Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE PHOTOCHEMISTRY OF AROMATIC COMPOUNDS
IV. PHOTOCHEMICAL BEHAVIOUR OF HEXAPHENYLDITIN

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(Received March 12th, 1970)

SUMMARY

The irradiation of hexaphenylditin yields "hot" triphenyltin radicals whose decomposition into diphenyltin and phenyl radicals competes with recombination and disproportionation.

INTRODUCTION

Little work has been done on the photochemistry of organotin compounds, and especially of aromatic tin derivatives. The light-induced reactions of alkyltin hydrides[1,2], triphenyltin azide[4], 1,1-diphenyl-1-stanna-2,6-cycloheptadiene[5] and tetraphenyl derivatives of Group IVA metals[6] are consistent with a homolytic cleavage. Electron spin resonance spectra of radicals formed on photolysis of various tin compounds have been recorded[2,3].

The photolytic behaviour of tetraethyltin[7] and hexaethylditin[7,8] has been investigated. Homolytic dissociation of the tin–tin bond in hexaphenylditin in its ground electronic state, was ruled out by Neumann *et al.*[9] but this was questioned by Hague and Prince[10]. In view of the current interest in the light-induced reactions of compounds having metal–metal bonds, we reexamined the photochemistry of hexaphenylditin.

METHODS AND RESULTS

Degassed solutions of hexaphenylditin, approximately $2 \cdot 10^{-3}$ *M* in cyclohexane, in thin Pyrex cells yielded on irradiation with a medium-pressure mercury lamp a mixture of tetraphenyltin, yellow polydiphenyltin and benzene. The products were quantitatively analysed by various methods. Tetraphenyl- and diphenyltin were formed in an approximate 1/1.5 ratio.

The presence of benzene was revealed by the appearance of its characteristic absorption spectrum in the solvent separated by distillation after photolysis. The amount of it was slightly higher than would be expected from the difference between the yields of tetraphenyl- and diphenyltin; this may be accounted for by the fact that polydiphenyltin absorbs light strongly and is expected to react in the same fashion as hexaphenylditin, giving rise to branched tin polymers.

The formation of benzene was not observed when triphenyltin radicals were formed by decomposition of azobis(isobutyronitrile) in presence of triphenyltin hydride and hexaphenylditin in cyclohexane solution. To ensure that the formation of benzene during photolysis was not due to the decomposition of electronically excited triphenyltin radicals, nearly monochromatic 275 nm light was used, which was wholly absorbed by hexaphenylditin and polydiphenyltin. Benzene was also effectively formed in these conditions.

Irradiation of hexaphenylditin in benzene solution similarly yielded tetraphenyltin and polydiphenyltin, together with biphenyl.

We planned to trap triphenyltin radicals as the corresponding chloride by irradiation in sec-butyl chloride as the solvent. The main products were tetraphenyltin, triphenyltin chloride, diphenyltin dichloride and phenyltin trichloride. The significance of this experiment is obscure because of the existence of the long wavelength absorption of triphenyltin chloride[11] and the catalytic action of the latter in the thermal decomposition of ditin compounds[12]. Moreover, diphenyltin is known to react with alkyl halides, giving rise to similar insertion and redistribution products[13].

Attempts to trap monomeric diphenyltin were not very successful. Thus photolysis in cyclohexane containing 10% 1-hexene yielded polymeric organotin compounds. Diphenylbis(ethylthio)tin was detected, however, by mass spectrometry, in small amount among the products obtained when a mixture of hexaphenylditin ($2\cdot10^{-3}$ *M*) and diethyl disulfide ($8\cdot10^{-3}$ *M*) was irradiated in cyclohexane; due to overlapping absorption it was not possible to prevent some decomposition of the disulfide. The same problem was encountered when a solution of hexaphenylditin and 2,3-dimethyl-1,3-butadiene (molar ratio 1/10) was irradiated; in such conditions, approximately 80% of the light was absorbed by the tin derivative. The mixture remained perfectly colourless and clear throughout the experiment but diphenyltin oxide, identified by its infrared absorption band[14] at 570 cm^{-1} precipitated when the sealed tube was opened, suggesting that diphenyltin had been trapped by the diene but that the adduct decomposed in presence of air.

The results reveal that at least 2,3-dimethylbutadiene (triplet energy 58 kcal[15]) does not quench the decomposition of hexaphenylditin. On the other hand, triphenylene (triplet energy[16] 66.6 kcal) was found to be inactive as a sensitizer.

The quantum yield of disappearance of hexaphenylditin was not determined in degassed solutions because of the formation of the yellow-coloured polymers. Air-equilibrated solutions, or solutions "deoxygenated" by a stream of pure nitrogen, became opalescent on irradiation, because of the precipitation of organotin oxides. Very dilute solutions were thus used to determine the rate of disappearance of hexaphenylditin, and they remained clear throughout the experiment. Potassium ferrioxalate was used as actinometer.

The quantum yield measured with air-equilibrated solutions was 0.32 ± 0.02 in cyclohexane, isopropanol, or 2% 1-hexene solution in cyclohexane. It was very slightly lower (0.29) for "deoxygenated" solutions where strongly absorbing tin chains may have been formed, and it was substantially lower (0.16 ± 0.05) in paraffin.

Irradiation at room temperature of pressed potassium bromide disks containing 1–2% hexaphenylditin (or triphenyltin hydride) produced tetraphenyltin, identified by its IR absorption band[17] at 460 cm^{-1} and by thin-layer chromatography, together with yellow polydiphenyltin. The latter must be responsible for the absorption at 675 cm^{-1}, which disappeared on oxidation.

Surprisingly, irradiation of the same matrices at low temperature resulted in the formation of a red "intermediate", stable at 77°K. Conceivably this red transient species is the one which was detected by spectroscopic flash photolysis of either hexaphenylditin, triphenyltin hydride or tetraphenyltin in degassed cyclohexane or paraffin solution. It was characterized by strong absorption up to 380 nm and two shoulders (400–460 nm and 500–570 nm).

The red species was detected even after 1 msec, but its lifetime could not be accurately measured. After the first flash, the absorption cut-off, initially at about 290 nm, was shifted to 320 nm (Ph_6Sn_2 and Ph_3SnH) or even 400 nm (Ph_4Sn); such degradation prevented further useful work with the solution*.

A transient species showing vibrational fine structure (λ_{max} 413, 435, 448 and 508 nm) was observed after two or more flashes. This was probably due to the photolysis of reaction products.

DISCUSSION

The formation of benzene (in cyclohexane solution) or biphenyl (in benzene solution) during the photolysis of hexaphenylditin, strongly suggests that free phenyl radicals are generated in the medium.

Since in hexaphenylditin, the tin–tin bond energy amounts to 30 kcal[19] while the carbon–tin bond energy is presumably approximately the same as in tetraphenyltin, *i.e.* 54 kcal[19], it seems safe to infer that the primary process must be the cleavage of the molecule into triphenyltin radicals which may remain in a tight radical pair because of their high molecular weight and thus low translational energy. However, recombination and disproportionation to Ph_4Sn and Ph_2Sn do not seem to be the only paths and decomposition of the radical into diphenyltin and phenyl radicals apparently also occurs.

Since we found that the thermally generated triphenyltin radicals did not decompose, it seems that the radicals produced by photodecomposition are energized. Indeed, the hexaphenylditin spectrum shows a strong absorption band at 247 nm which may be ascribed to the transition of a σ electron from the tin–tin bond into an antibonding orbital involving the tin *5d* orbitals[20]. The excited singlet state thus reached may be dissociative and the 95 to 105 kcal (300 to 275 nm) absorbed by the molecule would not dissipate vibrationally before homolytic breakdown. Even if the excited singlet state were not dissociative, strong spin–orbit coupling, due to the presence of tin atoms, would induce fast intersystem crossing to the triplet state. However, if the latter is the reactive state, we are inclined to think that dissociation occurs before any quenching is possible, and we did, indeed, find that the quantum yield of disappearance of Ph_6Sn_2 was not dependent on oxygen concentration.

The occurrence of photolysis in presence of 2,3-dimethylbutadiene and lack of sensitization by triphenylene suggest that, if a triplet state is involved in the photodissociation, its energy must exceed 66 kcal and it must be dissociative. The real quantum yield for homolytic dissociation of the tin–tin bond may thus be very near

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* Octaphenyltritin absorbs the light strongly till 330 nm[18].

unity and the 0.32 value found experimentally, would result from the recombination of the triphenyltin radicals.

The chemical yield of tetraphenyltin was lower than that of polydiphenyltin; this difference is significant, since tetraphenyltin was not photolyzed in these reaction conditions, nor by direct absorption nor, most likely, by triplet energy transfer from hexaphenylditin (the triplet energy of Ph_4Sn has been estimated as 79 kcal according to singlet–triplet absorption and phosphorescence spectra[21]). It seems thus reasonable to ascribe the formation of phenyl radicals to the breakdown of some of the triphenyltin radicals to give a relatively stable divalent tin compound. Interestingly enough, electron impact fragmentation of R_4Sn compounds yields mainly tetra- and divalent tin species[22].

In the absence of conclusive evidence for the assignment of the transient spectrum observed by flash photolysis, we note only that the only possible common intermediate in the photolysis of Ph_4Sn, Ph_6Sn_2 and Ph_3SnH are the triphenyltin radical, monomeric diphenyltin and phenyl radicals. In view of its short lifetime and low extinction coefficient, the phenyl radical must be discarded[23].

Hague and Prince[10] probably observed the same transient species upon flash photolysis, but only saw the stronger band beyond the hexaphenylditin absorption cut-off.

EXPERIMENTAL

Products

Hexaphenylditin[24] m.p. 233° and tetraphenyltin[25] m.p. 229° were synthesised by known procedures. Triphenyltin hydride, m.p. 106°, was obtained by $LiAlH_4$ reduction of very pure triphenyltin chloride.

Either Uvasol cyclohexane from Merck A.G. or p.a. cyclohexane freed of benzene by chromatography on silicagel, was used as solvent. Uvasol paraffin from Merck A.G. was purified by chromatography on silicagel.

2,3-Dimethyl-1,3-butadiene, b.p. 69°, was prepared from anhydrous pinacol[26], stored at $-10°$ on hydroquinone and distilled just before use.

Diethyl disulfide, b.p. 151°/750 mm, was prepared from ethanethiol[27].

Continuous irradiations

Thin Pyrex cells absorbing up to 275 nm were used for irradiation with a medium-pressure mercury lamp Philips HPK 125W. The solutions were thoroughly degassed by several freezing-pumping-thawing cycles.

Tetraphenyltin and unchanged hexaphenylditin were easily separated and recovered by preparative thin-layer chromatography on "Silicagel G nach Stahl" from Merck A.G., with a cyclohexane/benzene 3/1 mixture as eluent.

Polydiphenyltin was immediately oxidized on opening the vessel[28] to give diphenyltin oxide and bis(triphenyltin) oxide, the latter originating from the chain ends. Elution with ethyl acetate separated triphenyltin from di- and monophenyltin derivatives but, in such experiments, the amount of non-soluble polymeric diphenyltin oxide was evaluated by difference.

When both tetraphenyltin and diphenyltin were to be quantitatively determined, a double compartment cell was used, the former containing the hexaphenylditin solution and the second the same volume cyclohexane containing the stoechiometric amount of iodine required to cleave all the tin–tin bonds. After irradiation, both solutions were mixed and worked up in the dark. The solvent was first evaporated and partly replaced by benzene before paper-chromatography (Schleicher & Schüll 2043 b Mgl). A first elution with a pyridine/butanol 3/7 mixture saturated with water, yielded the triphenyltin derivatives migrating with the solvent front; then elution was carried halfway with benzene to separate Ph_4Sn from the non-migrating diphenyltin oxide and monophenyltin derivatives. The spots were developed by means of pyrocatechol violet, were cut off and finally mineralized in a mixture of nitric and sulfuric acids[29]. Sn^{4+} was reduced by thioglycolic acid and Sn^{2+} determined spectrophotometrically as its dithiol complex according to Sandell[30].

Benzene was determined by UV spectroscopy of the distilled solvent, blank experiments having shown that no benzene was liberated thermally from hexaphenylditin or phenyltin oxides.

Quantum yields

Quantum yields were measured on an optical bench using a Osram WB 200 high-pressure mercury arc, a Baush & Lomb high-intensity grating monochromator and a quartz beam splitter[31]. Potassium ferrioxalate was the actinometer.

Low-temperature irradiations

Low-temperature irradiations were run in a Pyrex cell with quartz vacuum-sealed twin windows; the external jacket was continuously filled with liquid nitrogen.

Flash photolysis

Flash photolysis was carried out in 20 cm quartz cells, the solution being degassed by freezing-pumping-thawing cycles, with a Northern Precision Ltd. equipment; the excitation flash was triggered by a 9 μF condenser charged at 12 kV, the spectroscopic flash was fired from a 1 μF condenser charged at 15 kV.

UV spectra were recorded on a Cary 14 spectrophotometer, mass spectra on a Hitachi Perkin–Elmer RMU-6D apparatus, and IR spectra on a Perkin–Elmer 125 grating spectrophotometer.

ACKNOWLEDGEMENT

We thank Professor R. H. Martin for his interest, and Dr. E. Van der Donckt for fruitful discussions. We express our gratitude to the Fonds de le Recherche Fondamentale Collective for financial support to the Laboratory.

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