Title	Partial Desulphurization of Dithioacetal Derivatives of Diaryl Ketones and Bis-sulphenylated Active Methylene Compounds using Sodium Telluride under Aprotic Conditions
Author(s)	Padmanabhan, Seetharamaiyer; Ogawa, Takuji; Suzuki, Hitomi
Citation	Journal of chemical research. Synopses. 1989, 1989(8), p. 266-267
Version Type	VoR
URL	https://hdl.handle.net/11094/2987
rights	
Note	

Partial Desulphurization of Dithioacetal Derivatives of Diaryl Ketones and Bis-sulphenylated Active Methylene Compounds using Sodium Telluride under Aprotic Conditions†

J. Chem. Research (S), 1989, 266–267†

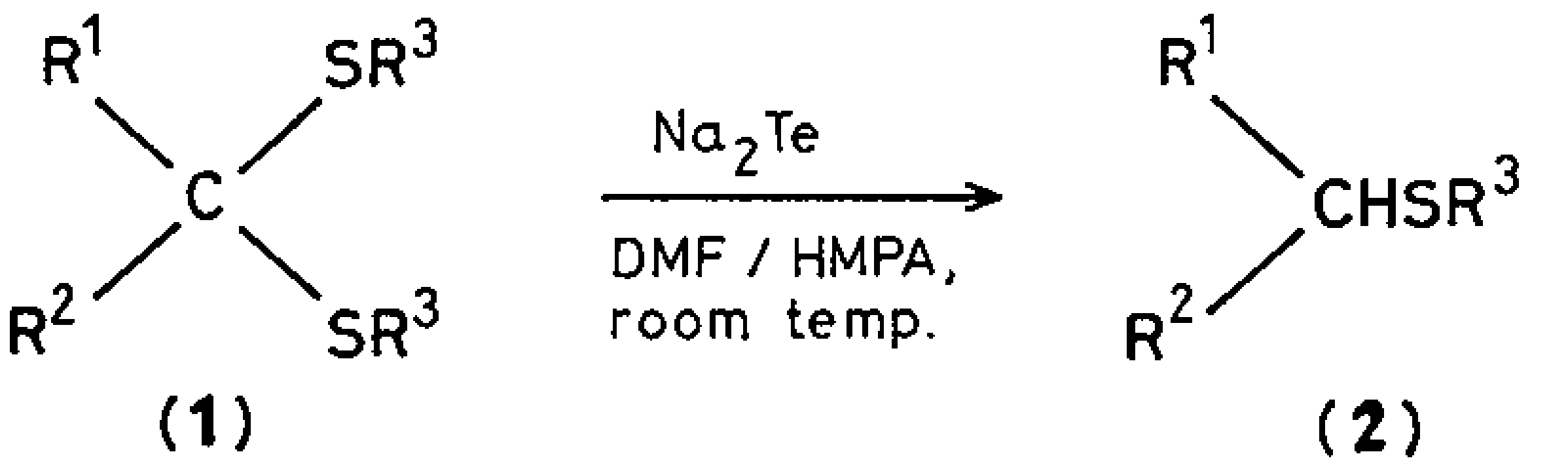
Seetharamaiyer Padmanabhan, Takuji Ogawa, and Hitomi Suzuki*

Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790, Japan

On treatment with sodium telluride in aprotic solvent at room temperature, the title compounds undergo partial desulphurization to afford the corresponding benzhydryl sulphides and monosulphenylated compounds in acceptable yields.

The preparation of dithioacetal derivatives using different catalysts,[1] methods for the regeneration of the parent carbonyl compounds, and desulphurization to hydrocarbons[2] are all well documented. The base catalysed fragmentation of 1,3-dithiolanes using n-butyl lithium[3,4] and lithium di-isopropylamide[5] has been studied recently, by which sulphides have been prepared by subsequent alkylation of the mercaptide anions. Pyridine–borane in trifluoroacetic acid[6,7] has been employed for the conversion of dithioacetals, derived from aldehydes and methyl ketones, into sulphides.

We have discovered a facile conversion of diethylthio acetal derivatives of diaryl ketones (**1a–e**) into benzhydryl ethyl sulphides (**2a–e**) in moderate yields using sodium telluride under aprotic conditions at room temperature (Table 1). Experiments were carried out using sodium telluride prepared from tellurium and sodium hydride in the presence of a mixture of dry *N*,*N*-dimethylformamide (DMF) and hexamethylphosphoric triamide (HMPA). The reaction occurred even in the absence of HMPA, but its presence shortened the reaction time considerably (Table 2). Complete removal of the sulphur unit was attempted, using excess sodium telluride (60 °C, 12 h), but was unsuccessful.



a; $R^1 = R^2 = Ph$, $R^3 = Et$
b; $R^1 = Ph$, $R^2 = 4\text{-}MeOC_6H_4$, $R^3 = Et$
c; $R^1 = Ph$, $R^2 = 4\text{-}ClC_6H_4$, $R^3 = Et$
d; $R^1 = Ph$, $R^2 = 4\text{-}BrC_6H_4$, $R^3 = Et$
e; R^1R^2 = 9-Fluorenyl, $R^3 = Et$
f; $R^1 = R^2 = MeCO$, $R^3 = Ph$
g; $R^1 = R^2 = CO_2Et$, $R^3 = Ph$
h; $R^1 = R^2 = PhCO$, $R^3 = Ph$
i; $R^1 = PhCO$, $R^2 = MeCO$, $R^3 = Ph$

The synthesis of alkyl/aryl benzhydryl sulphides is achieved by reaction of thiols with diazoketones,[8] benzhydrols,[9] or benzhydryl halides,[10] by treatment of diphenylmethane derivatives with arylsulphenyl chlorides,[11] or by the action of Grignard reagents on thiobenzophenones.[12,13] A similar conversion of benzophenone diphenylthioacetal using thiophenol under vigorous conditions (160–170 °C, 4 h) has been reported recently.[14] Our new method could prove a useful addition to the existing procedures as the reaction conditions employed are mild and the starting thioacetals are easily obtainable in good yields. However, its application to dithioacetal derivatives of benzaldehydes and acetophenones did not give encouraging results due to further reaction of the carbonyl compounds under basic conditions.

α-Sulphenylated carbonyl compounds are valuable intermediates in synthetic organic chemistry.[15] Controlled monosulphenylation using different reagents has often proved difficult.[16] Extension of the above procedure to the bis-sulphenylated active methylene compounds (**1f–i**) resulted in the isolation of the corresponding monosulphenylated products (**2f–i**) in moderate yields (Table 1) in addition to diphenyl disulphide. To our knowledge there is only one other report of a similar conversion of polysulphenylated compounds using sodium ethanethiolate.[17]

The formation of the products may be explained by an electron transfer by telluride anion to the substrate followed by the elimination of ethanethiolate anion from the diaryl dithioacetal derivatives [equation (1)] and of phenylthio radical from the bis-sulphenylated active methylene compounds [equation (2)], respectively. No such reduction was observed using sodium hydrogentelluride, which usually reacts as a soft nucleophile.

$$Ar_2C(SEt)_2 \xrightarrow{e} [Ar_2C(SEt)_2]^{-\bullet} \longrightarrow Ar_2\dot{C}SEt + EtS^- \qquad (1)$$

$$R_2C(SAr)_2 \xrightarrow{e} [R_2C(SAr)_2]^{-\bullet} \longrightarrow R_2\bar{C}SAr + ArS^\bullet \qquad (2)$$

The present method has advantages in terms of its mildness, simple manipulation, and use of non-aqueous solvents.

Experimental

All diethylthioacetal derivatives (**1a–e**) were prepared by the $TiCl_4$ catalysed[18] reaction of the corresponding carbonyl compounds with ethanethiol. The bis-sulphenylated active methylene compounds (**1f–i**) were obtained following the procedure reported by Mukaiyama and co-workers.[19] DMF and HMPA were dried over calcium hydride and sodium hydride, respectively, and distilled under reduced pressure prior to use. Melting points are uncorrected and boiling points refer to the Kugelrohr bath temperatures.

Preparation of Benzhydryl Ethyl Sulphides (**2a–e**); *General Procedure.*—Diaryl diethylthioacetal derivative (**1**) (2.0 mmol) in dry DMF (3 ml) was added to a pale yellow suspension of freshly prepared sodium telluride (1 mmol)[20] in a mixture of DMF (3 ml) and HMPA (3 ml) under nitrogen at room temperature. The colour of the reaction mixture gradually changed to deep violet and was stirred at room temperature for 12 h. The reaction was quenched by the addition of saturated aqueous ammonium chloride solution (10 ml) and the reaction mixture was extracted with benzene (10 ml). The extract was freed from inorganic insolubles by filtration through a thin bed of Celite and the aqueous layer was extracted with benzene. The combined benzene extracts were washed with water, dried over sodium sulphate, and evaporated to give the crude product. This was purified by chromatography over silica gel using hexane as eluent. Characterising data for sulphides (**2a–e**) are given in Table 1.

Preparation of Monosulphenylated Active Methylene Compounds (**2f–i**); *General Procedure.*—To a suspension of sodium telluride (1.0 mmol) in dry DMF (3 ml) under nitrogen at room temperature a solution of bis-sulphenylated active methylene compound (**1**; 1 mmol) in dry DMF (3 ml) was added. Immediate separation of tellurium occurred and the reaction went to completion in 1 h. The reaction was quenched by the addition of 0.5 M sulphuric acid

---

*To receive any correspondence.

†This is a Short Paper as defined in the Instructions for Authors [*J. Chem. Research (S)*, 1989, Issue 1, p. ii]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Preparation of benzhydryl sulphides (**2a**–**e**) and monosulphenylated active methylene compounds (**2f**–**i**)

Compound	Yield (%)[a]	B.p. (°C) (mmHg) or m.p. (°C) lit.	δ_H ($CDCl_3$/Me_4Si)	ν_{max} (cm^{-1})[b]
(**2a**)	76	118–122 (3)	1.13 (3 H, t), 2.32 (2 H, q), 5.11 (1 H, s), 7.1–7.4 (10 H, m)	1590, 1485, 1450, 1260, 1070, 1030, 745, 700
(**2b**)	51	157–163 (2)	1.11 (3 H, t), 2.30 (2 H, q), 3.64 (3 H, s), 5.07 (1 H, s), 6.7–7.4 (9 H, m)	1600, 1500, 1245, 1170, 1030, 695
(**2c**)	54	154–158 (3)	1.15 (3 H, t), 2.30 (2 H, q), 5.07 (1 H, s), 7.24 (9 H, br. s)	1480, 1440, 1080, 1005, 690
(**2d**)	41	165–168 (3)	1.13 (3 H, s), 2.35 (2 H, q), 5.07 (1 H, s), 6.9–7.5 (9 H, m)	1475, 1440, 1390, 1060, 1000, 690
(**2e**)	58	46–48 [46.5–47][c]		
(**2f**)	57	103–105 (2.5) [152–153 (22)][d]		
(**2g**)	67	145–147 (2.5) [148 (1.7)][d]		
(**2h**)	65	93–94 [93–94][d]		
(**2i**)	22[c]	59–63	2.31 (3 H, s), 7.08 (10 H, br. s), 17.65 (1 H, s)	1520, 1470, 1430, 1370, 730, 715, 690

[a] Yields refer to isolated compounds and are not optimised.

[b] Solids are measured as KBr pellets and liquids as neat films between NaCl plates.

[c] Ref. 21.

[d] Ref. 19.

[e] Benzoylacetone was obtained in 34% yield.

Table 2 Effect of variation in reaction conditions on the yield of benzhydryl ethyl sulphide (**2e**)

mmol of (**1e**)	mmol of Na_2Te	ml of HMPA	Reaction temperature (°C)	Yield (%)[a]
1	2	3	R.t.[b]	58
1	2	3	60	68
1	2	5	R.t.	72[c]
1	1	3	R.t.	69
1	2	0	R.t.	69[d]

[a] Yields refer to isolated compounds. Reaction time 12 h, unless otherwise stated.

[b] R.t. = room temperature.

[c] Reaction went to completion within 3 h.

[d] Reaction went to completion after 24 h.

saturated with sodium chloride followed by benzene (10 ml). The reaction mixture was stirred for 30 min and then filtered through a thin bed of Celite to remove insolubles. The aqueous layer was extracted with benzene and the combined organic extracts were washed with water, dried over sodium sulphate, and the solvent removed under reduced pressure to leave the crude product. This was purified by chromatography over silica gel using hexane as eluent to give diphenyl disulphide. Further elution with a mixture of hexane and dichloromethane gave the monosulphenylated compound. The reaction mixture obtained from (**1i**), after the elution of diphenyl disulphide, gave first the monosulphenylated product (**2i**) and then benzoylacetone.

We thank the Ministry of Education, Science and Culture, Japan, for a Scholarship (to S. P.).

Received, 18th January 1989; Paper E/9/00303G

References

1 T. W. Greene, 'Protective Groups in Organic Synthesis,' John Wiley, New York, 1981, pp. 129–133.
2 G. R. Pettit and E. E. van Tamelen, *Org. React.*, 1962, **12**, 356.
3 S. R. Wilson, G. M. Georgiadis, H. N. Khatri, and J. E. Bartmess, *J. Am. Chem. Soc.*, 1980, **102**, 3577.
4 S. R. Wilson, P. Caldera, and M. A. Jester, *J. Org. Chem.*, 1982, **47**, 3319.
5 H. Ikehira, S. Tanimoto, T. Oida, and T. Okano, *J. Org. Chem.*, 1983, **48**, 1120.
6 Y. Kikugawa, *Chem. Lett.*, 1981, 1157.
7 Y. Kikugawa, *J. Chem. Soc., Perkin Trans. 1*, 1984, 609.
8 A. Schonberg, O. Schutz, and J. Peter, *Chem. Ber.*, 1929, **62B**, 1663.
9 M. Micha-Screttas and C. G. Screttas, *J. Org. Chem.*, 1977, **42**, 1462.
10 M. M. Klenk, C. M. Suter, and S. J. Archer, *J. Am. Chem. Soc.*, 1948, **70**, 3846.
11 I. V. Koval, V. V. Andrushchenko, M. M. Kremlev, and A. I. Tarasenko, *Zh. Org. Khim.*, 1985, **21**, 1286.
12 M. Dagonneau and J. Vialle, *Bull. Soc. Chim. Fr.*, 1972, 2067.
13 M. Dagonneau and J. Vialle, *Tetrahedron*, 1974, **30**, 3119.
14 A. Schonberg, E. Singer, and W. Stephan, *Chem. Ber.*, 1984, **117**, 3388.
15 B. M. Trost, *Chem. Rev.*, 1978, **78**, 363.
16 J. M. Miller, S. R. Cater, K. H. So, and J. H. Clark, *Can. J. Chem.*, 1979, **57**, 2629.
17 J. S. Grossert and P. K. Dubey, *J. Chem. Soc., Chem. Commun.*, 1982, 1183.
18 V. Kumar and S. Dev, *Tetrahedron Lett.*, 1983, **24**, 1289.
19 T. Mukaiyama, S. Kobayashi, and T. Kumamoto, *Tetrahedron Lett.*, 1970, 5115.
20 H. Suzuki, H. Manabe, T. Kawaguchi, and M. Inouye, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 771.
21 F. G. Bordwell and A. H. Clemens, *J. Org. Chem.*, 1982, **47**, 2509.