= $(CH_2)_2$) was prepared from 100 mM of cyclohexanedione (**4**, n = 6) by the method A: IR (NaCl) 1730 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.30–2.00 (6 H, m, 3 × CH_2), 2.20–2.64 (2 H, m, CH_2C=O), 3.85 (4 H, m, $\overline{COCH_2CH_2O}$); bp 80 °C (3 mmHg) [lit.[10a] bp 115 °C (22 mmHg)].

2,2-Dimethoxycycloheptanone (6, n = 7; R^1 = Me) was prepared from 100 mM of cycloheptanedione (**4**, n = 7) by the method B: IR (NaCl) 1735 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.17–2.01 (8 H, m, 4 × CH_2), 2.22–2.63 (2 H, pseudo-t, CH_2C=O), 3.16 (6 H, s, 2 × OCH_3); bp 93 °C (7 mmHg). Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.57; H, 9.53.

2-Oxocycloheptane-1-spiro-2′-(1′,3′-dioxolane) (6, n = 7; $\overline{R^1R^1}$ = $(CH_2)_2$) was prepared from 100 mM of cycloheptanedione (**4**, n = 7) by the method B: IR (NaCl) 1720 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.42–2.09 (8 H, m, 4 × CH_2), 2.27–2.71 (2 H, m, CH_2C=O), 3.92 (4 H, s, $\overline{COCH_2CH_2O}$); bp 105 °C (8 mmHg).

2-Oxocyclooctane-1-spiro-2′-(1′,3′-dioxolane) (6, n = 8; $\overline{R^1R^1}$ = $(CH_2)_2$) was prepared from 100 mM of cyclooctanedione (**4**, n = 8) by the method A: IR (NaCl) 1720 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.10–1.19 (10 H, m, 5 × CH_2), 2.27–2.62 (2 H, m, CH_2C=O), 3.89 (4 H, s, $\overline{COCH_2CH_2O}$); bp 128 °C (8 mmHg). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.00; H, 8.97.

2-Oxocyclononane-1-spiro-2′-(1′,3′-dioxolane) (6, n = 9; $\overline{R^1R^1}$ = $(CH_2)_2$) was prepared from 10 mM of cyclononanedione (**4**, n = 9) by the method A: IR (NaCl) 1730 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.00–2.11 (12 H, m, 6 × CH_2), 2.27–2.62 (2 H, m, CH_2C=O), 3.55–4.04 (4 H, m, $\overline{COCH_2CH_2O}$).

2-Oxocyclodecane-1-spiro-2′-(1′,3′-dioxolane) (6, n = 10; $\overline{R^1R^1}$ = $(CH_2)_2$) was prepared from 7.7 mM of cyclodecanedione (**4**, n = 10) by the method A or from 9 mM of cyclodecanedione by azeotropic distillation in benzene–PTSA mixture: IR (NaCl) 1720 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.26–2.11 (14 H, m, 7 × CH_2), 2.62 (2 H, pseudo-t, CH_2C=O), 3.73–4.04 (4 H, m, $\overline{COCH_2CH_2O}$).

2-Oxocycloundecane-1-spiro-2′-(1′,3′-dioxolane) (6, n = 11; $\overline{R^1R^1}$ = $(CH_2)_2$) was prepared from 25 mM of cycloundecanedione (**4**, n = 11) by the method B: IR (NaCl) 1720 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.95–2.13 (16 H, m, 8 × CH_2), 2.35–2.77 (2 H, m, CH_2C=O), 3.55–4.05 (4 H, m, $\overline{COCH_2CH_2O}$). Anal. Calcd for $C_{13}H_{22}O_3$: C, 69.06; H, 10.04. Found: C, 68.99; H, 9.80.

2-Oxocyclododecane-1-spiro-2′-(1′,3′-dioxolane) (6, n = 12; $\overline{R^1R^1}$ = $(CH_2)_2$) was prepared from 25 mM of cyclododecanedione (**4**, n = 12) by the method B: IR (KBr) 1720 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.84–1.99 (18 H, m, 9 × CH_2 with br s at δ 1.27), 2.36–2.69 (2 H, pseudo t, CH_2C=O), 3.47–4.07 (4 H, m, $\overline{COCH_2CH_2O}$). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.79; H, 10.03.

General Procedure for the Preparation of Benzocyclobutenols 9. Reactions were carried out with magnetic stirring under a nitrogen atmosphere and monitored by GLC analysis.

A solution of t-BuOH (50 mM) in THF (or DME) (10 mL) was added dropwise to a suspension of $NaNH_2$ (200 mM for the ratio **7**/**8** = 0.5/1 or 220 mM for the ratio **7**/**8** = 1.1/1) in THF or DME (30 mL), and the mixture was heated at 45 °C for 2 h; the ketone **4** (50 mM) diluted in THF (or DME) (10 mL) was added at room temperature, and the reaction mixture was stirred for 2 h. A solution of bromobenzene (25 mM for the ratio **7**/**8** = 0.5/1 or 55 mM for the ratio **7**/**8** = 1.1/1) in THF (or DME) (20 mL) was slowly added at the temperature and for the time indicated in the Table III. Upon completion, the mass was poured on ice, extracted with diethyl ether, washed twice with water, and dried over $MgSO_4$. After evaporation of the solvents under reduced pressure, the different components of the mixture were separated by chromatography on a silica gel column or by HPLC for benzocyclobutenol ethylene acetal and only by HPLC for benzocyclobutenol dimethylacetal. Spectral data and melting points for compounds **9** are given in Table IV.

Registry No. **2** (n = 5), 120-92-3; **2** (n = 6), 108-94-1; **2** (n = 7), 502-42-1; **2** (n = 8), 502-49-8; **2** (n = 9), 3350-30-9; **2** (n = 10), 1502-06-3; **2** (n = 11), 878-13-7; **2** (n = 12), 830-13-7; **3** (n = 5), 52190-34-8; **3** (n = 6), 52190-35-9; **3** (n = 7), 52190-36-0; **3** (n = 8), 52190-37-1; **3** (n = 9), 100703-64-8; **3** (n 10), 100703-65-9; **3** (n = 11), 100703-66-0; **3** (n = 12), 52190-38-2; **4** (n = 5), 3008-40-0; **4** (n = 6), 765-87-7; **4** (n = 7), 3008-39-7; **4** (n = 8), 3008-37-5; **4** (n = 9), 3008-36-4; **4** (n = 10), 96-01-5; **4** (n = 11), 3008-34-2; **4** (n = 12), 3008-41-1; **5**, 100703-67-1; **6** (n = 5; R^4 = Me), 66057-04-3; **6** (n = 6; R^1 = Me), 38461-13-1; **6** (n = 6; $\overline{R^1R^1}$ = (CH_2)), 4746-96-7; **6** (n = 7; R^1 = Me), 89874-31-7; **6** (n = 7; $\overline{R^1R^1}$ $(CH_2)_2$), 89874-32-8; **6** (n = 8; $\overline{R^1R^1}$ = $(CH_2)_2$), 89874-33-9; **6** (n = 9; $\overline{R^1R^1}$ = $(CH_2)_2$), 100703-68-2; **6** (n = 10; $\overline{R^1R^2}$ = $(CH_2)_2$), 100703-69-3; **6** (n = 11; $\overline{R^1R^1}$ = $(CH_2)_2$), 100703-70-6; **6** (n = 12; $\overline{R^1R^1}$ = $(CH_2)_2$), 89874-34-0; **7**, 108-86-1; **9a**, 89874-22-6; **9b**, 89874-23-7; **9c**, 100765-51-3; **9d**, 89874-24-8; **9e**, 100703-71-7; **9f**, 100789-70-6; **9g**, 100703-72-8; **9h**, 100703-73-9; **9i**, 100703-74-0; **9j**, 100703-75-1; **9k**, 100703-76-2; **9l**, 100703-77-3; **9m**, 100837-45-4; MeSSMe, 624-92-0; 2-methyl-2-butanoyl-1,3-dioxolane, 61784-38-1; 2-methyl-2-(2-methylpropanoyl)-1,3-dioxolane, 61784-40-5; 2-methyl-2-pentanoyl-1,3-dioxolane, 61784-39-2.

Selective Protection of Carbonyl Compounds. Silica Gel Treated with Thionyl Chloride as an Effective Catalyst for Thioacetalization

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Silica gel treated with thionyl chloride was found to be an effective as well as highly selective catalyst for thioacetalization of aldehydes. With the use of this catalyst 1,3-dithioranes and 1,3-dithianes were obtained in excellent yields from various aldehydes. Under the same conditions ketones were similarly but more slowly thioketalized. This difference in reactivity between aldehydes and ketones was successfully utilized for the thioacetalization of aldehydes in the presence of ketones and also for the chemoselective conversion of keto aldehydes into the corresponding dithioacetals with the keto group remaining intact.

Introduction

The protection of carbonyl groups as acetals or dithioacetals is now commonly used as an important synthetic technique in the course of preparation of many organic compounds including multifunctional complex molecules. For thioacetalization, a number of methods using protic acids, Lewis acids, and some silicon reagents have been developed so far.[1] However, a convenient and at the same time highly chemoselective thioacetalization method capable of discrimination between aldehydes and ketones has not yet been described in spite of its great importance and

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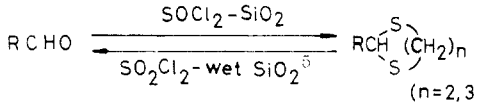
0022-3263/86/1951-1427$01.50/0

Table I. Thioacetalization of Aldehydes to 1,3-Dithioranes and 1,3-Dithianes with the Use of $SOCl_2$–SiO_2[a]

R	RCHO	dithiol	product	yield, %
$CH_3(CH_2)_5$–	**1a**	2	**1b**	99
		3	**1c**	99
$Ph(CH_3)CH$–	**4a**	2	**4b**	100
$H_2C{=}CH(CH_2)_8$–	**5a**	2	**5b**	100
Ph–	**6a**	2	**6b**	100[b]
		3	**6c**	97[b]
p-Tol–	**7a**	2	**7b**	98
PhCH=CH–	**8a**	2	**8b**	97
		3	**8c**	100
$CH_3CH{=}CH$–	**9a**	2	**9b**	100

[a] In the presence of $SOCl_2$–SiO_2 (0.2 g), aldehyde (1 mmol) and dithiol (1.1 mmol) were reacted for 5 h at 20 °C in benzene. [b] The reaction was carried out under N_2, otherwise oxidation of **6a** diminished the yield of **6b**.

necessity. As an extension of our recent studies regarding chemoselective reactions with the use of silica gel,[2-12] we started a work to develop highly chemoselective acetalization[12] and thioacetalization methods using inorganic supports.

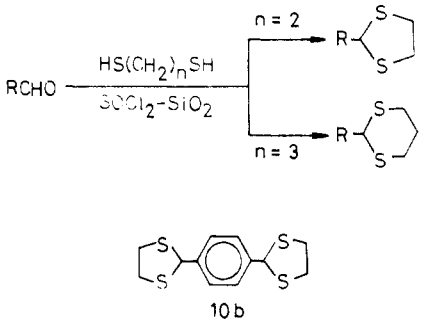


In this paper we wish to report a mild and highly chemoselective thioacetalization method for conversion of aldehydes to 1,3-dithioranes and 1,3-dithianes using silica gel treated with thionyl chloride ($SOCl_2$–SiO_2) as an effective catalyst. The reaction proceeds very cleanly and the workup procedure is very simple.

Results and Discussion

Thioacetalization of Aldehydes with the Use of $SOCl_2$–SiO_2. As a catalyst for the thioacetalization of aldehydes silica gel was tried first without other reagents. Heptanal (**1a**) was treated with three molar excess of 1,2-ethanedithiol (**2**) in the presence of silica gel, but only 11% of **1a** was converted to the corresponding 1,3-dithiorane (**1b**) after refluxing for 24 h in benzene. Thus silica gel itself was found not to be a good catalyst for thioacetalization of aldehydes. However, when silica gel treated with thionyl chloride ($SOCl_2$–SiO_2) was used as a catalyst in place of silica gel, **1a** was completely converted to **1b** by stirring it with equimolar amounts of **2** in benzene for 5 h even at room temperature. This catalyst can be easily obtained by treating silica gel (for column chromatography) with thionyl chloride (see Experimental Section). With the use of $SOCl_2$–SiO_2, thioacetalizations of several aldehydes were successfully performed and the results are summarized in Table I. As is seen in Table I, aliphatic as well as aromatic aldehydes **1a**–**8a** in which conjugated and unconjugated enals are included were all cleanly thioacetalized to the corresponding 1,3-dithioranes by **2** under mild conditions. Similarly, 1,3-dithianes were obtained in high yields when 1,3-propanedithiol (**3**) was used. It is worthy of note that the thioacetalization of crotonaldehyde (**9a**), which can not be thioacetalized[13] by ordinary acid catalysts, proceeded successfully by this method to afford **9b** quantitatively. Terephthalaldehyde (**10a**) was also thioacetalized by a threefold molar excess of **2** to the corresponding bis-1,3-dithiorane (**10b**) in 80% yield. These reactions proceeded quite cleanly under mild conditions and practically pure products were obtained after a simple workup procedure (see Scheme I).

Scheme I



10b

Scheme II

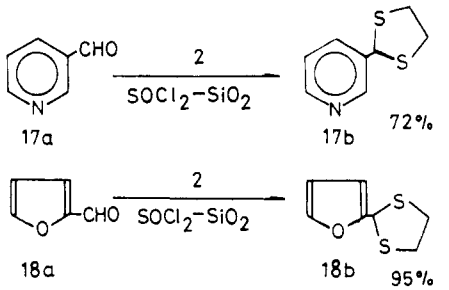


Table II. Thioacetalization of Substituted Benzaldehydes to 1,3-Dithiorane with the Use of $SOCl_2$–SiO_2[a]

substituent	aldehyde	1,3-dithiorane	yield, %
p-Cl	**11a**	**11b**	99
p-MeO	**12a**	**12b**	98
o-NO_2	**13a**	**13b**	93
p-HO	**14a**	**14b**	88[b,c]
p-Me_2N	**15a**	**15b**	91[d]
p-HO_2C	**16a**	**16b**	98

[a] In the presence of $SOCl_2$–SiO_2 (0.2 g), aldehyde (1 mmol) and **2** (1.1 mmol) were reacted for 5 h at 20 °C in benzene. [b] $SOCl_2$–SiO_2 (1 g) and **2** (3 mmol) were used. [c] Product was extracted with EtOH/acetone (1/1) from SiO_2. [d] $SOCl_2$–SiO_2 (1 g) was used in relfuxing benzene and product was extracted from SiO_2 with diethyl ether containing 10% of Et_3N.

Thioacetalization with the use of $SOCl_2$–SiO_2 was also examined with several substituted benzaldehydes and the results are listed in Table II. All these aldehydes bearing Cl, OMe, NO_2, OH, NMe_2, and CO_2H groups (**11a**–**16a**) were cleanly converted to the corresponding 1,3-dithioranes (**11b**–**16b**) in almost quantitative yields with these substituent groups remaining strictly unchanged. Heterocyclic aromatic aldehydes **17a** and **18a** which are thioacetalized with difficulty with the use of conventional acid catalysts were also converted to the corresponding thioacetals, **17b** and **18b**, in high yields (see Scheme II). In both cases the reaction proceeded quite cleanly and ^1H NMR spectra showed no indication of the presence of any byproducts and unreacted starting materials.

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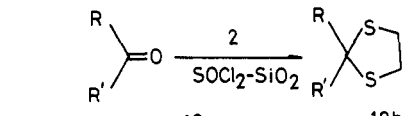
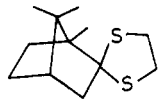
(12) Kamitori, Y.; Hojo, M.; Masuda, R.; Yoshida, T. *Tetrahedron Lett.* **1985**, *26*, 4767.

(13) 1,3-Dithiorane of **9a** is obtainable by the treatment of crotonaldehyde diethylacetal with **2**.

Scheme III



R= Ph, R'= CH_3 19a 19b
R,R'= $-(CH_2)_5-$ 20a 20b
R=R'= $PhCH_2$ 21a 21b
R=R'= Ph 22a 22b



23b

Table III. Thioacetalization of Ketones to 1,3-Dithiorane with the Use of $SOCl_2$-SiO_2

ketone	method[a]	1,3-dithiorane	yield, %
19a	A	**19b**	91
20a	A	**20b**	100
21a	A	**21b**	93
22a	A	**22b**	31[b]
	B	**22b**	48
23a	A	**23b**	32[b]
	B	**23b**	65

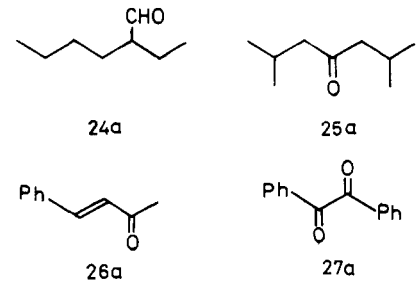
[a] Method A: ketone (1 mmol), **2** (3 mmol), and $SOCl_2$-SiO_2 (1 g) were reacted in refluxing toluene for 24 h. Method B: ketone (1 mmol), **2** (3 mmol) and $SOCl_2$-SiO_2 (1 g) were reacted for 24 h at 110 °C in a sealed tube without solvent. [b] Yield calculated on the basis of ^1H NMR spectra.

Thioacetalization of aldehydes with simple alkane thiols such as EtSH and MeSH in the presence of $SOCl_2$-SiO_2 resulted in recovery of most of the starting materials. This striking difference in reactivity is indicative of the mildness of the present catalyst and prompted us to investigate application of the present method to chemoselective thioacetalization.

Thioacetalization of Ketones with the Use of $SOCl_2$-SiO_2. Ketones were also thioacetalized to 1,3-dithioranes with the use of $SOCl_2$-SiO_2. However, the reaction of ketones occurred considerably more slowly compared to aldehydes and did not go to completion even in refluxing benzene. Therefore the reaction was carried out with a larger excess of **2** and $SOCl_2$-SiO_2 in refluxingg toluene, by which ketones **19a–21a** were successfully converted to the corresponding 1,3-dithioranes (**19b–21b**) in excellent yields. In the cases of benzophenone (**22a**) and camphor (**23a**), the reaction proceeded the more slowly and much of the substrate was recovered unchanged even in refluxing toluene. Thioacetalization of these compounds to **22b** and **23b** was achieved by heating the reagents at 110 °C in a sealed tube without solvent (see Scheme III and Table III).

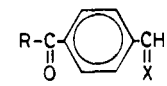
Selective Thioacetalization of Aldehydes in the Presence of a Keto Carbonyl Group. In order to examine selectivity of the present thioacetalization with the use of $SOCl_2$-SiO_2 two sets of experiments were performed. One was carried out by use of equimolar mixtures of an aldehyde and a ketone, and the other was done with keto aldehydes. In the former case several combinations of aliphatic as well as aromatic aldehydes and ketones were chosen (see Chart I). As shown in Table IV perfect chemoselectivity was observed in each case. None of the 1,3-dithioranes derived from these ketones were detected even by carefull inspection of ^1H NMR spectra of the crude products. As for the latter case, thioacetalization of keto aldehydes **28a–32a** also exhibited splendid selectivity towards the formyl group. For example the reaction of **30a** gave **30b** as a sole product in 97% yield (see Chart II).

Chart I

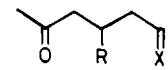


24a 25a 26a 27a

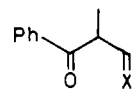
Chart II



R= CH_3, X= O 28a
R= CH_3, X= S S 28b
R= CH_3, X= S S 28c
R= Ph, X= O 29a
R= Ph, X= S S 29b



R= H, X= O 30a
R= H, X= S S 30b
R= H, X= S S 30c
R= Ph, X= O 31a
R= Ph, X= S S 31b
R= Ph, X= S S 31c



X= O 32a
X= S S 32b
X= S S 32c

Table IV. Thioacetalization of Mixture of Aldehyde and Ketone with the Use of $SOCl_2$-SiO_2[a]

RCHO	R'COR''	% conversion of aldehyde	% yield of dithiorane	% conversion[b] of ketone
6a	**19a**	100	92	0
11a	**19a**	96	94	0
24a	**21a**	100	89	0
12a	**25a**	100	88	0
4a	**26a**	83	75	0
1a	**27a**	100	91	0

[a] For a mixture of aldehyde and ketone (1 mmol/1 mmol), **2** (1.1 mmol) and $SOCl_2$-SiO_2 (0.2 g) were used in benzene at 20 °C. [b] These were calculated on the basis of ^1H NMR spectra.

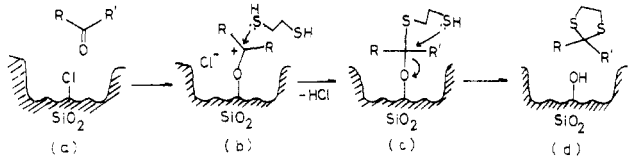
Table V. Selective Thioacetalization of Keto Aldehydes with the Use of $SOCl_2$-SiO_2[a]

substrate	dithiol	product	yield, %
28a	**2**	**28b**	90
	3	**28c**	99
29a	**2**	**29b**	78
30a	**2**	**30b**	89[b]
	3	**30c**	98
31a	**2**	**31b**	98
	3	**31c**	99
32a	**2**	**32b**	92
	3	**32c**	92

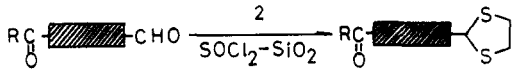
[a] Equimolar amounts of dithiol and $SOCl_2$-SiO_2 (1 g) were used for substrate (1 mmol) and reactions were carried out in relfuxing benzene for 24 h. [b] When this reaction was carried out at 20 °C for 5 h with the use of $SOCl_2$-SiO_2 (0.2 g), **30b** was obtained in 97% yield (see Experimental Section).

This striking selectivity with these keto aldehydes **28a–32a** may be emphasized by the fact that the thioacetalizations in Table V were carried out under enhanced reaction conditions, i.e., with the use of fivefold excess amounts of

Scheme IV



$SOCl_2$–SiO_2 and at the refluxing temperatures of benzene (*cf.* the reaction conditions in Tables I–IV). After completion of the reaction neither starting materials nor any byproducts derived from thioacetalization at keto carbonyl groups was observed. Thus the excellent selectivity of the present reaction is quite insensitive to both amounts of $SOCl_2$–SiO_2 and temperature.



Folman reported[14] that most of the OH groups on the surface of porous silicate glass are exchanged for Cl on treatment with $SOCl_2$ and this would be the case with the present catalyst, $SOCl_2$–SiO_2. These Si–Cl bonds should be reactive enough to trap carbonyl compounds to form carbenium species on the surface of the silica gel as illustrated in Scheme IV (b). The carbocationic center is then easily attacked by **2** to yield the 1,3 dithiorane. The reaction which occurs in such a relatively hindered environment, i.e., on the porous surface of silica gel, would favor aldehydes strongly in preference to ketones and thus produce striking chemoselectivity of the present thioacetalization.

In conclusion, $SOCl_2$–SiO_2 is a very effective and convenient catalyst for thioacetalization of aldehydes to 1,3-dithiorane and 1,3-dithiane, and high chemoselectivity of the reaction should be useful for selective protection of aldehydes in the presence of keto carbonyl groups. In addition the cleanness of the reaction and its simple procedure are suitable for use in syntheses of complex molecules by multistep processes. Striking chemoselectivity of the present reaction is ascribed to the difference in steric hindrance between aldehydes and ketones towards the porous surface of silica gel.

Experimental Section

Commercially available silica gel for column chromatography (Wakogel C-300)[15] was used as received. Solvents for the reactions were dried on 4-Å molecular sieves, $^1/_{16}$ before use. All ^{1}H NMR spectra were recorded at 60 MHz on JEOL PMX 60 SI or Hitachi R-24 spectrometers in $CDCl_3$ solutions containing tetramethylsilane as an internal standard. IR spectra were taken with a Hitachi model G3 spectrophotometer.

Products were identified on the basis of ^{1}H NMR spectra and at the same time by means of dethioacetalization back to the starting carbonyl compounds with the use of a reliable method which we developed previously[5] followed by comparison of their ^{1}H NMR and IR spectra with those of authentic samples. In some cases the results from elemental analysis were also utilized.

Preparation of $SOCl_2$–SiO_2. To well-stirred silica gel (20 g) in CH_2Cl_2 (40 mL) was added dropwise $SOCl_2$ (20 g) at room temperature. Evolution of copious amounts of HCl and SO_2 occurred instantaneously. After stirring for another 1 h, the solvent was removed to dryness under reduced pressure (1 torr). The $SOCl_2$–SiO_2 thus prepared was used in the following experiments and could be stored in sealed vessels for a few months without any critical decline of the activity.

(14) Folman, M. *Trans. Faraday Soc.* **1961**, *57*, 2000.

(15) Alternative silica gel which have grain size of about 300 mesh can be used instead of Wakogel C 300. For instance, a quite similar yield was obtained when $SOCl_2$–SiO_2 prepared from 300-mesh silicic acid (Mallinckrodt) was used for thioacetalization of **6a** to **6b**.

Reaction of Heptanal 1a with Ethanedithiol 2 in the Presence of SiO_2. To a mixture of SiO_2 (1 g) dried for 5 h at 170 °C under reduced pressure (0.1 torr) and **1a** (1 mmol) in dry benzene (5 mL) was added **2** (3 mmol), and the whole mixture was stirred for 24 h at the reflux temperature. Silica gel was filtered off and washed thoroughly with diethyl ether. Washings and the filtrates were combined, washed with 1 N aqueous NaOH, and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford 11% yield of **1b**, with recovery of some starting material **1a** (24%).

Thioacetalization of Aldehydes with the Use of $SOCl_2$–SiO_2. General Procedure (Refer to the Footnotes in Table I and Table II for 6a, 14a, and 15a). To a mixture of aldehyde (1 mmol) and $SOCl_2$–SiO_2 (0.2 g) in dry benzene (10 mL) was added dithiol (1.1 mmol), and the whole mixture was stirred for 5 h at 20 °C. Silica gel was filtered off and washed thoroughly with diethyl ether (ca. 20 mL). Washings and the filtrates were combined and washed with 1 N aqueous NaOH (in the case of **16b**, the latter process was omitted). After the mixture was dried over $MgSO_4$, the solvent (and dithiol) was removed under reduced pressure. Without further purification the crude products were practically pure **1b** (188 mg, 99%), **1c** (202 mg, 99%), **4b** (211 mg, 100%), **5b** (245 mg, 100%), **6b** (182 mg, 100%), **6c** (190 mg, 97%), **7b** (192 mg, 98%), **8b** (202 mg, 97%), **8c** (218 mg, 100%), **9b** (147 mg, 100%), **11b** (177 mg, 81%), **12b** (187 mg, 88%), **13b** (228 mg, 100%), and **16b** (222 mg, 98%). Recrystallization of crude **14b** and **15b** from cyclohexane to remove small amounts of impurities afforded pure **14b** (174 mg, 88%) and **15b** (203 mg, 90%). In the case of terephthalaldehyde (**10a**), $SOCl_2$ (0.2 g), **10a** (1 mmol), and **2** (3 mmol) were reacted for 5 h at 20 °C in benzene (10 mL) and product was extracted with CH_2Cl_2 (ca. 10 mL). The workup process described above afforded **10b** (226 mg, 79%). In the case of nicotinaldehyde (**17a**) $SOCl_2$–SiO_2 (0.2g), aldehyde (1 mmol), and **2** (1.1 mmol) were reacted in benzene (10 mL) for 24 h at the reflux temperature and in the case of furfural (**18a**) the reaction was carried out at 20 °C for 5 h. In each case products were extracted with diethyl ether containing 10% of Et_3N (ca. 20 mL) and usual workup as described above gave **17b** (132 mg, 72%) and **18b** (163 mg, 95%).

Thioacetalization of Ketones 19a–23a with the Use of $SOCl_2$–SiO_2 (Table III). Method A (19a–21a). To a mixture of ketone (1 mmol) and $SOCl_2$–SiO_2 (1 g) in toluene (10 mL) was added **2** (3 mmol), and the whole mixture was stirred for 24 h at the reflux temperature. Silica gel was filtered off and washed thoroughly with diethyl ether (ca. 50 mL). Washings and the filtrates were combined, washed with 1 N aqueous NaOH, and dried over $MgSO_4$. Solvent was removed under vacuum to afford **19b** (179 mg, 91%), **20b** (175 mg, 100%), and **21b** (266 mg, 93%). Without further purification the products were practically pure. **Method B (22a and 23a).** A mixture of ketone (1 mmol), **2** (3 mmol), and $SOCl_2$–SiO_2 (1 g) was heated to 110 °C in a sealed tube. After 24 h the reaction mixture was thoroughly extracted from silica gel with diethyl ether (ca. 50 mL). The extract was washed with 1 N aqueous NaOH and dried over $MgSO_4$. Removal of the solvent afforded crude **22b** or **23b**. Recrystallization of crude **22b** from cyclohexane gave pure **22b** (125 mg, 48%) and ball tube distillation of crude **23b** afforded pure 23b (148 mg, 65%).

Thioacetalization of the Mixture of Aldehyde and Ketone with the Use of $SOCl_2$–SiO_2 (Table IV). To a mixture of aldehyde (1 mmol), ketone (1 mmol), and $SOCl_2$–SiO_2 (0.2 g) in benzene (10 mL) was added **2** (1.1 mmol), and the whole mixture was stirred for 24 h at the reflux temperature. Silica gel was filtered off and washed thoroughly with diethyl ether (ca. 50 mL). Washings and the filtrates were combined, washed with 1 N aqueous NaOH, and dried over $MgSO_4$. The solvent was removed and residual materials were analyzed by ^{1}H NMR spectroscopy. From the equimolar mixtures mentioned above of **6a** and **19a**, **11a** and **19a**, **24a** and **21a**, **12a** and **25a**, **1a** and **27a**, and **4a** and **26a** were obtained a mixture of **6b** and **19a** (1/1, 279 mg), a mixture of **11b** and **19a** (96/91, 316 mg), a mixture of **24b** and **21a** (89/99, 401 mg), a mixture of **12b** and **25a** (88/17, 211 mg), a mixture of **1b** and **27a** (91/95, 372 mg), and a mixture of **4b**, **4a** and **26a** (75/24/99, 334 mg), respectively.

Thioacetalization of Keto Aldehydes 28a–32a with the Use of $SOCl_2$–SiO_2 (Table V). Keto aldehydes **28a–32a** were prepared by the methods shown in the literature.[16–19] Thio-

acetalization of **30a** was carried out according to general procedure to afford **30b** (185mg, 97%). Thioacetalization of keto aldehydes **28a–32a** were carried out as follows. To a mixture of keto aldehyde (1 mmol) and $SOCl_2$–SiO_2 (1 g) in benzene (10 mL) was added dithiol (1 mmol) and the whole mixture was stirred for 24 h at the reflux temperature. After silica gel was filtered off and washed thoroughly with diethyl ether (ca. 50 mL), washings and the filtrates were combined, washed with 1 N aqueous NaOH, and dried over $MgSO_4$. Removal of the solvent afforded **28b** (201 mg, 90%), **28c** (236 mg, 99%), **29b** (223 mg, 78%), **30b** (170 mg, 89%), **30c** (200 mg, 98%), **31b** (261 mg, 98%), **31c** (277 mg, 99%), **32b** (219 mg, 92%), and **32c** (231 mg, 92%). All these products were practically pure in this state. Microanalitical grade samples were obtained by recrystallization from cyclohexane for **28b**, **28c**, and **29b** and by ball tube distillation for **30b–32c**.

Dethioacetalization Procedure.[5] To a stirred mixture of thioacetal (0.5 mmol), H_2O (0.5 g), and SiO_2 (0.5 g) in CH_2Cl_2 (6 mL) was added dropwise a solution of SO_2Cl_2 (1 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The whole mixture was stirred for 3 h at 20 °C. Then finely powdered K_2CO_3 (0.6 g) was added to the mixture and stirring was continued for another 20 min. Insoluble materials were filtered off and washed thoroughly with CH_2Cl_2 (ca. 30 mL). Washings and the filtrates were combined, and the solvent was removed in vacuo to give the corresponding aldehydes. In some cases the procedure with the use of $Ce(NH_4)_2(NO_3)_6$[21] or $HgCl_2/CaCO_3$[22] was employed. The yields of **1a–23a** are as follows. **1a**: 50 mg (88%) from **1b**; 48 mg (85%) from **1c**. **4a**: 44 mg (65%) from **4b**. **5a**: 81 mg (97%) from **5b**. **6a**: 48 mg (90%) from **6b**; 39 mg (74%) from **6c**. **7a**: 43 mg (71%) from **7b**. **8a**: 37 mg (56%) from **8b**; 36 mg (55%) from **8c**. **9a**: 11 mg (31%) from **9b**. **10a**: 55 mg (82%) from **10b**. **11a**: 58 mg (82%) from **11b**. **12a**: 54 mg (79%) from **12b**. **13a**: 64 mg (85%) from **13b**. **14a**: 48 mg (79%) from **14b**. **15a**: 63 mg (84%) from **15b**. **16a**: 71 mg (95%) from **16b**. **17a**: 42 mg (79%) from **17b**. **18a**: 44 mg (91%) from **18b**. **19a**: 59 mg (99%) from **19b**. **20a**: 47 mg (96%) from **20b**. **21a**: 88 mg (84%) from **21b**. **22a**: 56 mg (61%) from **22b**. **23a**: 53 mg (70%) from **23b**.

The Physical and Spectroscopic Data for 1b–32c. 1b: oven temperature 130 °C (5 torr); ^1H NMR ($CDCl_3$) δ 4.48–4.27 (m, 1 H), 3.16 (s, 4 H), 2.00–0.87 (br, 13 H). **1c**: mp 74–76 °C; ^1H NMR ($CDCl_3$) δ 7.66–7.20 (m, 5 H), 5.07 (s, 1 H), 3.17–2.76 (m, 4 H), 2.31–1.66 (m, 2 H). **4b**: oven temperature 210 °C (6 torr); ^1H NMR ($CDCl_3$) δ 7.13 (s, 5 H), 4.73–4.63 (d, 1 H), 3.06 (s, 4 H), 3.25–2.70 (m, 1 H), 1.47–1.37 (d, 3 H). **5b**: oven temperature 210 °C (3 torr); ^1H NMR ($CDCl_3$) δ 6.00–5.40 (m, 1 H), 5.07–4.70 (m, 2 H), 4.38 (t, 1 H), 3.16 (s, 4 H), 2.20–1.17 (br, 16 H). **6b**: oven temperature 160 °C (3 torr); ^1H NMR ($CDCl_3$) δ 7.53–7.03 (br, 5 H), 5.52 (s, 1 H), 3.33 (s, 4 H). **6c**: mp 74 °C (from cyclohexane); ^1H NMR ($CDCl_3$) δ 7.66–7.20 (m, 5 H), 5.07 (s, 1 H), 3.17–2.76 (m, 4 H), 2.31–1.66 (m, 2 H). **7b**: mp 59 °C (from hexane); ^1H NMR ($CDCl_3$) δ 7.47–6.90 (q, 4 H), 5.57 (s, 1 H), 3.36 (d, 4 H), 2.30 (s, 3 H). **8b**: mp 58 °C; ^1H NMR ($CDCl_3$) δ 7.16 (s, 5 H), 6.42 (d, 1 H), 6.02 (q, 1 H), 5.10 (d, 1 H), 3.28 (s, 4 H). **8c**: oven temperature 180 °C (2 torr); ^1H NMR ($CDCl_3$) δ 7.20 (s, 5 H), 7.66 (d, 1 H), 6.10 (q, 1 H), 3.00–2.73 (m, 4 H), 2.20–1.60 (m, 2 H). **9b**: oven temperature 120 °C (5 torr); ^1H NMR ($CDCl_3$) δ 5.70–5.33 (m, 2 H), 4.85 (d, 1 H), 3.15 (s, 4 H), 1.67 (d, 3 H). **10b**: mp 198 °C; ^1H NMR ($CDCl_3$) δ 7.30 (s, 4 H), 5.48 (s, 2 H), 3.35 (m, 8 H). **11b**: mp 119 °C; ^1H NMR ($CDCl_3$) δ 7.40–7.20 (q, 4 H), 5.50 (s, 1 H), 3.00 (m, 4 H). **12b**: oven temperature 140 °C (2 torr); ^1H NMR ($CDCl_3$) δ 7.27 (d, 2 H), 6.75 (d, 2 H), 5.50 (s, 1 H), 3.70 (s, 3 H), 3.35 (m, 4 H). **13b**: mp 63 °C (from cyclohexane); ^1H NMR ($CDCl_3$) δ 8.10–7.10 (m, 4 H), 6.10 (s, 1 H), 3.40 (s, 4 H). **14b**: mp 116 °C; ^1H NMR ($CDCl_3$) δ 7.50–6.55 (q, 4 H), 5.54 (s, 1 H), 4.90 (br, 1 H), 3.36 (m, 4 H). **15b**: mp 107 °C; ^1H NMR ($CDCl_3$) δ 7.42–6.45 (q, 4 H), 5.57 (s, 1 H), 3.40 (d, 4 H), 2.89 (s, 6 H). **16b**: mp 166 °C (from CCl_4); ^1H NMR ($CDCl_3$) δ 8.70–8.40 (br, 1 H), 8.07–7.50 (q, 4 H), 5.66 (s, 1 H), 3.52 (d, 4 H). **17b**: oven temperature 220 °C (12 torr); ^1H NMR ($CDCl_3$) δ 8.55 (d, 1 H), 8.37 (d of d, 1 H), 7.78 (d of t, 1 H), 7.10 (t, 1 H), 5.53 (s, 1 H), 3.39 (m, 4 H). **18b**: oven temperature 110 °C (5 torr); ^1H NMR ($CDCl_3$) δ 7.23 (t, 1 H), 6.14 (d, 2 H), 5.50 (s, 1 H), 3.29 (s, 4 H). **19b**: oven temperature 125 °C (3 torr); ^1H NMR ($CDCl_3$) δ 7.80–6.97 (m, 5 H), 3.33 (s, 4 H), 2.10 (s, 3 H). **20b**: oven temperature 130 °C (3 torr); ^1H NMR ($CDCl_3$) δ 3.23 (s, 4 H), 2.17–1.33 (br, m, 10 H). **21b**: oven temperature 230 °C (15 torr); ^1H NMR ($CDCl_3$) δ 7.40–7.03 (m, 10 H), 3.18 (s, 4 H), 2.72 (s, 4 H). **22b**: mp 105 °C; ^1H NMR ($CDCl_3$) δ 7.63–7.06 (m, 10 H), 3.35 (s, 4 H). **23b**: oven temperature 140 °C (3 torr); ^1H NMR ($CDCl_3$) δ 3.33–3.00 (m, 4 H), 2.63–0.83 (m, 16 H). **28b**:[20] mp 95 °C; ^1H NMR ($CDCl_3$) δ 7.85–7.37 (q, 4 H), 5.55 (s, 1 H), 3.37 (d, 4 H), 2.54 (s, 3 H). **28c**:[20] mp 140 °C; ^1H NMR ($CDCl_3$) δ 7.83–7.30 (q, 4 H), 5.03 (s, 1 H), 3.17–2.80 (m, 4 H), 2.50 (s, 3 H), 2.27–1.83 (m, 2 H). **29b**:[20] mp 92 °C; ^1H NMR ($CDCl_3$) δ 7.73–7.23 (m, 9 H), 5.57 (s, 1 H), 3.40 (d, 4 H). **30b**:[20] oven temperature 170 °C (2 torr); ^1H NMR ($CDCl_3$) δ 4.50–4.23 (br, 1 H), 3.16 (s, 4 H), 2.57–2.27 (m, 2 H), 2.09 (s, 3 H), 1.97–1.50 (m, 4 H). **30c**:[20] oven temperature 220 °C (5 torr); ^1H NMR ($CDCl_3$) δ 4.13–3.80 (m, 1 H), 3.00–2.59 (m, 4 H), 2.59–2.17 (m, 2 H), 2.05 (s, 3 H), 2.03–1.57 (m, 6 H). **31b**:[20] oven temperature 180 °C (2 torr); ^1H NMR ($CDCl_3$) δ 7.17 (br, s, 5 H), 4.03 (q, 1 H), 3.40–3.00 (m, 5 H), 2.87–2.47 (m, 2 H), 2.20–1.90 (m, 2 H), 2.00 (s, 3 H). **31c**:[20] oven temperature 240 °C (3 torr); ^1H NMR ($CDCl_3$) δ 7.11 (s, 5 H), 3.33–2.74 (m, 2 H), 2.89–2.54 (m, 6 H), 1.97 (s, 3 H), 2.23–1.61 (m, 4 H). **32b**:[20] oven temperature 220 °C (2 torr); ^1H NMR ($CDCl_3$) δ 7.97–7.30 (m, 5 H), 4.82 (d, 1 H), 3.87–3.40 (m, 1 H), 3.20 (s, 4 H), 1.38 (d, 3 H). **32c**:[20] oven temperature 240 °C (1 torr); ^1H NMR ($CDCl_3$) δ 8.00–7.27 (m, 5 H), 4.37 (d, 1 H), 4.07–3.88 (m, 1 H), 2.97–2.67 (m, 4 H), 2.13–1.57 (m, 2 H), 1.33 (d, 3 H).

Registry No. **1a**, 111-71-7; **1b**, 6008-84-0; **1c**, 26958-42-9; **2**, 540-63-6; **3**, 109-80-8; **4a**, 93-53-8; **4b**, 83521-78-2; **5a**, 112-45-8; **5b**, 101033-01-6; **6a**, 100-52-7; **6b**, 5616-55-7; **6c**, 5425-44-5; **7a**, 104-87-0; **7b**, 23229-29-0; **8a**, 104-55-2; **8b**, 5616-58-0; **8c**, 26958-41-8; **9a**, 4170-30-3; **9b**, 61685-38-9; **10a**, 623-27-8; **10b**, 69922-37-8; **11a**, 104-88-1; **11b**, 23229-32-5; **12a**, 123-11-5; **12b**, 6712-20-5; **13a**, 552-89-6; **13b**, 101033-02-7; **14a**, 123-08-0; **14b**, 22068-49-1; **15a**, 100-10-7; **15b**, 31362-12-6; **16a**, 619-66-9; **16b**, 101033-03-8; **17a**, 500-22-1; **17b**, 101033-14-1; **18a**, 98-01-1; **18b**, 6008-83-9; **19a**, 98-86-2; **19b**, 5769-02-8; **20a**, 108-94-1; **20b**, 177-16-2; **21a**, 102-04-5; **21b**, 76312-47-5; **22a**, 119-61-9; **22b**, 6317-10-8; **23a**, 76-22-2; **23b**, 6787-91-3; **24a**, 123-05-7; **24b**, 101033-04-9; **25a**, 108-83-8; **26a**, 122-57-6; **27a**, 134-81-6; **28a**, 3457-45-2; **28b**, 101033-05-0; **28c**, 101033-06-1; **29a**, 20912-50-9; **29b**, 101033-07-2; **30a**, 505-03-3; **30b**, 101033-08-3; **30c**, 101033-09-4; **31a**, 75359-70-5; **31b**, 101033-10-7; **31c**, 101033-11-8; **32a**, 16837-43-7; **32b**, 101033-12-9; **32c**, 101033-13-0; $SOCl_2$, 7719-09-7; SiO_2, 7631-86-9.

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