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PRELIMINARY NOTE

Selectivity in the homolytic reduction of polyhaloalkanes with organosilicon hydrides*

Encouraged by recent developments in the chemistry of organosilicon free radicals[1-10], we have recently reported[11,12] that the reduction of carbon tetrachloride by triorganosilicon hydrides in the presence of benzoyl peroxide proceeds through a free radical chain mechanism as is shown in eqns. 1–4**, where In• is a radical produced from the initiator. The chains are moderately long, the reaction proceeding satisfactorily in the presence of about one mole per cent of the initiator[11]. As part of a general study of reactions of organosilicon hydrides[11,12,14] we now describe observations on aspects of selectivity in this reduction reaction.

In the present investigation, various polyhaloalkanes were treated with tri-

TABLE 1. PRODUCT DISTRIBUTION IN THE REDUCTION OF POLYHALOALKANES (80°, 10h)[a,b]

Halide	*Silane*	*Product*	
$CH_2ClCHCl_2$	Et_3SiH	CH_2ClCH_2Cl	(100)
		CH_3CHCl_2	(–)
$CH_2ClCHCl_2$	$PhMe_2SiH$	CH_2ClCH_2Cl	(100)
		CH_3CHCl_2	(–)
CH_2ClCCl_3	Et_3SiH	$CH_2ClCHCl_2$	(100)
		CH_3CCl_3	(–)
CH_2ClCCl_3	$PhMe_2SiH$	$CH_2ClCHCl_2$	(100)
		CH_3CCl_3	(–)
$CHCl_2CCl_3$	Et_3SiH	$CHCl_2CHCl_2$	(98)
		$CHClCCl_3$	(2)
$CHCl_2CCl_3$	$PhMe_2SiH$	$CHCl_2CHCl_2$	(98)
		$CHClCCl_3$	(2)
$CH_2ClCHClCH_2Cl$	$PhMe_2SiH$	$CH_2ClCHClCH_3$	(25)
		$CH_2ClCH_2CH_2Cl$	(75)
$CHClBrCHClBr$	$PhMe_2SiH$	$CHCl{=}CHCl$	(74)
		$CHClBrCH_2Cl$	(26)
		$CH_2BrCHClBr$	(–)
$CFCl_2CF_2Cl$	$PhMe_2SiH$	$CHFClCF_2Cl$	(100)
		$CFCl_2CHF_2$	(–)
		$CHCl_2CF_2Cl$	(–)
$Cl(CH_2)_4Br$	$PhMe_2SiH$	n-BuCl	(98)
		n-BuBr	(2)
$ClCH_2CH_2Br$	$PhMe_2SiH$	CH_3CH_2Cl	(100)
		CH_3CH_2Br	(–)
$BrCCl_3$	$PhMe_2SiH$	$CHCl_3$	(75)
		$CHBrCl_2$	(25)

[a] Each of the experiments was carried out in a sealed tube which was kept in a constant temperature bath.
[b] Analyses were made by means of vapor phase chromatography (Silicone Rubber, QF-1).

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** The proposed scheme has been further supported by the formation of 1,2-dicyclopropyltetramethyldisilane in the reaction of cyclopropyldimethylsilane with di-tert-butyl peroxide[13].

$$(C_6H_5COO)_2 \rightarrow 2\,\mathrm{In}^{\bullet} \qquad (1)$$

$$\mathrm{In}^{\bullet} + R_3SiH \rightarrow \mathrm{InH} + R_3Si^{\bullet} \qquad (2)$$

$$R_3Si^{\bullet} + CCl_4 \rightarrow R_3SiCl + Cl_3C^{\bullet} \qquad (3)$$

$$Cl_3C^{\bullet} + R_3SiH \rightarrow CHCl_3 + R_3Si^{\bullet} \qquad (4)$$

ethylsilane or phenyldimethylsilane in the presence of benzoyl peroxide. Table 1 summarises the product distributions as determined by vapour phase chromatographic analysis and it will be seen that the reactivity of the halogen atoms falls in the order: Br > Cl > F. This sequence is in accord with that found in homolytic reduction by organotin hydrides[15].

The reactivity sequence $Cl_3C > Cl_2HC > ClCH_2$ also applies, which means that stepwise reduction of carbon tetrachloride to methane can be carried out with reasonably good yields[16].

The greater reactivity of the chloromethylene group over the chloromethyl groups in 1,2,3-trichloropropane is consistent with the reactivity sequence found by Young and his co-workers in the photochemical reduction[6] of alkyl chlorides with trichlorosilane *viz.* tertiary C–Cl > secondary C–Cl > primary C–Cl. The polar effects of substituents[12] may also play a role, in this case resulting in the preferential attack on the chloromethylene group by the electron-donating organosilicon free radicals.

The vicinal dibromide, 1,2-dibromo-1,2-dichloroethane undergoes the radical debromination in preference to halogen–hydrogen exchange. Rather similar results have been observed by Kuivila and Menapace[15] for the organotin hydride reduction. The reversibility of the halogen atom addition to olefins[17] is presumably responsible for such homolytic eliminations.

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