Polarized Ketene Dithioacetals. Part 41.[1] Studies on Base-catalysed Rearrangements of 1,1-Bis(alkylthio)-2-aroylpenta-1,4-dienes to Novel 1,5-Bis(alkylthio)-2-aroylpenta-1,3-dienes *via* a 1,5-Alkylthio Shift

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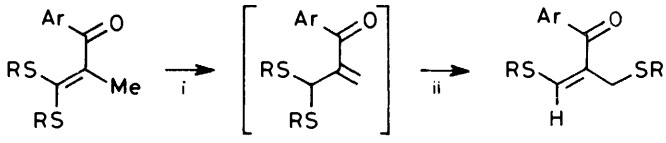
1,1-Bis(alkylthio)-2-aroylpenta-1,4-dienes (**7a—f**) undergo a facile rearrangement in the presence of sodium hydride and dimethylformamide–benzene to give novel (*1Z*, *3E*)-1,5-bis(alkylthio)-2-aroylpenta-1,3-dienes (**9a—f**), respectively. A probable mechanism involving the mobile oxopentadienyl intermediate (**12**), which on subsequent 1,5-alkylthio shift affords the dienes (**9**), has been suggested for this highly stereoselective rearrangement. Mechanistic studies have shown that the 1,5-alkylthio shift in this transformation is an intermolecular rather than a concerted process and involves the solvent-equilibriated enolate anion(**17**) formed by Michael addition of thiolate anion to (**12**). The synthesis of the α-allyloxoketene dithioacetals (**7a—f**) is also described.

In our earlier publications[2-3] we have reported that the α-oxoketene dithioacetals (**1**) derived from propiophenones undergo a facile base-catalysed 1,3-alkylthio shift to give the corresponding 3-alkylthio-2-alkylthiomethylacrylophenones (**3**) (Scheme 1). The mechanism of this novel rearrangement for the formation of compound (**3**) was shown to involve an initial mobile oxoallyl intermediate (**2**) followed by subsequent Michael addition and allylic displacement of alkylthiolate anion. Similar studies were also extended[3,4] to other α-methyleneoxoketene dithioacetals derived from dihydrochalcone, indan-1-one, 3,4-dihydronaphthalene-1(2*H*)-one, and 2,3-dihydro-1-benzothiopyran-4-one, which afforded either the rearranged products from a 1,3-alkylthio shift or those derived from subsequent transformations of 2-oxobis(methylthio)allyl anions. Our results demonstrated that the 1,3-alkylthio shift followed an ionic pathway rather than a concerted process. On the basis of these studies we further postulated that the α-oxoketene dithioacetals (**7**) carrying an allylic moiety at the 2-position should undergo a base-catalysed 1,3-prototropic shift to give the corresponding mobile oxodienyl intermediate (**12**) (see later); we considered these to be excellent systems for the study of facile 1,5-sigmatropic shifts. There are no examples of a 1,5-alkylthio shift in the literature and to the best of our knowledge this is the first report of its kind. Our efforts to isolate the key intermediate (**12**), however, were not successful, although our experiments on base-catalysed 1,3-prototropic shifts led directly to the formation of the expected dienes (**9**). It was therefore necessary to establish whether the observed 1,5-alkylthio shifts take place *via* an orbital-symmetry-allowed 1,5-sigmatropic shift or by an ionic pathway. Surprisingly our results are consistent with the latter.

Results and Discussion

The hitherto unreported α-allyl-α-oxoketene dithioacetals (**7a—f**) were conveniently prepared as shown in Scheme 2. When the dithioester (**4a**) was subjected to alkylation with allyl bromide in the presence of potassium carbonate only the rearranged α-*C*-allyl dithioester (**6a**) was formed in 80% yield. It is apparent that the intermediate dithioacetal (**5a**) underwent a facile thio-Claisen rearrangement[5] to give the ester (**6a**). The attempted alkylation of compound (**6a**) with methyl iodide in the presence of sodium hydride and dimethylformamide gave only a complex product mixture from which no well defined compound could be isolated; however, it was conveniently



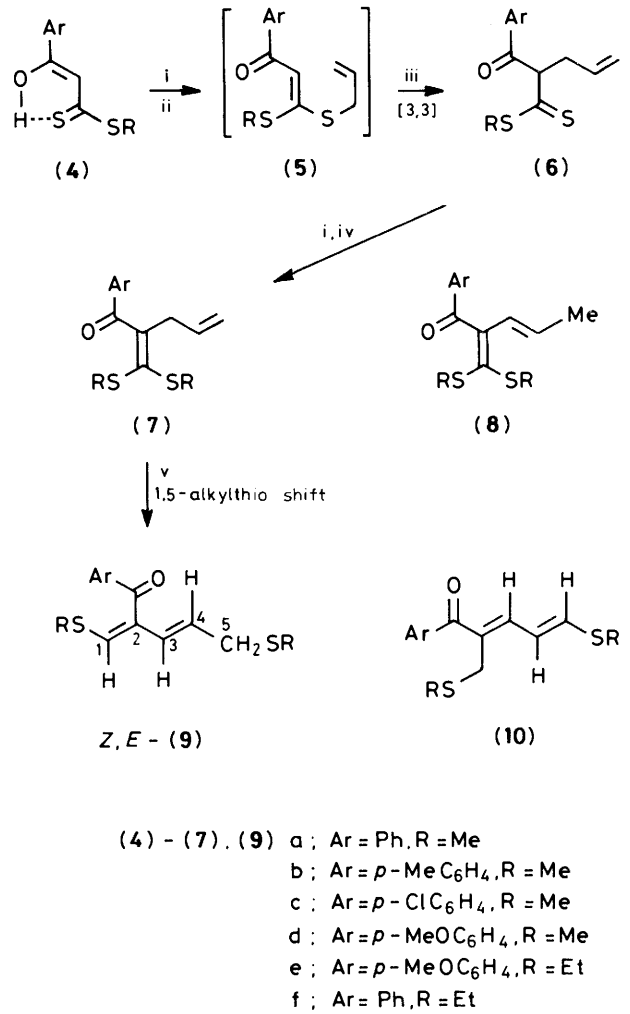
R = Me, Et, Pr^i

Scheme 1. *Reagents*: i, NaH/DMF; ii, R5

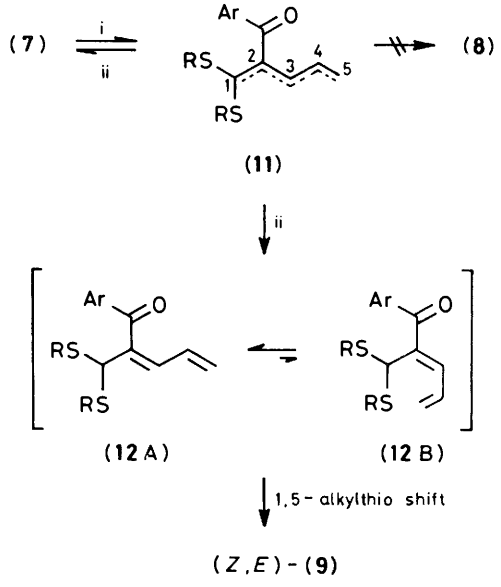
alkylated with methyl iodide in the presence of potassium carbonate in refluxing acetone to give the corresponding α-allyl dithioacetal (**7a**) in 70% yield. The presumed isomer (**8**) was not detected even as a contaminant with the acetal (**7a**), shown by the n.m.r. spectrum. The ketene dithioacetals (**7b**) and (**7c**) were similarly prepared in 65 and 60% yields, respectively. However it was found from subsequent experiments that the isolation of the α-allyldithioester (**6**) was not necessary, since direct methylation of the presumed intermediates (**6d—f**) yielded the corresponding dithioacetals (**7d—f**) in comparable yields.

Base-catalysed Rearrangements of Compounds (**7a—f**). When compound (**7a**) was stirred at 40—45 °C for 2 h with a suspension of sodium hydride in benzene–dimethylformamide, the formation of only one product was observed (t.l.c.) along with the uncharged starting material. Work-up and column chromatography of the reaction mixture gave a yellow oil (54%),† which was characterised as (1*Z*, 3*E*)-2-benzoyl-1,5-bis(methylthio)penta-1,3-diene (**9a**) on the basis of its spectral and analytical data. It analysed for $C_{14}H_{16}S_2O$ and exhibited in its mass spectrum a weak molecular ion peak at *m/z* 264(M^+). Its i.r. spectrum (neat) showed strong bands at 1 650, 1 630, and 1 600 cm^{-1} due to a conjugated carbonyl group and aliphatic double bonds. The final confirmation of the structure (**9a**) was obtained from its ^{1}H n.m.r. spectrum ($CDCl_3$). It showed two sharp singlets at δ 1.98 (3H) and 2.35 (3H) due to protons of two SMe groups attached to sp^3 and sp^2 carbon atoms, respectively. The methylene protons appeared as a doublet at δ 3.15 (2H, *J* 6 Hz) due to coupling with an olefinic proton (H_A), which rules out the formation of the isomeric diene (**10**). The multiplet at δ 5.7—6.1 (d t, 1H, *J* 6 and 15 Hz) was assigned to the olefinic

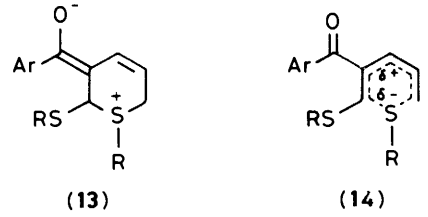
† Starting material (**7a**) (30%) was recovered.



Scheme 2. *Reagents*: i, K_2CO_3/acetone, ii, allyl bromide; iii, heat; iv, RI; v, NaH/benzene/DMF



Scheme 3. *Reagents*: i, Base; ii, (7)



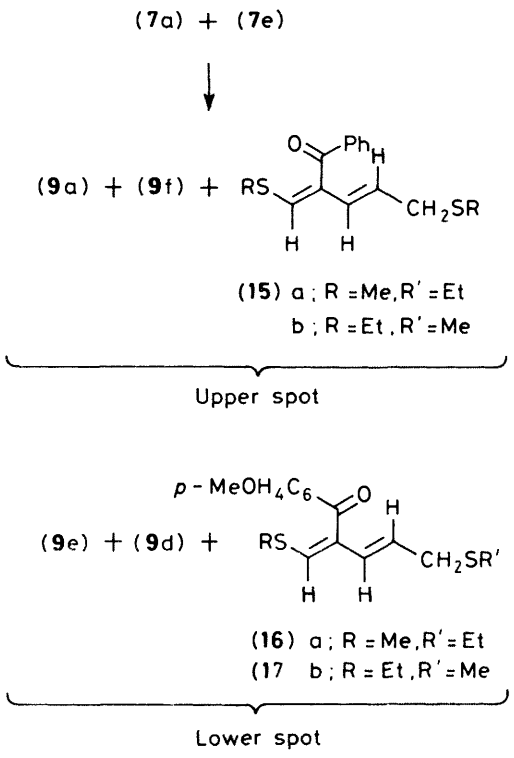
proton (H_A), the doublet at δ 6.25 (1H, *J* 15 Hz) to the olefinic proton (H_B), and the singlet at δ 6.75 (1H) to the olefinic proton (H_C). The aromatic protons appeared between δ 7.10—7.49 (m, 3H) and 7.51—7.78 (m, 2H). On the basis of the coupling constant (15 Hz) for H_B, the *trans*-(*E*)-configuration around the 3,4-double bond was assigned, while the (*Z*)-configuration around the 1,2-double bond was assigned on the basis of the position of the H_C signal (at δ 6.75), following our earlier observations of chemical shifts of olefinic protons in the rearrangement products (**3**).[3] The ^{13}C n.m.r. spectrum ($CDCl_3$) of compound (**9a**) was also consistent with the assigned structure (Experimental section).

The rearrangement was found to be generally applicable to other allyl dithioacetals (**7b—f**), which gave the corresponding (1*Z*,3*E*)-dienes (**9b—f**) in 52—70% overall yields. Also the rearrangement was found to be highly stereoselective, as no other stereoisomers could be isolated from the reaction mixture.

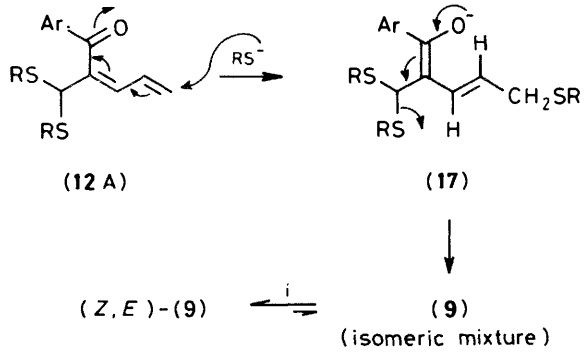
Mechanistic Studies.—The probable mechanism of the base-catalysed rearrangement is shown in Schemes 3 and 5, and appears to be similar to that described for the conversion of compounds (**1**)—(**3**).[3] The pentadienyl anion (**11**) generated under reversible conditions from compound (**7**), competes with sodium hydride in the deprotonation of (**7**) to give (**7**), the dithioacetal (**8**), or an unstable mobile oxopentadienyl intermediate (**12**). As no trace of compound (**8**) was observed in the reaction mixture, it appears that the protonation of the anion (**11**) occurs preferentially at C-1, rather than at C-5, giving (**12**). The intermediate (**12**) could then undergo a facile 1,5-alkylthio shift to give the thermodynamically more stable diene (**9**). It is probable that the intermediate (**12**) is present in the reaction mixture, although our efforts to isolate it were not successful. The 1,5-alkylthio shift can be intramolecular either involving a thermally allowed concerted process or *via* the tetrahydrothiopyrylium intermediate (**13**) by the sterically favourable *6-endo-trig* pathway or the antipolar transient complex (**14**).[6] However, our cross-over experiment with compounds (**7a**) and (**7e**) carried out under identical conditions with these for the 1,3-alkylthio shift in compounds (**1**)—(**3**),[3] revealed that the 1,5-alkylthio shift also takes place intermolecularly (Scheme 4); this could be the result of the intermediate (**12**) not adopting the configuration (**12B**) needed for a concerted 1,5-shift.

The intermolecular radical dissociation combination mechanism[7] was also ruled out on the basis of experiments using radical inhibitors (diphenylpicrylhydrazyl and hydroquinone). The rearrangement of compound (**12**) to give the dithioether (**9**) (Scheme 5) therefore takes place *via* an intermolecular ionic pathway, involving the solvent-equilibrated enolate anion (**17**); this anion would be formed by the Michael addition of thiolate anion to compound (**12**) followed by elimination of one of the alkylthio groups to give a mixture of stereoisomers (**9**), which in the presence of base rearrange to the thermodynamic products (*Z*, *E*)-(**9**).[8,9]

We presume that the intermolecularity and non-concertedness of this rearrangement do not necessarily eliminate the possibility of a thermal concerted 1,5-alkylthio shift, as the ionic pathway appears to predominate over the concerted process in



Scheme 4. *Reagents*: i, NaH



Scheme 5. *Reagents*: i, base

the presence of base. If the stable oxopentadienyl intermediate (**12**) could be prepared, it would be expected to undergo a concerted 1,5-alkylthio shift in neutral medium. The search for such a system is continuing.

Experimental

M.p.s were determined on a Boetius apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 297 spectrophotometer, while the ^{1}H n.m.r. spectra were obtained on a Varian EM-390 90 MHz n.m.r. spectrometer using $SiMe_4$ as the internal reference. In all the reactions a 50% suspension of sodium hydride was used. T.l.c. was carried out on a silica gel plate using EtOAc–benzene (5:95) as solvent.

Starting Materials.—The known α-oxodithioesters (**4a—d**) and the unknown dithioesters (**4e—f**) were prepared according to the method reported earlier.[10] *Ethyl* β-*oxo*-β-(p-*methoxyphenyl*)*dithioacetate* (**4e**) was obtained as yellow prisms (70%), m.p. 47—48 °C, $\nu_{max.}$(Nujol) 1 230, 1 560, 1 590, and 16 05 cm^{-1}; δ(CCl_4) 1.38 (t, 3H, SCH_2CH_3), 3.20 (q, 2H, SCH_2CH_3), 3.8 (s, 3H, OMe), 6.75 (s, 1H, vinylic), 6.82, 7.78 (dd, A_2B_2, 4H, arom.), and 15.1 (s, 1H, OH); *m/z* 254 (M^+) [Found: C, 56.9; H, 5.2. $C_{12}H_{14}O_2S_2$ (*M* 254) requires C, 56.69; H, 5.51%]. *Ethyl* β-*oxo*-β-*phenyldithioacetate* (**4f**) was obtained as red oil (75%) after purification by column chromatography over silica gel using hexane as eluant; $\nu_{max.}$(neat) 1 235, 1 570, 1 595, and 1 605 cm^{-1}; δ(CCl_4) 1.32 (t, 3H, SCH_2CH_3), 3.2 (q, 2H, SCH_2CH_3), 6.80 (s, 1H, vinylic), and 7.25—7.90 (m, 5H, arom.); *m/z* 224 (M^+) [Found: C, 59.2; H, 5.7. $C_{11}H_{12}OS_2$ (*M* 224) requires C, 58.93; H, 5.36%].

α-*Allyl*-α-*aroyldithioacetates* (**6a—c**); *General Procedure.*—To a solution of the β-oxodithioester (**4a—c**) (0.05 mol) in 100 ml of dry acetone, anhydrous potassium carbonate (14 g, 0.1 mol) was added and the reaction mixture was refluxed with stirring for 3 h. The reaction mixture was then cooled to room temperature and allyl bromide (6 g, 0.05 mol) in acetone (20 ml) was slowly added to it with stirring and the stirring continued at room temperature for 4 h. The reaction mixture was then refluxed with stirring at 70—80 °C for 6 h. The solvent was removed under reduced pressure and the residue was dissolved in water (100 ml), extracted with ethyl acetate (3 × 50 ml), the combined extract was washed with water (1 × 100 ml), dried (Na_2SO_4), and the solvent removed to give the crude product (**6a—c**) (>90% pure by t.l.c.), purified by column chromatography over silica gel using hexane as eluant. α-*Allyl*-α-*benzoyldithioacetate* (**6a**) was obtained as a red oil (10 g, 80%); $\nu_{max.}$(neat) 1 690, 1 595, and 1 220 cm^{-1}; δ(CCl_4) 2.48 (s, 3H, SMe), 2.62—3.15 (dd, 2 H, CH_2), 4.85—5.48 (m, 1 H, methine and 2 H, vinylic), 5.51—5.85 (m, 1 H, vinylic), 7.21—7.62 (m, 3H, arom.), and 7.82—8.20 (m, 2H, arom.); *m/z* 250 (M^+) [Found: C, 62.1; H, 5.9. $C_{13}H_{14}OS_2$ (*M* 250) requires C, 62.40; H, 5.60%]. α-*Allyl*-α-(p-*methylbenzoyl*)*dithioacetate* (**6b**) was obtained as red oil (10 g, 75%); $\nu_{max.}$ (neat) 1 685, 1 605, and 1 180 cm^{-1}; δ(CCl_4) 2.42 (s, 3 H, SMe), 2.58 (s, 3*H*, *p*-CH_3), 2.70—3.12 (dd, 2 H, CH_2), 4.82—5.32 (m, 1 H, methine and 2 H, vinylic), 5.56—5.90 (m, 1 H, vinylic), and 7.15, 7.85 (2d, A_2B_2, 4 H, arom.); *m/z* 264 (M^+) [Found: C, 63.58; H, 5.9. $C_{14}H_{16}OS_2$ (*M* 264) requires C, 63.64; H, 6.06%]. α-*Allyl*-α-(p-*chlorobenzoyl*)*dithioacetate* (**6c**) was obtained as a red oil (12 g, 85%); $\nu_{max.}$ (neat) 1 680, 1 590, and 1 210 cm^{-1}; δ(CCl_4) 2.40 (s, 3 H, SMe), 2.70—3.20 (dd, 2 H, CH_2), 4.90—5.22 (m, 1 H, methine and 2 H, vinylic), 5.60—5.90 (m, 1 H, vinylic), and 7.40, 7.75 (2 d, A_2B_2, 4 H, arom.); *m/z* 284 (M^+) [Found: C, 55.1; H, 4.2. $C_{13}H_{13}ClOS_2$ (*M* 284.5) requires C, 54.83; H, 4.57%].

α-*Allyl*-α-*aroylketene Dithioacetals* (**7a—c**). *General Procedure.*—A mixture of the dithioacetate (**6**) (0.05 mol) and anhydrous potassium carbonate (14 g, 0.01 mol) in dry acetone (75 mol) was refluxed with stirring at 70—75 °C for 3 h. The reaction mixture was ice-cooled and a solution of methyl/ethyl iodide (0.06 mol) in acetone (20 ml) slowly added with stirring. The reaction mixture was then stirred at room temperature for 10—15 h (monitored by t.l.c.). The solvent was removed under reduced pressure and the remaining residue was dissolved in water (100 ml), extracted with ethyl acetate (3 × 50 ml), the combined extract was washed with water (1 × 100 ml), dried (Na_2SO_4) and solvent removed to give the crude product (**7a—c**), purified by column chromatography over silica gel using hexane–EtOAc (9:1) as eluant. 2-*Allyl*-3,3-*bis*(*methylthio*)-1-*phenylprop*-2-*en*-1-*one* (**7a**) (9.2 g, 70%) was obtained as a red oil; $\nu_{max.}$(neat) 1 660, 1 610 cm^{-1}; δ($CDCl_3$) 2.0 (s, 3 H, SMe), 2.30 (s, 3 H, SMe), 3.35 (d, 2 H, CH_2), 4.81—5.15 (m, 2 H, vinylic), 5.43—5.91 (m, 1 H, vinylic), 7.20—7.51 (m, 3 H, arom.), and 7.75—7.90 (m, 2 H, arom.); *m/z* 264 (M^+) [Found: C, 64.0; H, 6.35. $C_{14}H_{16}OS_2$ (*M* 264) requires C, 63.64; H, 6.06%].

2-*Allyl*-3,3-*bis*(*methylthio*)-1-(p-*methylphenylprop*-2-*en*-1-*one*

(**7b**) (8 g, 65%) was obtained as a red oil; $\nu_{max.}$(neat) 1 665, 1 609 cm^{-1}; δ($CDCl_3$) 2.0 (s, 3 H, SMe), 2.33 (d, 6 H, SMe and *p*-Me), 3.20 (d, 2 H, CH_2), 4.80—5.10 (m, 2 H, vinylic), 5.40—5.80 (m, 1 H, vinylic), and 7.15—7.62 (2d, A_2B_2, 4 H, arom.); *m/z* 278 (M^+) [Found: C, 65.1; H, 6.9. $C_{15}H_{18}OS_2$ (*M* 278) requires C, 64.75; H, 6.47%].

2-*Allyl*-1-(p-*chlorophenyl*)-3,3-*bis*(*methylthio*)*prop*-2-*en*-1-*one* (**7c**) (9 g, 60%) was obtained as a red oil; $\nu_{max.}$(neat) 1 655, 1 595 cm^{-1}; δ($CDCl_3$) 2.03 (s, 3 H, SMe), 2.32 (s, 3 H, SMe), 3.56 (d, 2 H, CH_2), 4.90—5.20 (m, 2 H, vinylic), 5.50—5.82 (m, 1 H, vinylic), and 7.40, 7.80 (2d, A_2B_2, 4 H, arom.); *m/z* 298 (M^+) [Found: C, 56.0, H, 5.4. $C_{14}H_{15}ClOS_2$(*M* 298.5) requires C, 56.28; H, 5.02%].

α-*Allyl*-α-*aroylketene Dithioacetals* (**7d—f**); *Direct Method. General Procedure.*—The β-oxodithioesters (**4d—f**) (0.05 mol) were treated with allyl bromide (0.05 mol) in the presence of anhydrous potasium carbonate (14 g, 0.1 mol) as described above. When t.l.c. showed complete formation of the α-allyl-α-aroyldithioacetate (**6d—f**), the reaction mixture was cooled to room temperature, anhydrous potassium carbonate (14 g, 0.1 mol) added and the reaction mixture refluxed with stirring for another 2 h. It was then ice-cooled and added to it a solution of methyl/ethyl iodide (0.06 mol) in acetone (10 ml) and the stirring continued at room temperature for 10—15 h (monitored by t.l.c.). The reaction mixture after usual work-up as described above afforded the crude dithioacetal (**7d—f**), purified by column chromatography over silica gel using hexane–ethyl acetate (4:1) for (**7d—e**), or hexane–ethyl acetate (9:1) for (**7f**), as eluant. 2-*Allyl*-3,3-*bis*(*methylthio*)-1-(p-*methoxyphenyl*)*prop*-2-*en*-1-*one* (**7d**) (8.8 g, 60%) was obtained as a yellow oil; $\nu_{max.}$(neat) 1 680, 1 600 cm^{-1}; δ ($CDCl_3$) 2.05 (s, 3 H, SMe), 2.35 (s, 3 H, SMe), 3.40 (d, 2 H, CH_2), 3.83 (s, 3 H, OMe), 4.90—5.20 (m, 2 H, vinylic), 5.45—5.85 (m, 1 H, vinylic), and 6.85, 7.78 (2 d, A_2B_2, 4 H, arom.); *m/z* 294 (M^+) [Found: C, 61.6; H, 5.9. $C_{15}H_{18}O_2S_2$ (*M* 294) requires C, 61.22; H, 6.12%].

2-*Allyl*-3,3-*bis*(*ethylthio*)-1-(p-*methoxyphenyl*)*prop*-2-*en*-1-*one* (**7e**) (11.25 g, 70%) was obtained as a yellow oil; $\nu_{max.}$(neat) 1 660, 1 605 cm^{-1}; δ(CCl_4) 1.05 (t, 3 H, SCH_2CH_3), 1.30 (t, 3 H, SCH_2CH_3), 2.60 (q, 2 H, SCH_2CH_3), 2.80 (q, 2 H, SCH_2CH_3), 3.35 (d, 2 H, CH_2), 3.85 (s, 3 H, OMe), 4.80—5.20 (m, 2 H, vinylic), 5.50—5.90 (m, 1 H, vinylic), and 6.85, 7.72 (2 d, A_2B_2, 4 H, arom.); *m/z* 322 (M^+) [Found: C, 63.7; H, 7.05. $C_{17}H_{22}O_2S_2$ (*M* 322) requires C, 63.35; H, 6.83%].

2-*Allyl*-3,3-*bis*(*ethylthio*)-1-*phenylprop*-2-*en*-1-*one* (**7f**) (11 g, 75%) was obtained as a red oil; $\nu_{max.}$(neat) 1 660, 1 600 cm^{-1}; δ(CCl_4) 0.95 (t, 3 H, SCH_2CH_3), 1.25 (t, 3 H, SCH_2CH_3), 2.60 (q, 2 H, SCH_2CH_3), 2.85 (q, 2 H, SCH_2CH_3), 3.50 (d, 2 H, CH_2), 4.90—5.30 (m, 2 H, vinylic), 5.60—6.10 (m, 1 H, vinylic), and 7.50—8.20 (2 m, 5 H, arom.); *m/z* 292 (M^+) [Found: C, 65.6; H, 6.6. $C_{16}H_{20}OS_2$ (*M* 292) requires C, 65.75; H, 6.85%].

Rearrangement of the 1,1-*Bis*(*alkylthio*)-2-*aroylpenta*-1,4-*dienes* (**7a—f**) *to the* 1,5-*Bis*(*alkylthio*)-2-*aroylpenta*-1,3-*dienes* (**9a—f**). *General Procedure.*—To a suspension of sodium hydride (0.02 mol) in dry benzene–dimethylformamide (9:1) (50 ml), a solution of the dithioacetal (**7**) (0.01 mol) in the same solvent mixture (10 ml) was added and the reaction mixture was stirred at 40—45 °C for 2 h. It was then quenched over crushed ice (150 g), neutralized with dilute acetic acid, and extracted with chloroform (3 × 50 ml). The combined extract was washed with water (2 × 50 ml), dried (Na_2SO_4) and the solvent removed to give the crude residue, which was purified by column chromatography over silica gel. Elution with hexane–EtOAc (9:1) gave first the unchanged starting materials (**7a—f**) and further elution with hexane–EtOAc (4:1) yielded the pure rearranged penta-1,3-dienes (**9a—f**). 2-*Benzoyl*-1,5-*bis*(*methylthio*)*penta*-1,3-*diene* (**9a**) (1.45 g, 55%) was obtained as yellow oil; 0.8 g (30%) of (**7a**) was recovered. The i.r. and ^1H n.m.r. spectral data are described in the text. δ_C 67.89 MHz; $CDCl_3$) 14.4 (q, SMe), 18.4 (q, SMe), 36.9 (t, CH_2), 126.4 (d, C-4, vinylic), 129.2 (d, C-2′ and C-6′, arom.), 130.3 (d, C-3′ and C-5′, arom.), 132.3 (d, C-4′, arom.), 132.5 (d, C-3, vinylic), 133.3 (s, C-2, vinylic), 138.7 (s, C-1′, arom.), 146.2 (d, C-1, vinylic), and 194.2 (s, PhC=O) [Found: C, 63.4; H, 6.3. $C_{14}H_{16}OS_2$ (*M* 264) requires C, 63.64; H, 6.06%].

1,5-*Bis*(*methylthio*)-2-(p-*methylbenzoyl*)*penta*-1,3-*diene* (**9b**) (1.6 g, 57%) was obtained as a yellow oil; 0.9 g (30%) of (**7b**) was recovered; $\nu_{max.}$(neat) 1 650, 1 590, and 1 570 cm^{-1}; δ(CCl_4) 2.0 (s, 3 H, SMe), 2.40 (s, 6 H, SMe and *p*-Me), 3.17 (d, 2 H, CH_2), 5.7—6.12 (m, 1 H, H_A, olefinic), 6.28 (d, 1 H, *J* 15 Hz, H_B, olefinic), 6.80 (s, 1 H, H_C, olefinic), and 7.25—7.70 (2 d, 4 H, arom.); *m/z* 278 (M^+) [Found: C, 65.0; H, 6.2. $C_{15}H_{18}OS_2$ (*M* 278) requires C, 64.75; H, 6.47%].

2-(p-*Chlorobenzoyl*)-1,5-*bis*(*methylthio*)*penta*-1,3-*dienes* (**9c**) (1.65 g, 55%) was obtained as a red oil; 0.7 g (25%) of (**7c**) was recovered; $\nu_{max.}$(neat), 1 650, 1 590, and 1 570 cm^{-1}; δ(CCl_4) 2.0 (s, 3 H, SMe), 2.40 (s, 3 H, SMe), 3.20 (d, 2 H, CH_2), 5.70—6.10 (m, 1 H, H_A, olefinic), 6.25 (d, 1 H, *J* 15 Hz, H_B, olefinic), 6.85 (s, 1 H, H_C, olefinic), and 7.20—7.70 (2 d, A_2B_2, 4 H, arom.); *m/z* 298 (M^+) [Found: C, 56.8; H. 5.5. $C_{14}H_{15}ClOS_2$(*M* 298.5) requires C, 56.28; H, 5.02%].

1,5-*Bis*(*methylthio*)-2-(p-*methoxybenzoyl*)*penta*-1,3-*diene* (**9d**) (1.9 g, 65%) was obtained as a yellow oil; 0.7 g (24%) of (**7d**) was recovered; $\nu_{max.}$(neat) 1 645, 1 600, and 1 575 cm^{-1}; δ(CCl_4) 1.9 (s, 3 H, SMe), 2.30 (s, 3 H, SMe), 3.05 (d, 2 H, CH_2), 3.75 (s, 3 H, OMe), 5.55—5.95 (m, 1 H, H_A, olefinic), 6.20 (d, 1 H, *J* 15 Hz, H_B, olefinic), 6.60 (s, 1 H, H_C, olefinic), and 6.75, 7.55 (2 d, A_2B_2, 4 H, arom.); *m/z* 294 (M^+) [Found: C, 61.5; H, 6.4. $C_{15}H_{18}O_2S_2$ (*M* 294) requires C, 61.22; H, 6.12%].

1,5-*Bis*(*ethylthio*)-2-(p-*methoxybenzoyl*)*penta*-1,3-*diene* (**9e**) (2.25 g, 70%) was obtained as a yellow oil; 0.65 g (20%) of (**7e**) was recovered; $\nu_{max.}$(neat) 1 645, 1 600, and 1 575 cm^{-1}; δ(CCl_4) 1.0—1.35 [2t, 6 H, $(SCH_2CH_3)_2$], 2.40 (q, 2 H, SCH_2CH_3), 2.60 (q, 2 H, SCH_2CH_3), 3.15 (d, 2 H, CH_2), 3.77 (s, 3 H, OMe), 5.70—6.10 (m, 1 H, H_A, olefinic), 6.25 (d, 1 H, *J* 15 Hz, H_B, olefinic), 6.70—6.90 (m, 3 H, 1 H_C and 2 H_{arom}), and 7.65 (d, 2 H, arom.); *m/z* 322 (M^+) [Found: C, 63.2; H, 6.6. $C_{17}H_{22}O_2S_2$ (*M* 322) requires C, 63.35; H, 6.83%].

2-*Benzoyl*-1,5-*bis*(*ethylthio*)*penta*-1,3-*diene* (**9f**) (1.5 g, 52%) was obtained as a red oil; 0.95 g (32.5%) of (**7f**) was recovered; $\nu_{max.}$(neat) 1 640, 1 600, and 1 580 cm^{-1}; δ(CCl_4) 1.0—1.40 [2 t, 6 H, $(SCH_2CH_3)_2$], 2.30—2.80 [2 q, 4 H, $(SCH_2CH_3)_2$], 3.15 (d, 2 H, CH_2), 5.80—6.10 (m, 1 H, H_A, olefinic), 6.50 (d, 1 H, *J* 15 Hz, H_B, olefinic), 6.85 (s, 1 H, H_C, olefinic), and 7.30—7.70 (m, 5 H, arom.); *m/z* 292 (M^+) [Found: C, 65.9; H, 7.1. $C_{16}H_{20}OS_2$(*M* 292) requires C, 65.75; H, 6.85%].

Rearrangement of the Dithioacetals (**7a**) and (**7e**); A 'Cross-over' Reaction.—A suspension of compounds (**7a**) (2.64 g, 0.01 mol) and (**7e**) (3.22 g, 0.01 mol) and sodium hydride (2 g, 0.04 mol) in dry benzene–dimethylformamide (9:1) (100 ml) was stirred at 40—45 °C for 2 h. The reaction mixture, after usual work-up, was purified by column chromatography over silica gel. Elution with hexane–EtOAc (95:5) gave a mixture of unchanged starting materials (**7a**) and (**7e**) (t.l.c., i.r. and n.m.r.). Further elution with the same solvent mixture yielded a pure product (t.l.c. single spot, R_F *ca.* 0.5), which was found to be a mixture of compounds (**9a**) and (**9f**), 2-*benzoyl*-5-*ethylthio*-1-*methylthio penta*-1,3-*diene* (**15a**) and 2-*benzoyl*-1-*ethylthio*-5-*methylthiopenta*-1,3-*diene* (**15b**) (n.m.r. and mass spectra). The n.m.r. spectrum of the mixture showed the following signals: δ(CCl_4) 1.0—1.40 [2 t, $(SCH_2CH_3)_2$, 46 squares], 1.90 (s, SMe, 50 squares), 2.30 (s, SMe, 49 squares), 2.35—2.80 [2 q, $(SCH_2CH_3)_2$, 31 squares], 3.10 (d, CH_2, 38 squares), 5.70—6.80 (m, H, olefinic, 62 squares), and 7.20—7.45 (m, H, arom., 105 squares); which indicates the presence of cross-over products in

the mixture. The mass spectrum of this mixture gave the following prominent peaks, *m/z* 292, 278, 264, 245, 231, 217, 203, 185 *etc.* The peaks at *m/z* 292, 278, and 264 are the molecular ion peaks of compounds (**9f**), (**15a**) and/or (**15b**) and (**9a**), thus showing the presence of the cross-over products, particularly (**15a**) and/or (**15b**), in the mixture.

Further elution with hexane–EtOAc (4:1) gave an orange oil (t.l.c. single spot, R_F *ca.* 0.4), which was also found to be a mixture of compounds (**9e**) and (**9d**), *5-ethylthio-1-methylthio-2-(p-methoxypenzoyl)penta-1,3-diene* (**16a**) and *1-ethylthio-5-methylthio-2-(p-methoxybenzoyl)penta-1,3-diene* (**16b**). The n.m.r. spectrum of the mixture showed the following signals: δ(CCl_4) 1.10—1.45 [2 t, $(SCH_2CH_3)_2$, 75 squares], 1.90 (s, SMe, 39 squares), 2.35 (s, SMe, 41 squares), 2.40—2.90 [2 q, $(SCH_2CH_3)_2$, 52 squares], 3.0—3.25 (d, CH_2, 43 squares), 3.80 (s, OMe, 66 squares), 5.70—6.90 (m, H, arom. and H, olefinic, 105 squares), and 7.60 (d, H, arom., 42 squares); this indicates the presence of cross-over products in the mixture. The mass spectrum of the mixture displayed the following significant peaks, *m/z*) 322, 308, 294, 275, 261, 247, 214, 200 *etc.* The peaks at *m/z* 322, 308, and 294 are the molecular ion peaks of compounds (**9e**), (**16a**) and/or (**16b**) and (**9d**), thus showing the presence of the cross-over products particularly (**16a**) and/or (**16b**) in the mixture.

Rearrangement of the Ketene Dithioacetal (**7a**) *in the Presence of Diphenylpicrylhydrazyl–Hydroquinone.*—A mixture of compound (**7a**) (2.64 g, 0.01 mol) and diphenylpicrylhydrazyl (0.5 g) in dry benzene–dimethylformamide (9:1) (20 ml) was slowly added (15 min) to a suspension of sodium hydride (1 g, 0.02 mol) in the same solvent mixture (30 ml) and the reaction mixture was stirred at 40—45 °C for 2 h. The reaction mixture, after usual work-up and purification as described above, yielded the rearranged pentadiene (**9a**) (1.4 g, 53%); also 0.85 g (32%) of the starting material (**7a**) was recovered.

When the same reaction was carried out in the presence of hydroquinone (0.2 g) instead of diphenylpicrylhydrazyl, the yield of (**9a**) was 1.35 g (51%) along with 0.95 g (36%) of (**7a**).

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