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Novel room light-induced disproportionation reaction of organo-ditin and -dilead compounds with organic dichalcogenides: an efficient salt-free route to organo-tin and -lead chalcogenides

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Disproportionation of organo-ditin and -dilead compounds $(R_3M)_2$ (M = Sn, Pb) with organic dichalcogenides $(R'Z)_2$ (Z = S, Se, Te) is efficiently promoted by room light to produce the corresponding organo-tin and -lead chalcogenides R_3MZR' quantitatively.

Chalcogenides of heavier group 14 metals, R_3MZR' (M = heavier group 14 element; Z = chalcogen element) decompose upon heating to give composite metal chalcogenides which are useful for solar cells and other semiconductor applications.[1,2] They are also useful reagents in organic synthesis.[3] Conventional synthetic routes generally involve troublesome stoichiometric salt elimination reactions of R_3MX (X = halogen atom) with alkali metal chalcogenides.[3] However, the alkali metal salts concomitantly formed can be a serious contaminant that reduces the performance of the semiconductor materials derived *via* the MOCVD process of these metal chalcogenides as precursors.[2] Thus, an alternative, clean and salt-free route to R_3MZR' is highly desirable. During an extended research on the Pt-catalysed disproportionation of $(ArS)_2$ with $(SiCl_3)_2$[4] we accidentally came across a novel light-induced disproportionation.We disclose herein preliminary results of the light-induced disproportionation reaction of organic dichalcogenides $(R'Z)_2$ (Z = S, Se, Te; R′ = alkyl, aryl) with organo-ditin and -dilead compounds $(R_3M)_2$ (M = Sn, Pb) leading to R_3MZR' in excellent yields [eqn. (1)].[5]

$$(RZ)_2 + (R'_3M)_2 \xrightarrow{\text{room light}} 2RZMR'_3 \qquad (1)$$

$$Z = S, Se, Te;\ M = Sn, Pb$$

In a typical experiment, an equimolar mixture of $(PhS)_2$ and $(Me_3Sn)_2$ in C_6D_6 (0.5 M) was placed in a Pyrex tube under nitrogen and exposed to room light at 35 °C.[6] As confirmed by ^{1}H NMR spectroscopy, the starting materials were completely consumed within 20 min and $PhSSnMe_3$ was obtained quantitatively as the sole product. Irradiation was essential for this disproportionation; a control experiment carried out in the dark under similar conditions did not lead to $PhSSnMe_3$ even after 2 h.[7,8] The reaction proceeded equally well in other solvents such as toluene and chloroform. Particularly noteworthy is that even in the *absence* of the solvent, the reaction took place as efficiently. Thus, a colourless liquid of analytically pure $PhSSnMe_3$ was obtained by simply stirring a heterogeneous mixture of 10 mmol of $(PhS)_2$ (2.18 g) and an equivalent amount of $(Me_3Sn)_2$ (3.28 g) for 1 h at 35 °C in room light.

Table 1 demonstrates the wide applicability of the present light-induced disproportionation reaction. Other aromatic disulfides such as $(4\text{-}MeC_6H_4S)_2$, $(4\text{-}ClC_6H_4S)_2$, $(2,4,5\text{-}Cl_3C_6H_2S)_2$ and $(2\text{-}pyS)_2$ all reacted efficiently with $(Me_3Sn)_2$ to afford the corresponding trimethyltin sulfides in quantitative yields. Primary aliphatic disulfides such as $(BuS)_2$ reacted similarly. However, as the alkyl group became bulkier,

Table 1 Light-induced disproportionation of $(R_3M)_2$ (M = Sn, Pb) with $(R'Z)_2$ (Z = S, Se, Te)[a]

Run	$(RZ)_2$	$(R'_3M)_2$	*t*/h	Product	Yield (%)
1	$(PhS)_2$	$(SnMe_3)_2$	< 0.5	$PhSSnMe_3$	quant.
2	$(4\text{-}MeC_6H_4S)_2$	$(SnMe_3)_2$	1.5	$4\text{-}MeC_6H_4SSnMe_3$	quant.
3	$(4\text{-}ClC_6H_4S)_2$	$(SnMe_3)_2$	1.5	$4\text{-}ClC_6H_4SSnMe_3$	quant.
4	$(2,4,5\text{-}Cl_3C_6H_2S)_2$	$(SnMe_3)_2$	1.5	$2,4,5\text{-}Cl_3C_6H_2SSnMe_3$	quant.
5	$(2\text{-}pyS)_2$	$(SnMe_3)_2$	1.5	$2\text{-}pySSnMe_3$	quant.
6	$(BuS)_2$	$(SnMe_3)_2$	1.5	$BuSSnMe_3$	quant.
7	$(CyS)_2$	$(SnMe_3)_2$	4	$CySSnMe_3$	60 (95)[b]
8	$(Bu^tS)_2$	$(SnMe_3)_2$	2.5	Bu^tSSnMe_3	8
9	$(PhS)_2$	$(SnPh_3)_2$	1.5	$PhSSnPh_3$	quant.
10	$(4\text{-}ClC_6H_4S)_2$	$(SnPh_3)_2$	3	$4\text{-}ClC_6H_4SSnPh_3$	quant.
11	$(4\text{-}FC_6H_4S)_2$	$(SnPh_3)_2$	1	$4\text{-}FC_6H_4SSnPh_3$	quant.
12	$(BuS)_2$	$(SnPh_3)_2$	2	$BuSSnPh_3$	quant.
13	$(PhS)_2$	$(PbPh_3)_2$	3.5	$PhSPbPh_3$	quant.
14	$(BuS)_2$	$(PbPh_3)_2$	6	$BuSPbPh_3$	quant.
15	$(PhSe)_2$	$(SnMe_3)_2$	< 0.5	$PhSeSnMe_3$	quant.
16	$(PhSe)_2$	$(SnPh_3)_2$	1.5	$PhSeSnPh_3$	quant.
17	$(PhSe)_2$	$(PbPh_3)_2$	1.5	$PhSePbPh_3$	96[c]
18	$(PhTe)_2$	$(SnMe_3)_2$	9	$PhTeSnMe_3$	93[c]
19[d]	$(PhTe)_2$	$(PbPh_3)_2$	3	$PhTePbPh_3$	98[c]

[a] Unless otherwise stated, the reaction was performed as follows: 0.03–0.5 M benzene solution in a Pyrex tube irradiated with a 40 W fluorescent lamp at 35 °C. [b] Yields in parentheses obtained after 7 h reaction time.[c] Traces of decomposition products were also formed.[d] Irradiation with a 200 W tungsten lamp at 50 °C.

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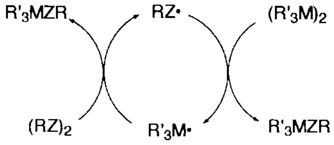
the reaction proceeded more slowly; the completion of the reaction between $(CyS)_2$ and $(Me_3Sn)_2$ required > 7 h and the formation of Bu^tSSnMe_3 in the reaction of $(Bu^tS)_2$ with $(Me_3Sn)_2$ under similar reaction conditions was only marginal. Although slower than $(Me_3Sn)_2$, $(Ph_3Sn)_2$ reacted with both aromatic and aliphatic disulfides to produce the corresponding triphenyltin sulfides in quantitative yields.

Similar disproportionation reactions did not take place with disilanes such as $(Me_3Si)_2$, $(MePh_2Si)_2$, $(Ph_3Si)_2$ or $(SiCl_3)_2$ under the same conditions. Digermanes such as $(Me_3Ge)_2$, $(ClMe_2Ge)_2$ and $(Ph_3Ge)_2$ did not react either. However, the reactions of $(Ph_3Pb)_2$ with $(PhS)_2$ and $(BuS)_2$ proceeded smoothly and quantitative yields of the products were obtained. $(PhSe)_2$ was as reactive as $(PhS)_2$ in the above disproportionation reactions. Similar reactions with $(PhTe)_2$ proceeded relatively slowly,[8] but ultimately afforded respectable yields.

$(Bu_3Sn)_2$ has no absorption maximum in the normal UV region. However, its λ_{max} at a wavelength < 215 nm displays strong end absorption that tails to 250–260 nm.[9] $(Ph_3Sn)_2$ and $(Ph_3Pb)_2$ display absorption maxima in the UV region (λ_{max} 248–260 nm for the former depending on the solvent and 294 nm for the latter).[9] Diphenyl dichalcogenides also have absorption maxima in the UV, near-UV or visible regions.[10] Because of these absorptions, various reactions involving ditins[11] or dichalcogenides[10] can very efficiently proceed under photolytic conditions by irradiation with a sunlamp through Pyrex.[12] With these precedents in mind, we envisioned that the present disproportionation reaction proceeds *via* a radical mechanism as shown in Scheme 1.[13] However, the initiation step is uncertain at the present time since precedents suggest that homolytic cleavage of both M–M[11] and Z–Z[10] bonds by light is possible to initiate the reaction. In agreement with the reactivity trends in other reactions of chalcogen-centered radicals (S > Se > Te),[10] the disproportionation of $(PhTe)_2$ proceeded most sluggishly. The decreasing trends in the reactivity of aliphatic disulfides, $(BuS)_2 > (CyS)_2 > (Bu^tS)_2$, appear to suggest that steric factors of the chalcogen-centered radicals also play an important role.[14]



Scheme 1

In summary, a clean and salt-free route to single source precursors for semiconductors has been presented and the process does not require the use of the volatile organic solvents. These features appear to meet the requirement for 'green' chemistry, which is of contemporary public concern.[15]

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6. Special irradiation apparatus is not necessary for the disproportionation of $(ArS)_2$ with $(Me_3Sn)_2$. Usually, mixing the two reagents in a flask placed about 2 m under a 40 W fluorescent lamp at room temperature for a few minutes leads to quantitative formation of the products. Only when the reactivity was low, was irradiation with a 200 W tungsten lamp performed.
7. $PhSSnMe_3$ was found to be formed only in *ca.* 15% yield by heating a benzene solution of $(PhS)_2$ and $(Me_3Sn)_2$ at 80 °C for 2 h in the dark.
8. Neither $(PhS)_2$ nor $(Me_3Sn)_2$ was detected by ^1H NMR spectroscopy when pure $PhSSnMe_3$ in benzene was exposed to the room light at room temperature, indicating the irreversibility of the disproportionation reaction. Similar phenomena were observed for $PhSeSnMe_3$ and $PhTeSnMe_3$, although decomposition of $PhTeSnMe_3$ (conversion 30%) to Ph_2Te and $(Me_3Sn)_2Te$ was found to have occurred after prolonged irradiation (44 h) at room temperature.
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13. In agreement with the radical mechanism, heating an equimolar mixture of $(Me_3Sn)_2$ and $(PhS)_2$ in C_6D_6 at 80 °C in the dark in the presence of 10 mol% of AIBN led to 95% conversion after 2 h, whereas the same treatment in the absence of AIBN showed only 15% conversion.
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15. Note added at proof: We have found very recently that the December 20 issue of *Chemical Abstracts* has compiled a paper on a new method for the synthesis of stannyl selenides; see V. A. Potapov, S. V. Amosova, V. Svetlana, I. P. Beletskaya, A. A. Starkova, A. V. Martynov and L. Hevesi, *Sulfur Lett.*, 1999, **22**, 237; *Chem. Abstr.*, 1999, **131**, 337113u.