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Useful Dethioacetalization with Soft Acid Metal Salts: Thallium Trinitrate and Mercuric Perchlorate

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Dethioacetalization with thallium trinitrate (TTN) was tried on thioacetals **3**—**13**, and good results were obtained. Then, the utility of co-solvents to be used with methanol was checked, and a wide range of co-solvents were shown to be available. The mechanism was also discussed.

Subsequently, dethioacetalization with mercuric perchlorate was found to be another excellent method. This procedure provided a great success for the dethioacetalization of compounds **4** and **11** which was not successful by the TTN procedure.

Keywords——dethioacetalization; thallium trinitrate; mercuric perchlorate; 1,3-dithianes; 1,3-dithiolanes; soft acid metal salts

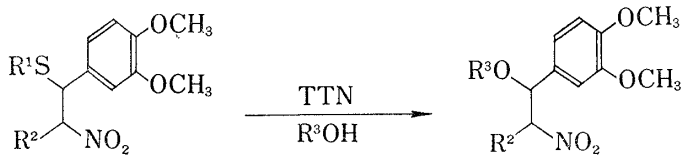
Recently, we have exploited new reactions utilizing "Soft-Soft specific affinity"[2] between trivalent thallium atom, Tl (III), and divalent sulfur atom. As a part of these investigations, we found a new reaction in which treatment of sulfides **1** with thallium trinitrate (TTN) for a short time gave ethers **2** in high yield[3] (See eq. (1)).

Table I. Dethioacetalization with TTN

Thioacetal	TTN (Mol Equiv.)	Solvent	Temp. (°C)	Time (min)	Yield (%)[a] of parent carbonyl compound
3	2.2	MeOH–THF (3:5)	25	30	73
4	2.2	MeOH–$CHCl_3$ (10:1)	25	15	many products
5	2.2	MeOH–ether (2:1)	25	5	98
6[4]	2.8	MeOH–THF (5:1)	25	30	82
7[5]	2.4	MeOH–THF (10:1)	25	5	99
8[6]	7[b]	MeOH–THF (8:1)	50	30	75
9	2.2	MeOH–ether (7:3)	25	5	77[c]
9	1.1	MeOH–ether (7:3)	25	5	79[d]
10	1.1	MeOH–$CHCl_3$ (1:1)	25	15	82
11	2.2	MeOH–$CHCl_3$ (1:1)	25	60	5 products[e]
12	2.2	MeOH–$CHCl_3$ (1:1)	25	5	83
13	2.2	MeOH–$CHCl_3$ (6:5)	25	5	82

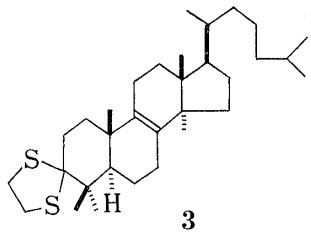
a) Isolated yield.
b) A large steric hindrance may be involved.
c) Diphenyl disulfide was obtained in 43% yield.
d) Diphenyl disulfide was obtained in 87% yield.
e) A spot whose *Rf* is identical with that of the parent aldehyde was recognized together with other four spots on TLC.

1) Location: *Uji, Kyoto-Fu, 611, Japan.*
2) R.G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963); T.-L. Ho, *Chem. Rev.*, **75**, 1 (1975).
3) Y. Nagao, K. Kaneko, M. Ochiai, and E. Fujita, *J. Chem. Soc. Chem. Commun.*, **1976**, 202.
4) E. Fujita, T. Fujita, K. Fuji, and N. Ito, *Tetrahedron*, **22**, 3423 (1966).
5) E. Fujita, T. Fujita, H. Katayama, and Y. Nagao, *Tetrahedron*, **25**, 1335 (1969).
6) T. Kubota, T. Matsuura, T. Tsutsui, S. Uyeo, H. Irie, A. Numata, T. Fujita, and T. Suzuki, *Tetrahedron*, **22**, 1659 (1966).



1 2 (1)

Application of this reaction to several thioacetals, compounds **3**—**13**, led to a useful way for their dethioacetalization.[7] The reaction conditions and the results are shown in Table I.



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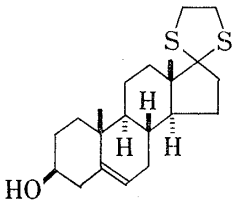

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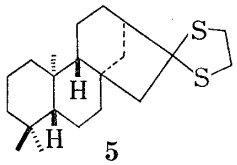

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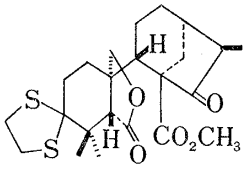

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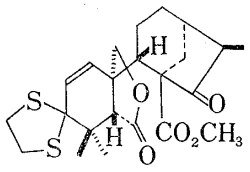

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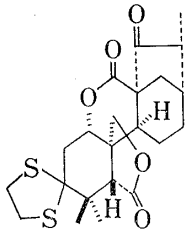

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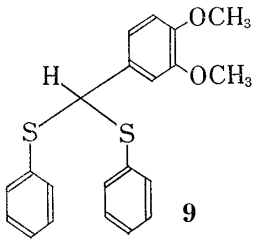

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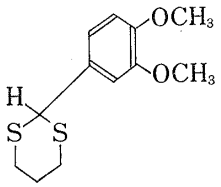

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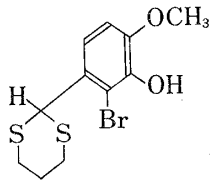

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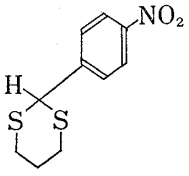

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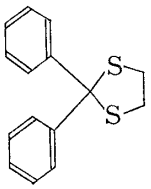

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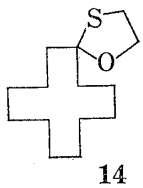

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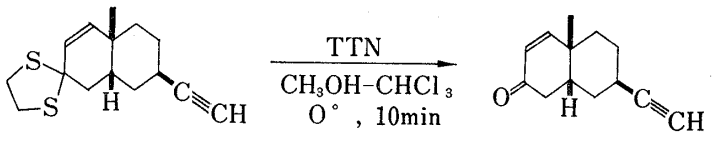
In this reaction, such functional groups as active methylene and methyne, ketone, ester, and lactone were not damaged at all (*cf.* compounds **6**, **7**, and **8**). The aromatic moiety was safe except for phenol **11**. Furthermore, also with compound **5** having the [3.2.1]bicyclooctane ring which was subject to a ring rearrangement,[8] the reaction proceeded smoothly to give the expected parent ketone in good yield. Thallium trinitrate has been known to react easily with olefins in methanol.[9] The reactions with olefinic dithioacetals, **3** and **7**, however,

7) The reactions with compounds **3**—**13** have been reported as a preliminary communication. See E. Fujita, Y. Nagao, and K. Kaneko, *Chem. Pharm. Bull.* (Tokyo), **24**, 1115 (1976).
8) *cf.* E. Fujita, T. Fujita, and Y. Nagao, *Tetrahedron*, **28**, 555 (1972) and references cited therein.
9) A. McKillop and E.C. Taylor, *Chem. in Britain*, **9**, 4 (1973).

were successful, although compound **4** on this reaction gave an inseparable complex mixture. It has been known that thallium (III) salts on the reactions with phenolic compounds gave quinoid products.[9] As described above, the reaction with compound **11** was unsuccessful showing five spots of the products on TLC, although one of these seemed to be the desired parent aldehyde. Dethioacetalizations with compounds **4** and **11**, however, were successful in the use of mercuric perchlorate instead of TTN (*vide infra*).

This useful dethioacetalization with TTN developed by us has also been successfully used for dithioacetal compound containing a triple bond. Thus, Harayama *et al.*[10] used our deacetalization procedure on dithioacetal **15** to give chamaecynone (**16**) in 73% yield (See eq. (2)).

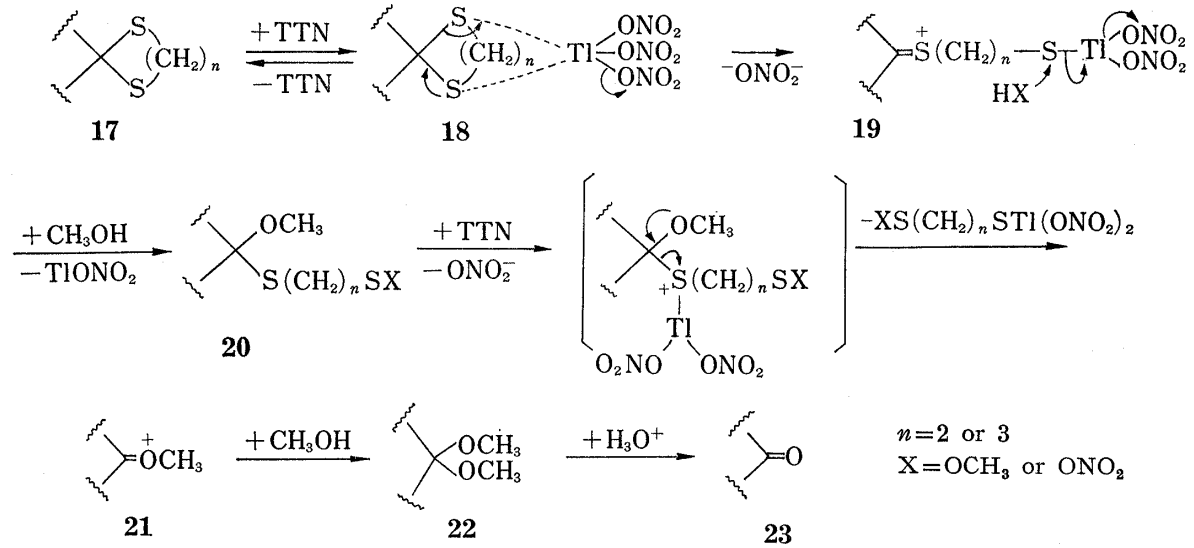


15 **16** (2)

Table II.[a] Dethioacetalization of Compound **7** with TTN in MeOH and Co-solvents Other than Those in Table I

Solvent		TTN (Mol Equiv.)	Reaction time (min)	Yield (%)[b] of parent carbonyl compound
MeCN–MeOH	(1:10)	2.4	10	94
DMF–MeOH	(4:1)	2.4	30	87
$MeCO_2Et$–MeOH	(4:1)	5	10	95
DMSO–MeOH	(4:1)	2.4	120	31[c]
DMSO–MeOH	(4:1)	12	30	72[d]

a) All reactions were performed at room temperature.
b) Isolated yield.
c) 51% recovery.
d) 23% recovery.



17 **18** **19** **20** **21** **22** **23**

Chart 1

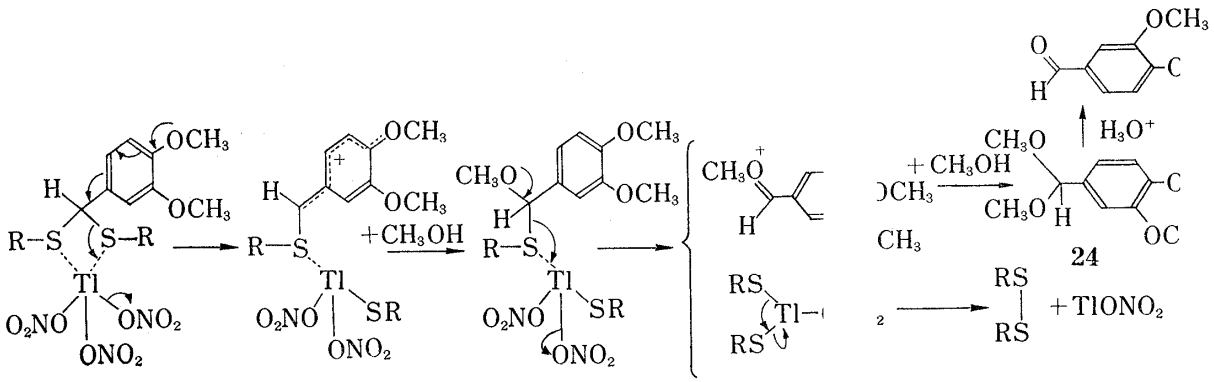
10) T. Harayama, H. Cho, and Y. Inubushi, *Tetrahedron Lett.*, **1977**, 3273; *idem*, *Chem. Pharm. Bull.* (Tokyo), **26**, 1201 (1978).

Subsequently, the utility of co-solvents to be used with methanol was checked by the reactions with dithioacetal **7**. The results are shown in Table II.

Thus, methanol alone or combinations of methanol with chloroform, tetrahydrofuran, ether, acetonitrile, and dimethylformamide, respectively, are shown to be useful in this reaction. In the use of ethyl acetate or dimethylsulfoxide as the cosolvent, an icreased amount of TTN was required, but the reaction was performed giving the satisfactory yield. The availability for such a wide range of solvents is an advantage of this reaction.

On treatment of dithioacetal **7** with 1.2 mol equivalent of TTN for 30 minutes, the reaction was found on TI nother 1.2 mol equivalent of TTN to this mixture i The same ol was obtained also in the case c ts of TTN a: ces- sary for dethioacetalization of these dithioacetals. We believe the pathwa d in Chart 1 to be reasonable.

On the other hand, the reactions for compounds **9** and **10** completed with 1.1 mol equivalent of TTN (See Table I). The mechanism for these cases must be as shown in Chart 2. The propriety of this mechanism was supported by the fact that the reaction of compound **12** with 1.1 mol equivalent of TTN proceeded only half and the further addition of another 1.1 mol equivalent of TTN completed the reaction.



$R = C_6H_5$ or R, $R = -(CH_2)_3-$

Chart 2

The reaction of compound **9** with 1.1 mol equivalent of TTN in the presence of equivalents of diisopropylamine as the nitric acid trapper yielded dimethyl acetal **24**. ' fact is not only supporting the rationality for the intermediacy of **22** and **24** shown in C 1 and 2, but shows that dethioacetalization for the acid-sensitive thioacetals should be ca out under the presence of an amine.

Previously Ho and Wong[11] carried out the dethioacetalization of simple 1,3-dithio and 1,3-dithiane derivatives with thallium tris(trifluoroacetate) (TTFA), $Tl(CF_3COO)_3$, u mild conditions, and got their parent carbonyl compounds in good yields. Compariso ours with their method indicated the following advantages for the former: 1) TTN is n cheaper and more easily available than TTFA. 2) The reaction mixture is generally colo and transparent in our case, while it is brownish in their case. Hence, the end point o reaction is more easily and clearly judged by the white precipitation of $TlONO_2$ in our met compared with their observation of the end point as the formation of emulsion. 3) method can be used for the compounds having functional groups (especially an alipl double bond) by the use of the suitable mol equivalents of the reagent, although it is not ex known in their case where only simple ketones and aldehydes were tested. 4) The wat

11) T.-L. Ho and C.M. Wong, *Can. J. Chem.*, **50**, 3740 (1972).

crystallization in TTN is available for the hydrolysis of the dimethyl acetals in the final step of the reaction.

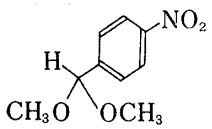
In general, the dethioacetalization with TTN has these superior features, but still some limitations for this method are recognized as described above. Thus, mercuric perchlorate (MPC), $Hg(ClO_4)_2 \cdot 3H_2O$, in which mercury has the isoelectronic structure of thallium (III) and is more soft acid metal than thallium (III) (hence expected to have more specific activity than thallium to the sulfur atom),[9,12] was explored for dethioacetalization. Treatment of dithioacetals with 2.2 mol equivalents of MPC in methanol or tetrahydrofuran at room temperature gave their parent carbonyl compounds in good yields (See Table III). In the use of 1.1 mol equivalent of MPC, only a half reaction proceeded. From this fact, the reaction mechanism is regarded as the same as in the reaction with TTN as shown in Chart 1. In the reaction of **12** in a mixture of methanol and dichloromethane, dimethyl acetal **25** was obtained in 96% yield. The acetal on treatment with acid gave the parent aldehyde in 92% yield. But the reaction in a mixture of tetrahydrofuran chloroform directly gave the parent aldehyde in 91% yield.

Table III. Dethioacetalization with MPC[a]

Thioacetal	Solvent		Yield (%)[b] of parent carbonyl compound
3	$MeOH-CHCl_3$	(4:3)	83
4	$MeOH-CHCl_3$	(4:3)	77
6	$MeOH-CHCl_3$	(2:1)	77
7	$MeOH-CHCl_3$	(1:1)	93
7	THF		91
8	MeOH–THF	(2:1)	96
10	$MeOH-CH_2Cl_2$	(5:3)	86
11	$MeOH-CHCl_3$	(3:5)	93
12	$MeOH-CH_2Cl_2$	(5:3)	88[c]
12	$THF-CHCl_3$	(1:1)	91
13	$MeOH-CHCl_3$	(4:3)	75
14[d]	$THF-CHCl_3$	(1:1)	95

a) All reactions were carried out at 25° for 5 min using 2.2 mol equivalents of MPC.
b) Isolated yield.
c) Overall yield.
d) In this case, only 1.1 mol equivalent of MPC is enough.

It is noteworthy that the MPC procedure provided a great success for the dethioacetalization of compounds **4** and **11** which was not successful by the TTN procedure. It may be due to the more soft character of MPC[Hg(II)] than TTN [Tl(III)] *i.e.* the more powerful specific affinity[12] of the former to a sulfur atom, and also to the lower oxidation ability[13] of the former which prevents the undesirable side reaction. Furthermore, dethioacetalization of compound **8** with TTN required an excess reagent (7 mol equivalents) under warming for 30 minutes to give 75% yield of the parent ketone, while that with MPC proceeded by



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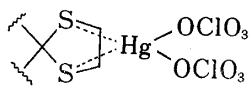

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12) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
13) Compare the standard redox potential of ($Tl^{3+}+2e \rightarrow Tl^{+}$): −1.25 V to that of ($Hg^{2+}+2e \rightarrow Hg$): −0.85 V.

only a stoichiometric amount of the reagent at room temperature for 5 minutes to give 96% yield of the product. This significant difference between two methods may be attributed to not only the more soft character of Hg(II) but its smaller size than Tl(III), which is more profitable for forming the transition state **26** than that in the case of TTN.

As the Hg(II) salts, $Hg(OAc)_2$,[14] $HgCl_2$–HgO,[14] $HgCl_2$–$CdCO_3$,[14] and HgO–BF_3 etherate[15] have been used for dethioacetalization hitherto. In comparison with these procedures, which have sometimes such weak points as low yield of the product, necessity of the co-reagent (s), and heterogeneity of the medium at least in the beginning of the reaction, the MPC method has the following characteristic advantages: 1) The reaction is completed within 5 minutes at room temperature. 2) The use of 2 mol equivalents of MPC does not give any damage to other functional groups. 3) The reaction is done under a homogeneous condition, because MPC is soluble in methanol and tetrahydrofuram. 4) The reaction is easily moniored by a change of the initial colorless transparent solution into an emulsion. 5) The water of crystallization in MPC is employed profitably, hence the original addition of water is not necessary. 6) Several combinations of methanol or tetrahydrofuran with other solvents are available.

The foregoing two procedures using TTN or MPC based on the Hard Soft Acids and Bases Principle[2] provide the excellent methods of dethioacetalization and are expected to be utilized for the development of the novel reactions of the organosulfur compounds and the synthesis of the complex natural products.

Experimental

Melting points were determined with a Yanagimoto microapparatus and uncorrected. IR spectra were measured in KBr discs on a Hitachi model EPI-S2 spectrophotometer. PMR spectra were taken with a Varian T-60 spectrometer in $CDCl_3$; signals were reported in ppm from TMS as internal standard. MS were determined on a JEOL model JMS-OISG double-focusing mass spectrometer. Extracts were dried over anhydrous Na_2SO_4. A mixture of Kieselgel 60 (70—230 mesh) (Merck) and silisic acid (Mallinckrodt) (4: 1) or neutral alumina (Woelm) was used for column chromatography. Thin-layer chromatography (TLC) plates were coated with Silica gel G nach Stahl (Merck). Thallium trinitrate ($Tl(ONO_2)_3 \cdot 3H_2O$) and Mercuric perchlorate ($Hg(OClO_3)_2 \cdot 3H_2O$) were purchased from Mitsuwa Chemicals Co., Ltd., Kyoto Japan. Dehydroepiandrosterone, veratraldehyde, *p*-nitrobenzaldehyde, and benzophenone were purchased from Nakarai Chemicals Co., Ltd., Kyoto Japan.

Dithioacetal 3——Lanosterol (2.4 g) was hydrogenated on Adam's catalyst in MeOH (5 ml) to give dihydrolanosterol (2.4 g) as needles, 2.2 g of which on Jones oxidation in acetone gave dihydrolanosterone (1.95 g, 88% yield) as plates, mp 118—119° (from CH_2Cl_2–MeOH). *Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.19; H, 11.95. IR ν_{max}: 1700 cm^{-1}. To a solution of dihydrolanosterone (400 mg) in $CHCl_3$ (10 ml) were added small excess of ethanedithiol and BF_3-etherate (47%) (0.4 ml). The mixture was stirred overnight at room temperature, then poured into aq. Na_2CO_3 containing ice and extracted with CH_2Cl_2. The usual work-up of the CH_2Cl_2 extract gave crude crystals (415 mg, 88%) which were purified by chromatography and recrystallization to give dithioacetal 3 (218 mg, 46%) as needles, mp 142—143°. (from $CHCl_3$–MeOH). *Anal.* Calcd. for $C_{32}H_{54}S_2$: C, 76.44; H, 10.83; M, 502. Found: C, 76.59; H, 10.84; M^+ *m/e*: 502. IR ν_{max}: 1635, 1465, 1388, 1370 cm^{-1}. NMR δ: 3.22 (4H, s).

Dithioacetal 4——To a solution of dehydroepiandrosterone (750 mg) in anhydrous $CHCl_3$ (20 ml) were added ethanedithiol (294 mg) and BF_3-etherate (1 ml) under ice-cooling. After stirring for 2 hr at room temperature, the reaction mixture on usual work-up yielded dithioacetal 4 (632 mg, 67%) as colorless needles, mp 165—167° (from CH_2Cl_2–MeOH). *Anal.* Calcd. for $C_{21}H_{32}OS_2$: C, 69.20; H, 8.85; M, 364.189. Found: C, 68.91; H, 8.98; M^+ *m/e*: 364.188. IR ν_{max} 3610 cm^{-1}. PMR δ: 0.95, 1.03, (each 3H, s), 1.84 (1H, s, OH, disappeared with D_2O), 3.21, 3.24 (each 2H, s, –S–$C\underline{H}_2$–$C\underline{H}_2$–S–), 5.36 (1H, broad d, J=5 Hz, C-6-H).

Dithioacetal 5——To a solution of ent-16-oxokaurane (274 mg)[16] in anhydrous $CHCl_3$ (20 ml) were added ethanedithiol (0.2 ml) and BF_3-etherate (0.2 ml). Then, the mixture was stirred at room temperature for 1 hr. The usual treatment of the reaction mixture afforded dithioacetal 5 (260 mg, 74%) as colorless plates, mp 133—134° (from $CHCl_3$–MeOH). *Anal.* Calcd. for $C_{21}H_{34}S_2$: C, 71.96; H, 9.78. Found: C, 71.72; H, 9.82. PMR δ: 0.80, 0.87, 1.03 (each 3H, s), 3.25 (4H, m, –S–$C\underline{H}_2$–$C\underline{H}_2$–S–).

14) E.J. Corey and B.W. Erickson, *J. Org. Chem.*, **36**, 3553 (1971).
15) E. Vedejs and P.L. Fucks, *J. Org. Chem.*, **36**, 366 (1971).
16) F.G. Jiménez, M.C. Perezamador, S.E. Flores, and J. Herrán, *Tetrahedron Lett.*, **1965**, 621.

Dithioacetal 7[5]——To a solution of enonoic acid methylester[5] (2 g) in anhydrous $CHCl_3$ (20 ml), ethanedithiol (750 mg) and BF_3-etherate (2 ml) were added under ice-cooling. After stirring at room temperature for 24 hr, usual work-up of the reaction mixture gave dithioacetal **7** (1.509 g, 87%) as colorless needles, mp 191—192° (from CH_2Cl_2–MeOH). *Anal.* Calcd. for $C_{23}H_{30}O_5S_2$: C, 61.32; H, 6.71. Found: C, 61.24, H, 6.74. IR ν_{max} 1773, 1741, 1717 cm^{-1}. PMR δ: 1.10 (3H, d, J=6.5 Hz, C-15-H_3) 1.15, 1.49 (each 3H, s), 2.76 (1H, s, C-5-H), 3.10—3.52 (4H, m, –S–C$\underline{H}_2$–C$\underline{H}_2$–S–), 3.77 (3H, s, –COOCH_3) 3.90, 4.11 (2H, AB type, J=10 Hz, C-20-H_2), 5.62, 6.11 (each 1H, AB type, J=10 Hz, –C$\underline{H}$=C$\underline{H}$–).

Dithioacetal 8[6]——To a solution of bisdehydrodihydroenmein (270 mg) in anhydrous $CHCl_3$ (10 ml) were added ethanedithiol (0.5 ml) and BF_3-etherate (0.5 ml). The mixture was stirred at room temperature for 2 days. Then, usual work-up gave dithioacetal **8** (215 mg, 66%) as colorless needles, mp 252—254° (from $CHCl_3$–MeOH) (lit.[6] 242—245°). *Anal.* Calcd. for $C_{22}H_{28}O_5S_2$: C, 60.54; H, 6.47. Found: C, 60.30; H, 6.50. IR ν_{max} 1775 (infl), 1765, 1725 cm^{-1}. PMR δ: 1.15 (3H, d, J=7 Hz, C-15-H_3) 1.30, 1.51 (each 3H, s), 3.36 (4H, broad, s, –S–C$\underline{H}_2$–C$\underline{H}_2$–S–), 4.35, 4.09 (2H, AB type, J=10 Hz, C-20-H_2), 4.76 (1H, q, J=11, 7 Hz, C-1-H).

Dithioacetal 9——To a solution of veratralaldehyde (2.685 g) in dry $CHCl_3$ (30 ml) were added benzenethiol (4.229 g) and BF_3-etherate (5 ml) under ice-cooling. The mixture was stirred at *ca.* 0° for 10 min and then poured into some ice-water. Usual work-up of the mixture gave dithioacetal **9** (5.127 g, 86%) as colorless needles, mp 63—64° (from $CHCl_3$–MeOH). *Anal.* Calcd. for $C_{21}H_{20}O_2S_2$: C, 68.47; H, 5.47. Found: C, 68.24; H, 5.37. IR ν_{max} 1583, 1512 cm^{-1}. NMR δ: 3.71, 3.73 (each 3H, s), 5.27 (1H, s), 6.67—6.87 (3H, m), 7.00—7.49 (10H, m).

Dithioacetal 10——To a solution of veratraldehyde (2 g) in anhydrous $CHCl_3$ (50 ml) were added 1,3-propanedithiol (1.56 g) and BF_3-etherate (1 ml) under ice-cooling. The mixture was stirred at room temperature for 2 hr and then usual work-up gave a crude solid, whose purification on silica gel column yielded dithioacetal **10** (2.88 g, 94%) as colorless needles, mp 83—84° (from CH_2Cl_2–MeOH). *Anal.* Calcd. for $C_{12}H_{16}O_2S_2$: C, 56.24; H, 6.29; M, 256. Found: C, 56.00; H, 6.33; M^+ *m/e*: 256. IR ν_{max} 1602, 1587, 1260, 1138, 1019 cm^{-1}. NMR δ: 1.69—2.36 (2H, m, –S–CH_2–C$\underline{H}_2$–CH_2–S–), 2.85—3.16 (4H, m, –S–C$\underline{H}_2$–CH_2–C$\underline{H}_2$–S–), 3.87, 3.90 (each 3H, s, –O–CH_3), 5.14 (1H, s, $\begin{matrix}-S\diagdown\\ \quad\ CH-\\ -S\diagup\end{matrix}$), 6.70—7.16 (3H, m).

Dithioacetal 11——To a solution of 2-bromoisovanillin (1 g) in anhydrous CH_2Cl_2 (200 ml) were added 1,3-propanedithiol (514 mg) and BF_3-etherate under ice-cooling. After stirring at room temperature for 1 hr, usual work-up of the reaction mixture gave a colorless solid, which was chromatographed on silica gel column by CH_2Cl_2 to give dithioacetal **11** (1.3 g, 95%) as colorless needles, mp 198—199.5° (from CH_2Cl_2–MeOH). *Anal.* Calcd. for $C_{11}H_{13}BrO_2S_2$: C, 41.13; H, 4.05; M, 321. Found: C, 40.89; H, 4.06; M^+ *m/e*: 322 and 320. IR ν_{max}: 1602, 1487, 1288, 1034 cm^{-1}. NMR δ: 1.85—2.37 (2H, m, –S–CH_2–C$\underline{H}_2$–CH_2–S–), 2.62—3.33 (4H, m, –S–C$\underline{H}_2$–CH_2–C$\underline{H}_2$–S), 3.90 (3H, s, –O–CH_3), 5.56 (1H, s, $\begin{matrix}-S\diagdown\\ \quad\ CH-\\ -S\diagup\end{matrix}$), 6.02 (1H, broad s, $1/2W$=3 Hz, OH, disappeared with D_2O), 6.82, 7.22 (2H, AB type, J=8 Hz, C-5-H, C-6-H).

Dithioacetal 12——To a solution of 4-nitrobenzaldehyde (2 g) in anhydrous $CHCl_3$ (50 ml) were added 1,3-propanedithiol (1.72 g) and BF_3-etherate (1 ml) under ice-cooling. After stirring at room temperature for 1 hr, the reaction mixture was poured into some ice-water. Usual work-up afforded a pale yellow crude product which was purified on silica gel column by CH_2Cl_2 to give dithioacetal **10** (2.66 g, 83%) as pale yellow needles, mp 144—145° (from CH_2Cl_2–MeOH). *Anal.* Calcd. for $C_{10}H_{11}NO_2S_2$: C, 49.79; H, 4.60; N, 5.81; M, 241. Found: C, 49.55; H, 4.72; N, 5.70; M^+ *m/e*: 241. IR ν_{max}: 1601, 1514, 1489, 1350, 1342 cm^{-1}. NMR δ: 1.74—2.51 (2H, m, –S–CH_2–C$\underline{H}_2$–CH_2–S–), 3.04 (4H, dd, J=9 Hz, 4 Hz, –S–C$\underline{H}_2$–CH_2–C$\underline{H}_2$–S–), 5.23 (1H, s, $\begin{matrix}-S\diagdown\\ \quad\ CH-\\ -S\diagup\end{matrix}$), 7.63, 8.17 (4H, AB type, J=9 Hz, C-2-H, C-3-H).

Dithioacetal 13——To a solution of benzophenone (1 g) in anhydrous $CHCl_3$ (8 ml) were added ethanedithiol (600 mg) and BF_3-etherate (0.5 ml). After stirring at room temperature for 2 days, the reaction mixture was treated as usual to give crude crystals, which were recrystallized from $CHCl_3$–MeOH to afford dithioacetal **13** (1.004 g, 71%) as colorless prism, mp 104—105°. *Anal.* Calcd. for $C_{15}H_{14}S_2$: C, 69.75; H, 5.46. Found: C, 69.54; H, 5.24. IR ν_{max}: 1592, 1482, 1445 cm^{-1}. NMR δ: 3.40 (4H, s, –S–C$\underline{H}_2$–C$\underline{H}_2$–S–), 7.08—7.73 (10H, m).

Monothioacetal 14——To a solution of cyclododecanone (1 g) in anhydrous $CHCl_3$ (20 ml) were added 2-mercaptoethanol (943 mg) and BF_3-etherate (0.5 ml) under ice-cooling. After addition of $CaCl_2$ (100 mg), the mixture was stirred at room temperature for 5 hr. Usual treatment gave an oil, whose purification on a short silica gel column afforded monothioacetal **14** (995 mg, 75%) as colorless needles, mp 33° (from $CHCl_3$). *Anal.* Calcd. for $C_{14}H_{26}OS$: M, 242.170. Found: M^+ *m/e*: 242.170. NMR δ: 3.06 (2H, t, J=6 Hz, –O–CH_2–C$\underline{H}_2$–S–), 4.14 (2H, t, J=6 Hz, –O–C$\underline{H}_2$–CH_2–S–).

General Procedures for Dethioacetalization Using TTN——(1) A colorless solution of TTN (279 mg, 2.2 mol equiv) in MeOH (2 ml) was dropwise added to a solution of dithioacetal **5** (100 mg) in MeOH (4 ml)–

ether (3 ml) under stirring. Stirring was maintained for 5 min at 25° after complete addition. In the course of this time, a white crystalline precipitate ($TlONO_2$) appeared. The precipitate was filtered off and the filtrate was evaporated *in vacuo* to give a solid residue, which was extracted with $CHCl_3$ after addition of water. The extract was washed with some brine, dried, and evaporated *in vacuo* to afford the parent ketone[16] (87 mg, 98%) as colorless needles, mp 118—120° (from $CHCl_3$–MeOH) (lit.[16] 116—117°).

The white crystalline precipitate was confirmed to be thallium (I) nitrate ($TlONO_2$) by the following evidence: i) mp (205—206°) was identical with that of the authentic sample. ii) The aqueous solution was negative for the iodostarch reaction. iii) Addition of 35% HCl to the aqueous solution gave white precipitate of TlCl. iv) *Anal.* Calcd. for $TlNO_3$: N, 5.25. Found: N, 5.26.

(2) To a solution of dithioacetal **10** (100 mg) in $CHCl_3$ (3 ml) was dropwise added a solution of TTN (191 mg, 1.1 mol equiv) in MeOH (3 ml). The mixture was stirred at room temperature for 15 min. The white crystalline precipitate was filtered off and the filtrate was treated as usual to give the parent aldehyde (53 mg, 82%) as colorless needles, mp 43° (from $CHCl_3$–MeOH) (lit.[17] 42.5—43.5°).

Investigations for the Stoichiometry on the Dethioacetalization with TTN——(1) To a solution of dithioacetal **7** (100 mg) in MeOH (8 ml)–THF (1 ml) was dropwise added a solution of TTN (119 mg, 1.2 mol equiv.) in MeOH (2 ml). After the mixture was stirred at 25° for 30 min, TLC of the reaction mixture showed the presence of two spots of the starting dithioacetal **7** and the parent ketone in almost equal amounts. Further addition of TTN (119 mg) in MeOH (2 ml) to this reaction mixture made this dethioacetalization complete immediately. Usual treatment of the reaction mixture afforded the parent ketone (80 mg, 96%) as colorless needles, mp 251° (from $CHCl_3$–MeOH).

(2) To a solution of dithioacetal **3** (100 mg) in ether (10 ml)–MeOH (4 ml) was dropwise added a solution of TTN (98 mg, 1.1 mol equiv.) in MeOH (1 ml). When the mixture was stirred at 25° for 2 hr, the reaction was shown on TLC to proceed approximately half. Further addition of another 1.1 mol equiv. of TTN (98 mg) in MeOH (1 ml) immediately completed the reaction (TLC analysis). Then, a usual work-up yielded the parent ketone (65 mg, 76%) as colorless plates, mp 118—119° (from CH_2Cl_2–MeOH).

Transacetalization from Diphenylthioacetal 9 into Dimethylacetal 24——To a solution of diphenylthioacetal **9** (200 mg) in anhydrous ether (6 ml), anhydrous MeOH (8 ml) and diisopropylamine (133 mg) was dropwise added a solution of TTN (266 mg) in anhydrous MeOH (2 ml). The mixture was stirred at room temperature for 10 min. In the course of this time, brownish color of the reaction medium changed into transparent pale yellow and then a white precipitate came out. After addition of K_2CO_3, the reaction medium was condensed *in vacuo* to one third in volume. Extraction with $CHCl_3$ after addition of water, washing with brine, drying over K_2CO_3, and evaporation *in vacuo* gave an oily residue, which was chromatographed on neutral alumina column with CH_2Cl_2 to afford an oily dimethylacetal **24** (86 mg, 75%). PMR δ: 3.33 (6H, s, $-OCH_3$ of acetal), 3.90 (6H, s, $-OCH_3$ on aromatic ring), 5.36 (1H, s, $(CH_3O)_2CH-$), 6.80—7.49 (3H, m, aromatic protons).

General Procedures for Deacetalization using MPC——(1) To a solution of dithioacetal **4** (100 mg) in $CHCl_3$ (3 ml)–MeOH (1 ml) was dropwise added a colorless solution of MPC (274 mg) in MeOH (3 ml) under stirring. From the reaction mixture, a white fine precipitate immediately came out. After 5 min at 25°, the filtrate from the precipitate was neutralized with an aqueous sodium carbonate solution, then extracted with $CHCl_3$. The $CHCl_3$ layer, after washing with brine and drying, was evaporated off *in vacuo* to leave an oily residue. Purification by passing on a short neutral alumina column (CH_2Cl_2) gave the parent ketone (61 mg, 77%) as colorless needles, mp 148—150° (from $CHCl_3$–MeOH) (lit.[18] 148°).

(2) To a solution of dithioacetal **11** (100 mg) in $CHCl_3$ (5 ml) was dropwise added a solution of MPC (312 mg) in MeOH (3 ml) under stirring. After 5 min at 25°, the filtrate from a white precipitate was treated as usual to give the parent aldehyde (67 mg, 93%) as colorless needles, mp 208—209° (from EtOH) (lit.[19] 211—212°).

Dethioacetalization of Compound 12 with MPC——(1) To a solution of dithioacetal **12** (100 mg) in CH_2Cl_2 (3 ml) was dropwise added a solution of MPC (414 mg) in MeOH (3 ml) under stirring. After 5 min at 25°, white fine precipitate was filtered off and the filtrate was immediately poured onto ice-water, then extracted with $CHCl_3$. The extract was washed with brine, dried, and evaporated *in vacuo* to give an oily residue, which was purified on neutral alumina column by CH_2Cl_2 to give dimethylacetal **25** (78 mg, 96%) as an oily product. *Anal.* Calcd. for $C_9H_{11}NO_4$: M, 197. Found: M^+ *m/e*: 197. PMR δ: 3.37 (6H, s, $2\times OCH_3$), 5.49 (1H, s, $(CH_3O)_2\underline{C}H-$), 7.64, 8.22 (4H, AB type, $J=9$ Hz, aromatic protons).

To a solution of dimethylacetal **25** (78 mg) in CH_2Cl_2 (3 ml)–water (1 ml) was added 69% $HClO_4$ (0.5 ml) under ice-cooling. After stirring at 25° for 1 hr, the reaction mixture was poured onto ice-water and then

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18) E.S. Wallis and E. Fernholz, *J. Am. Chem. Soc.*, **57**, 1504 (1935).
19) T.A. Henry and T.M. Sharp, *J. Chem. Soc.*, **1930**, 2279.

neutralized with an aqueous saturated sodium carbonate. Extraction with CH_2Cl_2, washing with brine, drying, and evaporation *in vacuo* left a pale yellow oil. Its purification on silica gel column gave *p*-nitrobenzaldehyde (55 mg, 92% from **25**, 88% in over all) as colorless needles, mp 107° (from CH_2Cl_2–MeOH).

(2) To a solution of dithioacetal **12** (100 mg) in THF (3 ml)–$CHCl_3$ (5 ml) was dropwise added a solution of MPC (414 mg) in THF (2 ml) under stirring. After 5 min at 25°, white fine precipitates were filtered off and the filtrate was allowed to the usual treatment to give *p*-nitrobenzaldehyde (57 mg, 91%) as colorless needles, mp 107° (from CH_2Cl_2–MeOH).

Simple Investigation for the Stoichiometry on the Dethioacetalization with MPC——To a solution of dithioacetal **10** (100 mg) in CH_2Cl_2 (3 ml) was dropwise added a solution of MPC (195 mg, 1.1 mol equiv.) in MeOH (3 ml) under stirring. After stirring at 25° for 30 min, the reaction was observed on TLC to proceed approximately half. Further addition of another 1.1 mol equiv of MPC (195 mg) in MeOH (3 ml) to this mixture immediately completed this reaction (TLC analysis). Usual work-up of the reaction mixture afforded the parent aldehyde (56 mg, 86%), as colorless needles, mp 44—44.5° (from CH_2Cl_2–MeOH), (lit.[17] 42.5—43.5°).

Treatment of Monothioacetal 14 with MPC——To a solution of compound **14** (100 mg) in THF (2 ml)–$CHCl_3$ (5 ml) was dropwise added a solution of MPC (200 mg) in THF (3 ml) under stirring. After 5 min at 25°, a white fine precipitate was filtered off and the filtrate was treated as usual to give the parent ketone (71 mg, 95%) as colorless prisms, mp 55—56° (from $CHCl_3$–MeOH).

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