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PRELIMINARY COMMUNICATION

THE REACTION OF TRIETHYLIODOSILANE WITH ALKYL HALIDES*

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The homolytic reduction of a variety of haloalkanes with organosilicon hydrides was first reported by Haszeldine and Young[1] and later confirmed by other workers[2,3] A radical chain mechanism involving alternate formation of silyl and alkyl radicals was proposed, and it has been shown that the ease of reaction decreases in the order: bromides > chlorides ≫ iodides[4]. From consideration of the carbon–halogen bond energies one would expect the reactivity order to be iodides > bromides > chlorides,

$$\equiv Si^{\cdot} + RX \rightarrow \equiv SiX + R^{\cdot} \quad (1)$$

$$R^{\cdot} + \equiv SiH \rightarrow RH + \equiv Si^{\cdot} \quad (2)$$

$(X = Cl \text{ or } Br)$

and so the inertness of alkyl iodides seemed somewhat surprising. It has been explained in terms of the endothermicity of reaction (1) when X = I[4], from which it follows that reaction (3) should be exothermic, and that the combination of two exothermic reactions

$$R^{\cdot} + \equiv SiI \rightarrow RI + \equiv Si^{\cdot} \quad (3)$$

(1) and (3) might constitute a new example of chain propagation. The correctness of this reasoning has now been illustrated by observation of the novel halogen–halogen exchange reaction (4):

$$\equiv SiI + RX \rightarrow \equiv SiX + RI \quad (4)$$

$(X = Cl \text{ or } Br)$

The irradiation of triethyliodosilane[5] and a six molar excess of normal amyl chloride for 100 h at 20° gave triethylchlorosilane (18%) and normal amyl iodide (12%). A small amount of hexaethyldisilane was detected in the reaction mixture by means of vapour-phase chromatography. Increased formation of triethylchlorosilane resulted when photolysis of triethyliodosilane was carried out in isopropyl chloride (25%) or in tertiary butyl chloride (78%). The same iodosilane gave triethylchlorosilane on photolysis in methylene chloride (15%), in chloroform (62%) and in carbon tetrachloride (92%), also. In every case, qualitative analysis of the product mixtures indicated the formation of the corresponding iodoalkanes.

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Alkyl bromides reacted in a similar fashion with triethyliodosilane to give triethylbromosilane as well as the expected alkyl iodide. These reactions proceeded more readily than those of alkyl chlorides. The reactivity sequence was found to fall in the order: tertiary (C–Br) > secondary (C–Br) > primary (C–Br). The reactions of primary and secondary halides did not occur in the dark to any detectable extent, but tertiary halides did react very slowly in the dark.

These results are consistent with the predicted chain mechanism (1) + (3). Triethyliodosilane showed a significant absorption in the region 2200–2800 Å in cyclohexane, with a maximum near 2600Å. As irradiation was carried out using light mainly with a wavelength of 2537Å, it is not unlikely that the homolytic dissociation of excited molecules of triethyliodosilane initiates the reaction. The possibility of photodissociation of alkyl halides cannot be excluded, however.

Thermal reaction also took place between triethyliodosilane and an alkyl chloride to give the expected halogen–halogen exchange products. For instance, a 2:1 mixture of isopropyl chloride and triethyliodosilane heated at 80° for 10 h furnished triethylchlorosilane (12%) and isopropyl iodide (8%). The reactivity sequence of alkyl chlorides for the thermal reaction was again in the orders: tertiary (C–Cl) > secondary (C–Cl) > primary (C–Cl) and $CCl_4 > CHCl_3 > CH_2Cl_2$. In this case a homolytic pathway is possible but was not definitely demonstrated. Benzoyl peroxide did not act as catalyst in this system, but this may be because it reacts very rapidly with the triethyliodosilane.★ Further studies on both the photochemical and thermal reactions of iodosilanes are at present under way.

The photolyses were carried out in sealed quartz tubes employing a 160 watt mercury lamp whereas the dark thermal reactions were performed in sealed Pyrex glass tubes.

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★Mixing the two components caused immediate blackening. A preliminary analysis of the products suggested the reaction to be expressed by the equation:

$$2Et_3SiI + (PhCO_2)_2 \rightarrow I_2 + 2PhCO_2SiEt_3$$