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PHOTOLYSIS OF DIORGANODITELLURIDES IN THE PRESENCE OF TERTIARY PHOSPHINES

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Summary

Ultraviolet irradiation of solutions of R_2Te_2 (R = Et or $PhCH_2$) produces R_2Te and Te quantitatively. In the presence of tertiary phosphines, $R'_3P[R'_3 = Ph_2Me$ or $Ph_2(CH_2PPh_2)]$, the reactions are accelerated via the formation of R'_3PTe, which decomposes to liberate Te and reform R'_3P. A rapid (on the NMR timescale) equilibrium between R'_3PTe and R'_3P + Te is established in solution. All the reactions can satisfactorily be interpreted in terms of an initiation step involving photochemical cleavage of Te—C bonds. Comparisons with analogous reactions of R_2S_2 and R_2Se_2 suggest that element—carbon bonds are more easily cleaved by UV radiation as the group is descended, whereas element—element bond cleavage becomes less important.

Photochemical reactions between diorganodisulphides, R_2S_2, and tertiary phosphines [1] or olefins [2] are well documented. Both involve thiyl radicals produced by UV cleavage of S—S bonds. Scission of sulphur—carbon bonds has also been observed but this is unimportant unless high-energy radiation is used or the relevant carbon radicals are stabilised [3].

Few studies have been made on photochemical reactions of diorganodiselenides. Ultraviolet irradiation of $(PhCH_2)_2Se_2$ leads to $(PhCH_2)_2Se$ and Se quantitatively [4]. The reaction route (eq. 1—5) involves initial photochemical cleavage of Se—C, and any cleavage of Se-Se simply reverses.

$$R_2Se_2 \xrightarrow{h\nu} RSe_2^{\cdot} + R^{\cdot} \qquad (1)$$

$$RSe_2^{\cdot} \rightarrow RSe^{\cdot} + Se \qquad (2)$$

$$R^{\cdot} + R_2Se_2 \rightarrow R_2Se + RSe^{\cdot} \qquad (3)$$

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$$R^{\cdot} + RSe^{\cdot} \rightarrow R_2Se \quad (4)$$

$$2\ RSe^{\cdot} \rightarrow R_2Se_2 \quad (5)$$

We have shown that under analogous conditions, diorganodiselenides react with tertiary phosphines to produce R'_3PSe and R_2Se [5]. Furthermore, though selenium—carbon cleavage may contribute, the most important initiation process is selenium—selenium cleavage (eqn. 6), followed by a cyclic chain process (eqns. 7, 8, and 3).

$$R_2Se_2 \xrightarrow{h\nu} 2\ RSe^{\cdot} \quad (6)$$

$$RSe^{\cdot} + R'_3P \rightarrow [R'_3PSeR]^{\cdot} \quad (7)$$

$$[R'_3PSeR]^{\cdot} \rightarrow R'_3PSe + R^{\cdot} \quad (8)$$

We report here some related photochemical reactions of diorganoditellurides.

Experimental

UV irradiations were carried out using a Hanovia PCR 11 medium pressure mercury lamp. UV/visible spectra were recorded on a Unicam SP800B spectrophotometer. NMR spectra were recorded on either JEOL C-60 HL or Varian T-60 instruments. $(PhCH_2)_2Te_2$ and Et_2Te_2 were made by standard methods [6].

Deuteriobenzene solutions of the ditellurides (ca. 0.14 mol l^{-1}), both alone and with one equivalent of tertiary phosphine added, were irradiated under nitrogen in inverted pyrex NMR tubes. These were kept immersed in a water bath at 285 K to avoid complicating thermal side reactions. The reactions were interrupted regularly (2 min intervals for $(PhCH_2)_2Te_2$ and 30 min intervals for Et_2Te_2) to monitor their progress by NMR spectrometry and to remove deposited tellurium (which would ultimately have scattered all the UV radiation). Inversion of the tubes during irradiation ensured that the Te did not affect the resolution of the spectra, and facilitated its removal since it adhered to the glass at the top of the tube.

With the exception of $(PhCH_2)_2Te$, all the reactants and ultimate products were known compounds, and their identification from NMR spectra was confirmed by observing complete superimposition of the resonances with those of authentic samples. Our attempts to isolate and fully characterise a sample of $(PhCH_2)_2Te$ from the photolysis of $(PhCH_2)_2Te_2$ failed. As the photolysis proceeded, the resonance at δ (C_6D_6) 3.95 due to the methylene signals of $(PhCH_2)_2$-Te_2 diminished, and a signal at δ 3.75, which we assign to $(PhCH_2)_2Te$, grew. Decomposition of this material to bibenzyl (δ 2.75) and tellurium began before the reaction was complete. A typical experiment on a larger scale (0.46 mmol of $(PhCH_2)_2Te_2$ in 25 ml of ether) produced $(PhCH_2)_2Te$ (58%) and bibenzyl (18%), with 24% unreacted starting material, after 23 h irradiation. Attempts to isolate dibenzylmonotelluride from this mixture led to continued decomposition to bibenzyl and Te, even with only occasional exposures to diffuse daylight, suggesting that $(PhCH_2)_2Te$ might be thermally as well as photochemically sensitive.

Results and discussion

Solutions of both dibenzylditelluride or diethylditelluride reacted quantitatively to produce tellurium and the monotelluride under UV irradiation.

$$R_2Te_2 \xrightarrow{h\nu} R_2Te + Te$$

Presumably steps analogous to reactions 1—4 operate, initiated by cleavage of tellurium—carbon bonds. The benzyl derivative photolysed more rapidly than the ethyl compound (times to 50% reaction are given in Table 1), and both reacted more rapidly than their selenium analogues [5]. These relative rates would be expected from the ease of cleavage of the element—carbon bonds.

When the diorganoditellurides were photolysed in the presence of diphenylmethylphosphine, the monotelluride and tellurium metal were again produced, but at a slightly faster rate (see table 1). Also, tellurium deposition on the walls of the reaction tubes continued for some time after irradiation was interrupted. These differences can be accounted for by the formation of some diphenylmethylphosphine telluride. Phosphine tellurides are unstable when aryl groups are involved, and their decomposition to phosphine and tellurium is accelerated by glass surfaces [7].

$$Ph_2MePTe \rightarrow Ph_2MeP + Te$$

No separate ^1H NMR signals for Ph_2MePTe were observed, but the methyl doublet of Ph_2MeP was found to shift downfield with reduced coupling constant (sometimes to zero) during and after irradiation of the $R_2Te_2/MePh_2P$ mixtures, indicating the establishment of a rapid equilibrium between Ph_2MeP and Ph_2MePTe (eqn. 9).

$$Ph_2MePTe \rightleftharpoons Ph_2MeP + Te \tag{9}$$

Variable temperature NMR measurements on these reaction products and on mixtures of Ph_2MeP and powdered tellurium showed that the phenomenon was temperature dependent, but failed to give reproducible results, probably due to the heterogeneous nature of the system.

Mixtures of $(PhCH_2)_2Te_2$ and Ph_2MeP deposited tellurium even after very short irradiation periods, but no free tellurium was apparent after irradiating

TABLE 1

RELATIVE REACTION TIMES

Reactants	Time to 50% [a] reaction (min)
$(PhCH_2)_2Te_2$	13.5
$(PhCH_2)_2Te_2 + Ph_2MeP$	9
$(PhCH_2)_2Te_2 + Ph_2PCH_2PPh_2$	12
Et_2Te_2	150
$Et_2Te_2 + Ph_2MeP$	105

[a] Values quoted are the mean of two closely comparable reactions. Errors are estimated at ±0.5 min for the $(PhCH_2)_2Te_2$ reactions, but ±30 min for the Et_2Te_2 reactions owing to the difficulty of accurately integrating partly overlapping signals in the NMR spectra.

Et_2Te_2 and Ph_2MeP for up to 120 min, although the methyl doublet was again narrowed and shifted downfield. This suggested that either the tellurium depicted in equilibrium (9) remained in solution, or that it could be transferred from phosphorus to phosphorus by a bimolecular route and was never completely released *. To test the latter possibility, mixtures of $Ph_2PCH_2PPh_2$ and Et_2Te_2 were irradiated briefly and examined, in the hopes of finding intramolecular transfer. The deuteriobenzene solutions remained clear, but the entire methylene triplet of the diphosphine was partially collapsed and moved downfield. Thus the tellurium transfer involves intermolecular migration in this case also and we are unable to distinguish which mechanism operates. Longer irradiation of either Ph_2MeP/Et_2Te_2 or $Ph_2PCH_2PPh_2/Et_2Te_2$ leads to the deposition of tellurium, as does even brief irradiation of mixtures of $Ph_2PCH_2PPh_2$ and $(PhCH_2)_2Te_2$. Also, the clear solutions after short irradiations deposit tellurium on standing.

The phosphine tellurides may be produced by the operation of steps analogous to reactions (7) and (8) involving $RTe^{\bullet}$ radicals, or by direct reaction of the phosphine and elemental tellurium [7], (if the latter, the faster reaction rates observed for the decomposition of R_2Te_2 in the presence of R'_3P would be caused by less light-scattering by deposited tellurium). The reaction between tertiary phosphines and diorganodiselenides proceeds via steps (7) and (8) after the photochemical cleavage of selenium—selenium bonds [5]. Even if the phosphine tellurides in this work are formed via the attack of $RTe^{\bullet}$ on R'_3P, it seems more likely that the initiation step will be the photochemical cleavage of Te—C [which can lead to $RTe^{\bullet}$ via steps analogous to (2) and (3)] rather than of Te—Te, since, unlike the selenium case [5], the increase in reaction rate in the presence of tertiary phosphine is not marked (see table 1).

It therefore appears that the ease of cleavage of element—carbon bonds by UV irradiation increases in the series $R_2S_2 < R_2Se_2 < R_2Te_2$, whereas the ease of cleavage of element—element bonds is the reverse (though in the case of the disulphides, light of wavelength down to ca 250 nm may be needed to excite the bond-rupturing $n \rightarrow \sigma^*$ absorption [8]). Photochemical cleavage of Te—C bonds has been observed in tellurophenes [9]. Interestingly, the monotellurides Et_2Te and $(PhCH_2)_2Te$ also decomposed on prolonged irradiation. In an attempt to isolate and characterise $(PhCH_2)_2Te$ by irradiating solutions of the ditelluride alone it was discovered that although $(PhCH_2)_2Te$ was produced in the early stages of photolysis, at no time was it possible to obtain complete reaction of the ditelluride without producing substantial amounts of bibenzyl. Similarly, ethylene was identified (by comparison of NMR signals with those of an authentic sample) as a by-product from the prolonged photolysis of Et_2Te_2, with or without added phosphine.

In cyclohexane solutions Et_2Te_2 has UV absorptions at 400 nm ($\epsilon = 2.28 \times 10^3$) and 300 nm ($\epsilon = 1.37 \times 10^3$), and $(PhCH_2)_2Te_2$ has absorptions at 380 nm ($\epsilon = 1.30 \times 10^3$) and at 280 nm (sh).

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* *Note added in proof:* A recent communication [10] describes a related phenomenon in $t\text{-}Bu_3PTe/t\text{-}Bu_3P$ mixtures, and proposes linear $R_3P\text{-}Te\text{-}PR_3$ intermediates.

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