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CATALYSIS OF HYDROSILYLATION OF OLEFINS BY tert-BUTYL PEROXIDE UNDER UV IRRADIATION

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SUMMARY

The scope of the hydrosilylation of olefins catalysed by tert-butyl peroxide under UV irradiation has been studied briefly. Some conclusions are as follows: (*i*) The reaction between trichlorosilane and 1-hexene is not much affected by temperature change in the range −20 to +40°; (*ii*) good yields of trichlorosilane adduct can be obtained from trichlorosilane and 1-hexene, 1-octene and cyclohexene; but yields are very poor with 2-octene and 2-methyl-2-butene; (*iii*) dichloro(methyl)silane gives acceptable yields though markedly lower than those from trichlorosilane, but triethylsilane, triethoxysilane, triphenylsilane and 1,1,1,3,5,5,5-heptamethyltrisiloxane do not give detectable yields of adducts under the conditions used.

Trichlorosilane has been found to react with benzene under similar conditions to give phenyltrichlorosilane in 16% yield.

INTRODUCTION

It was recently shown that the addition of trichlorosilane to 1-octene and cyclohexene is effectively catalysed by tert-butyl peroxide under UV irradiation; thus, trichloro-n-octylsilane was obtained in 95% yield from 1-octene after 12 h irradiation at 40° [1]. Only very small yields were obtained from trimethylsilane under comparable conditions.

We describe below a brief study of the influence of some variables on this type of hydrosilylation, and also report the formation of trichloro(phenyl)silane from benzene under similar conditions. The study was essentially comparative, and no attempt was made to maximise yields by, for example, using more powerful irradiation or higher concentrations of peroxide.

RESULTS

(*a*). *Effect of change of temperature*

Since one of the possible advantages of hydrosilylation by the technique under investigation is that it can be carried out at low temperatures, the effect of temperature was studied for the reaction between trichlorosilane (0.035 mole) and 1-hexene (0.024 mole) in the presence of tert-butyl peroxide (0.6 mmole) under irradiation from

TABLE 1

INTERACTION OF SILICON HYDRIDES WITH OLEFINS UNDER UV IRRADIATION IN PRESENCE OF TERT-BUTYL PEROXIDE[a]

Olefin	Silane	Temp. (°C)	Time (h)	Vessel	Yield of adduct (%)
1-Hexene	Cl_3SiH	−20	6	Pyrex	31
		0	9	Pyrex	76
		20	16	Pyrex	79
		40	14	Pyrex	78
		30	24	Quartz	88
		40	14*	Pyrex	61
1-Hexene	$MeCl_2SiH$	30	40	Pyrex	27
		30	40	Quartz	42
1-Hexene	$(EtO)_3SiH$	30	16	Pyrex	0
1-Hexene	Et_3SiH	40	38	Pyrex	0
1-Hexene	$(Me_3SiO)_2MeSiH$	30	16	Pyrex	0
1-Hexene	Ph_3SiH	40	14	Pyrex	0
1-Octene	Cl_3SiH	30	8	Quartz	63
		40	14*	Pyrex	78
1-Octene	$MeCl_2SiH$	40	14*	Pyrex	23
1-Octene	$(EtO)_3SiH$	40	14*	Pyrex	0
1-Octene	Ph_3SiH	40	14*	Pyrex	0
Cyclohexene	Cl_3SiH	40	14*	Quartz	62
Cyclohexene	$MeCl_2SiH$	40	14*	Quartz	10
2-Octene	Cl_3SiH	40	14	Pyrex	6[b]
2-Octene	$MeCl_2SiH$	40	14	Pyrex	2[b]

[a] 0.6 mmole of the peroxide was used with 0.024 mole of olefin and 0.035 mole of the hydride. The sample was normally positioned about 4 cm from a 125 W lamp, but for cases in which an asterisk is shown against the reaction time a 500 W lamp was used at a distance of 20 cm. [b] Mixed isomers.

a 125 W lamp immersed in a water bath. Yields of 78, 79, and 76% of trichloro-n-octylsilane (determined after conversion into trimethyl-n-octylsilane) were obtained after 14 h at 40°, 16 h at 20°, and 9 h at 0°, respectively. A similar experiment for 6 h in a methanol bath at −20°C gave a 31% yield of adduct. The apparent lowering of the yield in this case may be due to the effect of the change of the bath on the irradiation efficiency rather than to the temperature change itself. The experiments at 0–40° show that temperature change does not have a large effect on the rate of reaction, and it is clear that reactions at low temperatures are practicable.

(*b*). *Variations of the olefin*

The use of quartz vessels appears to give some advantage. Good yields of n-alkyltrichlorosilane were obtained from either 1-hexene or 1-octene and trichlorosilane (see Table 1). The maximum yield obtained from 1-octene, *viz.* 78%, was lower than that reported previously[1], but little significance can be attached to this difference, since a rather more powerful irradiation system was used in the earlier work.

While a 62% yield of adduct was obtained from cyclohexene, the yield of adduct from 2-octene under similar conditions was only about 6%.

(*c*). *Variation of the silane*

Of the other silicon hydrides examined (see Table 1) only methyldichlorosilane gave significant yields of adducts with 1-hexene or 1-octene. The hydrides Et_3SiH,

$(EtO)_3SiH$, and $(Me_3SiO)_2MeSiH$ and Ph_3SiH did not give detectable quantities of adduct.

(*d*). *Effect of solvent*

Use of an equal volume of light petroleum (b.p. 60–80°) as solvent lowered the yield of adduct in the reaction of trichlorosilane with 1-hexene from 78 to 58%. The lowering of the yield was less marked with 1-octene, namely from 57 to 54%. Clearly use of a solvent would be practicable if it were needed, as for example with a solid olefin.

(*e*). *Reactions with benzene*

Free radical silylation of benzene was first carried out by UV irradiation of a solution of bis(trimethylsilyl)mercury in benzene, which gave trimethyl(phenyl)-silane in 21% yield[2]. Later triethyl(phenyl)silane was obtained in 16% yield by heating a mixture of triethylsilane, tert-butyl peroxide, and benzene at 135° for 20 h[3]. We have now found that trichloro(phenyl)silane is formed in 16% yield from UV irradiation (500 W lamp) of a mixture of trichlorosilane and benzene containing a little tert-butyl peroxide for 16 h in a quartz vessel under the conditions used for hydrosilylation of olefins, as described below. Only a trace (< 2%) of triethyl(phenyl)-silane was obtained from triethylsilane under similar conditions, however.

EXPERIMENTAL

Materials

No impurities (*i.e.* < 1%) could be detected by GLC in the olefins used.

Reaction procedure

Reactions were usually carried out in sealed Pyrex glass ampoules. For example, a mixture of 1-hexene (3.0 ml, 0.024 mole), trichlorosilane (3.5 ml, 0.035 mole), and tert-butyl peroxide (0.60 mmole) was sealed in a Pyrex ampoule which was placed about 4 cm from a 125 W medium pressure mercury arc immersed in a water bath at 20°. After 14 h the ampoule was opened and n-decane (3.0 ml) was added as internal standard. A small sample was then withdrawn, and the yield of trichloro-n-hexylsilane was determined by GLC after conversion to 1-hexyltrimethylsilane as described below.

In some experiments, as indicated in Table 1, the mixture was exposed to the light from a 500 W medium pressure mercury arc at a distance of 20 cm.

Analysis of products

Yields of adducts were determined by GLC by measurement of peak areas in conjunction with an internal standard (n-nonane, n-decane, or n-hexadecane) and calibration with authentic samples of the expected products, organotrichloro- and organomethyldichlorosilanes being converted into the corresponding organotrimethylsilanes by treatment with an excess of methyllithium in ether after the addition of the internal standard. Tests on mixtures of known compositions showed that yields could be determined in this way with an accuracy of ±4%.

The GLC columns were of 5% SE 30 on 100–120 mesh acid-washed Chromosorb G.

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