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Photolysis of *tert*-Butyl Peroxylaurate

Sir:

It has been reported[1] that the photolysis of neat *tert*-butyl peroxycaprate and *tert*-butyl peroxylaurate produces high yields of the corresponding carboxylic acids, capric, and lauric acids. By reinvestigation[2] of the photolysis, using *tert*-butyl peroxylaurate as substrate, we have found that little or no carboxylic acid is formed.

The titration procedure used to determine the acid in the original work[1] was tested and found erroneous principally because the perester itself is saponified in the procedure. We then tried other methods of analysis and found them suitable for the detection of lauric acid in the presence of peroxylaurate. The methods employed thin-layer chromatography, and infrared and NMR spectroscopy. Using those methods, no lauric acid was detected in the photolyzed *tert*-butyl peroxylaurate.

We have also discovered some striking effects caused by a small pyridine impurity such as was present in the peresters studied originally. Those peresters were prepared by the pyridine-acylation method of Silbert and Swern[3] and the recrystallization procedure of that method does not remove the pyridine completely. When we came to suspect the effects of that slight impurity, we were able to remove it completely by chromatography on a silica gel column, using a 10% solution of diethyl ether in petroleum ether as eluting agent.[4]

The UV spectrum of *tert*-butyl peroxylaurate reported in the original work[1] showed a band at 2700 Å. That band is spurious and disappears when the perester is completely freed of pyridine. The highly purified perester has a structureless spectrum in the range 3000–2100 Å, the absorbance rising smoothly with decreasing wavelength. Pyridine has a strong band close to 2700 Å ($\epsilon \sim 3000$).[5] The very strong absorption by the pyridine in that spectral region plays an important role when peresters are photolyzed with 2537-Å radiation.

The radiation photolyzes the pyridine as well as the perester and produces a coloration that progresses from yellow to reddish brown during the process. The strong absorption by the pyridine also diminishes the quantum yield of decomposition of the perester. The value of ϕ_{D} for the *tert*-butyl peroxylaurate was 1.76 in the original work[1] but rose to 7.0 at the same radiation intensity with the pyridine-free perester. In the absence of pyridine the photolyzed perester was colorless and the ϕ_{D} value was not lowered by saturation of the perester with oxygen gas.

The rate of photodecomposition of the chromatographed *tert*-butyl peroxylaurate followed a three-halves-order dependence on the perester concentration over times up to 3 h. Since that kinetic behavior and the high ϕ_{D} value indicated a chain reaction, EPR spectroscopy was used to detect any radicals produced during photolysis. The neat perester was photolyzed directly in the spectrometer cavity at 10 °C. A single-line spectrum was observed and the radical was apparently an alkyl peroxy radical ($g = 2.0150$, peak-to-peak width ~6 G). It was observed that if pyridine was present the signal was enhanced, showing a stabilization of the radical. Such stabilization might be expected to lower the induced decomposition of the perester.

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Photolysis of Organopolysilanes. Formation and Reactions of Substituted 1-Silacyclopropene and 1-Sila-1,2-propadiene

Sir:

Despite widespread interest in the photochemical studies of the organopolysilanes,[1-5] there have been no reports of the photolysis of 1-alkynylpolysilanes. Recently we demonstrated that irradiation of vinyldisilanes produces reactive silicon–carbon double-bonded intermediates in high yields *via* photorearrangement of a silyl group to the terminal carbon of a vinyl group.[6] In this communication we report a novel photo-