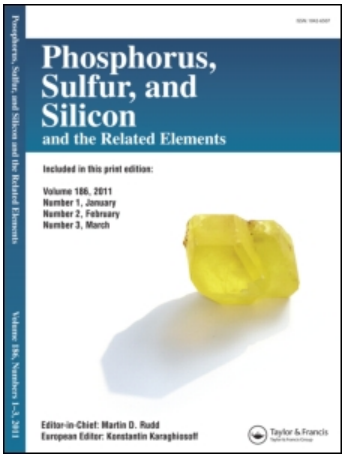

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Tellurium Tetrachloride as a Mild Deprotection Reagent for Acetals and Thioacetals

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To cite this Article Tani, Hiroyuki , Inamasu, Tokuo , Masumoto, Kazunori , Tamura, Rui , Shimizu, Hiroshi and Suzuki, Hitomi(1992) 'Tellurium Tetrachloride as a Mild Deprotection Reagent for Acetals and Thioacetals', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 261 — 266
To link to this Article: DOI: 10.1080/10426509208045846
URL: http://dx.doi.org/10.1080/10426509208045846

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 261–266
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TELLURIUM TETRACHLORIDE AS A MILD DEPROTECTION REAGENT FOR ACETALS AND THIOACETALS

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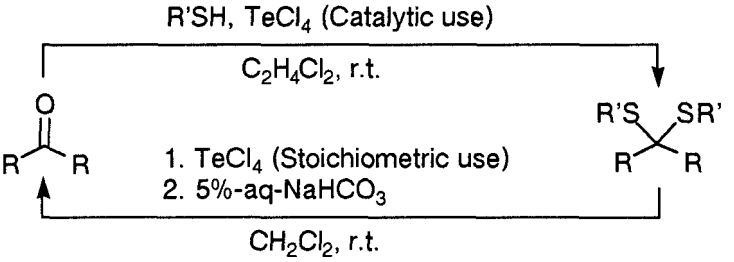
Abstract On treatment with tellurium tetrachloride in dichloromethane at room temperature, acetals and thioacetals are easily cleaved to regenerate original carbonyl compounds in good yields.

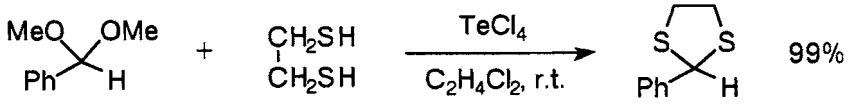
Although tellurium tetrachloride ($TeCl_4$) is widely used as a telluration reagent for a variety of electron-rich organic compounds, its use as a mild Lewis acid has not been explored in organic synthesis as yet.[1] Recently, we have reported that aldehydes and ketones react easily with alkanethiols in the presence of a catalytic amount of $TeCl_4$ to form dithioacetals in good yields.[2] We now wish to report that acetals and thioacetals are easily cleaved in the presence of an equimolar amount of $TeCl_4$ to regenerate original carbonyl compounds in high yields. Thus $TeCl_4$ exhibits the dual property as a Lewis acid; used in a small amount it acts as an efficient catalyst for masking carbonyl functions with thiols, whereas it is a good unmasking reagent for acetal and thioacetal functions in stoichiometric uses.



PROTECTION OF CARBONYL FUNCTIONS

When aldehydes were allowed to react with alkanethiols in 1,2-dichloroethane in the presence of a small amount of $TeCl_4$ at room temperature, the thioacetalization proceeded

smoothly to give the corresponding dithioacetals in good yields. Aliphatic ketones were also converted to dithioacetals, but aromatic ketones remained almost intact. Under similar conditions, dimethylacetals readily underwent the acetal exchange with alkanethiols to afford the expected dithioacetals in high yields. The transacetalization was incomplete with acetals derived from aromatic ketones.

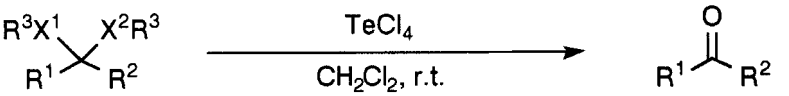


$TeCl_4$ is not effective as catalyst for the acetalization of carbonyl compounds.

General procedure for the protection of carbonyl groups with alkanethiols: To a solution of carbonyl compound (5 mmol) and thiol (10 mmol) or dithiol (5 mmol) in 1,2-dichloroethane (10 ml) was added powdered $TeCl_4$ (0.25 mmol, 5 mol%), and the resulting mixture was stirred for 2-3 h at room temperature. During the course of this period, free tellurium gradually separated as a black deposit. The reaction was quenched by the addition of sodium hydrogencarbonate (ca. 0.2 g) and the insoluble material was removed by filtration. The filtrate was dried over sodium sulfate and the solvent was evaporated under reduced pressure to leave a crude dithioacetal **3**, which was purified either by chromatography over silica gel or by bulb-to-bulb distillation.

DEPROTECTION OF ACETALS AND THIOACETALS

Acetals (1a, 1b), monothioacetals (2a, 2b) and dithioacetals (3a-3o) were all easily cleaved by treatment with an equimolar amount of $TeCl_4$ in dichloromethane at room temperature to regenerate original carbonyl compounds in most cases in good yields (Table I). The reaction was clean and no polymeric substances were formed. Bis(phenylthio)acetals (3c and 3i) behaved somewhat differently, where bis(phenylthio) telluride and diphenyl disulfide were formed as important side products.



1: $X^1=X^2=O$
2: $X^1=O$, $X^2=S$
3: $X^1=X^2=S$

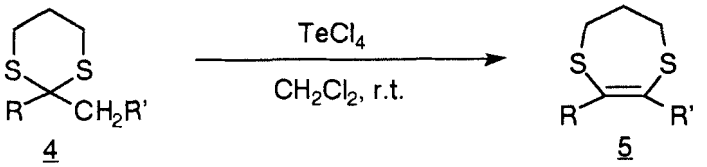
General procedure for the deprotection of acetals and thioacetals: To a solution of acetal (1) or thioacetal (2 or 3; 1.0 mmol) in dichloromethane (20 ml) was added powdered $TeCl_4$ (1.1 mmol) and the resulting suspension was stirred for 1-2 h at room temperature. The reaction mixture was quenched by the addition of 5% aqueous sodium hydrogencarbonate and the insoluble material was removed by filtration. The organic layer was separated, dried over magnesium sulfate and evaporated under reduced pressure to leave a crude product, which was purified by chromatography on silica gel or by Kugel-rohr distillation to obtain pure carbonyl compound.

TABLE I Deprotection of acetals, monothioacetals and dithioacetals by $TeCl_4$

Compound	R^1	R^2	R^3	X^1	X^2	Yield/%[a]
1a	Ph	H	Me	O	O	95
1b	Ph	Ph	$(CH_2)_2$	O	O	99
2a	Ph	H	$(CH_2)_2$	O	S	99
2b	Ph	Ph	$(CH_2)_2$	O	S	94
3a	Ph	Ph	Et	S	S	99
3b	Ph	H	Et	S	S	94
3c	Ph	H	Ph	S	S	34[b]
3d	Ph	H	$(CH_2)_2$	S	S	47
3e	Ph	H	$(CH_2)_3$	S	S	74
3f	4-ClC_6H_4	H	Et	S	S	99
3g	4-HOC_6H_4	H	$(CH_2)_3$	S	S	48
3h	4-CNC_6H_4	H	Et	S	S	87
3i	4-CNC_6H_4	H	Ph	S	S	53[b]
3j	4-CNC_6H_4	H	$(CH_2)_2$	S	S	98
3k	PHCH=CH	H	Et	S	S	55
3l	$PhCH_2CH_2$	H	Et	S	S	51
3m	Ph	Ph	$(CH_2)_2$	S	S	91
3n	Ph	Ph	$(CH_2)_3$	S	S	98
3o	$(CH_2)_5$		$(CH_2)_2$	S	S	--[c]

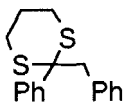
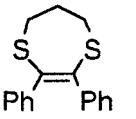
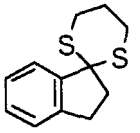
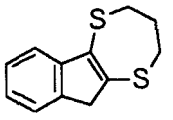
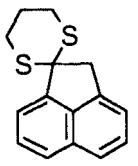
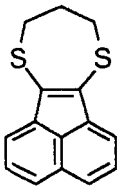
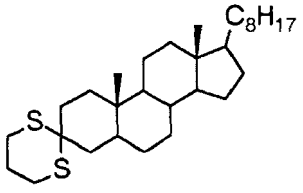
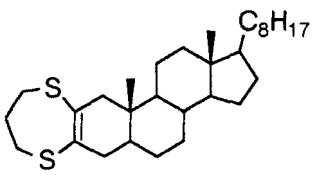
a) Yields refer to isolated compounds.
b) $(PhS)_2Te$ and $(PhS)_2$ were formed as by-products.
c) 5,6-Tetramethylene-2,3-dihydro-1,4-dithiin was obtained in 82% isolated yield.

When the above deprotection procedure was applied to five membered cyclic thioacetals derived from dialkyl or alkyl aryl ketones (1,3-dithiolanes and 1,3-oxathiolanes), a facile ring enlargement by one carbon atom took place via the 1,2-migration of sulfur atom, giving dihydro-1,4-dithiins and dihydro-1,4-oxathiins respectively in good to moderate yield.[3] Extension of this reaction to six-membered cyclic dithioacetals (5) also led to ring expansion, but the yields of dihydro-1,4-dithiepins (6) were moderate (Table II).[4]



4 5

TABLE II $TeCl_4$ induced ring expansion reaction of 1,3-dithianes to dihydro-1,4-dithiepins

Entry	1,3-Dithiane (4)	1,4-Dithiepin (5)	Yield/%[a]
a			39
b			47
c			56
d			34[b]

a) Yields refer to isolated compounds and are not optimized.
b) The reaction was carried out in 1,2-dichloroethane.

When the deprotection of acetal and dithioacetal was carried out in the presence of $TeCl_4$ and a silyl enol ether (6), the acetal carbon was alkylated to give the corresponding β-alkoxy and β-alkylthio ketones (7) in fair to moderate yields (Table III). Replacement of silyl enol ether by non-enolizable aldehyde led to the expected acetal at -78°C, but β-chloroketone was mainly obtained at room temperature.

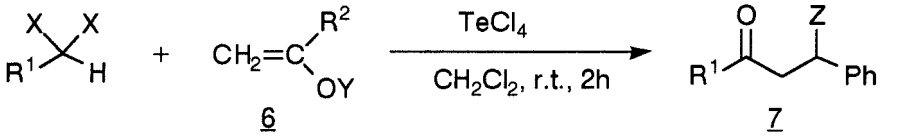


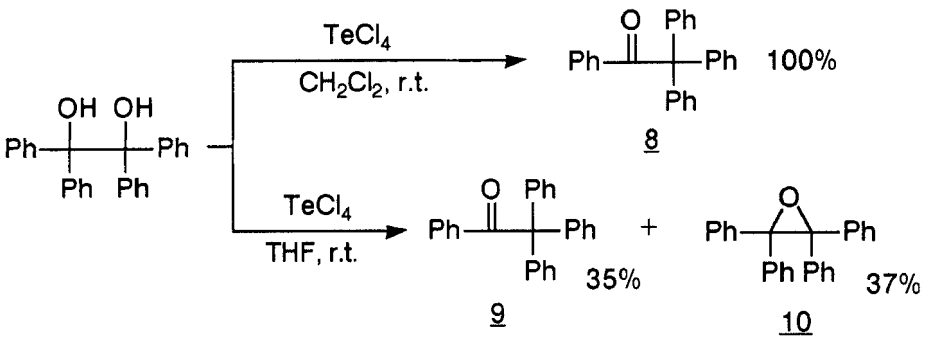
TABLE III $TeCl_4$ mediated condensation of acetal and thioacetal with silyl enol ethers

Entry	R^1	R^2	X	Y[a]	Z	Temp./°C	Yield/%[b]
a	Ph	Ph	OMe	TMS	OMe	-78	43
b	4-MeC_6H_4	Ph	SEt	TMS	-[c]	r.t.	85
c	4-CNC_6H_4	Ph	SEt	TMS	SEt	-45	50
d	4-CNC_6H_4	Ph	SEt	TMS	SEt	-78	56
e	Ph	MeO	SEt	TBDMS	Cl	-78	20
f	Ph	Ph	=O	TMS	Cl	r.t.	40
g	Ph	Ph	=O	TMS	OH	-78	48

a) TMS=trimethylsilyl; TBDMS=tert-butyldimethylsilyl.
b) Yields refer to isolated compounds and are not optimized.
c) Chalcone was the product.

$TeCl_4$ is insoluble in polychlorohydrocarbons, but in the presence of non-enolizable carbonyl compound it dissolves without change to form a pale yellow homogeneous solution. Lewis acid ability of $TeCl_4$ varies considerably depending on the solvent employed; benzopinacol (8) was converted quantitatively into benzopinacolone (9) by $TeCl_4$ in dichloromethane at room temperature, while a comparable mixture of 9 and tetraphenylethylene oxide (10) was obtained in THF.

$TeCl_4$ is an easily handled stable solid, commercially available at moderate price. The major advantages of the protection and deprotection procedures based on $TeCl_4$ are mild reaction conditions, cleanness of reaction, and simplicity of performance.



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2. H. Tani, K. Masumoto, T. Inamasu, and H. Suzuki, Tetrahedron Lett., 32, 2039 (1991). For a general survey see: T. W. Greene, Protective Groups in Organic Synthesis, (John Wiley and Sons, New York, 1981).
3. H. Tani, T. Inamasu, R. Tamura, and H. Suzuki, Chem. Lett., 1323 (1990).
4. All compounds 5a-5d gave satisfactory elemental analyses, mass, infrared and NMR spectra.

   5a: m.p. 148-149°C; ^{1}H NMR($CDCl_3$) δ=2.13(2H, quintet, J=6.1Hz), 3.71(4H, t, J=6.1Hz), 7.0-7.2(10H, m); ^{13}C NMR($CDCl_3$) δ=28.82, 32.21, 126.95, 127.56, 130.98, 131.27, 141.24; IR(KBr) 1520, 1475, 1435, 1400, 1290, 760, 745, 725, 690cm^{-1} ; MS(20eV) m/z(rel intensity) 284(M^+; 100), 210(49), 178(46), 121(31), 106(41).

   5b: oil; ^{1}H NMR($CDCl_3$) δ=2.29(2H, quintet, J=5.8Hz), 3.40(2H, s), 3.45(2H, t, J=7.0Hz), 3.47(2H, t, J=6.4Hz), 7.1-7.3(4H, m); ^{13}C NMR($CDCl_3$) δ=31.59, 32.20, 32.55, 117.77, 122.57, 124.29, 126.40, 131.55, 135.45, 140.75, 144.95; IR(NaCl) 2930, 1605, 1525, 1465, 1420, 1305, 1255, 760, 720cm^{-1}; MS(20eV) m/z(rel intensity) 220(M^+; 99), 187(13), 146(100), 115(19).

   5c: m.p. 92-94°C; ^{1}H NMR($CDCl_3$) δ=2.39(2H, quintet, J=5.8Hz), 3.45(4H, t, J=5.8Hz), 7.4-7.5(4H, m), 7.66(2H, d, J=7.6Hz); ^{13}C NMR($CDCl_3$) δ=32.19, 33.30, 120.33, 126.55, 127.40, 127.65, 127.71, 132.35, 139.71; IR(KBr) 1490, 1440, 1425, 1290, 1190, 835, 780cm^{-1}; MS(20eV) m/z(rel intensity) 256(M^+; 100), 227(24), 184(50).

   5d: m.p. 127-128°C; ^{1}H NMR($CDCl_3$) δ=0.6-2.1(46H, m), 2.73(1H, t, J=4.3Hz), 2.79(1H, t, J=4.3Hz), 3.69(2H, quintet, J=7.9Hz); ^{13}C NMR($CDCl_3$) δ=11.47, 11.93, 18.65, 21.01, 22.53, 22.78, 23.80, 24.16, 27.80, 27.95, 28.15, 30.74, 31.47, 31.48, 31.56, 35.23, 35.28, 35.73, 36.12, 38.91, 39.46, 39.81, 41.74, 42.39, 48.75, 53.51, 56.18, 56.29, 126.57, 127.20; IR(KBr) 2900, 2850, 1600, 1460, 1440, 1400, 1375, 1290cm^{-1} ; MS(20eV) m/z(rel intensity) 474(M^+; 100).