diluted with water and extracted with ether. The ethereal phase was washed with water, 5% $Na_2S_2O_3$ (aqueous), 5% $KHCO_3$ (aqueous), and water and dried with Na_2SO_4, and the solvent was evaporated in vacuo. The residue was dissolved in a petroleum ether–benzene mixture (2:1) and filtered through a pad of aluminum oxide. The filtrate was evaporated, and the product was crystallized from aqueous methanol to give 6β,19-epoxycholest-4-en-3β-yl acetate (24 mg): mp 57–59 °C; $[\alpha]_D$ −90° (c 1.5); ^1H NMR 0.72 (s, 3 H, 18-H), 2.02 (s, 3 H, CH_3CO_2), 3.37 and 4.12 (AB system, J = 8 Hz, 2 H, 19-H), 4.48 (d, J = 4 Hz, 1 H, 6α-H), 5.23 (m, $W/2$ = 8 Hz, 1 H, 3α-H), 5.57 (s, 1 H, 4-H).

Anal. Calcd for $C_{29}H_{46}O_3$: C, 78.67; H, 10.49. Found: C, 78.90; H, 10.66.

Acknowledgment. We thank Dr. S. Vašíčková for measurement of IR spectra, Drs. J. Zajíček, M. Buděšínský, Mrs. J. Jelínková, and Mrs. M. Snopková for measurement of NMR spectra, and Drs. V. Hanuš and M. Smrčina for mass spectra.

Reformatsky Reaction on α-Oxo Ketene Dithioacetals: Synthesis of Substituted and Fused Ethyl 2-Hydroxy-6-(methylthio)benzoates, 6-(Methylthio)pyran-2-ones, and 6-(Methylthio)-2(1*H*)-pyridone Derivatives

Apurba Datta, Hiriyakkanavar Ila,* and Hiriyakkanavar Junjappa*

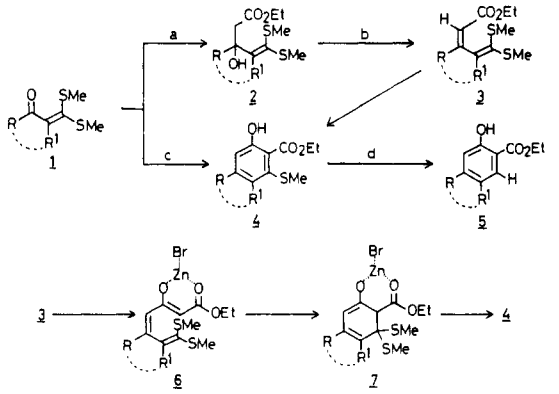
Department of Chemistry, North-Eastern Hill University, Shillong 793 003, Meghalaya, India

Received October 6, 1989

A novel cycloaromatization reaction leading to substituted and annelated ethyl 2-hydroxy-6-(methylthio)benzoates **4** by condensation of α-oxo ketene dithioacetals with an excess of Reformatsky reagent from ethyl bromoacetate through intermediate dienes **3** has been described. The reaction has also been extended for the synthesis of substituted ethyl 3-hydroxy-5-(methylthio)stilbenecarboxylates **9** by using cinnamoyl ketene dithioacetals **8**. A few of the benzoates **4** were desulfurized to the corresponding salicylate derivatives **5**. Reaction of acyclic oxo ketene dithioacetals with ethyl(bromozincio)acetate in the presence of cuprous iodide afforded 4- (or 4,5-) substituted 6-(methylthio)pyran-2-ones **15** in moderate to good yields. A probable mechanism for the formation of **15** is suggested. Cyclization of the acyclic dienes **3** or the carbinols **10** with ammonium acetate in refluxing acetic acid afforded the corresponding 4- (or 4,5-) substituted 6-(methylthio)-2(1*H*)-pyridones **22**.

The α-oxo ketene dithioacetals **1** have been extensively investigated as three-carbon units, which have been shown to undergo regio-, stereo-, and chemoselective C–C bond forming reactions.[1] As a part of our programmed studies, we have shown that these intermediates undergo exclusive 1,2-addition with methylmagnesium iodide while the higher alkyl and aryl Grignard reagents add sequentially in 1,4 and 1,2 fashion.[2] However, the allylmagnesium halide adds in an exclusive 1,2 fashion to yield the corresponding carbinol acetals, which undergo cycloaromatization in the presence of boron trifluoride etherate to afford the benzoannelated products in good yields.[3] Similarly, propargyl,[4] acetonitrile,[5] 2-picolyl,[6] and 5-methylisoxazolyl[7] anions were shown to undergo 1,2-addition followed by cycloaromatization in the presence of Lewis acids to afford a variety of aromatic and heteroaromatic compounds. However, the reaction of benzylmagnesium chloride with **1** was found to undergo sequential 1,4 and 1,2 addition to afford the corresponding carbinol acetals, which underwent similar Lewis acid assisted cycloaromatization involving aromatic ring π-participation to yield the corresponding naphthoannelated products.[8] These results have since been reviewed.[9] The lithioacetate and ethyl (bromozincio)acetate have also been reacted with **1** in a 1,2 manner to afford the hydroxy esters

Scheme I[a]



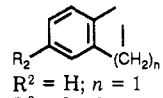
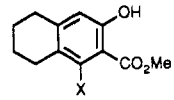
[a] (a) $BrZnCH_2CO_2Et$ (1.5 equiv)/C_6H_6/Δ; (b) I_2/C_6H_6/Δ; (c) $BrZnCH_2CO_2Et$(4 equiv)/C_6H_6/Et_2O/Δ; (d) Raney Ni/EtOH/Δ.

in high yields, which have been further converted either to the corresponding pyran-2-ones[10] or to the dienes **3** (Scheme I) under iodide ion catalyzed dehydration.[11] In our preliminary communication these dienes were further shown to react with (bromozincio)acetate to yield the corresponding substituted and annelated ethyl 2-hydroxy-6-(methylthio)benzoates **4** in good yields[12] (Scheme I). This two-step reaction involving intermediates **6** and **7** could be achieved in one pot in equally high yields by reacting **1** with an excess of ethyl (bromozincio)acetate. We now report a full account of these studies, including the scope and limitations. The intermediate dienes **3** and the carbinols **10** have also been utilized for the synthesis

(1) For a review, see: Dieter, R. K. *Tetrahedron* **1986**, *42*, 3029.
(2) Singh, G.; Purkayastha, M. L.; Ila, H.; Junjappa, H. *J. Chem. Soc., Perkin Trans. I* **1985**, 1289.
(3) Singh, G.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1984**, *25*, 5095.
(4) Gupta, A. K.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1987**, *28*, 1459.
(5) Gupta, A. K.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1988**, *29*, 6633.
(6) Balu, M. P.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1987**, *28*, 3023.
(7) Balu, M. P.; Pooranchand, D.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1988**, *29*, 501.
(8) Balu, M. P.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1986**, *27*, 117.
(9) Junjappa, H.; Ila, H.; Asokan, C. V. *Tetrahedron Rep.* In press.
(10) (a) Dieter, R. K.; Fishpaugh, J. R. *J. Org. Chem.* **1983**, *48*, 4439. (b) Dieter, R. K.; Fishpaugh, J. R. *Tetrahedron Lett.* **1986**, *27*, 3823.
(11) Apparao, S.; Datta, A.; Ila, H.; Junjappa, H. *Synthesis* **1985**, 169.
(12) Datta, A.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1988**, *29*, 497.

0022-3263/90/1955-5589$02.50/0

Table I. Synthesis of 4-(or 4,5-)Substituted and Annelated 2-Hydroxy-6-(methylthio)benzoates 4 and Salicylates 5

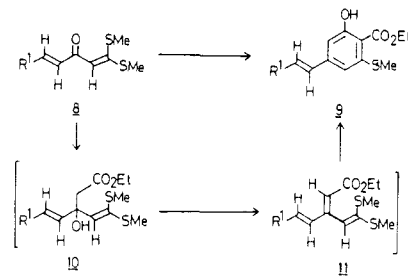
entry	startg matrl	product	R	R^1	% yield 4, 5	mp, °C
1	**1a**	**4a**, **5a**	$4\text{-ClC}_6\text{H}_4$	H	63, 88	108–109
2	**1b**	**4b**	C_6H_5	H	60	72–73
3	**1c**	**4c**	$4\text{-MeOC}_6\text{H}_4$	H	62	104–105
4	**1d**	**4d**	2-naphthyl	H	63	117–118
5	**1e**	**4e**	2-furyl	H	58	91–92
6	**1f**	**4f**	2-thienyl	H	63	91–92
7	**1g**	**4g**, **5g**	CH_3	H	60, 84	78–79
8	**1h**	**4h**	CH_3	CH_3	32	58
9	**1i**	**3i**	H	C_6H_5	66	48–49
10	**1i**		C_2H_5	CH_3		
11	**1k**		C_6H_5	CH_3		
12	**1l**	**4l**	$-(CH_2)_3-$		52	67–68
13	**1m**	**4m**	$-(CH_2)_4-$		57	137–138
14	**1n**	**4n**, **5n**	$-(CH_2)_5$		60, 72	128
15	**1o**	**4o**, **5o**	 R^2 = H; n = 1		55, 63	116–117
16	**1p**	**4p**, **5p**	R^2 = MeO; n = 2		58, 81	147–148
17	**1m**	$BrZnCH_2CO_2Me$	 **4q**, X = SMe		56	104–105
			5q, X = H		79	39–40 (lit.[13] 41)

of novel substituted pyridones **22**, while the acyclic α-oxo ketene dithioacetals have been shown to follow a different path when reacted with (bromozincio)acetate in the presence of cuprous iodide to afford 4-(or 4,5-)substituted 6-(methylthio)pyran-2-ones **15**.

Results and Discussion

Synthesis of Substituted and Annelated Ethyl 2-Hydroxy-6-(methylthio)benzoates 4. The diene **3a** obtained from **1a** was reacted with ethyl (bromozincio)-acetate. The reaction mixture after workup afforded the corresponding ethyl 4-(4-chlorophenyl)-2-hydroxy-6-(methylthio)benzoate (**4a**) in 72% yield. However **4a** could directly be obtained in identical yield when **1a** was reacted with an excess of (bromozincio)acetate (4 equiv) in a one-pot reaction. The entries 1 to 8 (Table I) represent the conversion of acyclic oxo ketene dithioacetals to **4**. The oxo ketene dithioacetal **1h** in which the α-hydrogen was replaced by a methyl group (entry 8) yielded the corresponding **4h** only in 32% yield, while **1i** yielded the corresponding diene **3i** in 65% yield. The other two α-alkyl acetals **1j** and **1k** failed to give either of the products and were recovered unchanged under the described conditions. Steric crowding in these systems appears to be the main reason either for low yield or for total failure. Entries 12–16 represent the conversion of cyclic ketene dithioacetals **1l–p** to the corresponding 4,5-annelated 2-hydroxybenzoates **4l–p** in good yields (Table I). The regiochemistry was confirmed by subjecting some of the (methylthio)benzoates (**4a,g,n–p**) to Raney nickel desulfurization, leading to the corresponding salicylates **5** (Scheme I) (Table I). The ^1H NMR chemical shift values for methyl and aromatic protons in ethyl *m*-cresotate (**5g**) were found to be very similar to those of methyl *m*-cresotate.[13] Similarly, the known cyclic methyl salicylate (**5q**) (entry 17) was prepared by desulfurization of the corresponding **4q** obtained by reacting methyl (bromozincio)-acetate with **1m**, thus confirming the regiochemistry of the product. The cinnamoyl ketene dithioacetals **8a–j** were

Scheme II



entry	startng matrl	product	R^1	% yield	mp, °C
1	**8a**	**9a**	C_6H_5	66	104–105
2	**8b**	**9b**	$4\text{-ClC}_6\text{H}_4$	69	136–137
3	**8c**	**9c**	$4\text{-MeOC}_6\text{H}_4$	61	106–107
4	**8d**	**9d**	$4\text{-NO}_2\text{C}_6\text{H}_4$	60	192–193
5	**8e**	**9e**	$3\text{-MeOC}_6\text{H}_4$	67	97–98
6	**8f**	**9f**	$2\text{-ClC}_6\text{H}_4$	61	123–124
7	**8g**	**9g**	$3,4\text{-(MeO)}_2\text{C}_6\text{H}_3$	60	124–125
8	**8h**	**9h**	3,4-(methylenedioxy)C_6H_3	61	166–167
9	**8i**	**9i**	$3,4\text{-Cl}_2\text{C}_6\text{H}_3$	72	142–143
10	**8j**	**9j**	$2,6\text{-Cl}_2\text{C}_6\text{H}_3$	69	130–131
11	**8k**	**11k**	Me	58	oil
12	**8l**	**11l**	Et	61	oil
13	**8a**	**11a**	C_6H_5	70	oil
14	**8b**	**11b**	$4\text{-ClC}_6\text{H}_4$	74	oil

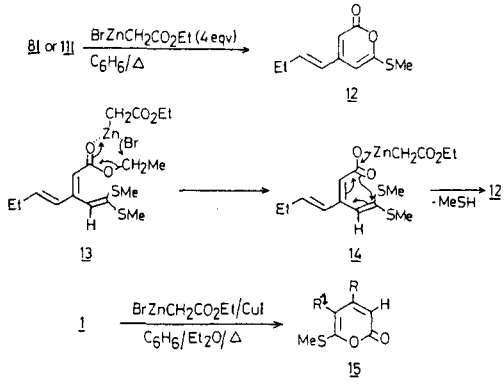
next examined. Thus **8a** when reacted with ethyl (bromozincio)acetate under similar reaction conditions, the expected ethyl 3-hydroxy-5-(methylthio)stilbene-4-carboxylate (**9a**) was obtained in 66% yield. The other substituted stilbenes (**9b–j**) were similarly obtained in 60–72% overall yields (Scheme II). The intermediacy of cross-conjugated trienes **11** (Scheme II) was established by isolation of **11a** and **11b** by curtailing the reaction time. Under similar reaction conditions, α-propenoyl (**8k**) and α-butenoyl (**8l**) ketene dithioacetals, however, yielded the corresponding trienes **11k** and **11l**, respectively (Scheme II). However **8l** or **11l** on prolonged heating (26 h) with ethyl (bromozincio)acetate yielded a product characterized as 4-(1-butenyl)-6-(methylthio)pyran-2(1*H*)-one (**12**) (Scheme III). A plausible mechanism for the conversion of **8l** to **12** involves electrocyclization of the triene **11l** followed by dealkylation and elimination of the MeSH group. However, **11l** on prolonged heating alone did not yield **12** and required (bromozincio)acetate for cyclization, though it did not participate in the reaction. Thus it appears that electrophilicity of the ester carbonyl group in **11k** and **11l** is considerably altered due to hyperconjugation of the δ-alkyl group, and (bromozincio)acetate may simply complex with the ester carbonyl group as depicted in **13**, which may undergo dealkylation followed by cyclization to afford **12** (Scheme III).

Reaction of 1 with Ethyl (Bromozincio)acetate in the Presence of Cuprous Iodide. It was considered of interest to examine the reactivity of ethyl (bromozincio)-acetate with **1** in the presence of cuprous iodide to explore the possibilities of 1,4-addition. When **1b** and (bromozincio)acetate (2 equiv) were reacted in the presence of cuprous iodide, the product isolated was characterized as 6-(methylthio)-4-phenyl-2(1*H*)-pyrone (**15a**) (62%) (Scheme III). However, its physical and spectral properties did not match with the known regioisomeric 4-(methylthio)-6-phenyl-2(1*H*)-pyrone.[14] Thus the structure of **15a** was established by subjecting it to Raney Ni desulfurization to afford the known 4-phenyltetrahydropyran-2-one

(13) Chan, T. H.; Brownbridge, P. *J. Am. Chem. Soc.* **1980**, *102*, 3534.

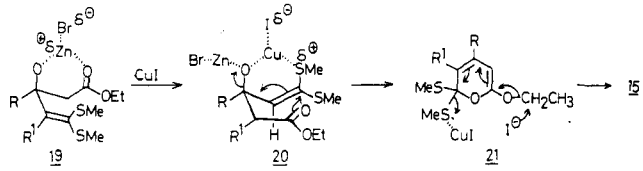
(14) Tominaga, Y.; Ushrogochi, A.; Matsuda, Y. *J. Heterocycl. Chem.* **1987**, *24*, 1557.

Scheme III

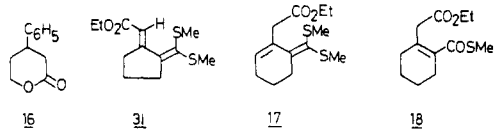


entry	1	15	R	R^1	% yield	mp, °C
1	**1b**	**15a**	C_6H_5	H	62	84–85
2	**1c**	**15b**	4-$MeOC_6H_4$	H	53	122–123
3	**1d**	**15c**	2-naphthyl	H	58	107–108
4	**1e**	**15d**	2-furyl	H	58	116–117
5	**1f**	**15e**	2-thienyl	H	60	68–69
6	**1g**	**15f**	CH_3	H	60	68–69
7	**1h**	**15g**	CH_3	CH_3	48	54–55

Scheme IV



(16),[15] which was found to be identical. Under similar reaction conditions, the substituted pyrones **15b–g** were obtained in 48–60% overall yields from **1c–h**. The cyclic ketene dithioacetals **1l** and **1m**, however, gave inconsistent results under similar reaction conditions. Thus the dithioacetal **1l** yielded only the corresponding diene **3l** in 57% yield, while **1m** yielded a mixture of the corresponding diene **17** (38%) and the δ-keto thioester **18** (16%).

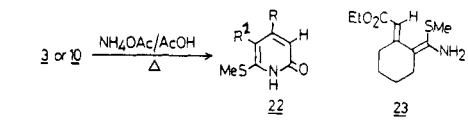


The mechanism altering the course of this reaction appears interesting (Scheme IV). The addition of cuprous iodide to the preformed carbinol **2** or the diene **3** did not yield the pyrone even after prolonged heating and the unreacted starting materials were recovered. However, when cuprous iodide was added 3 h after the addition of (bromozincio)acetate to **1a** and the reaction mixture was further refluxed for 13 h, the pyrone **15a** was obtained in 62% yield. Thus it appears that the softer Cu^+ ion replaces the zinc and preferentially coordinates with soft base sulfur so that the free acetate moiety is pushed to the rear side, facilitating the attack by ester carbonyl oxygen on the electrophilic bis(methylthio)carbon as shown in **20** (Scheme IV) to form **21**, which on iodide ion assisted dealkylation and elimination of MeSH group affords **15**.

Synthesis of 6-(Methylthio)-4,5-substituted-2-(1*H*)-pyridones 22. The reactivity of the dienes **3** with nitrogen nucleophiles was next examined. Thus the pyridones **22a–e** were obtained in 60–70% yields when the corresponding dienes **3** were heated with ammonium

(15) Irwin, A. J.; Jones, J. B. *J. Am. Chem. Soc.* **1977**, *99*, 556.

Scheme V



entry	startng matrls	product	R	R^1	% yield	mp, °C
1	**3e**	**22a**	2-furyl	H	65	192–193
2	**3g**	**22b**	Me	H	69	192–193
3	**3h**	**22c**	Me	Me	60	130–131
4	**3q**	**22d**	4-MeC_6H_4	H	70	178–179
5	**3r**	**22e**	4-BrC_6H_4	H	68	207–208
6	**10a**	**22f**	$C_6H_4CH{=}CH$	H	70	177–178
7	**10c**	**22g**	4-$MeOC_6H_5CH{=}CH$	H	70	189–190
8	**10m**	**23**	$-(CH_2)_4-$		45	53–54

acetate in glacial acetic acid (Scheme V). It was not necessary to isolate the dienes and the corresponding carbinol acetals (**10a,10c**) could also be reacted with ammonium acetate to afford pyridones (entries 6 and 7). However the cyclic dienes **3l–p** or the corresponding carbinols failed to yield the respective pyridones and the reaction mixture gave only the intractable tar. Only **10m** yielded the corresponding δ-amino ester **23** in 45% yield, which failed to cyclize under varying conditions.

Conclusion

The reaction of α-oxo ketene dithioacetals **1** with ethyl (bromozincio)acetate provides a novel route for regiospecifically substituted 2-hydroxy-6-(methylthio)benzoates **4**. The reaction is shown to proceed through the intermediate dienes **3**, though the entire sequence can be accomplished in a one-pot reaction by using an excess of ethyl bromozinc acetate. The reaction of **1** with ethyl (bromozincio)acetate follows a different course in the presence of cuprous iodide to yield the corresponding pyrones **15**. A possible mechanism to account this deviation is proposed. It may be pertinent to note that Dieter and co-workers have reported a new general method for substituted pyrones involving 1,2-addition of ester, ketone, or hydrazone enolate to **1** followed by acid-promoted rearrangement to the corresponding thioesters or acids and their subsequent enol lactonization in the presence of a mixture of trifluoroacetic acid and its anhydride.[10] The present method provides a single-step procedure for the synthesis of pyrones **15** though limited in its application. The dienes **3** and the carbinols have also been reacted with ammonium acetate to afford the corresponding substituted 2(1*H*)-pyridones **22**.

Experimental Section

Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. IR spectra of solids were recorded in KBr pellets. ^{13}C NMR spectra were recorded at 67.89 MHz.

The known ketene dithioacetals **1a–p**, cinnamoyl ketene dithioacetals **8a–j**, and alkenoyl ketene dithioacetals **8k,l** were prepared according to the reported procedures.[16–18]

Synthesis of Ethyl 2-Hydroxy-4-(or 4,5-)substituted-6-(methylthio)benzoates 4. General Procedure. To a refluxing solution of the Reformatsky reagent [prepared from zinc (2.6 g, 0.04 g atom) and ethyl bromoacetate (3.4 g, 0.02 mol)] in 30 mL of dry ether was added a solution of the appropriate α-oxo ketene dithioacetal (0.005 mol) in dry benzene (30 mL) dropwise (30 min), and the reaction mixture was further refluxed for 38–46 h

(16) Potts, K. T.; Cipullo, M. J.; Ralli, P.; Theodoris, G. *J. Org. Chem.* **1982**, *47*, 3027 and references therein.
(17) Thuillier, A.; Vialle, J. *Bull. Soc. Chim. Fr.* **1962**, 2182.
(18) Asokan, C. V.; Balu, M. P.; Ila, H.; Junjappa, H. *Synthesis* **1988**, 727.

Table II. Spectral and Analytical Data for the Products 4, 5, and 9

compd	mol form.	IR ν_{max}, cm^{-1}	^1H NMR,[a] δ	m/z (rel int) M^+	Anal. Calcd/Found	
					C	H
4a	$C_{16}H_{15}ClO_3S$	3422, 1658	1.48 (t, 3 H, CH_3), 2.42 (s, 3 H, SCH_3) 4.47 (q, 2 H, OCH_2), 6.71 (br s, 1 H, *H*-5), 6.85 (br s, 1 H, *H*-3), 7.29–7.51 (m, 4 H, Ar*H*), 10.0 (br s, 1 H, O*H*)	323, 321 (19, 45)	59.53/59.26	4.65/4.38
4b	$C_{16}H_{16}O_3S$	3300, 1655	1.48 (t, 3 H, CH_3), 2.46 (s, 3 H, SCH_3), 4.50 (q, 2 H, OCH_2), 6.85 (br s, 1 H, *H*-5), 6.93 (br s, 1 H, *H*-3), 7.41–7.63 (m, 5 H, Ar*H*), 11.45 (br s, 1 H, O*H*)	288 (65)	66.67/66.88	5.56/5.80
4c	$C_{17}H_{18}O_4S$	3410, 1650	1.47 (t, 3 H, CH_3), 2.46 (s, 3 H, SCH_3), 3.85 (s, 3 H, OCH_3), 4.51 (q, 2 H, OCH_2), 6.82 (br s, 1 H, *H*-5), 6.90–7.61 (m, 4 H, H-3, Ar*H*), 11.49 (s, 1 H, O*H*)	318 (59)	64.15/64.37	5.66/5.92
4d	$C_{20}H_{18}O_3S$	3400, 1648	1.48 (t, 3 H, CH_3), 2.46 (s, 3 H, SCH_3), 4.48 (q, 2 H, OCH_2), 6.91 (br s, 1 H, *H*-5), 7.03 (br s, 1 H, *H*-3), 7.40–8.01 (m, 7 H, Ar*H*), 11.50 (s, 1 H, O*H*)	338 (54)	71.01/71.30	5.33/5.57
4e	$C_{14}H_{14}O_4S$	3420, 1656	1.47 (t, 3 H, CH_3), 2.49 (s, 3 H, SCH_3), 4.51 (q, 2 H, OCH_2), 6.42–6.53 (m, 1 H, furyl), 6.73 (d, 1 H, furyl), 7.0 (s, 2 H, *H*-3, *H*-5), 7.51 (br s, 1 H, furyl), 11.47 (s, 1 H, O*H*)	278 (34)	60.43/60.21	5.04/5.24
4f	$C_{14}H_{14}O_3S_2$	3430, 1645	1.50 (t, 3 H, CH_3), 2.48 (s, 3 H, SCH_3), 4.49 (q, 2 H, OCH_2)8 6.88 (br s, 1 H, *H*-5), 6.94 (br s, 1 H, *H*-3), 7.02–7.46 (m, 3 H, thienyl), (s, 1 H, O*H*)	294 (100)	57.14/57.33	4.76/5.00
4g	$C_{11}H_{14}O_3S$	3250, 1700	1.33 (t, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 2.42 (s, 3 H, SCH_3), 4.29 (q, 2 H, OCH_2), 6.30 (br s, 1 H, *H*-5), 6.40 (br s, 1 H, *H*-3), 10.59 (s, 1 H, O*H*)	226 (72)	58.41/58.73	6.19/5.98
4h	$C_{12}H_{16}O_3S$	3250, 1690	1.42 (t, 3 H, CH_3), 2.29 (s, 6 H, CH_3), 2.48 (s, 3 H, SCH_3), 4.45 (q, 2 H, OCH_2), 6.74 (s, 1 H, *H*-3), 12.72 (s, 1 H, O*H*)	240 (55)	60.0/59.78	6.67/6.49
4l	$C_{13}H_{16}O_3S$	3440, 1680	1.42 (t, 3 H, CH_3), 2.02 (t, 2 H, CH_2), 2.31 (s, 3 H, SCH_3), 2.92 (m, 4 H, CH_2), 4.43 (q, 2 H, OCH_2), 6.87 (s, 1 H, *H*-7), 10.02 (br s, 1 H, O*H*)	252 (50)	61.90/61.66	6.35/6.13
4m	$C_{14}H_{18}O_3S$	3304, 1695	1.48 (t, 3 H, CH_3), 1.62–1.93 (m, 4 H, CH_2), 2.32 (s, 3 H, SCH_3), 2.61–3.05 (m, 4 H, CH_2), 4.49 (q, 2 H, OCH_2) 6.73 (s, 1 H, *H*-8), 9.15 (br s, 1 H, OH)	226 (25)	63.16/63.42	6.77/6.98
4n	$C_{15}H_{20}O_3S$	3248, 1695	1.39 (t, 3 H, CH_3), 1.42–1.94 (m, 6 H, CH_2), 2.30 (s, 3 H, SCH_3), 2.68–2.88 (m, 2 H, CH_2), 3.10–3.32 (m, 2 H, CH_2), 4.41 (q, 2 H, OCH_2) 6.74 (s, 1 H, *H*-9)	280 (27)	64.28/64.55	7.14/7.37
4o	$C_{17}H_{16}O_3S$	3280, 1695	1.50 (t, 3 H, CH_3), 2.44 (s, 3 H, SCH_3), 3.92 (s, 2 H, CH_2), 4.49 (q, 2 H, OCH_2), 7.29–7.84 (m, 5 H, Ar*H*), 10.52 (br s, 1 H, O*H*)	300 (54)	68.00/68.25	5.33/5.17
4p	$C_{19}H_{20}O_4S$	3375, 1705	1.42 (t, 3 H, CH_3), 2.29 (s, 3 H, SCH_3), 2.68–2.89 (m, 2 H, CH_2), 3.02–3.27 (m, 2 H, CH_2), 3.84 (s, 3 H, OCH_3), 4.50 (q, 2 H, OCH_2), 6.73 (s, 1 H, *H*-8), 7.28–7.69 (m, 3 H, Ar*H*),, 9.47 (br s, 1 H, O*H*)	344 (71)	66.28/66.49	5.81/5.57
4q	$C_{13}H_{16}O_3S$	3250, 1700	1.57–1.85 (m, 4 H, CH_2), 2.29 (s, 3 H, SCH_3), 2.62–3.0 (m, 4 H, CH_2), 3.98 (s, 3 H, OCH_3), 6.67 (s, 1 H, *H*-8)	252 (42)	61.90/62.13	6.35/6.59
5a	$C_{15}H_{13}ClO_3$	3320, 1676	1.33 (t, 3 H, CH_3), 4.35 (q, 2 H, CH_2), 7.0–7.89 (m, 7 H, Ar*H*), 10.77 (s, 3 H, O*H*)	275 (7)	65.10/64.89	4.70/4.92
5g	$C_{10}H_{12}O_3$	3240, 1680	1.38 (t, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 4.32 (q, 2 H, OCH_2), 6.56 (br s, *J* = 8, 1 H, *H*-5), 6.68 (br s, 1 H, *H*-3), 7.60 (d, *J* = 8, 1 H, *H*-6), 10.60 (s, 1 H, O*H*)	180 (36)	66.67/66.81	6.67/6.42
5n	$C_{14}H_{18}O_3$	3420, 1685	1.25–1.38 (t, 3 H, CH_3), 1.50–1.89 (m, 6 H, CH_2), 2.51–2.84 (m, 4 H, CH_2), 4.33 (q, 2 H, -OCH_2), 6.62 (br s, 1 H, *H*-9), 7.43 (br s, 1 H, *H*-6), 10.45 (br s, 1 H, O*H*)	234 (31)	71.79/71.52	7.69/7.92
5o	$C_{16}H_{14}O_3$	3310, 1685	1.39 (t, 3 H, CH_3), 3.76 (s, 2 H, CH_2), 4.43 (q, 2 H, OCH_2) 6.77–7.62 (m, 6 H, Ar*H*), 10.81 (s, 1 H, O*H*)		75.59/75.86	5.51/5.79
5p	$C_{18}H_{18}O_4$	3380, 1710	1.41 (t, 3 H, CH_3), 2.82 (br s, 4 H, CH_2), 3.83 (s, 3 H, OCH_3), 4.41 (q, 2 H, OCH_2), 6.78–7.71 (m, 5 H, Ar*H*), 10.68 (br s, 1 H, O*H*)	298 (91)	72.48/72.71	6.04/6.33
5q	$C_{12}H_{14}O_3$	3230, 1696	1.56–1.78 (m, 4 H, ring CH_2), 3.80 (s, 3 H, OCH_3), 6.52 (br s, 1 H, *H*-8), 7.38 (br s, 1 H, *H*-5), 10.39 (br s, 1 H, O*H*)		69.90/70.13	6.79/7.02
9a	$C_{18}H_{18}O_3S$	3410, 1646, 1633	1.46 (t, 3 H, CH_3), 2.39 (s, 3 H, SCH_3), 4.41 (q, 2 H, OCH_2), 6.72 (s, 1 H, *H*-2), 6.84 (s, 1 H, *H*-6), 7.0–7.11 (two s, 2 H, =C*H*), 7.22–7.66 (m, 5 H, Ar*H*)	314 (100)	68.79/69.00	5.73/5.98
9b	$C_{18}H_{17}ClO_3S$	3420, 1648, 1605	1.48 (t, 3 H, CH_3), 2.36 (s, 3 H, SCH_3), 4.38 (q, 2 H, CH_2), 6.68 (s, 1 H, *H*-2), 6.82 (s, 1 H, *H*-6), 6.96 (s, 2 H, =C*H*), 7.34–7.74 (m, 4 H, Ar*H*) δ_C 14.26 (SCH_3), 16.50 (CH_3), 62.12 (OCH_2), 109.55 (*C*-4, ArCH), 110.67, 113.97 (*C*-2, *C*-6, ArCH), 128.0, 128.94 (C-2′, C-3′, C-5′, C-6′, ArCH and =CH), 130.78 (=CH), 134.05 (C-1′), 134.95 (*C*-4′), 142.23 (*C*-1), 144.47 (*C*-5), 163.56 (*C*-3), 170.19 (CO_2Et)[a]	348, 350 (100, 72)	61.98/62.26	4.88/4.63
9c	$C_{19}H_{20}O_4S$	3401, 1644, 1595	1.45 (t, 3 H, CH_3), 2.47 (s, 3 H, SCH_3), 3.85 (s, 3 H, OCH_3), 4.42 (q, 2 H, OCH_2), 6.73 (s, 1 H, *H*-2), 6.84 (s, 1 H, *H*-6), 6.73 (s, 1 H, *H*-2), 6.84 (s, 1 H, *H*-6), 6.90–7.58 (m, 6 H, Ar*H*, =C*H*) δ_C 14.26 (SCH_3), 16.50 (CH_3), 55.30 (OCH_3), 62.01 (OCH_2), 108.97 (*C*-4), 110.34, 113.79 (*C*-2, *C*-6, ArCH), 114.21 (*C*-3′, *C*-5′, ArCH), 125.12 (*C*-1′), 128.21 (*C*-2′, *C*-6′, ArCH), 129.27 131.78 (=CH), 143.05 (*C*-1), 144.23 (*C*-5), 159.92 (*C*-4′), 163.59 (*C*-3), 170.28 (CO_2Et)[a]	344 (100)	66.28/66.51	5.81/6.04
9d	$C_{18}H_{17}NO_5S$	3422, 1648	1.83 (t, 3 H, CH_3), 2.80 (s, 3 H, SCH_3), 4.78 (q, 2 H, OCH_2), 7.03 (br s, 1 H, *H*-2), 7.19 (br s, 2 H, *H*-6), 7.46 (s, 2 H, =C*H*), 7.43 (d, 2 H, Ar*H*), 8.14 (d, 2 H, Ar*H*), 11.83 (s, 1 H, O*H*)	359 (61)	60.17/60.44	4.74/5.02
9e	$C_{19}H_{20}O_4S$	3320, 1647, 1596	1.47 (t, 3 H, CH_3), 2.49 (s,3 H, SCH_3), 3.83 (s, 3 H, OCH_3), 4.46 (q, 2 H, OCH_2), 6.75 (br s, 1 H, *H*-2), 6.91 (br s, 1 H, *H*-6), 7.07–7.51 (m, 6 H, Ar*H*, =C*H*), 11.52 (s, 1 H, O*H*) δ_C 14.17 (SCH_3), 16.42 (CH_3), 55.19 (OCH_3), 62.00 (OCH_2), 109.34 (*C*-4), 110.65, 112.06 (C-2, C-6, ArCH), 113.96, 114.10 (C-2′, C-5′, ArCH), 119.56 (C-6′, ArCH), 127.56 (*C*-5′), 129.64, 132.01 (=CH), 137.89, 142.49 (C-1′, ArCh), 144.35 (*C*-5), 159.90 (*C*-3′), 163.54 (*C*-3), 177.22 (CO_2Et)[a]	344 (100)	66.28/66.51	5.81/6.04

Table II (Continued)

compd	mol form.	IR ν_{max}, cm^{-1}	^1H NMR,[a] δ	m/z (rel int) M^+	Anal. Calcd/Found C	Anal. Calcd/Found H
9f	$C_{18}H_{17}ClO_3S$	3422, 1650, 1600	1.49 (t, 3 H, CH_3), 2.46 (s, 3 H, SCH_3), 4.48 (q, 2 H, CH_2), 6.80 (br s, 1 H, *H*-2), 6.97 (br s, 1 H, *H*-6), 7.12–7.48 (m, 6 H, Ar*H*, =C*H*), 11.51 (s, 1 H, *H*-2), 6.97 (br s, 1 H, *H*-6), 7.12–7.48 (m, 6 H, Ar*H*, =C*H*), 11.51 (s, 1 H, O*H*)	348, 350 (65.52)	61.98/61.77	4.88/4.61
9g	$C_{20}H_{22}O_5S$	3422, 1647, 1592	1.50 (t, 3 H, CH_3), 2.49 (s, 3 H, SCH_3), 3.88 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.48 (q, 2 H, CH_2), 6.71–7.18 (m, 7 H, Ar*H*, =C*H*), 11.62 (s, 1 H, O*H*)	374 (100)	64.17/64.40	5.88/6.12
9h	$C_{19}H_{18}O_5S$	3422, 1643, 1594	1.44 (t, 3 H, CH_3), 2.43 (s, 3 H, SCH_3), 4.43 (q, 2 H, CH_2, 5.98 (s, 2 H, OCH_2O), 6.65–7.10 (m, 7 H, Ar*H*, =C*H*), 11.49 (br s, 1 H, O*H*)	354 (100)	63.69/63.95	5.03/4.80
9i	$C_{18}H_{16}Cl_2O_3S$	3420, 1650, 1605	1.40 (t, 3 H, CH_3), 2.82 (s, 3 H, SCH_3), 4.35 (q, 2 H, CH_2), 6.49 (br s, 1 H, *H*-2), 6.62 (br s, 1 H, *H*-6), 7.13–7.64 (m, 5 H, Ar*H*), 10.68 (s, 1 H, OH)	385, 383 (53, 73)	56.40/56.63	4.18/4.38
9j	$C_{18}H_{16}Cl_2O_3S$	3422, 1648, 1599	1.43 (t, 3 H, CH_3), 2.46 (s, 3 H, SCH_3), 4.44 (q, 2 H, CH_2), 6.72 (br s, 1 H, *H*-2), 6.87 (br s, 1 H, *H*-6), 7.07–7.45 (m, 5 H, Ar*H*, =C*H*), 11.51 (s, 1 H, O*H*) δ_C 14.21 (SCH_3), 16.44 (CH_3), 62.13 (OCH_2), 109.85 (*C*-4), 110.97, 114.12 (*C*-2, *C*-6, ArCH), 126.02 (C-4, ArCH), 128.55 (*C*-1), 128.61 (*C*-3′, *C*-5′), 133.79, 135.64 (=CH), 134.61 (*C*-2′, *C*-6′), 142.01 (*C*-1), 144.57 (*C*-5), 163.56 (*C*-3), 170.24 (CO_2Et)[a]	384, 382 (26, 38)	56.40/56.67	4.18/4.42

[a] In $CDCl_3$.

(monitored by TLC). It was then cooled and poured into 5% sulfuric acid (100 mL), and the organic layer separated and washed once with water, dried (Na_2SO_4), and concentrated to give the crude products, which were then purified by being passed through silica gel column. Elution with hexane/ethyl acetate (19:1) yielded the pure hydroxybenzoates **4** in overall good yields (Table II). The samples for elemental analysis were obtained by crystallization from chloroform.

The reaction of oxo ketene dithioacetal **1i** with ethyl (bromozincio)acetate under identical conditions afforded the corresponding **1,1-bis(methylthio)-2-phenyl-4-(ethoxycarbonyl)-1,3-butadiene (3i)**: light yellow solid ($CHCl_3$); mp 48–49 °C; IR (KBr) 1710, 1605 cm^{-1}; ^1H NMR (CCl_4) 1.20 (t, 3 H, CH_3), 2.11 (s, 6 H, SCH_3), 4.21 (q, 2 H, OCH_2), 5.45 (d, J = 15, *H*-4), 7.10–7.72 (m, 5 H_{arom}), 8.52 (d, J = 15 Hz, *H*-3). Anal. Found: C, 61.32; H, 6.38. Calcd for $C_{15}H_{18}O_2S_2$: C, 61.14; H, 6.11.

General Procedure for Raney Nickel Desulfurization of 4. Synthesis of 4-Substituted and 4,5-Annelated Ethyl Salicylates 5. Freshly prepared W-4 Raney nickel (10 g) was added to a solution of the appropriate (methylthio)hydroxybenzoate **4** (0.5 g) in ethanol (20 mL), and the reaction mixture was refluxed with stirring for 1 h. It was then filtered through Kieselgel and washed with hot chloroform (3 × 100 mL), and the solvent was evaporated from the combined filtrate to give the crude salicylates **5**, which were further purified by being passed through a silica gel column, using hexane as eluent (Table I).

Ethyl 3-Hydroxy-5-(methylthio)stilbene-4-carboxylate (9). The general procedure was followed. In the case of trienes **11a** and **11b**, the reaction was stopped after refluxing for 3 h and worked up in the similar manner as described for **4**. However the pure products were found to decompose on prolonged storage (72 h).

1,1-Bis(methylthio)-3-(carbethoxymethylene)-5-phenyl-1,4-pentadiene (11a): red viscous liquid; yield 70%; IR (neat) 1702, 1601, 1590 cm^{-1}; ^1H NMR (CCl_4) 1.26 (t, 3 H, CH_3), 2.21 (s, 3 H, SCH_3), 2.43 (s, 3 H, SCH_3), 4.10 (q, 2 H, OCH_2), 6.93 (br s, 1 H, *H*-2), 6.75 (s, 1 H, =*H*CCO), 6.88 (s, 2 H_{styryl}), 7.23–7.64 (m, 5 H_{arom}).

1,1-Bis(methylthio)-3-(carbethoxymethylene)-5-(4-chlorophenyl)-1,4-pentadiene (11b): red viscous liquid; yield 74%; IR (neat) 1704, 1597 cm^{-1}; ^1H NMR (CCl_4) 1.28 (t, 3 H, CH_3), 2.29 (s, 3 H, SCH_3), 2.33 (s, 3 H, SCH_3), 4.19 (q, 2 H, OCH_2), 5.76 (s, 1 H, *H*-2), 6.37 (s, 1 H, =C*H*CO), 6.65 (d, J = 15, 1 H, *H*-4), 7.20–7.44 (m, 4 H_{arom}), 8.32 (d, J = 15, 1 H, *H*-5).

Reaction of Alkenoyl Ketene Dithioacetals 8k,l with Reformatsky Reagent. The general procedure was followed. The pure trienes **11k,l** were obtained (refluxing time 12 h) by column chromatography of the reaction mixture over silica gel, using hexane as eluent.

1,1-Bis(methylthio)-3-(carbethoxymethylene)-1,4-hexadiene (11k): red viscous oil; yield 58%; IR (neat) 1700, 1638 cm^{-1}; ^1H NMR (CCl_4) 1.29 (t, 3 H, CH_3), 1.90 (d, J = 6, 3 H, CH_3), 2.24 (s, 3 H, SCH_3), 2.57 (s, 3 H, SCH_3), 4.18 (q, 2 H, OCH_2), 5.78–6.19 (m, 1 H, *H*-5), 6.25 (d, J = 15, 1 H, *H*-4), 6.48 (br s, 1 H, *H*-2), 6.68 (br s, 1 H, C*H*CO). Anal. Found: C, 56.06; H, 7.25. Calcd for $C_{12}H_{18}O_2S_2$: C, 55.81; H, 6.98. MS: m/z 258 (M^+, 6).

1,1-Bis(methylthio)-3-(carbethoxymethylene)-1,4-heptadiene (11l): red viscous oil; yield 61%; IR (neat) 1703, 1620 cm^{-1}; ^1H NMR (CCl_4) 1.06, 1.25 (two t, 6 H, CH_2CH_3 and OCH_2CH_3), 2.28 (s, 3 H, SCH_3), 2.31 (br quint, 2 H, CH_2CH_3), 2.40 (s, 3 H, SCH_3), 4.12 (q, 2 H, OCH_2), 5.58 (br s, 1 H, *H*-2), 6.11 (d, J = 16, 1 H, *H*-4), 5.71–6.06 (m, 1 H, *H*-5), 6.63 (br s, 1 H, =C*H*CO_2Et). Anal. Found: C, 57.63; H, 7.50. Calcd for $C_{13}H_{20}O_2S_2$: C, 57.35; H, 7.35. MS: m/z 272 (M^+, 8).

4-(1-Butenyl)-6-(methylthio)-2*H*-pyran-2-one (12) was obtained when **8l** or **11l** was reacted with ethyl (bromozincio)-acetate under identical conditions to those described and the reaction mixture was refluxed for 26 h: yellow solid ($CHCl_3$); yield 47%; mp 61–62 °C; IR (KBr) 1728, 1640, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) 1.09 (t, J = 7, 3 H, CH_3), 2.26 (br quint, 2 H, CH_2CH_3), 2.45 (s, 3 H, SCH_3), 5.67 (s, 1 H, *H*-5), 6.04 (d, J = 16, 1 H, *H*-$1_{butenyl}$), 6.13 (s, 1 H, *H*-3), 6.48 (dt, J = 16, 6.5, 1 H, *H*-$2_{butenyl}$). Anal. Found: C, 60.98; H, 6.38. Calcd for $C_{10}H_{12}O_2S$: C, 61.22; H. 6.12. MS: m/z 196 (M^+, 39).

Reaction of 1 with Ethyl (Bromozincio)acetate in the Presence of Cuprous Iodide. Synthesis of 4-(and 4,5-)Substituted-6-(methylthio)-2*H*-pyran-2-one (15). General Procedure. To the Reformatsky reagent [prepared from zinc (2.6 g, 0.04 g atom) and ethyl bromoacetate (3.4 g, 0.02 mol)] in dry ether (30 mL) was added cuprous iodide (1.9 g, 0.01 mol) under a nitrogen atmosphere, and the reaction mixture was refluxed with stirring for 15 min. A solution of the appropriate α-oxo ketene dithioacetals **1** (0.01 mol) in dry benzene (40 mL) was then added dropwise and refluxing continued for 20–24 h. The reaction mixture was then cooled and poured into dilute sulfuric acid (100 mL, 10%), the organic layer was separated, washed once with water, dried (Na_2SO_4), and the solvent was evaporated to give the crude pyran-2-ones, which were further purified by being passed through a silica gel column. Elution with hexane/ethyl acetate (9:1) afforded the pyrones **15** as crystalline solids (Table III). The cylic oxo ketene dithioacetals **1l** and **1m** afforded only the open-chain dienes **3l** and **17** and ester **18**, respectively, under identical conditions to those described above.

1-(Carbethoxymethylene)-2-[bis(methylthio)methylene]-cyclopentane (3l): light yellow solid ($CHCl_3$); yield 57%; mp 42–43 °C; IR (neat) 1703, 1620 cm^{-1}; ^1H NMR (CCl_4) 1.21 (t, 3 H, CH_3), 1.70 (t, J = 7, 2 H, ring CH_2), 2.33 [s, 6 H, $(SCH_3)_2$], 2.68 (t, J = 7.5, 2 H, ring CH_2), 3.0 (dt, J = 1.5, 7, 2 H, ring CH_2), 4.17 (q, 2 H, OCH_2), 7.0 (t, J = 1.5, 1 H, =C*H*). Anal. Found: C, 56.08; H, 6.70. Calcd for $C_{12}H_{18}O_2S_2$: C, 55.81; H, 6.98.

1-[Bis(methylthio)methylene]-2-(carbethoxymethyl)-cyclohex-2-ene (17): yellow liquid; yield 38%; IR (neat) 1730 cm^{-1}; ^1H NMR (CCl_4) 1.22 (t, J = 7, 3 H, CH_3), 1.48–1.62 (m, 2 H, CH_2 cyclic), 2.36–2.58 (m, 4 H, CH_2 cyclic), 3.61 (s, 2 H,

Table III. Spectral and Analytical Data for Pyrones 15

compd	mol form.	IR ν_{max}, cm^{-1}	^1H NMR,[a] δ	m/z (rel int) M^+	Anal. calcd/found C	Anal. calcd/found H
15a	$C_{12}H_{10}O_2S$	1710, 1605	2.58 (s, 3 H, SCH_3), 6.24 (d, J = 2, 1 H, H-5), 6.41 (d, J = 2, 1 H, H-3), 7.52 (br s, 5 H, ArH)	218 (38)	66.06/65.79	4.59/4.84
15b	$C_{13}H_{12}O_3S$	1705, 1600	2.53 (s, 3 H, SCH_3), 3.78 (s, 3 H, OCH_3), 6.21 (d, J = 2, 1 H, H-3), 6.35 (d, J = 2, 1 H, H-5), 6.80–7.59 (dd, 4 H, ArH)	248 (34)	62.90/63.17	4.84/5.10
15c	$C_{16}H_{12}O_2S$	1730, 1610	2.58 (s, 3 H, SCH_3), 6.53 (d, J = 2, 1 H, H-5), 6.50 (d, J = 2, 1 H, H-3), 7.41–8.03 (m, 7 H, ArH)	268 (34)	71.64/71.91	4.48/4.74
15d	$C_{10}H_8O_3S$	1700, 1610	2.52 (s, 3 H, SCH_3), 6.24 (d, J = 2, 1 H, H-3), 6.33 (d, J = 2, 1 H, H-5), 6.40–6.51 (m, 1 H, furyl), 6.82 (d, J = 2, 1 H, furyl), 7.60 (d, J = 2, 1 H, furyl)	208 (23)	57.69/57.93	3.85/4.12
15e	$C_{10}H_8O_2S_2$	1715, 1605	2.52 (s, 3 H, SCH_3), 6.29 (d, J = 2, 1 H, H-5), 6.37 (d, J = 2, 1 H, H-3), 7.12–7.25 (m, 1 H, thienyl), 7.42–7.52 (m, 2 H, thienyl)	224 (39)	53.57/53.30	3.57/3.28
15f	$C_7H_8O_2S$	1710, 1600	2.28 (s, 3 H, CH_3), 2.41 (s, 3 H, SCH_3), 6.22 (d, J = 2, 1 H, H-5), 6.38 (d, J = 2, 1 H, H-3)	156 (12)	53.85/54.09	5.13/5.40
15g	$C_8H_{10}O_2S$	1710, 1612	2.20 (s, 6 H, two CH_3), 2.51 (s, 3 H, SCH_3), 6.29 (br s, 1 H, H-3)		56.47/56.70	5.88/6.11

[a] In $CDCl_3$.

Table IV. Spectral and Analytical Data for Pyridones 22

compd	mol form.	IR ν_{max}, cm^{-1}	^1H NMR,[a] δ	m/z (rel int) M^+	Anal. calcd/found C	Anal. calcd/found H	Anal. calcd/found N
22a	$C_{10}H_9NO_2S$	3350, 1648	2.53 (s, 3 H, SCH_3), 6.50 (d, J = 1.5, 1 H, H-5), 6.56–6.61 (m, 1 H, furyl), 6.65 (d, J = 1.5, 1 H, H-3), 7.14 (d, J = 3, 1 H, furyl), 7.75 (d, J = 2, 1 H, furyl)	207 (100)	57.97/58.24	4.35/4.60	6.76/7.05
22b	C_7H_9NOS	3440, 1660	2.27 (s, 3 H, CH_3), 2.48 (s, 3 H, SCH_3), 6.06 (br s, 1 H, H-5), 6.19 (br s, 1 H, H-3)		54.19/54.42	5.81/6.07	9.03/9.33
22c	$C_8H_{11}NOS$	3400, 1658	2.27 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 2.48 (s, 3 H, SCH_3), 6.35 (br s, 1 H, H-3)		56.81/57.04	6.51/6.78	8.28/8.59
22d	$C_{13}H_{13}NOS$	3360, 1655	2.33 (s, 3 H, CH_3), 2.51 (s, 3 H, SCH_3), 6.40 (d, J = 2, 1 H, H-5), 6.43 (d, J = 2, 1 H, H-3), 7.27 (d, 2 H, ArH), 7.50 (d, 2 H, ArH)	231 (100)	67.53/67.76	5.63/5.91	6.06/6.35
22e	$C_{12}H_{10}BrNOS$	3380, 1652	2.52 (s, 3 H, SCH_3), 6.39 (d, J = 1.5, 1 H, H-5), 6.61 (d, J = 1.5, 1 H, H-3), 7.60 (s, 4 H, ArH)	297, 295 (100, 95)	48.65/48.90	3.38/3.66	4.73/5.03
22f	$C_{14}H_{13}NOS$	3400, 1650, 1610	2.52 (s, 3 H, SCH), 6.40 (br s, 1 H, H-5), 6.61 (br s, 1 H, H-3), 7.18 (d, J = 15, 1 H, =CH), 7.43–7.80 (m, 6 H, ArH, =CH)		69.14/69.33	5.35/5.63	5.76/6.00
22g	$C_{15}H_{15}NO_2S$	3410, 1610, 1595	2.52 (s, 3 H, SCH_3), 3.80 (s, 3 H, OCH_3), 6.23 (br s, 1 H, H-5), 6.39 (br s, 1 H, H-3), 6.70 (d, J = 16, 1 H, =CH), 6.85 (d, 2 H, ArH), 7.18 (d, J = 16, 1 H, =CH), 7.46 (d, 2 H, ArH)	273 (100)	65.93/66.21	5.50/5.78	5.13/5.40

[a] In DMSO-d_6.

CH_2CO_2Et), 4.03 (q, 2 H, CH_2CH_3), 5.50 (t, J = 1.5, 1 H, =CH). Anal. Found: C, 57.08; H, 7.15. Calcd for $C_{13}H_{20}O_2S_2$: C, 57.31; H, 7.40.

Methyl 2-(carbethoxymethyl)cyclohexene-1-thiocarboxylate (18): yellow oil; yield 16%; IR (neat) 1730, 1640 cm^{-1}; ^1H NMR (CCl_4) 1.23 (t, 3 H, CH_3), 1.62–1.80 (m, 4 H, CH_2 cyclic), 2.05–2.46 (m, 4 H, CH_2 cyclic), 2.61 (s, 3 H, SCH_3), 3.0 (br s, 2 H, CH_2CO_2Et), 4.01 (q, 2 H, CH_2CH_3). Anal. Found: C, 59.68; H, 7.71. Calcd for $C_{12}H_{18}O_3S$: C, 59.47; H, 7.49.

4-Phenyltetrahydropyran-2-one (16)[15] was obtained by Raney Ni desulfurization of **15a** at room temperature (3 h) as described; oil, 50%; IR (neat) 1736 cm^{-1}; ^1H NMR (CCl_4) 2.0–2.21 (m, 2 H, H-5), 2.48–2.83 (m, 2 H, H-3), 3.01–3.30 (m, 1 H, H-4), 4.29–4.57 (m, 2 H, OCH_2), 7.11–7.53 (m, 5 H, ArH). Anal. Found: C, 75.27; H, 7.01. Calcd for $C_{11}H_{12}O_2$: C, 75.0; H, 6.82.

Synthesis of 4-(or 4,5-)Substituted-6-(methylthio)-2-(1H)-pyridones 22a–g. General Procedure. A suspension of the appropriate diene **3** (0.01 mol) or the corresponding crude carbinols **10** (0.01 mol) (obtained by the reaction of the corresponding oxo ketene dithioacetals with Reformatsky reagent as described earlier) and excess of ammonium acetate (10 g) in glacial acetic acid (25 mL) was refluxed with stirring for 10 h. The reaction mixture was cooled and poured into ice-cold water (100 mL), and the precipitated yellow solids were filtered and recrystallized from chloroform to give pure pyridones **2** in good yields (Table IV).

Ethyl [2-[(methylthio)aminomethylene]cyclohexylidene]acetate (23): white solid ($CHCl_3$); yield 45%; mp 53–54 °C; IR (KBr) 3120, 1648, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) 1.39 (t, 3 H, CH_3), 1.54–1.88 (m, 4 H, ring CH_2), 2.32–2.52 (m, 4 H, ring CH_2), 2.60 (s, 3 H, SCH_3), 4.09 (q, 2 H, OCH_2), 5.24 (s, 1 H, =CH), 11.04 (br s, 2 H, NH_2, exchangeable with D_2O, NH_2). Anal. Found: C, 59.92; H, 8.12; N, 6.09. Calcd for $C_{12}H_{19}NO_2S$: C, 59.75; H, 7.88; N, 5.81.

Registry No. **1a**, 41467-26-9; **1b**, 13636-88-9; **1c**, 33868-76-7; **1d**, 98606-76-9; **1e**, 78078-05-4; **1f**, 41467-29-2; **1g**, 17649-86-4; **1h**, 17649-87-5; **1i**, 4254-65-3; **1j**, 51507-08-5; **1k**, 61541-58-0; **1l**, 17649-89-7; **1m**, 17649-90-0; **1n**, 61539-01-3; **1o**, 61402-25-3; **1p**, 51507-10-9; **3e**, 128950-89-0; **3g**, 128950-90-3; **3h**, 128950-91-4; **3i**, 128950-92-5; **3l**, 128950-93-6; **3m**, 128950-94-7; **3q**, 128950-95-8; **3r**, 128950-96-9; **4a**, 117530-23-1; **4b**, 117530-24-2; **4c**, 128950-97-0; **4d**, 128950-98-1; **4e**, 117530-26-4; **4f**, 117530-25-3; **4g**, 117530-22-0; **4h**, 128950-99-2; **4l**, 117530-27-5; **4m**, 117530-28-6; **4n**, 117530-29-7; **4o**, 117530-30-0; **4p**, 117530-31-1; **4q**, 128951-00-8; **5a**, 128951-01-9; **5g**, 60770-00-5; **5n**, 20894-49-9; **5o**, 7213-92-5; **5p**, 128951-02-0; **5q**, 52888-73-0; **8a**, 89812-50-0; **8b**, 89812-53-3; **8c**, 89812-52-2; **8d**, 128951-03-1; **8e**, 114577-54-7; **8f**, 128951-04-2; **8g**, 117672-14-7; **8h**, 89812-54-4; **8i**, 128951-05-3; **8j**, 128951-06-4; **8k**, 128951-07-5; **8l**, 128951-08-6; **9a**, 128951-09-7; **9b**, 128951-10-0; **9c**, 128951-11-1; **9d**, 128951-12-2; **9e**, 128951-13-3; **9f**, 128951-14-4; **9g**, 128951-15-5; **9h**, 128951-16-6; **9i**, 128951-17-7; **9j**, 128951-18-8; **10a**, 128951-19-9; **10c**, 128951-20-2; **10m**, 128951-21-3; **11a**, 128951-22-4; **11b**, 128951-23-5; **11k**, 128951-24-6; **11l**, 128951-25-7; **15a**, 128951-26-8; **15b**, 128951-27-9; **15c**, 128951-28-0; **15d**, 128951-29-1; **15e**, 128951-30-4; **15f**, 128951-31-5; **15g**, 128951-32-6; **16**, 25547-53-9; **17**, 128951-33-7; **18**, 128951-34-8; **22a**, 128951-35-9; **22b**, 128951-36-0; **22c**, 128951-37-1; **22d**, 128951-38-2; **22e**, 128951-39-3; **22f**, 128951-40-6; **22g**, 128951-41-7; **23**, 128951-42-8; $BrCH_2CO_2Me$, 96-32-2; ethyl bromoacetate, 105-36-2.