A Novel Cyclization Reaction of Alkylthiodiphenylcyclopropenium Ions with Acyclic 1,3-Diketones to Give Cyclopentadienols

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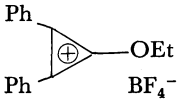
Reaction of methylthio-, ethylthio-, and benzylthiodiphenylcyclopropenium salts with 2,4-pentanedione (**3a**) and ethyl acetoacetate (**3b**) yielded the cyclopentadienol derivatives (**4**) by ring expansion. One of the products **4a** was shown to be 4-acetyl-5-hydroxy-5-methyl-1-methylthio-2,3-diphenyl-1,3-cyclopentadiene by X-ray crystallography. Chemical transformation of the products yielded some cyclopentenones. Triphenylcyclopropenium perchlorate reacted with **3a** and **3b** affording the ketocyclopropene in good yields.

Cyclopropenium ions with phenyl, amino, and alkylthio groups as substituents condense with nitrogenous nucleophiles such as hydrazine, aliphatic amines, and azides to give 5- or 6-membered nitrogen heterocycles,[1-4] whereas 1,2-diphenyl-3-ethoxycyclopropenium tetrafluoroborate (**1**) reacts with 1,3-diketones yielding fulvenes.[5,6] In the course of our studies on the chemistry of some cyclopropenone derivatives[7,8] we found a novel cyclization reaction of 3-alkylthio-1,2-diphenylcyclopropenium salts (**2**) with 2,4-pentanedione (**3a**) or ethyl acetoacetate (**3b**).



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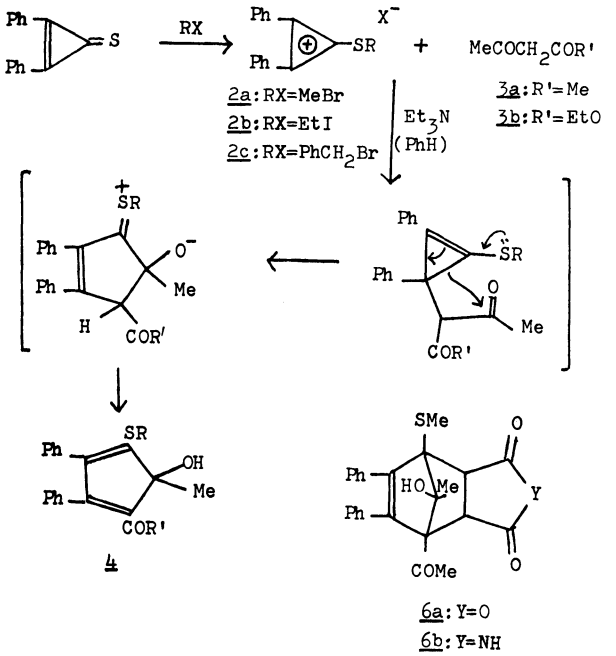
Diphenylcyclopropenethione reacted easily with alkyl halides, such as methyl bromide, ethyl iodide, or benzyl bromide, to give the corresponding cyclopropenium salts (**2a—c**) in good yields. A mixture of **2**, **3**, and triethylamine in approximately 1 : 1.2 : 2 molar ratio was stirred in benzene at room temperature for 20 min. Column chromatography of the products on silica gel afforded pale yellow crystals of the cyclopentadienols (**4**) (Table 1). The use of acetonitrile as reaction solvent or diisopropylamine as base lowered the yield of **4a**. Although many isomeric structures are mechanistically possible for the products, the ^{1}H- and ^{13}C-NMR, and mass spectra did not permit clear choice to be made.

TABLE 1. REACTIONS OF CYCLOPROPENIUM SALTS **2** OR **11** WITH CARBONYL COMPOUNDS **3**.

Product	Reactant		R	R′	Yield/%[a]
4a	**2a**	**3a**	Me	Me	73, 59,[b] 61[c]
4b	**2a**	**3b**	Me	EtO	36
4c	**2b**	**3a**	Et	Me	71
4d	**2b**	**3b**	Et	EtO	45
4e	**2c**	**3a**	$PhCH_2$	Me	65
4f	**2c**	**3b**	$PhCH_2$	EtO	14
12a	**11**	**3a**	—	Me	73
12b	**11**	**3b**	—	EtO	61

Tertiary amine and solvent used: a) triethylamine in benzene, b) triethylamine in acetonitrile, c) diisopropylamine in acetonitrile.

The structure of 4-acetyl-5-hydroxy-5-methyl-1-methylthio-2,3-diphenylcyclopentadiene (**4a**) was ascertained by an X-ray crystal structure determination. There are two molecules of **4a** in the asymmetric unit and their relationship is shown in the stereo diagram, Fig. 1. Thermal ellipsoid plots of both molecules are shown in Fig. 2 and some of the more interesting bond lengths and angles are presented in Tables 2 and 3. There are no significant differences between the parameters for the two molecules. The two phenyl groups make angles of ≈58° (range 55.6—61°) in the same sense with the best plane through the respective cyclopentadiene ring. The bond length data suggests that there is electron delocalization from the sulfur atom through the butadiene system and into the acetyl group. In particular the S(1)–C(1) and C(2)–C(3) single bonds are shortened and the carbon-carbon and carbon-oxygen double bonds lengthened. The *S*-methyl carbons lie almost in the plane of their respective cyclopentadiene rings (deviation from plane: C(6)-0.307, C(6A)-0.211 Å)



Scheme 1.

Table 2. Bond lengths for **4a** with e.s.d.'s in parentheses

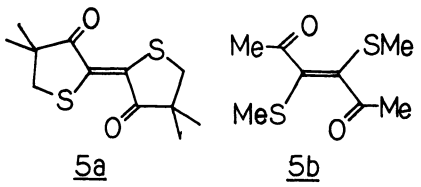
Bond length	l/Å	
	Molecule 1	Molecule 1A
S(1)–C(1)	1.744(6)	1.732(7)
S(1)–C(6)	1.769(8)	1.747(9)
O(1)–C(19)	1.235(7)	1.234(7)
O(2)–C(5)	1.440(7)	1.450(8)
C(1)–C(2)	1.359(8)	1.355(8)
C(1)–C(5)	1.504(8)	1.513(9)
C(2)–C(3)	1.389(8)	1.468(8)
C(2)–C(7)	1.481(8)	1.478(8)
C(3)–C(4)	1.351(8)	1.354(8)
C(3)–C(13)	1.484(8)	1.491(8)
C(4)–C(5)	1.523(8)	1.517(9)
C(4)–C(19)	1.456(8)	1.461(9)
C(5)–C(21)	1.525(9)	1.502(9)
C(19)–C(20)	1.502(9)	1.491(9)

Carbon-carbon bond lengths in the phenyl rings range between 1.361 and 1.397 Å with e.s.d.'s ranging from 0.008 to 0.011 Å.

Table 3. Bond angles for **4a** with e.s.d.'s in parentheses

Bond angle	ϕ/°	
	Molecule 1	Molecule 1A
C(1)–S(1)–C(6)	107.4(4)	109.4(4)
S(1)–C(1)–C(2)	122.1(5)	124.0(5)
S(1)–C(1)–C(5)	126.4(5)	126.0(5)
C(2)–C(1)–C(5)	110.7(5)	109.6(6)
C(1)–C(2)–C(3)	107.3(5)	109.2(5)
C(1)–C(2)–C(7)	127.6(6)	126.0(6)
C(3)–C(2)–C(7)	125.2(5)	124.8(5)
C(2)–C(3)–C(4)	110.3(5)	109.3(5)
C(2)–C(3)–C(13)	119.7(5)	122.0(5)
C(4)–C(3)–C(13)	129.9(5)	128.8(6)
C(3)–C(4)–C(5)	108.6(5)	109.4(6)
C(3)–C(4)–C(19)	132.0(6)	132.1(6)
C(5)–C(4)–C(19)	119.3(6)	118.4(6)
O(2)–C(5)–C(1)	109.7(5)	109.5(6)
O(2)–C(5)–C(4)	111.7(5)	113.3(6)
O(2)–C(5)–C(21)	110.6(5)	110.5(5)
C(1)–C(5)–C(4)	102.6(5)	102.3(5)
C(1)–C(5)–C(21)	112.1(6)	111.3(6)
C(4)–C(5)–C(21)	110.0(5)	109.8(6)
O(1)–C(19)–C(4)	119.4(6)	118.4(7)
O(1)–C(19)–C(20)	117.9(6)	119.0(7)
C(4)–C(19)–C(20)	122.7(6)	122.4(6)

C–C–C bond angles at the phenyl ring carbons vary between 118.2 and 121.3° with e.s.d.'s ranging between 0.6 and 0.8°.



5a 5b

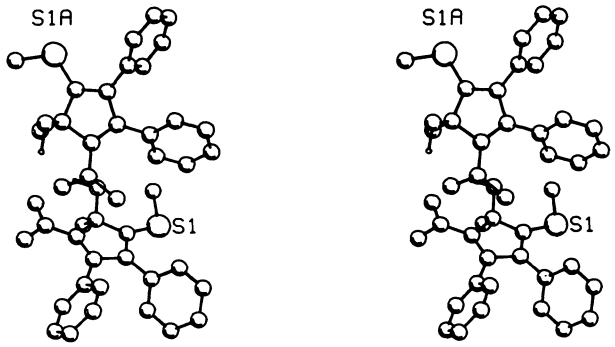


Fig. 1. A stereo view of the contents of the asymmetric unit of the crystal structure of **4a** drawn with SNOOPI.[10]

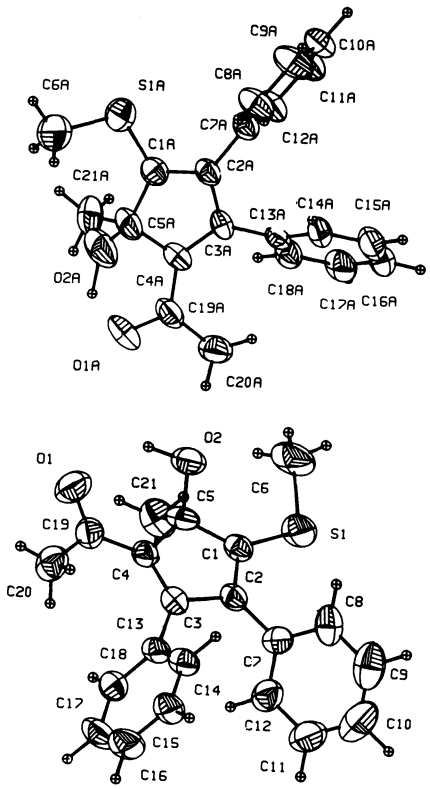
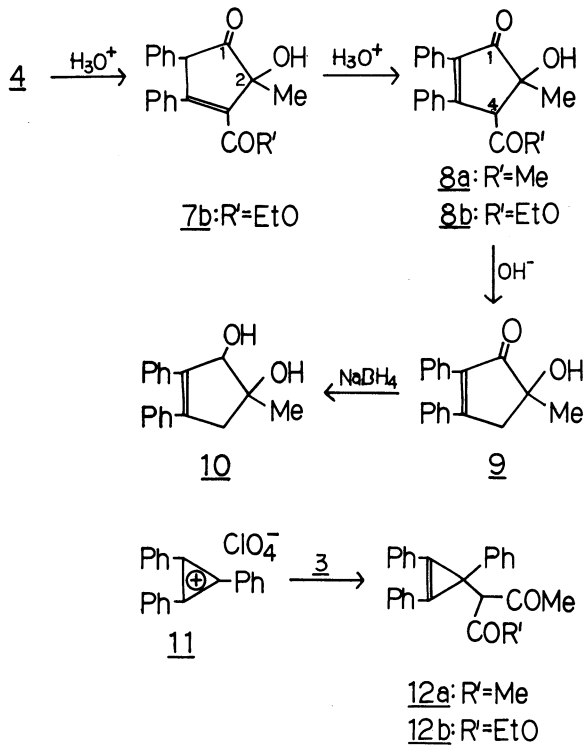


Fig. 2. Thermal ellipsoid plots, drawn at the 50% level of the two independent molecules of **4a** drawn with SNOOPI.[10]

suggesting that the conjugated sulfur lone pair is in an essentially p-type orbital. From a comparison with the accurately measured[9] bond length data for *trans*-$\Delta^{2,2'}$-bis(4,4-dimethylthiolan-3-one) (**5a**) and *trans*-3,4-bis-(methylthio)-3-hexene-2,5-dione (**5b**) it would appear that electron delocalization from sulfur into an acetys group through a butadiene system was more effectivel than through just one carbon-carbon double bond. Thus the average C(1)–S(1) bond and the average C(4)–C(19) bond in **4a** are both shorter (by 0.010 and 0.028 Å respectively) while all the double bonds are longer than the equivalent bonds in **5a** and **5b**. However this may be misleading since further shortening of the bonds



joining the sulfur and acetyl moieties to the double bond in **5a**, **b** would further reduce the distance between the sulfur and carbonyl oxygen which is already (2.8 Å) within the sum of the van der Waals radii for these two atoms (3.2 Å).

The other compounds listed in Table 1 and given similar structures have similar spectra. In agreement with the dienol structure, **4a** underwent Diels-Alder reactions with maleic anhydride and maleimide at room temperature in benzene to give the adducts **6a** and **6b** in 81 and 66% yields and both showed characteristic AB quartets due to the two methine protons in their ^{1}H-NMR spectra.

Chemical transformation of **4** yielded some new cyclopentene derivatives **7**—**10**, the structures of which are based on their spectra and the reagents employed. Raney nickel (W1 and W5) desulfurization of **4a** and **4b** gave only tarry mixtures.

On hydrolysis with a mixture of trifluoroacetic acid–mercury(II) chloride–water–chloroform, both **4a** and **4c** gave the cyclopentenone (**8a**) in 88 and 81% yield respectively. In the absence of the mercury(II) chloride the product was a tarry mixture. In contrast, **4b** and **4d** were hydrolyzed easily with hydrochloric acid in ethanol to give β,γ-unsaturated cyclic ketone **7b**, which isomerized to **8b** under further acid treatment.

On heating in aqueous sodium hydroxide **8a** and **8b** smoothly cleaved to yield the cyclopentenone (**9**) in good yields. This type of cleavage of vinylogous β-keto esters or diketones has been studied.[11]

Reduction of **9** with sodium borohydride gave the cyclic glycol **10** quantitatively. The structure of **7**—**10** are consistent with their ^{1}H- and ^{13}C-NMR, IR, and mass spectra. The mass spectra of **8**—**9** showed peaks at *m/e* 178, corresponding to PhC≡CPh, indicaing that the PhC=CPh grouping splits out intact; **7b** showed no such peak. Since ^{1}H- and ^{13}C-NMR spectra indicated that only one isomer was obtained for **8a**, **8b**, and **10**, their structures were not settled.

Eicher and his coworkers have reported reactions of **1**, with various carbon nucleophiles,[12] at position 1 or 3 of the cyclopropene ring depending on the conditions and reactant used.

Although the reactions of **2** with **3** were expected to give similar products to those obtained from **1**, several attempts (careful column chromatography or varieties of reaction conditions) to isolate products other than **4** were unsaccessful.

In contrast to the behavior of **2**, triphenylcyclopropenium perchlorate (**11**) with **3** in the presence of triethylamine in benzene produced the triphenylcyclopropenes (**12**) (Table 1). Their structures are clear from their ^{1}H-NMR (one proton exchanged by NaOD) and IR (2000—1700 cm^{-1} due to the cyclopropene ring) spectra. These cyclopropenes **12** were stable at 100 °C in the presence or absence of triethylamine.

The marked difference in reaction between **2** and **11** may be ascribed to electron-releasing properties of the alkylthio group.[13] The exact mechanism for the formation of **4** is not clear but most probably involves the formation of an intermediate corresponding to **12**, ring expansion, and proton movement as shown in Scheme 1.

Experimental

General. Melting points are uncorrected. The ^{13}C FT NMR spectra were recorded on a JEOL JNM FX-60 spectrometer (15.04 MHz), and ^{1}H-NMR spectra, on a Hitachi-Perkin Elmer R-24 (60 MHz). The IR spectra were recorded on a JASCO A-3 spectrometer.

Preparation of Alkylthiodiphenylcyclopropenium Salts (2a—c). The alkyl halide (25 mmol) was added in one portion to a solution of diphenylcyclopropenthione (4.3 g) in benzene (50 ml), and after 2 d at room temperature the precipitated salt **2** was collected, washed with dry benzene, and all solvent removed under reduced pressure. The following were prepared: *methylthiodiphenylcyclopropenium bromide (2a)*: yield 88%; mp 131—132 °C; ^{1}H-NMR ($CDCl_3$–10% CF_3CO_2H) δ=3.24 (3H, s, MeS) and 7.1—8.3 (10H, m, Ph). *Ethylthiocyclopropenium iodide (2b)*: yield 62%; mp 130—132 °C; ^{1}H-NMR ($CDCl_3$–10% CF_3CO_2H) δ=1.52 (3H, t, J=7.5 Hz, $\underline{Me}CH_2$), 3.66 (2H, q, CH_2), and 7.1—8.3 (10H, m, Ph). *Benzylthiodiphenylcyclopropenium bromide (2c)*: yield 79%; mp 131—134 °C; ^{1}H-NMR ($CDCl_3$–10% CF_3CO_2H) 5.09 (2H, s, $Ph\underline{CH_2}$) and 7.1—8.3 (15H, m, Ph).

The Reactions of Alkylthiodiphenylcyclopropenium Ions (2) with 2,4-Pentanedione (3a) or Ethyl Acetoacetate (3b). (a): Methylthiodiphenylcyclopropenium bromide with **3a**. A mixture of **2a** (10 mmol), **3a** (12 mmol), and triethylamine (20 mmol) in dry benzene (100 cm^3) was stirred for 20 min. After filtration from the precipitate, the benzene solution was concentrated and chromatographed over silica gel (petroleum ether : benzene : ethyl acetate, 10 : 2 : 1 v/v) to give *4-acetyl-5-hydroxy-5-methyl-1-methylthio-2,3-diphenyl-1,3-cyclopentadiene (4a)*, yellow crystals (73%): mp 105—106 °C; IR (KBr) 3300—3500 (OH) and 1615 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ=1.79 (3H, s, MeCO), 1.82 (3H, s, $\underline{Me}COH$), 2.39 (3H, s, MeS), 4.36 (1H, s, OH), and 6.9—7.5 (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=15.0 (q, MeS), 27.1 (q, $\underline{Me}COH$), 29.7 (g, $\underline{Me}CO$) 87.2 (s, COH), 127.7 (d), 128.2 (d), 128.6 (d),

129.7 (d), 133.4 (s), 134.7 (s), 139.6 (s), 143.6 (s), 154.0 (s), 155.4 (s), and 196.0 (s, C=O); MS (*m/e*) 336 (M^+); Found: C, 74.73; H, 5.91%. Calcd for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99%.

Acetonitrile as reaction solvent gave 61% of **4a**, and replacing the triethylamine by diisorpylamine as well reduced the yield to 59%.

The subsequent reactions were carried out in benzene as described above. (*b*): Methylthiodiphenylcyclopropenium bromide (**2a**) with ethyl acetoacetate (**3b**) yielded *4-ethoxycarbonyl-5-hydroxy-5-methyl-1-methylthio-2,3-diphenyl-1,3-cyclopentadiene* (***4b***) (36%): mp 96—97 °C; IR (KBr) 3300—3500 (OH) and 1670 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=0.99 (3H, t, J=7.5 Hz, MeCH_2), 1.78 (3H, s, MeCO), 2.31 (3H, s, MeS) 3.88 (1H, s, OH), 4.06 (2H, q, MeCH_2), and 7.0—7.6 (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=13.6 (q, MeS), 15.1 (q, MeCH_2O), 21.6 (q, MeCOH), 59.9 (t, CH_2O), 86.1 (s, COH), 127.1 (d), 127.5 (d), 128.1 (d), 129.7 (d), 133.5 (s), 134.2 (s), 134.7 (s), 139.9 (s), 154.2 (s), 155.1 (s), and 164.1 (s, CO_2); MS (*m/e*) 366 (M^+); Found: C, 71.74; H, 5.98%. Calcd for $C_{22}H_{22}O_3S$: C, 72.12; H, 6.05%. (*c*): Ethylthiodiphenylcyclopropenium iodide (**2b**) with 2,4-pentanedione (**3a**) yielded *4-acetyl-1-ethylthio-5-hydroxy-5-methyl-2,3-diphenyl-1,3-cyclopentadiene* (***4c***) (71%): mp 107—107.5 °C; IR (KBr) 3300—3500 (OH) and 1610 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ=1.13 (3H, t, J=7.5 Hz, MeCH_2), 1.74 (3H, s, MeC=O), 1.78 (3H, s, MeCOH), 2.4—3.6 (2H, m, CH_2), 4.05 (1H, s, OH), and 6.8—7.4 (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=15.1 (q, MeCH_2), 25.8 (t, CH_2S), 27.5 (q, MeCOH), 29.4 (q, MeC=O), 87.2 (s, COH), 127.7 (d), 128.2 (d), 128.6(d), 129.6(d), 133.6 (s), 134.8 (s), 140.6 (s), 144.0 (s), 153.4 (s), 155.2 (s), and 195.9 (s, C=O); MS (*m/e*) 350 (M^+); Found: C, 75.50; H, 6.28%. Calcd for $C_{22}H_{22}O_2S$: C, 75.40; H, 6.23%. (*d*) Ethylthiodiphenylphenylcyclopropenium iodide (**2b**) with ethyl acetoacetate (**3b**) yielded *4-ethoxycarbonyl-1-ethylthio-5-hydroxy-5-methyl-2,3-diphenyl-1,3-cyclopentadiene* (***4d***) (45%): mp 62—63 °C; IR (KBr) 3300—3500 (OH) and 1660 cm^{-1} (CO): ^{1}H-NMR ($CDCl_3$) δ=0.98 (3H, t, J=7.5 Hz, MeCH_2O), 1.15 (3H, t, J=7.5 Hz, MeCH_2S), 1.77 (3H, s, MeCOH), 2.4—3.6 (2H, m, CH_2), 4.08 (2H, q, J=7.5 Hz, CH_2O), and 6.8—7.4 (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=13.7 (q, MeCH_2S), 15.2 (q, MeCH_2O), 25.8 (t, CH_2S), 26.4 (q, MeCOH), 59.9 (t, CH_2O), 86.1 (s, COH), 127.0 (d), 127.3 (d), 127.6 (d), 127.7 (d), 128.9 (d), 129.6 (d), 133.7 (s), 134.2 (s), 135.2 (s), 141.1 (s), 150.5 (s), 154.1 (s), and 164.2 (s, CO_2); MS (*m/e*) 380 (M^+); Found: C, 72.50; H, 6.48%. Calcd for $C_{23}H_{24}O_3S$: C, 72.60; H, 6.36%. (*e*): Benzylthiodiphenylcyclopropenium bromide (**2c**) with 2,4-pentanedione (**3a**) yielded *4-acetyl-1-benzylthio-5-hydroxy-5-methyl-2,3-diphenyl-1,3-cyclopentadiene* (***4e***) (65%): mp 116—117 °C; IR (KBr) 3300—3500 (OH) and 1620 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ=1.76 (3H, s, MeCO), 1.99 (3H, s, MeCOH), 4.04 and 4.30 (2H, ABq, J=13 Hz, CH_2), 4.16 (1H, s, OH), and 6.7—7.4 (15H, m, Ph); MS (*m/e*) 412 (M^+); Found: C, 78.61; H, 5.97%. Calcd for $C_{27}H_{24}O_2S$: C, 78.61; H, 6.06%. (*f*): Benzylthiodiphenylcyclopropenium bromide (**2c**) with ethyl acetoacetate (**3b**) gave *1-benzylthio-4-ethoxycarbonyl-5-hydroxy-5-methyl-2,3-diphenyl-1,3-cyclopentadiene* (***4f***) (14%): mp 120—121 °C; IR (KBr) 3300—3500 (OH) and 1675 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ=0.98 (3H, t, J=7.5 Hz, MeCH_2), 1.76 (3H, s, MeCOH), 4.08 (2H, q, CH_2O), 4.08 (1H, s, OH), 4.13 (2H, s, PhCH_2) and 6.6—7.7 (15H, m, Ph); MS (*m/e*) 442 (M^+); Found; C, 76.28; H, 6.09%. Calcd for $C_{28}H_{26}O_3S$: C, 75.99; H, 5.92%.

Diels-Alder Reaction of ***4a***. (*a*): A solution of **4a** (1 mmol) and maleic anhydride (2 mmol) in benzene (25 cm^3) was stirred at room temperature for 3 h. The precipitate of needles was collected, washed with small amount of benzene, and dried to give *the adduct* **6a** (81%): mp 151—165 °C; IR (KBr) 3450 (OH), 1855, 1770, and 1690 cm^{-1}; ^{1}H-NMR ($CDCl_3$–DMSO-d_6 1/1) δ=1.63 (3H, s, MeCOH), 2.03 (3H, s, MeCO), 2.22 (3H, s, MeS), 3.10 (1H, bs, OH), 4.33 (1H, d, J=9 Hz, CH), 4.83 (1H, d, CH), and 6.6—7.6 (10H, m, Ph) MS (*m/e*) 434 (M^+); Found: C, 68.54; H, 5.01%. Calcd for $C_{25}H_{20}O_5S$: C, 69.11; H, 5.10%. (b) A solution of **4a** (1 mmol) and maleimide (1 mmol) in ethanol (50 cm^3) was left at room temperature for 3 h. The solvent was removed *in vacuo* and the residual crystalline mass washed with benzene and hot ethanol to yield *the adduct* **6b** (66%): mp 234—238 °C; IR (KBr) 3475 (OH), 1860, 1780, and 1700 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$: DMSO-d_6, 1 : 1) δ=1.06 (3H, s, MeCOH), 2.14 (3H, s, MeCO), 2.16 (3H, s, MeS), 3.24 (1H, s, OH), 3.86 (1H, d, J=7.5 Hz, CH), 4.52 (1H, d, CH), 5.91 (1H, s, NH), and 6.6—7.3 (10H, m, Ph); MS (*m/e*) 443 (M^+); Found: C, 68.44; H, 5.12; N, 3.10%. Calcd for $C_{25}H_{21}NO_4S$: C, 69.26; H, 5.35; N, 3.23%.

Hydrolysis of ***4a***. A mixture of **4a** (160 mg, 0.48 mmol), mercury(II) chloride (260 mg, 0.96 mmol), trifluoroacetic acid (0.56 cm^3, 48 mmol), water (0.4 cm^3), and chloroform (15 cm^3) was vigorously stirred at room temperature for 3 d. Water (15 cm^3) was added and the organic layer separated. Removal of the solvent and chromatography of the residue over silica gel (chloroform: ethyl acetate, 3 : 1, v/v) yielded *4-acetyl-5-hydroxy-5-methyl-2,3-diphenyl-2-cyclopentenone* (**8a**) (88%): mp 184—185 °C (2-propanol); IR (KBr) 3450 (OH), 1700, 1690 (sh) (CO), and 1620 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.60 (3H, s, MeCOH), 2.20 (3H, s, MeCO), 2.92 (1H, OH, D_2O exchangeable), 4.28 (1H, s, CH), and 7.28—7.31 (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=27.3 (q, MeCOH), 30.5 (q, MeCO), 67.7 (d, C_4H), 78.4 (s, C_5), 128.3 (d), 128.6 (d), 128.8 (d), 129.2 (d), 129.5 (d), 130.5 (d), 131.2 (s), 134.2 (s), 138.0 (s), 163.2 (s), 204.9 (s, MeC=O), and 206.8 (s, C_1=O); MS (*m/e*) 304 (M^+); Found: C, 78.28; H, 5.83%. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92%.

Hydrolysis of ***4b*** *to* ***7b***. A solution of **4b** (270 mg, 0.55 mmol) and concentrated hydrochloric acid (0.4 cm^3) in ethanol (10 cm^3) was stirred at 10 °C for 2 d. The mixture was quenched with water and the product was extracted with chloroform. The extract was dried and evaporated under reduced pressure to give colorless crystals of *3-ethoxycarbonyl-2-hydroxy-2-methyl-4,5-diphenyl-3-cyclopentenone* (***7b***) (86% crude yield) which after recrystallization from 2-propanol (48%) has mp 150—151 °C: IR (KBr) 3450 (OH), 1730, 1710 (CO), and 1630 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.16 (3H, t, J=7 Hz, MeCH_2), 1.60 (3H, s, MeC_2), 3.01 (1H, s, OH), 4.06 (1H, s, CH), 4.07 (2H, q, CH_2), and 7.0—7.4 (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=13.7 (q, MeCH_2), 26.4 (q, MeCOH), 61.0 (d, C_5H), 61.7 (t, CH_2), 78.1 (s, C_2), 128.3 (d), 128.5 (d), 129.2 (d), 130.0 (d), 130.3 (d), 131.3 (s), 134.1 (s), 137.9 (s), 161.0 (s), 169.6 (s, CO_2), and 206.2 (s, C_1=O); MS (*m/e*) 396 (M^+); Found: C, 75.08; H, 5.83%. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99%.

Similar treatment of **4d** yielded **7b** in 83% yield.

Isomerization of ***4b*** *to* ***8b***. A solution of **4b** (0.5 mmol) and concentrated HCl (1 cm^3) in ethanol (10 cm^3) was left at 25 °C for 2 d. The mixture was quenched with water, extracted with chloroform and the dried extracts evapolated *in vacuo* to yield a crystalline mass of *4-ethoxy-5-hydroxy-5-methyl-2,3-diphenylcyclopent-2-enone* (***8b***) (83%) mp: 158—159 °C (benzene–petroleum ether); IR (KBr) 3470 (OH), 1730, and 1710 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ=1.06 (3H, t, J=7.5 Hz, MeCH_2), 1.46 (3H, s, MeC_5), 3.13 (1H, s, OH, D_2O exchangeable), 4.08 (2H, q, CH_2), 4.27 (1H, s, CH), and 7.0—7.5 (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=14.0 (q, MeCH_2), 21.7 (q, Me), 60.0 (t, CH_2), 61.2 (d, CH), 77.2 (s,

MeCOH), 128.4 (d), 128.4 (d), 129.5 (d), 130.1 (d), 130.9 (s), 134.3 (s), 137.3 (s), 163.5 (s), 169.8 (s, CO_2), and 206.3 (s, C=O); MS (*m/e*) 396 (M^+) and 178 (PhC≡CPh); Found: C, 74.75; H, 5.85%. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99%.

The compound **8b** was prepared in the same way from **7b** in 96% yield.

*Preparation of 2,3-Diphenyl-5-hydroxy-5-methylcyclopent-2-en-1-one (**9**).* A suspension of **8a** (272 mg, 0.89 mmol) in 20% aqueous hydroxide (15 cm^3) was refluxed for 20 min. The first formed red solution precipitated crystals. After cooling these were collected and purified by chromatography over silica gel (ethyl acetate : chloroform, 1 : 3, v/v) to give **9** (60%): mp 146—147 °C (benzene); IR (KBr) 3425 (OH) and 1690 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ=1.53 (3H, s, Me), 2.68 (1H, s, OH), 2.94 and 3.31 (2H, d, J=18 Hz, CH_2), and 7.1—7.4 (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=24.1 (q, Me), 44.2 (t, CH_2), 73.2 (COH), 126.4 (d), 126.8 (d), 127.7 (d), 128.6 (d), 130.4 (s), 133.4 (s), 134.2 (s), 163.5 (s), and 207.2 (s, C=O); MS (*m/e*) 264 (M^+) and 178 (PhC≡CPh); Found: C, 81.55; H, 6.00%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%. similar treatment of **8b** with aqueous sodium hydroxide yielded **9** in a 74% yield.

*Reduction of **9** with Sodium Borohydride.* A solution of **9** (1 mmol) and sodium borohydride (1 mmol) in ethanol (25 cm^3) was stirred at room temperature for 1 d, quenched with water and extracted with chloroform. The extract was chromatographed over silica gel (chloroform : ethyl acetate, 3 : 1, v/v) to yield *3,4-diphenyl-1-methyl-3-cyclopentene-1,2-diol (**10**)* (75%): mp 110—111 °C; IR (KBr) 3100—3700 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=1.45 (3H, s, Me), 2.20 (2H, s, OH), 2.58 and 3.20 (2H, d, J=16 Hz, CH_2), 4.07 (1H, s, CH), and 7.1—7.3 (10H, m, Ph); MS (*m/e*) 266 (M^+) and 178 (PhC≡CPh); Found: C, 80.58; H, 6.84%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

*Reactions of Triphenylcyclopropenium Perchlorate (**11**).* *(a) With 2,5-Pentanedione (**3a**)*: A mixture of **11** (0.5 mmol), **3a** (0.6 mmol), and triethylamine (1.0 mmol) in benzene (10 cm^3) was stirred for 20 min. The solution was concentrated and chromatographed over silica gel (petroleum ether : ethyl acetate, 4 : 1, v/v). Evaporation of the elute gave a solid which recrystallized from 2-propanol to give *3-(1,2,3-triphenyl-2-cyclopropenyl)-2,4-pentanedione (**12a**)* (73%): mp 135—137 °C; IR (KBr) 1810, 1730, and 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.07 (6H, s, MeCO), 5.22 (1H, s, CH), and 7.0—8.1 (15H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=31.2 (q, Me), 33.0 (s, C_3), 72.1 (d, CH), 116.9 (s), 125.9 (d), 126.2 (d), 128.0 (d), 128.2 (s), 128.3 (d), 128.6 (d), 128.9 (d), 129.7 (d), 144.3 (s), and 204.2 (C=O); MS (*m/e*) 366 (M^+); Found: C, 85.28; H, 6.00%. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05%. *(b) With Ethyl Acetoacetate **3b***: A mixture of **11** (0.5 mmol), ethyl acetoacetate **3b** (0.6 mmol), and triethylamine (1 mmol) in benzene yielded *ethyl 2-(1,2,3-triphenyl-2-cyclopropenyl)-3-oxobutyrate (**12b**)* (61%): mp 133—134 °C; IR (KBr) 1950, 1890, 1730, and 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.94 (3H, t, J=7 Hz, $\underline{Me}CH_2$) 2.12 (s, MeCO), 3.98 (2H, q, CH_2O), 4.96 (1H, CH), and 7.1—8.0 (15H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=13.6 (q, $\underline{Me}CH_2$), 30.3 (q, $\underline{Me}CO$), 32.5 (s, C_3), 61.1 (t, CH_2O), 64.6 (d, CH), 116.0 (s), 116.3 (s), 125.8 (d), 126.2 (s), 128.0 (s), 128.2 (d), 128.7 (d), 129.0 (d), 129.7 (d), 129.8 (d), 144.2 (s), 169.1 (s, CO_2), and 202.5 (s, $\underline{C}OMe$); MS (*m/e*) 396(M^+); Found: C, 81.99; H, 6.28%. Calcd for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10%.

Crystal Structure Determination. *Crystal Data*: $C_{21}H_{20}O_2S$, M_r 336.5, monoclinic, $P2_1/n$, a=10.365(4), b=24.659(8), c=14.394(5) Å, β=101.63(3)°, U=3603.4 Å, Z=8, D_c=1.25 g cm^{-3}, μ=0.19 mm^{-1} (Mo $K\alpha$), R=0.053 for 2225 observed reflections.

A crystal of **4a** mounted on a glass fibre, was transferred to a CAD-4F four-circle diffractometer. Cell dimensions were determined from the positions of strong reflections located by the SEARCH routine and intensity data was collected by $\omega/2\theta$ scans out to 2θ=44° with periodic checking of the intensity and orientation of three standered reflections. After the application of Lorentz and polarization corrections, elimination of systematic absences and the merging of equivalent reflections, 3520 structure amplitudes were derived. The structure was solved using MULTAN 80[14] whic hlocated all but one of the non-hydrogen atoms. The structure was refined by blocked-matrix least squares with isotropic temperature factors and with Waser constrains[15] applied to the phenyl ring (bond lengths: 1.40 Å, e.s.d. 0.01 Å, bond angles: 120°, e.s.d. 0.5°). The missing atom was located by a difference Fourier synthesis and refinement continued with anisotropic temperature factors. The hydroxyl hydrogen atoms were placed from a difference Fourier synthesis but all the other hydrogens were placed geometrically and all were assigned an isotropic temperature factor of 0.075 and excluded from the refinement. The constrains on the phenyl ring were removed and weights for the final rounds of refinement were computed from Chebyshev series $w=[19.33t_0(x)+25.87t_1(x)+8.733t_2(x)]^{-1}$, where $(x)=F_o/F_{max}$.[16] The structure converged at an R-value of 0.053. All calculations were performed with the CRYSTALS[17] package on a VAX 11/750 computer.

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