p. 70—110 °C at 1 mmHg; $\nu_{max.}$ 1 735, 1 435, and 1 240 cm^{-1}; δ 2.00 (3 H, s), 2.04 (3 H, s), 3.45 (3 H, s), and 7.10—7.80 (5 H, m) (Found: C, 49.0; H, 4.8; Cl, 24.6. $C_{12}H_{14}Cl_2O_2S$ requires C, 49.2; H, 4.8; Cl, 24.2%).

Methyl (1-Phenylthiocyclopentyl)glyoxylate (49).—(*a*) *From the acetoxy-chloro-ester* (48). A solution of the acetoxy-chloro-ester (48) (0.47 g) in dilute dioxan (75%, 4 ml) was heated under reflux for 30 min. The reaction mixture was diluted with water and extracted with ether. The combined extracts were washed with water and brine, and solvent evaporated off to give the *glyoxylate* (49) (0.37 g, quantitative), b.p. 70—110 °C at 1 mmHg; $\nu_{max.}$ 1 735, 1 705, 1 440, and 1 295 cm^{-1}; δ 1.20—2.40 (8 H, m), 3.85 (3 H, s), and 7.26 (5 H, s) (Found: C, 63.4; H, 6.2. $C_{14}H_{16}O_3S$ requires C, 63.6; H, 6.1%). The glyoxylate (49) was also obtained in quantitative yield by distillation of the acetoxy-chloro-ester (48) at 120 °C and 1 mmHg.

(*b*) *From the dichloro-ester* (54). A solution of the dichloro-ester (54) (0.4 g) in dilute dioxan (75%, 6 ml) was heated under reflux for 14 h. Work-up in the same manner and preparative t.l.c. on silica gel of the crude product (0.37 g) [light petroleum–diethyl ether (5 : 1)] gave the *glyoxylate* (49) (0.044 g, 17%).

(*c*) *From the bis(trifluoroacetoxy)-ester* (55). To a solution of the α-phenylsulphinylacrylate (2) (0.1 g) in dichloromethane (2 ml) was added dropwise a solution of trifluoroacetic anhydride (0.3 ml) in dichloromethane (2 ml) at 0 °C, and the reaction mixture was stirred at 0 °C for 30 min. Evaporation of the solvent under reduced pressure without heating gave *methyl α,β-bis(trifluoroacetoxy)-α-(phenylthio)cyclopentylacetate* (55) (0.18 g, quantitative); $\nu_{max.}$ 1 800, 1 785, 1 750, and 1 220 cm^{-1}; δ 1.60—2.20 (4 H, m), 2.20—2.90 (4 H, m), 3.45 (3 H, s), and 7.10—7.90 (5 H, m).

A solution of the bis(trifluoroacetoxy)-ester (55) [obtained from 0.19 g of the α-phenylsulphinylacrylate (2)] in dilute dioxan (75%, 4 ml) was heated under reflux for 30 min and

worked up in the same manner to yield the *glyoxylate* (49) (0.2 g, quantitative).

Methyl (*Cyclopent*-1-*enyl*)*glyoxylate* (50).—To a solution of the glyoxylate (49) (0.36 g) in dichloromethane (5 ml) was added dropwise a solution of *m*-chloroperbenzoic acid (0.28 g, 1.0 equiv.) in dichloromethane (5 ml), and the reaction mixture was stirred at 0 °C for 30 min. The usual work-up gave the sulphoxide. A solution of this crude sulphoxide and 2-mercaptobenzothiazole (0.27 g, 1.2 equiv.) [20] in carbon tetrachloride (10 ml) was heated under reflux for 30 min. The solvent was removed by distillation under atmospheric pressure. Preparative t.l.c. of the residue on silica gel [light petroleum–diethyl ether (5 : 1)] gave crude product (0.15 g), which was still contaminated with crystalline impurities. A portion of this substance was carefully distilled to yield the *glyoxylate* (50), b.p. 100 °C at 20 mmHg; $\nu_{max.}$ 1 740, 1 675, and 1 610 cm^{-1}; δ 1.60—2.30 (2 H, m), 2.30—2.90 (4 H, m), 3.80 (3 H, s), and 7.03 (1 H, br s) (Found: C, 62.1; H, 6.9. $C_8H_{10}O_3$ requires C, 62.3; H, 6.5%).

Methyl Cyclopentylglyoxylate (51).—To a slurry of deactivated Raney nickel (prepared from 1 g of the alloy) in ethanol (*ca.* 5 ml) was added a solution of the glyoxylate (49) (0.17 g) in methanol (2 ml), and the mixture was stirred at room temperature for 15 min and then heated under reflux for 15 min. After removal of the nickel by filtration, the filtrate was evaporated to dryness; preparative t.l.c. of the residue on silica gel [light petroleum–diethyl ether (5 : 1)] gave the *glyoxylate* (51), which was identified with an authentic sample prepared according to the reported procedure.[17]

Methyl [2-(*Phenylthio*)*but*-2-*yl*]*glyoxylate* (57).—A solution of the acetoxy-chloro-ester (56) (0.2 g) in dilute dioxan (80%, 5 ml) was heated under reflux for 1.5 h. The mixture was diluted with water and extracted with ether. The combined extracts were washed with water and brine, and solvent evaporated off. Preparative t.l.c. of the residue (0.14 g) on silica gel [light petroleum–diethyl ether (4 : 1)] gave the *glyoxylate* (57) (0.11 g, 70%); b.p. 60—80 °C at 1 mmHg; $\nu_{max.}$ 1 745, 1 705, 1 440, 1 275, 1 195, and 1 055 cm^{-1}; δ 1.00 (3 H, t, *J* 7.0), 1.28 (3 H, s), 1.87 (2 H, m), 3.88 (3 H, s), and 7.32 (5 H, br s) (Found: C, 62.1; H, 6.4. $C_{13}H_{16}O_3S$ requires C, 61.9; H, 6.4%).

Methyl [2-(*Phenylthio*)*prop*-2-*yl*]*glyoxylate* (59).—(*a*) *From the acetoxy-chloro-ester* (58). A solution of the acetoxy-chloro-ester (58) (0.14 g) in dilute dioxan (75%, 4 ml) was heated under reflux for 1 h. Work-up in the same manner as described in the preceding experiment gave the *glyoxylate* (59) (0.09 g, 86%); b.p. 40—70 °C at 1 mmHg; $\nu_{max.}$ 1 740, 1 710, and 1 050 cm^{-1}; δ 1.43 (6 H, s), 3.88 (3 H, s), and 7.30 (5 H, br s) (Found: C, 60.4; H, 5.8. $C_6H_{14}O_3S$ requires C, 60.5; H, 5.9%).

(*b*) *From the* α-*phenylsulphinylacrylate* (17) via *the bis*-(*trifluoroacetoxy*)-*ester*. To a solution of the α-phenylsulphinylacrylate (17) (0.18 g) in dichloromethane (3 ml) was added dropwise a solution of trifluoroacetic anhydride (0.5 ml) in dichloromethane (5 ml) at 0 °C, and the reaction mixture was stirred at room temperature for 20 min. After removal of the solvent, the residual oil was dissolved in dilute dioxan (75%, 4 ml), and the solution was heated under reflux for 30 min. Work-up in the same manner as described above and preparative t.l.c. of the crude product on silica gel [light petroleum–diethyl ether (5 : 1)] gave the *glyoxylate* (59) (0.063 g, 35%).

Methyl [1-(*Phenylthio*)*propyl*]*glyoxylate* (62).—A solution of the acetoxy-chloro-ester (61) (0.3 g) in dioxan (10 ml) and water (2 ml) was heated under reflux for 20 h. The reaction mixture was diluted with water and extracted with ether. The combined extracts were washed with water and brine, and treated with an excess of ethereal diazomethane (because the product was partially hydrolysed during the reaction). Evaporation of the ether left an oily residue; preparative t.l.c. on silica gel [light petroleum–diethyl ether (4 : 1)] gave the *glyoxylate* (62) (0.17 g, 75%), b.p. 70—90 °C at 1 mmHg; $\nu_{max.}$ 1 750 (sh), 1 720, 1 440, 1 240, and 1 050 cm^{-1}; δ 1.03 (3 H, t, *J* 7.0), 1.33—2.00 (2 H, m), 3.85 (3 H, s), 4.05 (1 H, t, *J* 7.0), and 7.30 (5 H, s) (Found: C, 60.3; H, 6.1. $C_{12}H_{14}O_3S$ requires C, 60.5; H, 5.9%).

Methyl [1-(*Phenylthio*)-2-*methylpropyl*]*glyoxylate* (65).—A solution of the acetoxy-chloro-ester (64) (0.16 g) in dilute dioxan (75%, 4 ml) was heated under reflux for 35 h. Work-up in the usual manner and preparative t.l.c. of the crude product (0.22 g) on silica gel [light petroleum–diethyl ether (4 : 1)] gave the *glyoxylate* (65) (0.06 g, 49%); b.p. 80—110 °C at 1 mmHg; $\nu_{max.}(CHCl_3)$ 1 730, 1 715, 1 240, and 1 050 cm^{-1}; δ 0.96 (3 H, d, *J* 7.0), 1.21 (3 H, d, *J* 7.0), 1.67—2.35 (1 H, m), 3.83 (3 H, s), 3.91 (1 H, d, *J* 9.0), and 7.30 (5 H, br s) (Found: C, 62.1; H, 6.3. $C_{13}H_{16}O_3S$ requires C, 61.9; H, 6.4%).

5,6,7,7a-*Tetrahydro*-3-(*phenylsulphinyl*)*benzofuran*-2(4H)-*one* (67).—To a solution of (66) [19] (9.03 g) in dichloromethane (60 ml) was added dropwise a solution of trifluoroacetic anhydride (6.7 ml) in dichloromethane (20 ml) at 0 °C, and the reaction mixture was stirred at 0 °C for 30 min and then at room temperature for 3.5 h. The mixture was evaporated to dryness under reduced pressure to remove trifluoroacetic acid and anhydride, and dissolved again in dichloromethane. The solution was washed with dilute sodium hydroxide solution, water, and brine. Evaporation of the solvent under reduced pressure and chromatography of the residue (8.65 g) on silica gel [120 g; eluant light petroleum alone to light petroleum–diethyl ether (1 : 1)] gave the 3-(*phenylthio*)*furanone* (22) (5.1 g, 61%).

Oxidation of this compound (22) (2.43 g) with *m*-chloroperbenzoic acid and work-up were carried out in the same manner as described earlier to give the 3-(*phenylsulphinyl*)-*furanone* (67) (2.70 g, quantitative); $\nu_{max.}(CHCl_3)$ 1 755, 1 635, and 1 045 cm^{-1}; δ 0.60—2.70 (7 H, m), 3.86 (1 H, m), 4.63 (1 H, m), and 7.20—8.10 (5 H, m). This compound was fairly unstable and could not be purified even by chromatography (rearrangement took place on silica gel).

Reactions of the 3-(*Phenylsulphinyl*)*furanone* (67).—(*a*) *With dilute sulphuric acid–dioxan*. A solution of compound (67) (0.32 g) in 6N sulphuric acid (1 ml) and dioxan (4 ml) was heated under reflux for 4 h. The reaction mixture was diluted with water and extracted with ether. The combined extracts were washed with water and brine, and evaporated to dryness. Preparative t.l.c. of the residue (0.34 g) on silica gel [light petroleum–diethyl ether (1 : 1)] gave the thermally very unstable (polymerised on standing) 5,6-*dihydro*-3-(*phenylthio*)*benzofuran*-2(4H)-*one* (68) (0.053 g, 18%); $\nu_{max.}$ 1 775, 1 655, 1 590, and 980 cm^{-1}; δ 1.30—2.60 (6 H, m), 5.68 (1 H, t, *J* 4.0), and 7.00—7.60 (5 H, m), and 5,6,7,7a-*tetrahydro*-7a-*hydroxy*-3-(*phenylthio*)*benzofuran*-2(4H)-*one* (69) (0.075 g, 24%); m.p. 135—136 °C (from carbon tetrachloride); $\nu_{max.}(CHCl_3)$ 3 300, 1 755, 1 640, and 975 cm^{-1}; δ 0.70—3.00 (8 H, m), 4.10—5.70 (1 H, br, OH), and 6.90—7.70 (5 H, m) (Found: C, 63.8; H, 5.4. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.4%).

(*b*) *With acetic anhydride–methanesulphonic acid*. A

solution of compound (67) (0.29 g) in acetic anhydride (2 ml) containing a small amount of methanesulphonic acid was heated under reflux for 1 h. The reaction mixture was diluted with ether, and the resulting solution was washed with dilute sodium hydroxide solution, water, and brine, and evaporated to dryness. Preparative t.l.c. of the residue (0.23 g) on silica gel [light petroleum–diethyl ether (1 : 1)] gave the *diene–lactone* (68) (0.12 g, 44%).

(*c*) *With acetic anhydride.* A solution of compound (67) (0.22 g) in acetic anhydride (3 ml) was heated under reflux for 3.5 h. The reaction mixture was diluted with ether, and the resulting solution was washed with dilute sodium hydroxide solution, water, and brine, and evaporated to dryness. Preparative t.l.c. of the residue (0.17 g) on silica gel [light petroleum–diethyl ether (1 : 1)] gave the *diene–lactone* (68) (0.027 g, 13%) and 3,3a-*diacetoxy*-3a,4,5,6,7,7a-*hexahydro*-3-(*phenylthio*)*benzofuran*-2(3H)-*one* (70) (0.06 g, 20%); $\nu_{max.}$ 1 790, 1 765, 1 365, and 1 200 cm^{-1}; δ 1.00—3.00 (8 H, m), 2.00 (3 H, s), 2.10 (3 H, s), 4.66 (1 H, m), and 7.00—7.50 (5 H, m) (Found: C, 59.2; H, 5.7. $C_{18}H_{20}O_6S$ requires C, 59.3; H, 5.5%).

(*d*) *With pyridine–acetic anhydride.* A solution of compound (67) (0.3 g) in a mixture of pyridine (1 ml) and acetic anhydride (0.5 ml) was stirred overnight at room temperature. The reaction mixture was diluted with ether, and the resulting solution was successively washed with dilute sodium hydroxide solution, dilute sulphuric acid, water, and brine, and evaporated to dryness. Preparative t.l.c. of the residue (0.27 g) on silica gel [light petroleum–diethyl ether (1 : 1)] gave 7a-*acetoxy*-5,6,7,7a-*tetrahydrobenzofuran*-2(4H)-*one* (71) (0.1 g, 45%); b.p. 90—100 °C at 2 mmHg; $\nu_{max.}$ 1 800, 1 770, 1 660, and 1 205 cm^{-1}; δ 0.83—3.00 (8 H, m), 2.03 (3 H, s), and 5.70 (1 H, d, *J* 1.5) (Found: C, 61.5; H, 6.2. $C_{10}H_{12}O_4$ requires C, 61.2; H, 6.2%).

(*e*) *With pyridine–water.* A solution of compound (67) (0.26 g) in dilute pyridine (75%, 2 ml) was stirred at room temperature for 2 h. The reaction mixture was diluted with ether, and the resulting solution was washed with dilute sulphuric acid, water, and brine, and then evaporated to dryness. Preparative t.l.c. of the residue (0.22 g) on silica gel [light petroleum–diethyl ether (5 : 4)] gave 5,6,7,7a-*tetrahydro*-7a-*hydroxybenzofuran*-2(4H)-*one* (72) (0.083 g, 54%); m.p. 87.5—88.5 °C (from light petroleum–diethyl ether); $\nu_{max.}$($CHCl_3$) 3 300, 1 745, 1 655, and 1 190 cm^{-1}; δ 1.00—3.00 (8 H, m), 3.67—5.07 (1 H, br, OH), and 5.67 (1 H, d, *J* 1.5) (Found: C, 62.3; H, 6.7. $C_8H_{10}O_3$ requires C, 62.3; H, 6.5%). Acetylation of this compound (72) with acetic anhydride–pyridine at room temperature for 15 h gave the *acetate* (71) in 67% yield.

(*f*) *With acetyl chloride.* To a solution of compound (67) (0.65 g) in dichloromethane (10 ml) was added dropwise a solution of acetyl chloride (0.5 ml) in dichloromethane (3 ml) at 0 °C. The reaction mixture was stirred at 0 °C and gradually warmed to room temperature during 1.5 h. After removal of the solvent under reduced pressure, preparative t.l.c. of the residue (0.88 g) on silica gel [light petroleum–diethyl ether (6 : 1)] gave 3,3a-*dichloro*-3a,4,5,6,7,7a-*hexahydro*-3-(*phenylthio*)*benzofuran*-2(3H)-*one* (74) (a mixture of the stereoisomers; 0.5 g, 64%); m.p. 93.5—94.5 °C (from diethyl ether–carbon tetrachloride); $\nu_{max.}$($CHCl_3$) 1 790 and 1 440 cm^{-1}; δ 0.83—2.50 (8 H, m), 4.60 and 5.00 (total 1 H, m), and 7.00—7.93 (5 H, m) (Found: C, 52.4; H, 4.3; Cl, 21.7. $C_{14}H_{14}Cl_2O_2S$ requires C, 53.0; H, 4.5; Cl, 22.4%); 3-*acetoxy*-3a-*chloro*-3a,4,5,6,7,7a-*hexahydro*-3-(*phenylthio*)*benzofuran*-2(3H)-*one* (75) (0.075 g, 9%); δ 0.80—2.74 (8 H, m), 1.83 (3 H, s), 4.40 (1 H, m), and 7.00—8.00 (5 H, m) (this compound did not give satisfactory analyses because of thermal instability), but gave a positive halogen test; and the 3-(*phenylthio*)*furanone* (22) (0.074 g, 12%).

Cyclopent-1-*enyl*(*phenylthio*)*acetic Acid* (78).—A solution of (1-hydroxycyclopentyl)(phenylthio)acetic acid (77) [10] (2.52 g) and anhydrous toluene-*p*-sulphonic acid (a catalytic amount) in benzene (30 ml) was heated under reflux for 1 h using a water-separator. After removal of the solvent, the residue was dissolved in ether, and the resulting solution was passed through a short column of active-charcoal (upper)–silica gel. Evaporation of the ether left the viscous *unsaturated acid* (78) (2.24 g, quantitative); $\nu_{max.}$($CHCl_3$) 3 500—2 500, 1 705, 1 645, and 1 580 cm^{-1}; δ 1.45—2.79 (6 H, m), 4.40 (1 H, s), 5.68 (1 H, br s), 6.95—7.56 (5 H, m), and 12.04 (1 H, s). Treatment of this compound with ethereal diazomethane gave the methyl ester which was identified by comparison with an authentic sample.[10]

Cyclopentylidene(*phenylthio*)*methyl Methyl Ketone* (79).—To a solution of the unsaturated acid (78) (0.94 g, 4 mmol) in carbon tetrachloride (6 ml) was added dropwise a solution of thionyl chloride (0.57 g, 4.8 mmol) in carbon tetrachloride (3 ml) under nitrogen, and the reaction mixture was heated at 70—75 °C for 2.5 h. Evaporation of the solvent and distillation of the remaining oil under reduced pressure gave the *acid chloride* (0.77 g, 76%); b.p. 120—130 °C at 1 mmHg; δ 1.50—1.92 (6 H, m), 4.85 (1 H, s), 5.65 (1 H, br s), and 6.96—7.45 (5 H, m). Similarly, the reaction of the unsaturated acid (78) with oxalyl chloride in benzene at 40—45 °C for 2.5 h gave the *acid chloride* in 75% yield.

A solution of freshly prepared lithium dimethylcuprate (7.0 mmol) in ether (26 ml) was added dropwise to a solution of the acid chloride (1.47 g, 5.82 mmol) in ether (10 ml) at −60 °C under nitrogen, and the reaction mixture was stirred at −60 °C for 30 min. Saturated ammonium chloride solution was added, and the water layer was extracted twice with ether. The combined ether layers were thoroughly washed with water and brine, and solvent evaporated off. Chromatography of the residue (1.32 g) on silica gel [30 g, eluant light petroleum alone to light petroleum–diethyl ether (9 : 1)] gave the *unsaturated ketone* (79) (0.55 g, 41%); b.p. 100—110 °C at 1 mmHg; $\nu_{max.}$ 1 675, 1 580, 1 480, and 1 355 cm^{-1}; δ 1.33—2.04 (4 H, m), 2.15 (3 H, s), 2.22—3.00 (4 H, m), and 6.75—7.31 (5 H, m) (Found: C, 72.1; H, 6.8. $C_{14}H_{16}OS$ requires C, 72.4; H, 6.9%).

(E)-(2-*Acetoxycyclopentylidene*)*methyl Methyl Ketone* (81).—To a solution of the unsaturated ketone (79) (0.23 g) in dichloromethane (3 ml) was added dropwise a solution of *m*-chloroperbenzoic acid (0.2 g, 1 equiv.) in dichloromethane (7 ml) at 0 °C, and the reaction mixture was stirred at 0 °C for 30 min. The unstable product decomposed during the usual work-up (especially alkali washing) or isolation (silica gel t.l.c.). Thus, the reaction mixture was concentrated, without the removal of acid material, under reduced pressure. The residue was dissolved in dilute pyridine (75%, 4 ml), and the resulting solution was stirred at room temperature for 17 h. The mixture was diluted with water, acidified with 3N hydrochloric acid (indicator Congo Red) with ice-cooling, and extracted twice with ether. The combined extracts were washed with water and brine, and solvent evaporated off. Preparative t.l.c. of the residue (0.29 g) on silica gel [light petroleum–diethyl ether (1 : 2)] gave the unstable (E)-(2-*hydroxycyclopentylidene*)*methyl methyl ketone* (80) (0.03 g, 20%); δ 1.17—1.93 (4 H, m), 2.12

(3 H, s), 2.50—2.90 (2 H, m), 3.17 (1 H, s), 4.29 (1 H, br t, *J* 7.0), and 6.14 (1 H, q, *J* 2.0).

A solution of the above hydroxy-ketone (80) in pyridine (1 ml) and acetic anhydride (1 ml) was allowed to stand at room temperature for 15 h. After the usual work-up, preparative t.l.c. of the residue on silica gel [light petroleum–diethyl ether (7 : 3)] gave the *acetoxy-ketone* (81) (>30%); b.p. 60—65 °C at 1 mmHg; $\nu_{max.}$(neat) 1 735, 1 685, 1 630, 1 370, and 1 235 cm^{-1}; $\delta(CDCl_3)$ 1.33—1.96 (4 H, m), 2.07 (3 H, s), 2.20 (3 H, s), 2.60—3.00 (2 H, m), 5.47 (1 H, br t, *J* 7.0), and 6.22 (1 H, q, *J* 2.0) (Found: C, 65.9; H, 7.9. $C_{10}H_{14}O_3$ requires C, 65.9; H, 7.7%).

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