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

ORGANOSILICON COMPOUNDS
XLV*. CATALYSIS OF HYDROSILYLATION BY BIS(TRIMETHYLSILYL)MERCURY OR tert-BUTYL PEROXIDE UNDER ULTRAVIOLET IRRADIATION

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(Received September 9th, 1969)

SUMMARY

Addition of trichlorosilane to 1-octene or cyclohexene is very effectively catalysed by bis(trimethylsilyl)mercury or tert-butyl peroxide under UV irradiation at 40°. The mercurial is somewhat the more effective, and in its presence n-octyltrichlorosilane is formed in almost quantitative yield in only 2 h under the conditions used.

Small yields of addition products are obtained from trimethylsilane in 12 h under similar conditions.

INTRODUCTION

Hydrosilylation of olefins in the presence of free-radical initiators is a well studied process[2-4]. Thermal decomposition of an initiator such as an organic peroxide is most frequently used to generate radicals, which abstract hydrogen atoms from the silicon hydride to give silicon radicals, and these then take part in a chain process[4]. Since bis(trimethylsilyl)mercury generates silicon radicals, *viz.* trimethylsilyl radicals, directly under UV irradiation[5], we have examined the use of this radical source in hydrosilylation, and we find it to provide very effective catalysis. tert-Butyl peroxide under irradiation is also very effective, but less so than the mercurial.

RESULTS AND DISCUSSION

An equimolar mixture of olefin and silicon hydride containing a little bis(trimethylsilyl)mercury or tert-butyl peroxide was sealed in a glass ampoule and exposed to UV light at 40°. The yields of addition products were determined by GLC. Results obtained after 12 h irradiation are shown in Table 1, and it will be seen that an almost quantitative yield of n-octyltrichlorosilane was obtained from 1-octene and trichlorosilane in presence of either the mercurial or the peroxide. Lower, but still very good, yields of addition product were obtained from cyclohexene. (With both olefins very little hydrosilylation occurred under irradiation in absence of the radical sour-

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* For Part XLIV see ref. 1.

TABLE 1

YIELDS OF ADDITION PRODUCTS OBTAINED IN 12 HOURS IRRADIATION AT 40°

Initiator	Olefin	Silane	Product	Yield (%)
$(Me_3Si)_2Hg$	1-Octene	Cl_3SiH	$n\text{-}C_8H_{17}SiCl_3$	97
$(tert\text{-}BuO)_2$				95
None				2
$(Me_3Si)_2Hg$	1-Octene	Me_3SiH	$n\text{-}C_8H_{17}SiMe_3$	8
$(tert\text{-}BuO)_2$				9
None				0
$(Me_3Si)_2Hg$	Cyclohexene	Cl_3SiH	$C_6H_{11}SiCl_3$	80
$(tert\text{-}BuO)_2$				84
None				1
$(Me_3Si)_2Hg$	Cyclohexene	Me_3SiH	$C_6H_{11}SiMe_3$	2
$(tert\text{-}BuO)_2$				1
None				0

ces.) Trimethylsilane gave only very low yields of addition products under these conditions.

In a comparison of the relative effectiveness of bis(trimethylsilyl)mercury and tert-butyl peroxide, the yields of addition product obtained from trichlorosilane and 1-octene after various times were determined, as shown in Table 2. It will be seen that reaction is about twice as fast in presence of the mercurial up to about 80% of reaction, and, that a virtually quantitative yield is obtained in only 2 h in presence of the mercurial.

TABLE 2

VARIATION WITH TIME OF THE YIELD OF n-OCTYLTRICHLOROSILANE FROM TRICHLOROSILANE AND 1-OCTENE AT 40°

Time (h)	Yields (%) of $n\text{-}C_8H_{17}SiCl_3$	
	$(Me_3Si)_2Hg$ as initiator	$(tert\text{-}BuO)_2$ as initiator
0.2	32	16
0.4	58	30
0.6	74	39
0.8	80	44
1.0	85	52
1.5	93	61
2.0	97	74
2.5	96	86
3.0	96	90
4.0	97	95
5.0	97	95
12.0	97	95

As far as we are aware, UV irradiation has not previously been used in conjunction with a peroxide or other free radical source for catalysis of hydrosilylation, and the very full account of hydrosilylation by Lukevits and Voronkov[3] contains no mention of such a procedure. The combination may be of value, since it is clearly much more effective than irradiation alone, and the temperatures which can be used are lower than those necessary when the radical sources are decomposed thermally. The temperature used for the combined radical source-irradiation process could probably be substantially lowered without serious effect on the ease of hydrosilylation, if this were desirable.

EXPERIMENTAL

A degassed mixture of the olefin (0.010 mole) and the silane (0.010 mole) containing bis(trimethylsilyl)mercury[6] (0.2 mmole) or tert-butyl peroxide (0.2 mmole) was sealed in a Pyrex glass ampoule and exposed to the light from a 500 watt medium pressure mercury arc (Hanovia model U.V.S. 500A) at a distance of about 20 cm. Separate tests showed that the temperature within the ampoules was raised to about 40°.

Yields of addition products were determined after appropriate calibration with a Pye Series 104 dual-flame chromatograph, with packings of 5% S.E. 30 and of 5% Carbowax on 100–120 mesh silanized Chromosorb G, and with hydrocarbons as internal standards.

ACKNOWLEDGEMENTS

We thank the Science Research Council for general support and for the award of a Research Studentship (to S.W.B.)

REFERENCES

1 C. Eaborn, B. N. Ghose, and D. R. M. Walton, *J. Organometal. Chem.*, 18 (1969) 371.
2 C. Eaborn, *Organosilicon Compounds*, Butterworths, London, 1960, pp. 45–51.
3 E. Ya. Lukevits and M. G. Voronkov, *Organic Insertion Reactions of Group IV Elements*, Consultants Bureau, New York, 1966.
4 C. Eaborn and R. W. Bott, in A. G. MacDiarmid (Ed.), *Organometallic Compounds of the Group IV Elements*, Vol. 1, Part 1, Dekker, New York, 1968, pp. 213–231.
5 C. Eaborn, R. A. Jackson and R. W. Walsingham, *Chem. Commun*, (1965) 300; C. Eaborn, R. A. Jackson and R. Pearce, *Chem. Commun*, (1967) 920.
6 C. Eaborn, R. A. Jackson and R. W. Walsingham, *J. Chem. Soc., C*, (1967) 2188.