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The reaction of organosilicon hydrides with organic hydroperoxidic compounds

Recent work of Sommer and Parker has been reported to show that treatment of R_3SiH with excess of peroxybenzoic acid in benzene solvent at room temperature for 12 hours gave a 40% yield of R_3SiOH[1]. As part of a detailed investigation of the reaction of organosilicon hydrides with a variety of organic peroxides, we have been also studying the peroxyacid oxidation and wish to report our own results as to the yields and kinetics.

$$R_3SiH + PhCO_3H \rightarrow R_3SiOH + PhCO_2H$$

An exothermic reaction took place when 5 g of triethylsilane was added to 140 ml of a benzene solution (0.3 mole/l) of peroxybenzoic acid at room temperature. After standing overnight, the standard iodometric titration[2] revealed that practically all of the peroxybenzoic acid used was consumed during the reaction. Vaccum distillation resulted in the collection of 4.0 g (70%) of triethylsilanol boiling at 81° (40 mm). Vapor phase chromatographic analysis (QF-1 2.5 m, 117°) of the original reaction mixture showed almost complete disappearance of triethylsilane as well as formation of triethylsilanol. Since there was also no evidence for the presence of hexaethyldisiloxane, the reaction may be regarded as virtually quantitative. The somewhat decreased yield calculated from the amount of the isolated product is apparently due to the condensation which occurred during distillation[*].

In a similar fashion, dimethylphenylsilane and methyldiphenylsilane gave the corresponding silanol in a 60 and 58% yield, respectively. Identities for these products were confirmed by comparing their physical properties with those of authentic samples prepared from the corresponding chlorosilanes[4-6]. This peroxyacid oxidation thus possesses an advantage in that silanols can be made in non-aqueous systems.

A kinetic study of the reaction has been accomplished in benzene at 20° by determining the concentration of the peroxybenzoic acid at intervals. Excellent second order kinetics (first order in each reactant) were observed for the above three silanes up to at least 90% completion[**]. Values of the second order rate constant ($\times 10^3$ $l \cdot mol^{-1} \cdot sec^{-1}$) were found to be 10.0, 2.82 and 1.38 for triethylsilane, dimethylphenylsilane and methyldiphenylsilane, respectively. These figures suggest the electrophilic attack of peroxybenzoic acid on the organosilicon hydrides and this trend is in keeping with the mode of action of peroxybenzoic acid on other nucleophiles[2,8,9].

For the peroxybenzoic acid oxidation of organosilicon hydrides, Sommer[1] has proposed a three-center-type ionic mechanism, $(S_N i - S_E i) - Si$. However, a molecular pathway cannot be ruled out. Recently, Sakurai and coworkers[9] have observed similar oxygen insertion reaction between organodisilanes and peroxybenzoic acid

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[*] Sommer and coworkers[3] noted the extended stability of triethylsilanol at reflux temperature even in the presence of 0.1 *N* HCl. It should be noted, however, that dehydration of silanols is fairly easy to bring about in the presence of suitable catalysts. Impurities which catalyze the condensation processes might have been present in the reaction mixture.

[**] The reaction of the organosilicon hydrides with iodine did not interfere with the kinetic measurements to any great extent probably because of the heterogeneity of the solution to be titrated[7].

in non-polar solvents for which a three-center-type molecular mechanism was suggested. In this case, the reaction rate has no dependence on solvent polarity[10]. The rather small rate differences observed in the present work seem to be more compatible with a molecular mechanism*, but further work is obviously necessary to obtain the right answer to this problem.

Oxidation of triethylsilane was further extended using tert-butyl hydroperoxide. An exothermic reaction also occurred to give triethylsilanol in a 49% yield. Since, however, no reaction was observed with dibenzoyl peroxide and with di-tert-butyl peroxide at room temperature, the presence of a hydroperoxy group seems necessary to cause oxidation** of an organosilicon hydride to the corresponding silanol.

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* This hypothesis is also consistent with a retentive stereochemistry in the peroxybenzoic acid oxidation of organosilicon hydrides[1].
** For somewhat different types of oxidation, see ref. 11.