

The Reaction of Cyclic 1,3-Diketones with Alkylthiocyclopropenium Ions to Yield 2-Alkylthio-substituted 2*H*-Pyrans

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This study treats the reactions of methylthio-, ethylthio-, or benzylthiodiphenylcyclopropenium ion (**1**) with 5-, 6-, and 7-membered cyclic 1,3-diketones, giving either 2-alkylthio-2*H*-pyrans or dienone derivatives. Treatment of **1** with 1,3-cyclopentanedione, 1,3-cyclohexanedione, 5,5-dimethyl-1,3-cyclohexanedione, 4-hydroxy-6-methyl-2-pyrone, 4-hydroxycoumarin, and 1,3-cycloheptanedione in the presence of triethylamine afforded 2-alkylthio-2*H*-pyrans. The structure of the products was elucidated on the basis of their elemental analyses, IR, ¹H-NMR, ¹³C-NMR, and mass spectroscopic data, as well as chemical transformations. 2-Alkylthio-2*H*-pyrans with mercury(II) chloride in an alcohol underwent conversion to the corresponding 2-alkoxy-2*H*-pyrans. The ¹H- and ¹³C-NMR data of these compounds clearly show that the equilibrium lies completely on the side of the 2*H*-pyran. In contrast, the reaction of **1** with 1,3-indandione yielded the ring-opened dienone derivative as a mixture of *E* and *Z* isomers.

2*H*-Pyrans are apparently not well known.¹⁾ Electrocyclic ring openings of 2*H*-pyrans and ring closures of dienones have been of considerable interest in view of the yet unresolved questions of how the presence of heteroatoms in a conjugated chain exerts influence on the electrocyclic process.²⁾ Although some synthetic routes to the stable 2*H*-pyrans like halogen-substituted 2*H*-pyrans have been developed,²⁾ neither physical nor chemical properties of sulfur-containing 2*H*-pyrans have been reported. Quite recently, we have communicated³⁾ the reaction of alkylthiodiphenylcyclopropenium salts **1** which acyclic 1,3-diketones to give the cyclopentadienol derivatives. Here we describe a novel cyclization reaction of **1** with cyclic 1,3-diketones to produce 2-alkylthio-substituted 2*H*-pyrans.

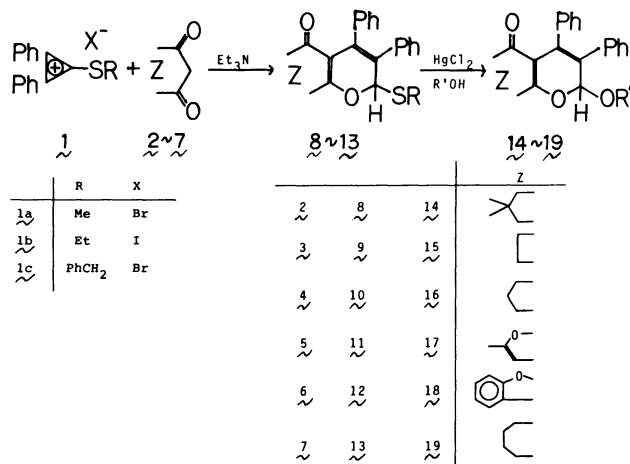
Methylthio-, ethylthio-, and benzylthiodiphenylcyclopropenium salts **1a–c** were prepared by the previously reported method.³⁾ A mixture of **1**, cyclic 1,3-diketone, and triethylamine in a molar ratio of 1:1:2 was stirred in dry benzene at room temperature for 15 min. The product was then purified by recrystal-

lization or by column chromatography. Cyclic 1,3-diketones such as 5,5-dimethyl-1,3-cyclohexanedione (**2**), 1,3-cyclopentanedione (**3**), 1,3-cyclohexanedione (**4**), 4-hydroxy-6-methyl-2-pyrone (**5**), 4-hydroxycoumarin (**6**) and 1,3-cycloheptanedione (**7**) gave the corresponding 2-alkylthio-2*H*-pyrans **8–13** in good yield as shown in Table 1. Treatment of the compounds with mercury (II) chloride in an alcohol yielded the corresponding desulfurization products: 2-alkoxy-2*H*-pyrans **14–19**.

The 2-alkylthio- and 2-alkoxy-2*H*-pyran structures of the products **8–19** were elucidated on the basis of elemental analyses, MS, ¹H- and ¹³C-NMR spectroscopic studies. For example, the ¹H- and ¹³C-NMR spectrum of **8a** showed a singlet at $\delta=6.03$ for one hydrogen and an sp³ carbon bonded to one hydrogen at $\delta=88.3$.

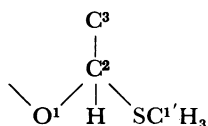
TABLE 1. ALKYLTHIO- AND ALKOXY-2*H*-PYRAN DERIVATIVES

Reactant		Product	Yield/%
1a	2	8a (R = Me)	84
1b	2	8b (R = Et)	58
1c	2	8c (R = PhCH ₂)	67
1a	3	9 (R = Me)	89
1a	4	10 (R = Me)	74
1a	5	11 (R = Me)	90
1a	6	12 (R = Me)	84
1a	7	13 (R = Me)	63
8a	MeOH	14a (R' = Me)	93
8a	EtOH	14b (R' = Et)	78
8a	<i>i</i> -PrOH	14c (R' = <i>i</i> -Pr)	80
8b	MeOH	14a (R' = Me)	83
9	MeOH	15a (R' = Me)	87
9	EtOH	15b (R' = Et)	81
10	MeOH	16 (R' = Me)	74
11	EtOH	17 (R' = Et)	89
12	EtOH	18 (R' = Et)	65
13	EtOH	19 (R' = Et)	61



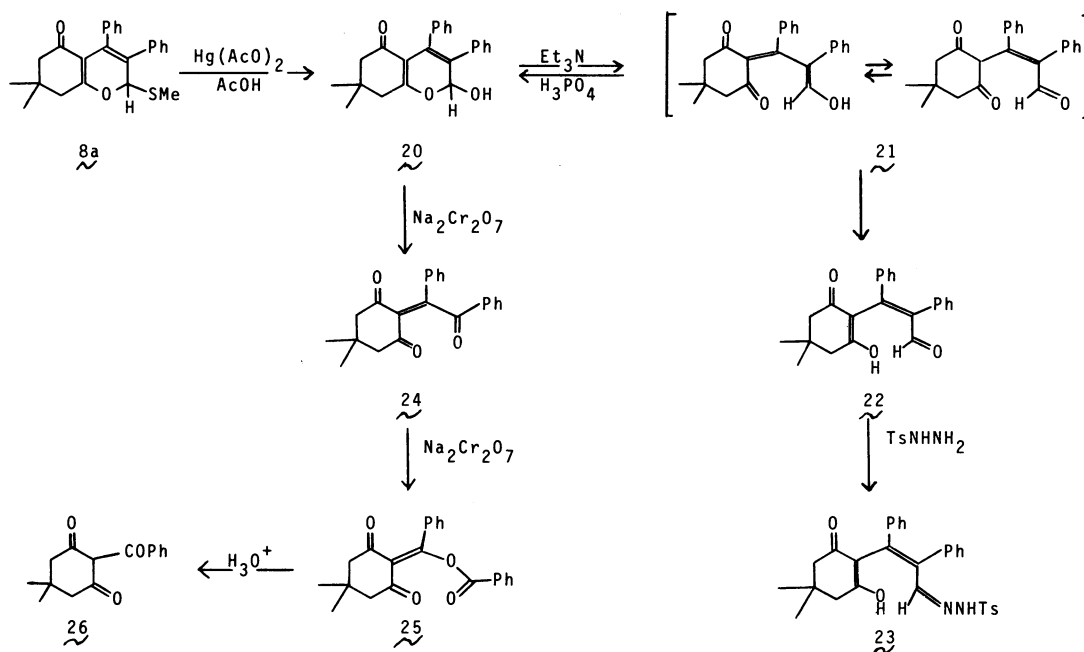
Scheme 1.

Coupling constants were $^1J_{\text{C}^2\text{H}}=170$ Hz and $^3J_{\text{C}^2\text{SC}^1\text{H}}=$
 $^3J_{\text{HC}^2\text{SC}^1\text{H}}=3$ Hz, thus indicating the framework:

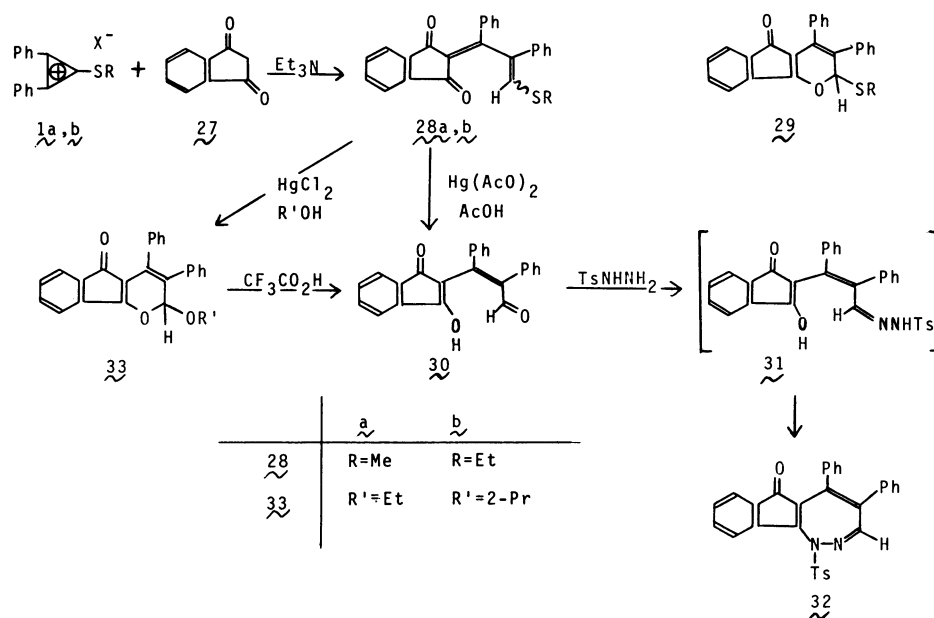


On treatment with mercury(II) acetate in acetic acid 2-alkylthio-2*H*-pyrans **8a** and **8b** gave 2-hydroxy-2*H*-pyran (**20**). The $^1\text{H-NMR}$ spectroscopic studies of **20** were interesting. A chloroform-*d* solution of **20** which showed a singlet at $\delta=5.76$ due to the C-2 hydrogen, gave two new singlets at 9.22 (D_2O exchangeable, OH)

and 9.80 ($\text{HC}=\text{O}$) on addition of a small amount of triethylamine to the solution. Attempt at isolation of the expected α,β -unsaturated aldehyde **22** failed, and **20** was recovered from the solution. However, treatment of a solution with *p*-toluenesulfonylhydrazide in ethanol containing 10% of triethylamine yielded the corresponding *p*-tolylsulfonyl hydrazone **23** in 38% yield. The unsaturated aldehyde **22** must be stabilized as enolate anion, since **20** was soluble in aqueous sodium hydroxide and acidification of the solution with phosphoric acid yielded **20**. These results indicate that 2-hydroxy-2*H*-pyran **20** is not stable in a basic solvent, but under acidic or neutral conditions the equilibrium lies completely on the side of 2*H*-



Scheme 2.



Scheme 3.

pyran **20**. The aldehyde **22** may be formed *via* either isomerization of **20** or electrocyclic ring opening of **20** to give **21**, followed by keto-enol isomerization.

Oxidation of **20** with sodium dichromate in acetic acid yielded the benzoylphenylmethylene derivative **24** as an initial oxidation product in 45% yield; further oxidation under the same reaction conditions gave **25** in 24% yield. The latter product **25** produced the known 2-benzoyl-5,5-dimethyl-1,3-cyclohexanedione (**26**)⁴ on hydrolysis in an acidic medium (Scheme 2).

A spontaneous reaction took place between **1a** (or **1b**) and 1,3-indandione (**27**) in the presence of triethylamine. In contrast to the reactions of 1,3-diketones **2**–**7**, the product isolated by column chromatography showed no peak corresponding to the 2*H*-pyran structure **29** in ¹H- and ¹³C-NMR spectra. The product is most likely to be an *E,Z*-isomer mixture of the dienone **28**, since the ¹H-NMR spectrum gave olefinic protons at $\delta=6.60$ and 6.71 in a 1:2 ratio.

Treatment of **28** with mercury(II) acetate in acetic acid yielded a resinous crystalline mass, the structure of which was established to be the ring-opened vinyl aldehyde **30**. The ¹H-NMR spectrum of **30** showed two singlets at $\delta=4.44$ (OH) and 9.59 (HC=O). The aldehyde **30** was converted by *p*-toluenesulfonylhydrazide to the diazepine **32**⁵ *via* the *p*-tolylsulfonylhydrazone **31** intermediate. In contrast, the reaction of **28a** with mercury(II) chloride in an alcohol afforded 2-alkoxy-2*H*-pyran **33** (the C-2 hydrogen as a singlet at around $\delta=6.0$). Addition of a small amount of trifluoroacetic acid to a solution of **33** in CDCl₃ yielded a ¹H-NMR spectrum in agreement with the structure **30**.

The reaction mechanism shown in Scheme 4 is proposed. The initial step involves a nucleophilic attack of the carbanion generated from 1,3-diketone on the cyclopropene ring of **1**. Subsequent elimination of the acidic methine hydrogen and ring opening gives either a conjugated betaine or a dienone intermediate, followed by intramolecular cyclization leading to the 2-alkylthio-2*H*-pyran. A cyclic 1,3-diketone like 1,3-indandione (**27**), which has little flexibility, gave no cyclization product, while 5-, 6-, and 7-membered flexible 1,3-diketones **2**–**7** yielded only 2-alkyl-

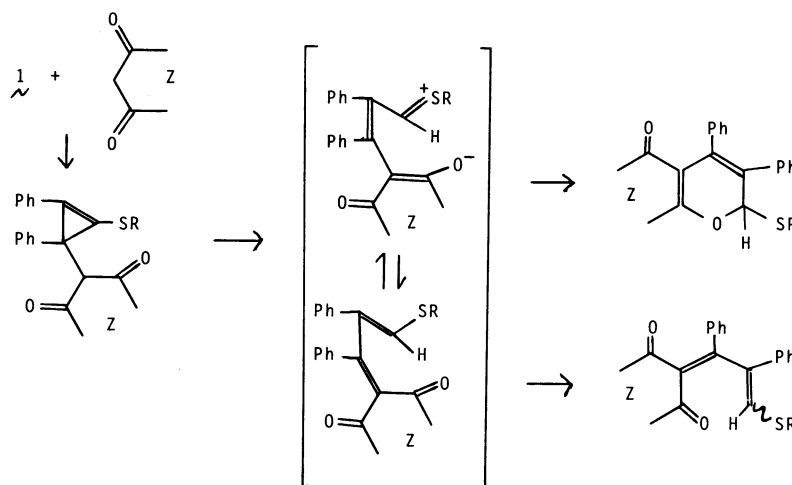
thio-2*H*-pyran derivatives.

Experimental

General. Melting points are uncorrected. The ¹³C FT NMR spectra were recorded on a JEOL JNM FX-60 spectrometer (15.04 MHz), and ¹H-NMR spectra, on a Hitachi-Perkin-Elmer R-24 (60 MHz). The IR spectra were recorded on a JASCO A-3 spectrometer, and mass spectra on a Hitachi RMU-7M mass spectrometer.

Alkylthiodiphenylcyclopropenium Ions 1a–c. Methylthio-, ethylthio-, and benzylthiodiphenylcyclopropenium ions **1a–c** were prepared as previously described.³⁾

The Reaction of Alkylthiodiphenylcyclopropenium Salts 1a–c with Cyclic 1,3-Diketones 2–7. (a) **The Reaction of 1a with 2:** A mixture of **1a** (1 mmol), **2** (1 mmol), and triethylamine (2 mmol) in dry benzene (15 cm³) was stirred for 20 min at room temperature. After the separation of the precipitate, the benzene solution was condensed and chromatographed over silica gel (chloroform) to give colorless crystals of 7,7-dimethyl-3,4-diphenyl-2-methylthio-5,6,7,8-tetrahydro-2*H*-1-benzopyran-5-one (**8a**) in 84% yield. **8a:** mp 190–192 °C; IR (KBr) 1670 and 1630 cm⁻¹; ¹H-NMR (CDCl₃) $\delta=1.16$ (3H, s, Me), 1.21 (3H, s, Me), 2.30 (5H, s, MeS and CH₂), 2.48 (2H, s, CH₂), 6.03 (1H, s, CH), and 6.9–7.2 (10H, m, 2Ph); ¹³C-NMR (CDCl₃) $\delta=13.9$ (q, MeS), 27.3 and 29.4 (q, 2Me), 31.8 (s), 42.9 (t), 51.7 (t), 88.3 (d), 116.5 (s), 123.4 (s), 126.6 (d), 127.0 (d), 127.4 (d), 127.8 (d), 129.2 (d), 132.4 (s), 136.9 (s), 137.8 (s), 168.5 (s), and 193.5 (s); MS (*m/z*) 376 (*M*⁺). Found: C, 76.33; H, 6.44%. Calcd for C₂₄H₂₄O₂S: C, 76.56; H, 6.42%. (b) **The Reaction of 1b with 2:** A similar reaction of **1b** with **2** yielded 7,7-dimethyl-3,4-diphenyl-2-ethylthio-5,6,7,8-tetrahydro-2*H*-1-benzopyran-5-one (**8b**) in 58%. **8b:** mp 152–154 °C; IR (KBr) 1650 and 1620 cm⁻¹; ¹H-NMR (CDCl₃) $\delta=1.17$ (3H, s, Me), 1.22 (3H, s, Me), 1.37 (3H, t, *J*=7.5 Hz, MeCH₂), 2.28 (2H, s, CH₂CO), 2.48 (2H, s, CH₂C=C), 2.77 (2H, q, CH₂S), 6.16 (1H, s, CH), and 6.8–7.4 (10H, m, 2Ph); MS (*m/z*) 390 (*M*⁺). Found: C, 77.02; H, 6.79%. Calcd for C₂₅H₂₆O₂S: C, 76.89; H, 6.71%. (c) **The Reaction of 1c with 2:** Similar reaction of **1c** with **2** yielded 2-benzylthio-7,7-dimethyl-3,4-diphenyl-5,6,7,8-tetrahydro-2*H*-1-benzopyran-5-one (**8c**) in 67% yield. **8c:** mp 157–159 °C; IR (KBr) 1665, 1650, and 1620 cm⁻¹; ¹H-NMR (CDCl₃) $\delta=1.11$ (3H, s, Me), 1.18 (3H, s, Me), 2.25 (2H, s, CH₂C=C), 2.29 (2H, CH₂CO), 3.94 (2H, dd, *J*=2.5 and 14.5 Hz, PhCH₂S), 6.06 (1H, s, CH), and 6.8–7.4 (15H, m, 3Ph); MS (*m/z*) 452 (*M*⁺). Found: C, 79.37; H, 6.14%. Calcd for C₃₀H₂₈O₂S: C, 79.61;



Scheme 4.

H, 6.24%. (d) *The Reaction of 1a with 3*: Similar treatment of **1a** with **3** afforded 3,4-diphenyl-2-methylthio-6,7-dihydrocyclopenta[b]pyran-5(2H)-one (**9**) in 89%. **9**: mp 175 °C; IR(KBr) 1670 and 1620 cm⁻¹; ¹H-NMR (CDCl₃) δ=2.32 (3H, s, MeS), 2.4–2.9 (4H, m, CH₂CH₂), 6.35 (1H, s, CH), 6.8–7.6 (10H, m, 2Ph); ¹³C-NMR (CDCl₃) δ=13.8 (q, MeS), 25.9 (t), 34.6 (t), 91.3 (d), 117.5 (s), 123.2 (s), 127.4 (d), 128.0 (d), 129.5 (d), 130.0 (d), 131.6 (s), 134.0 (s), 136.3 (s), 183.1 (s), and 198.3 (s); MS (*m/z*) 334 (M⁺). Found: C, 75.15; H, 5.63%. Calcd for C₂₁H₁₈O₂S: C, 75.42; H, 5.43%. (e) *The Reaction of 1a with 4*: Similar treatment of **1a** with **4** yielded 3,4-diphenyl-2-methylthio-5,6,7,8-tetrahydro-2H-1-benzopyran-5-one (**10**) in 74% yield. **10**: mp 174–176 °C; IR (KBr) 1660 and 1640 cm⁻¹; ¹H-NMR (CDCl₃) δ=1.8–2.8 (6H, m, CH₂CH₂CH₂), 2.28 (3H, s, MeS), 6.04 (1H, s, CH), and 6.8–7.6 (10H, m, 2Ph); ¹³C-NMR (CDCl₃) δ=14.0 (q, MeS), 20.0 (t), 29.4 (t), 37.8 (t), 88.2 (d), 117.7 (s), 123.5 (s), 126.6 (d), 127.1 (d), 127.4 (d), 127.8 (d), 128.3 (d), 129.3 (d), 132.5 (s), 137.0 (s), 137.9 (s), 169.9 (s), and 193.5 (s); MS (*m/z*) 348 (M⁺). Found: C, 75.68; H, 5.84%. Calcd for C₂₂H₂₀O₂S: C, 75.83; H, 5.79%. (f) *The Reaction of 1a with 5*: Similar treatment of **1a** with **5** yielded **11** in 90%. **11**: mp 162–164 °C; IR (KBr) 1700 and 1640 cm⁻¹; ¹H-NMR (CDCl₃) δ=2.20 (3H, s, MeC=C), 2.23 (3H, s, MeS), 5.92 (1H, s, HC=SMe), 6.06 (1H, s, HC=C), and 6.8–7.3 (10H, m, 2Ph); ¹³C-NMR (CDCl₃) δ=14.1 (q, MeS), 20.2 (q), 88.0 (d), 100.2 (d), 103.4 (s), 125.2 (s), 127.1 (d), 127.2 (d), 127.5 (d), 127.8 (d), 128.2 (d), 129.2 (d), 129.4 (d), 132.0 (s), 136.1 (s), 136.7 (s), 163.0 (s), and 163.8 (s); MS (*m/z*) 315 (M⁺–SMe). Found: C, 72.99; H, 5.25%. Calcd for C₂₂H₁₈O₃S: C, 72.91; H, 5.04%. (g) *The Reaction of 1a with 6*: Similar treatment of **1a** with **6** yield **12** in 84% yield. **12**: mp 204 °C; IR (KBr) 1720 and 1610 cm⁻¹; ¹H-NMR (CDCl₃) δ=2.27 (3H, s, MeS), 6.29 (1H, s, CH), and 6.7–8.1 (14H, m, Arom); ¹³C-NMR (CDCl₃) δ=13.8 (q, MeS), 88.4 (d, MeSC₂H), 105.6 (s), 115.6 (s), 116.6 (d), 122.6 (d), 124.0 (d), 126.8 (s), 127.2 (d), 127.5 (d), 127.6 (d), 127.9 (d), 129.2 (d), 129.4 (d), 132.3 (s), 132.4 (d), 136.2 (s), 136.5 (s), 153.5 (s), 157.8 (s), and 158.2 (s); MS (*m/z*) 351 (M⁺–SMe). Found: C, 75.63; H, 4.72%. Calcd for C₂₅H₁₈O₃S: C, 75.63; H, 4.55%. (h) *The Reaction of 1a with 7*: Similarly **13** was obtained in 63% yield. **13**: mp 138–140 °C; IR (KBr) 1660 cm⁻¹; ¹H-NMR (CDCl₃) δ=1.5–2.1 (4H, m, COCH₂CH₂CH₂CH₂), 2.24 (3H, s, MeS), 2.3–2.9 (4H, m, COCH₂CH₂CH₂CH₂), 6.00 (1H, s, CH), and 6.7–7.4 (10H, m, 2Ph); ¹³C-NMR (CDCl₃) δ=13.8 (q), 21.7 (t), 22.9 (t), 32.3 (t), 42.9 (t), 87.8 (d), 121.2 (s), 122.9 (s), 126.6 (d), 126.9 (d), 127.5 (d), 127.7 (d), 129.1 (d), 134.3 (s), 137.0 (s), 138.1 (s), 163.5 (s), and 199.9 (s); MS (*m/z*) 315 (M⁺–SMe). Found: C, 76.34; H, 6.19%. Calcd for C₂₃H₂₂O₂S: C, 76.21; H, 6.12%.

Desulfurization of **8**–**13** with Mercury(II) Chloride.

(a) *The Reaction of 8a in Methanol*: A mixture of **8a** (0.5 mmol) mercury(II) chloride (0.55 mmol), methanol (5 cm³), and dichloromethane (10 cm³) was stirred for 2 h to give a clear solution. The solution was quenched in water and extracted with chloroform. The chloroform extract was evaporated *in vacuo* to give colorless crystals (98%), and recrystallization from chloroform–hexane yielded 7,7-dimethyl-3,4-diphenyl-2-methoxy-5,6,7,8-tetrahydro-2H-1-benzopyran-5-one (**14a**) in 93% yield. **14a**: mp 175–177 °C; IR (KBr) 1670 and 1630 cm⁻¹; ¹H-NMR (CDCl₃) δ=1.11 (3H, s, Me), 1.20 (3H, s, Me), 2.26 (2H, s, CH₂), 2.58 (2H, s, CH₂), 3.59 (3H, s, MeO), 5.56 (1H, s, CH), and 6.8–7.7 (10H, m, 2Ph); ¹³C-NMR (CDCl₃) δ=27.3 (q), 29.3 (q), 31.7 (s), 42.6 (t), 51.8 (t), 55.3 (q), 101.4 (d), 113.9 (s), 123.5 (s), 126.5 (d), 126.7 (d), 127.7 (d), 129.2 (d), 129.3 (d), 132.0 (s), 137.1 (s), 138.0 (s), 167.2 (s), and 193.6 (s); MS (*m/z*) 360 (M⁺). Found: C, 79.88; H, 6.54%. Calcd for C₂₄H₂₄O₃: C, 79.97; H, 6.71%. (b) *The Reaction of 8a in Ethanol*: Similar treatment of **8a** in ethanol afforded 7,7-dimethyl-3,4-diphenyl-2-ethoxy-5,6,7,8-tetrahydro-2H-1-benzopyran-5-one (**14b**) in 78% yield. **14b**: mp

116–118 °C; IR (KBr) 1660 and 1620 cm⁻¹; ¹H-NMR (CDCl₃) δ=1.13 (3H, s, Me), 1.22 (3H, s, Me), 1.32 (3H, t, *J*=7 Hz, CH₃CH₂), 2.25 (2H, s, CH₂), 2.53 (2H, s, CH₂), 3.88 (2H, dd, *J*=6 and 7 Hz, CH₂O), 5.63 (1H, s, CH), and 6.5–7.5 (10H, m, 2Ph); MS (*m/z*) 374 (M⁺). Found: C, 80.11; H, 7.06%. Calcd for C₂₅H₂₆O₃: C, 80.18; H, 7.00%. Similar treatment of **8b** in ethanol yielded **14b** in 82% yield. (c) *The Reaction of 8a in 2-Propanol*: Similarly **14c** was obtained in 80% yield. **14c**: mp 163–164 °C; IR(KBr) 1660 cm⁻¹; ¹H-NMR (CDCl₃) δ=1.07 and 1.16 (6H, s, CMe₂), 1.25 (6H, d, *J*=7 Hz, CHMe₂), 2.21 and 2.49 (4H, s, CH₂CMe₂CH₂), 4.21 (1H, sept, CHMe₂), 5.65 (1H, s, OCHO), and 6.7–7.4 (10H, m, 2Ph); MS (*m/z*) 345 (M⁺–CHMe₂) and 329 (M⁺–OCHMe₂). Found: C, 80.20; H, 7.36%. Calcd for C₂₆H₂₈O₃: C, 80.38; H, 7.26%. (d) *The Reaction of 9 in methanol* yielded 3,4-diphenyl-2-methoxy-6,7-dihydrocyclopenta[b]pyran-5(2H)-one (**15a**) in 87% yield. **15a**: mp 130–133 °C; IR (KBr) 1690 and 1630 cm⁻¹; ¹H-NMR (CDCl₃) δ=2.3–3.0 (4H, m, CH₂CH₂), 3.63 (3H, s, MeO), 5.83 (1H, s, CH), and 6.5–7.6 (10H, m, 2Ph); MS (*m/z*) 318 (M⁺). Found: C, 79.11; H, 5.82%. Calcd for C₂₁H₁₈O₃: C, 79.23; H, 5.70%. (e) *The reaction of 9 in ethanol* yielded **15b** in 81% yield. **15b**: mp 157–158 °C; IR (KBr) 1680 and 1620 cm⁻¹; ¹H-NMR (CDCl₃) δ=1.26 (3H, t, *J*=7 Hz, CH₃CH₂), 2.3–2.9 (4H, m, COCH₂CH₂), 3.5–4.2 (2H, m, CH₂O), 5.84 (1H, s, CH), and 6.7–7.3 (10H, m, 2Ph); MS (*m/z*) 332 (M⁺). Found: C, 79.30; H, 6.09%. Calcd for C₂₂H₂₀O₃: C, 79.49; H, 6.06%. (f) *The reaction of 10 in methanol* yielded 3,4-diphenyl-2-methoxy-5,6,7,8-tetrahydro-2H-1-benzopyran-5-one (**16**) in 79% yield. **16**: mp 175–177 °C; IR(KBr) 1660 and 1620 cm⁻¹; ¹H-NMR (CDCl₃) δ=1.7–2.8 (6H, m, –(CH₂)₃–), 3.53 (3H, s, MeO), 5.49 (1H, s, CH), and 6.5–7.5 (10H, m, 2Ph); MS (*m/z*) 318 (M⁺); Found: C, 76.62; H, 6.06%. Calcd for C₂₂H₂₀O₃: C, 79.50; H, 6.06%. (g) *The reaction of 11 in ethanol* yielded **17** in 65% yield. **17**: mp 202–205 °C; IR (KBr) 1710, 1640, and 1620 cm⁻¹; ¹H-NMR (CDCl₃) δ=1.29 (3H, t, *J*=7 Hz, CH₃CH₂), 2.22 (3H, s, MeC=C), 3.5–4.2 (2H, m, CH₂O), 5.68 (1H, s, CH), 5.99 (1H, s, CH), and 6.8–7.4 (10H, m, 2Ph); ¹³C-NMR (CDCl₃) δ=15.3 (q), 20.2 (q), 64.6 (t), 100.0 (d), 100.2 (d), 101.5 (s), 125.5 (s), 127.0 (d), 127.5 (d), 127.8 (d), 129.3 (d), 129.6 (d), 131.5 (s), 136.5 (s), 137.1 (s), 160.1 (s), 162.2 (s), and 163.1 (s); MS (*m/z*) 360 (M⁺). Found: C, 76.38; H, 5.49%. Calcd for C₂₃H₂₀O₄: C, 76.65; H, 5.59%. (h) *The reaction of 12 in ethanol* yielded **18** in 89% yield. **18**: mp 172–174 °C; IR (KBr) 1720, 1630, and 1610 cm⁻¹; ¹H-NMR (CDCl₃) δ=1.26 (3H, t, *J*=7 Hz, CH₃CH₂), 3.5–4.3 (2H, m, CH₂), 5.89 (1H, s, CH), and 6.8–8.2 (10H, m, Arom); ¹³C-NMR (CDCl₃) δ=15.4 (q), 64.6 (t), 100.4 (d), 104.4 (s), 115.5 (s), 116.6 (d), 122.6 (d), 124.0 (d), 126.9 (s), 127.1 (d), 127.2 (d), 127.6 (d), 127.9 (d), 129.2 (d), 129.5 (d), 131.6 (s), 132.2 (d), 136.6 (s), 136.9 (s), 153.4 (s), 157.0 (s), and 158.6 (s); MS (*m/z*) 395 (M⁺–1). Found: C, 78.96; H, 4.92. Calcd for C₂₆H₂₀O₄: C, 78.77; H, 5.08%. (i) *The reaction of 13 in ethanol* yielded **19** in 61% yield. **19**: mp 120–122 °C; IR (KBr) 1650 and 1630 cm⁻¹; ¹H-NMR (CDCl₃) δ=1.25 (3H, t, *J*=7 Hz, CH₃), 1.6–2.2 (4H, m, COCH₂(CH₂)₂), 2.3–2.9 (4H, m, COCH₂(CH₂)₂CH₂), 3.5–4.1 (2H, m, CH₃CH₂), 5.56 (1H, s, CH), and 6.7–7.3 (10H, m, 2Ph); ¹³C-NMR (CDCl₃) δ=15.4 (q), 21.6 (t), 22.9 (t), 31.8 (t), 42.7 (t), 63.6 (t), 99.8 (d), 118.6 (s), 123.0 (s), 126.4 (d), 126.5 (d), 127.4 (d), 127.5 (d), 129.1 (d), 133.4 (s), 137.4 (s), 138.2 (s), 161.8 (s), and 200.8 (s); MS (*m/z*) 315 (M⁺–EtO). Found: C, 80.22; H, 6.66%. Calcd for C₂₄H₂₄O₃: C, 79.97; H, 6.71%.

The Reaction of 8a in Acetic Acid.

A mixture of **8a** (0.5 mmol) and mercury(II) acetate (0.55 mmol) in acetic acid (5 cm³) was stirred at room temperature for 2 h to give a clear solution. The solution was poured into water and extracted with chloroform. The extract was treated with aqueous sodium hydroxide (5%, 20 cm³) and aqueous layer was sep-

arated. Acidification of the aqueous extract with phosphoric acid, extraction with chloroform, and condensation of the chloroform extract under reduced pressure yielded a resinous mass (86%). Crystallization from benzene and petroleum ether yielded scales, 7,7-dimethyl-3,4-diphenyl-2-hydroxy-5,6,7,8-tetrahydro-2H-1-benzopyran-5-one (**20**) in 57%. **20**: mp 105–107 °C; IR (KBr) 3300 (OH), 1640, and 1620 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =1.09 (3H, s, Me), 1.11 (3H, s, Me), 2.23 (2H, s, CH_2), 2.26 (2H, s, CH_2), 5.76 (1H, s, CH), and 6.6–7.6 (10H, m, 2Ph); $^{13}\text{C-NMR}$ (CDCl_3) δ =26.9 (q), 29.7 (q), 31.4 (s), 42.9 (t), 51.3 (t), 95.0 (d), 113.6 (s), 125.5 (s), 126.7 (d), 126.9 (d), 127.5 (d), 127.7 (d), 128.3 (d), 129.3 (d), 130.5 (s), 136.7 (s), 137.6 (s), 168.2 (s), and 194.8 (s); MS (m/z) 328 (M^+ –18). Found: C, 79.94; H, 6.74%. Calcd for $\text{C}_{23}\text{H}_{22}\text{O}_3$: C, 79.74; H, 6.40%.

The $^1\text{H-NMR}$ spectrum of **20** in $\text{CDCl}_3\text{-Et}_3\text{N}$ (100:3, v/v) showed δ =1.05 (6H, br, s, Me_2), 2.25 (4H, br, s, CH_2CH_2), 6.8–7.5 (10H, m, 2Ph), 9.22 (1H, s, exchangeable with D_2O) and 9.80 (1H, s, CH) indicating the structure to be the unsaturated aldehyde **22**. The reaction of **22** with *p*-toluenesulfonylhydrazide was carried out as follows. A solution of **20** (0.5 mmol), *p*-toluenesulfonylhydrazide (1 mmol), triethylamine (3 mmol) in ethanol (3 cm^3) was allowed at room temperature for 2 d. The precipitated needles were collected and recrystallized from ethanol to give the hydrazone **23** in 38%. **23**: mp 125–127 °C; IR (KBr) 3400 and 1710 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =0.91 (6H, s, Me_2), 2.30 (3H, s, $\text{CH}_3\text{C}_6\text{H}_4$), 2.41 (2H, s, CH_2), 3.21 (2H, s, CH_2), 6.6–7.8 (15H, m, 2Ph, C_6H_4 , and NH), and 8.59 (1H, s, CH=N); MS (m/z) 497 (M^+ –OH). Found: C, 69.78; H, 5.87; N, 5.42%. Calcd for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_4\text{S}$: C, 70.02; H, 5.88; N, 5.44%.

Oxidation of 20 with Sodium Dichromate. (a): A mixture of **20** in acetic acid (1 mmol in 5 cm^3) and sodium dichromate in water (1 mmol in 2 cm^3) was stirred for 10 min. The resulting solution was diluted with water and extracted with chloroform. The chloroform extract was condensed and chromatographed over silica gel (chloroform, petroleum ether, and ethyl acetate in 4:4:1, v/v). 2-(Benzoylphenylmethylene)-5,5-dimethyl-1,3-cyclohexanedione (**24**) was obtained in 45% yield. **24**: mp 156–157 °C; IR (KBr) 1710 and 1670 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =1.12 (6H, s, Me_2), 2.57 (2H, s, CH_2), 2.63 (2H, s, CH_2), and 7.0–7.9 (10H, m, 2Ph); $^{13}\text{C-NMR}$ (CDCl_3) δ =28.5 (q), 29.9 (s), 53.1 (t), 54.5 (t), 128.2 (d), 128.3 (d), 128.7 (d), 129.0 (d), 129.8 (d), 133.2 (d), 133.3 (s), 133.6 (s), 134.8 (s), 161.9 (s), 194.7 (s), 196.6 (s), and 197.6 (s); MS (m/z) 332 (M^+). Found: C, 79.28; H, 6.07. Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_3$: C, 79.50; H, 6.06. (b): Further oxidation of **24** was carried out as follows. A mixture of **24** (1 mmol) and sodium dichromate (2 mmol) in acetic acid (20 cm^3) was stirred at room temperature for 5 h. The resulting solution was treated as above to yield 2-[α -(benzoyloxy)benzylidene]-5,5-dimethyl-1,3-cyclohexanedione (**25**) in 24% yield. **25**: mp 146–148 °C; IR (KBr) 1730, 1680, and 1660 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =1.25 (6H, s, Me_2), 2.46 (2H, s, CH_2), 2.78 (2H, s, CH_2), and 6.9–8.1 (10H, m, 2Ph); $^{13}\text{C-NMR}$ (CDCl_3) δ =28.2 (q), 33.1 (s), 42.2 (t), 51.0 (t), 127.7 (s), 128.3 (s), 128.5 (d), 128.9 (d), 130.0 (d), 133.6 (d), 134.1 (d), 136.6 (s), 162.8 (s), 166.3 (s), 192.1 (s), and 196.4 (s); MS (m/z) 348 (M^+). Found: C, 75.82; H, 5.66%. Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_4$: C, 75.84; H, 5.79%.

Hydrolysis of 25. In a mixture of concd HCl (1 cm^3) and 20% aqueous ethanol (20 cm^3), some **25** (0.3 mmol) was kept for 2 d. The resulting solution was quenched in water and extracted with chloroform. The chloroform extract was condensed under reduced pressure and then dissolved in 30 cm^3 of ether. The solution was shaken with an aqueous saturated solution of copper(II) acetate (0.3 mmol) and the resulting precipitate was separated. The precipitate was treated with 3 M hydrochloric acid (1 M=1 mol dm^{-3})

to give colorless crystals. The crystals were collected and recrystallized from petroleum ether to yield the known 2-benzoyl-5,5-dimethyl-1,3-cyclohexanedione **26** in 36% yield. **26**: mp 120–121 °C (lit.⁴ mp 120–122 °C); $^1\text{H-NMR}$ (CDCl_3) δ =1.08 (6H, s, Me_2), 2.24 (2H, s, CH_2), 2.49 (2H, s, CH_2), and 7.1–7.5 (5H, br s, Ph); MS (m/z) 244 (M^+).

The Reaction of 1a or 1b with 1,3-Indandione 27. The reaction was carried out as was described in the reaction of **1a** with **2**. The salt **1a** gave **28a** in 41% yield. **28a**: mp 190–191 °C; IR (KBr) 1690 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =2.18 (3H, s, MeS), 6.60 and 6.71 (1H, s, 1:2, C=CH), and 6.8–8.1 (14H, m, Arom); MS (m/z) 381 (M^+ –1). Found: C, 78.22; H, 4.66%. Calcd for $\text{C}_{25}\text{H}_{18}\text{O}_2\text{S}$: C, 78.50; H, 4.74%. The salt **1b** yielded **28b** in 37% yield. **28b**: mp 134–136 °C; IR (KBr) 1650 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =1.11 (3H, t, J =7 Hz, CH_3), 2.54 (2H, q, CH_2), 6.49 and 6.58 (1H, s, 1:2, C=CH), and 6.8–8.0 (14H, m, Arom); MS (m/z) 396 (M^+). Found: C, 78.43; H, 4.96%. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_2\text{S}$: C, 78.76; H, 5.08%.

The Reaction of 28a with Mercury(II) Acetate in Acetic Acid.

The compound **28a** was treated in a way similar to that described in the reaction of **8a** with mercury(II) acetate in acetic acid; **30** was obtained in 50% yield. **30**: resinous; IR (KBr) 3400, 1700, and 1680 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =4.44 (1H, s, exchangeable with D_2O , OH), 6.4–8.3 (14H, m, Arom), and 9.59 (1H, s, CHO); MS (m/z) 352 (M^+). Found: C, 81.66; H, 4.67%. Calcd for $\text{C}_{24}\text{H}_{16}\text{O}_3$: C, 81.80; H, 4.57%.

The reaction of **30** with *p*-toluenesulfonylhydrazide in ethanol at room temperature for 2 d yielded the corresponding diazepine **32** in 44% yield. **32**: mp 280–281 °C; IR (KBr) 1730 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =2.30 (3H, s, CH_3), 6.5–9.1 (18H, m, Arom), and 8.38 (1H, s, N=CH); MS (m/z) 502 (M^+). Found: C, 74.06; H, 4.50; N, 5.70%. Calcd for **31**, $\text{C}_{31}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$: C, 71.52; H, 4.65; N, 5.38% and for **32**, $\text{C}_{31}\text{H}_{22}\text{N}_2\text{O}_5\text{S}$: C, 74.08; H, 4.41; N, 5.57%.

The Reaction of 28a with Alcohol in the Presence of Mercury(II) Chloride.

The compound **28a** was treated as described in the reaction of **8a**. The reaction of **28a** in ethanol yielded **33a** in 84%. **33a**: mp 133–134 °C; IR (KBr) 1690 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =1.23 (3H, t, J =7 Hz, CH_3), 3.82 (2H, q, CH_2), 5.93 (1H, s, CH), and 6.6–7.7 (14H, m, Arom); MS (m/z) 380 (M^+). Found: C, 82.01; H, 5.27%. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_3$: C, 82.08; H, 5.29%.

The reaction of **28a** in 2-propanol gave **33b** in 63% yield. **33b**: mp 135–136 °C; IR (KBr) 1700 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ =1.26 (6H, d, J =7 Hz, Me_2), 4.24 (1H, sept, OCHMe_2), 6.13 (1H, s, CH), and 6.9–7.4 (14H, m, Arom); $^{13}\text{C-NMR}$ (CDCl_3) δ =23.2 (q), 73.2 (d, CHMe_2), 106.1 (d, CH), 118.3 (d), 121.7 (d), 122.4 (s), 126.9 (d), 127.4 (s and d), 127.6 (s), 127.8 (d), 129.5 (d), 130.2 (d), 130.3 (d), 131.0 (d), 132.6 (d), 134.5 (s), 135.0 (s), 137.0 (s), 188.8 (s); MS (m/z) 394 (M^+). Found: C, 82.34; H, 5.55%. Calcd for $\text{C}_{27}\text{H}_{22}\text{O}_3$: C, 82.21; H, 5.62%.

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- 4) W. Kirokor and J. Baranowicz, *Lodz. Towarz. Nauk. Wydział III, Acta Chim.*, **8**, 69 (1962); *Chem. Abstr.*, **59**, 7415d (1963).
- 5) The assignment of the structure **32** was tentative. Attempted conversion of **23** to the corresponding 1H-1,2-diazepine was unsuccessful, even on refluxing in toluene or on treating with trifluoroacetic acid in benzene, presumably because of steric repulsion between toluenesulfonyl and two methyl groups.