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Photolysis of tert-Butyl Peroxylaurate

Sir:

It has been reported¹ 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 reinvestigation² 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 work¹ 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 Swern³ 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 work¹ 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 work¹ 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 siliconcarbon 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 photoScheme I



chemical behavior of (pentamethyldisilanyl)phenylacetylene (1). In marked contrast with vinyldisilanes, the photolysis of 1 has been found to proceed simultaneously by two different routes, one of which, a main route, involves the production of 1-silacyclopropene (A), and the other, a minor one, comprises the transient formation of a new type of silicon-carbon double-bonded intermediate (B) (see Scheme I).

When a solution of 1 (4.31 mmol) in 110 ml of dry benzene in the presence of 0.5 ml of acetone was irradiated at room temperature for 6 h with a low-pressure mercury lamp bearing a Vycor filter (2537Å) under a purified nitrogen atmosphere, four products, 2,2,5,5-tetramethyl-3-trimethylsilyl-4-phenyl-1-oxa-2-silacyclo-3-pentene^{7,8} (2) (NMR (CCl₄) δ -0.25 (CH₃-SiMe₂, s, 9 H), 0.26 (CH₃-SiMe, s, 6 H), 1.23 (CH₃-CMe, s, 6 H), 6.9-7.4 (ring protons, m, 5 H); m/e 290 (M⁺)), 2,2,5,5-tetramethyl-3-phenyl-4-trimethylsilyl-1oxa-2-silacyclo-3-pentene (3) (NMR (CCl₄) δ -0.10 (CH₃-SiMe₂, s, 9 H), 0.16 (CH₃-SiMe, s, 6 H), 1.40 (CH₃-CMe, s, 6 H), 6.9-7.4 (ring protons, m, 5 H); m/e 290 (M^+) , phenyltrimethylsilylacetylene⁹ (4), and 1-phenyl-1trimethylsilyl-3-methyl-1,2-butadiene (5) (NMR (CCl₄) δ 0.19 (CH₃-SiMe₂, s, 9 H), 1.77 (CH₃-CMe, s, 6 H), 7.14 (ring protons, broad s, 5 H), m/e 216 (M⁺), IR (neat) 1940 cm^{-1}) were obtained in 51, 2, 10, and 5% yield, respectively, with 81% conversion of the starting disilane. The formation of products 2-5 can be best understood by assuming intermediacy of both 1-silacyclopropene (A) and a silicon-carbon double-bonded species, 1-sila-1,2-propadiene (B). Insertion of acetone into the silicon-carbon bond in silacyclopropene A generates five-membered compounds 2 and 3. Liberation of dimethylsilylene species from either direct photolysis of 1 or decomposition of A results in the formation of 4. The dimethylsilylene could easily be trapped by diethylmethylsilane.¹⁰ Compound 5 can be rationalized in terms of cycloaddition of acetone¹¹ to intermediate B to afford silaoxetane¹² (C) followed by loss of the Me_2SiO moiety.

To establish whether or not acetone was involved in the photoisomerization, we irradiated 1 (3.43 mmol) with a lowpressure mercury lamp in the absence of acetone at -78 °C for 4 h in 110 ml of dry toluene. After the irradiation was stopped, 2 ml of acetone was added to the reaction mixture. Here, three products derived from A, 2, 3, and 4, were obtained in 44, 2, and 7% yield,¹³ respectively. However, as expected, no compound 5 arising from the reaction of short-lived intermediate B with acetone was detected by GLC analysis. Scheme II



Further evidence for the photochemical generation of A and B was obtained from photolysis of 1 in the presence or absence of methyl alcohol (see Scheme II). Irradiation of 1 (4.50 mmol) at -78 °C for 5 h in 110 ml of toluene, followed by addition of 2 ml of dry methyl alcohol at the same temperature, afforded two compounds which can be expected from reaction of the silacyclopropene with methyl alcohol, 14 (E)-1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethylene (6) (NMR $(CCl_4) \delta - 0.06 (CH_3 - SiMe_2, s, 9 H), 0.24 (CH_3 - SiMe, s, 6$ H), 3.41 (CH₃-O, s, 3 H), 7.0-7.3 (ring protons, m, 5 H), 7.77 (vinylic proton, s, 1 H), m/e 264 (M⁺)) and (E)-1-phenyl-1-methoxydimethylsilyl-2-trimethylsilylethylene (7) (NMR CCl₄) δ -0.20 (CH₃-SiMe₂, s, 9 H), 0.09 (CH₃-SiMe, s, 6 H), 3.34 (CH₃-O, s, 3 H), 6.35 (vinylic proton, s, 1 H), 6.8-7.3 (ring protons, m, 5 H), m/e 264 (M⁺)) in 62 and 7% yield, respectively, in addition to 5% yield of 4. On the other hand, photolysis of 1 in the presence of dry methyl alcohol under similar conditions gave, via the expected addition of methyl alcohol across the silicon-carbon double bond on intermediate B, (E)-1-phenyl-1-trimethylsilyl-2-methoxydimethylsilylethylene (10) (NMR (CCl₄) δ -0.24 (CH₃-SiMe, s, 6 H), 0.06 (CH₃-SiMe₂, s, 9 H), 3.25 (CH₃-O, s, 3 H), 6.25 (vinylic proton, s, 1 H), 6.8-7.3 (ring protons, m, 5 H), m/e 264 (M⁺)) and (Z)-1-phenyl-1-trimethylsilyl-2-methoxydimethylsilylethylene (11) (NMR (CCl₄) δ 0.12 (CH₃-SiMe₂, s, 9 H), 0.23 (CH₃-SiMe, s, 6 H), 3.44 (CH₃-O, s, 3 H), 6.17 (vinylic proton, s, 1 H), 6.8-7.3 (ring protons, m, 5 H), m/e 264 (M⁺)) in 12 and 9% yield, in addition to 6 (33%) and 7 (7%). Moreover, in this case, photochemical isomerization of the initial products, 6 and 7, took place to give (Z)-1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethylene $(8)^{15}$ and (Z)-1phenyl-1-methoxydimethylsilyl-2-trimethylsilylethylene (9)¹⁶ in 18 and 4% yield, respectively. Such photochemical isomerization was confirmed by the fact that the photolysis of the isolated pure compounds, 6, 7, and 10, gave the corresponding equilibrium mixture (6/8 = 1.2, 7/9 = 1.4, and 10/11 = 1.6)under the same conditions.17

The structure of photoisomers, 8, 9, and 11, could be distinguished from that of 6, 7, and 10, respectively, on the basis of comparison of the NMR spectra of the isomer pairs. For example, the proton NMR of 8 showed an upfield shift for the dimethylmethoxysilyl group due to the ring current of the phenyl ring *cis* to this dimethylmethoxysilyl group, while its isomer 6 showed the upfield shift for the trimethylsilyl group but not for dimethylmethoxysilyl group, and we therefore assign the *E* structure to 6 and *Z* structure to 8.

We could also confirm the formation of 1-silacyclopropene A by means of NMR techniques.¹⁸ The proton NMR spectrum of a mixture containing $25\%^{19}$ of A produced by photolysis of 1 in *benzene* at room temperature showed two sharp resonances at δ 0.23 and 0.30 with relative intensities of 3:2, in addition to two peaks at δ 0.19 and 0.31 assignable, respectively, to Me₃Si and Me₂Si protons of 1.

The silacyclopropene A in solution seems to be relatively stable at room temperature. When a reaction mixture containing $44\%^{19}$ of A and 22% of unchanged 1 was allowed to stand for 8 h at room temperature, only 6.6% of A was decomposed to give mainly a nonvolatile product. We are continuing this investigation to stabilize intermediate A.

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Stereoselection in the Aldol Condensation

Sir:

Dubois and co-workers have shown that the aldol condensation is subject to kinetic stereoselection, with (Z)-enolates giving predominantly the *erythro* aldol (eq 1), and (E)-enolates leading preferentially to the *threo* isomer (eq 2).¹ House and co-workers found that the use of preformed lithium enolates in the presence of chelating divalent cations such as Zn^{2+} and Mg^{2+} leads to product mixtures rich in the more stable *threo* aldol, regardless of enolate geometry.² We have examined the use of preformed lithium enolates and find that, under the proper conditions, *complete kinetic stereoselection* may be achieved.

Reactions are carried out by preforming the enolate at -72°C in THF or ether by addition of the ketone to a 1 M solution of lithium diisopropylamide (LDA).³ After 15 min, the aldehyde is added in one portion to the rapidly stirring enolate solution. The reaction mixture is guenched by the addition of saturated aqueous $NH_4Cl 5$ s after addition of the aldehyde. After separation of the layers, the aqueous layer is extracted with ether and the combined organic layers are dried (anhydrous MgSO₄) and evaporated to afford the aldol in good yield. Further purification is achieved by distillation and/or recrystallization of the crude product. Diastereomer ratios were determined from the carbinol resonances in the ¹H NMR spectra of the crude aldol product, using the well-established fact that $J_{threo} > J_{erythro}$.² In cases where both diastereomeric aldols are not produced in the condensation, the kinetic aldol was equilibrated so that both stereoisomers were in hand.

Our results may be summarized as follows: In aldol condensations of the type typified by eq 1 and 2, complete kinetic stereoselection is observed, with the (Z)-enolate giving the *erythro* aldol and the (E)-enolate giving the *threo* aldol when R is bulky (*tert*-butyl, 1-adamantyl, mesityl, trimethylsilyl). When R is smaller (ethyl, isopropyl, phenyl, methoxy, *tert*butoxy, diisopropylamino), stereoselectivity diminishes or disappears.

$$\xrightarrow{R} \xrightarrow{\text{LDA}} \xrightarrow{\text{R'CHO}} \xrightarrow{\text{HO}} \xrightarrow{\text{O}} \xrightarrow{\text{O}}$$

An example is provided by the condensation of ethyl tertbutyl ketone (1, 100% (Z)-enolate) with benzaldehyde to yield erythro aldol 2. The crude aldol product in this reaction, obtained in quantitative yield, shows no measurable amount of threo aldol. Pure aldol 2 (mp 55-56 °C) is obtained in 78% yield after distillation (bp 105°/0.3 Torr) and trituration with a small amount of hexane. On the other hand, ethyl mesityl ketone (3, 92% (E)-enolate, 8% (Z)-enolate) reacts with benzaldehyde to afford 92% of threo aldol 4 and 8% of erythro aldol 5. Pure 4 (mp 97-99 °C) is obtained in 52% yield after two recrystallizations from hexane. To gain further support for the supposition that (Z)-enolates give erythro aldols and (E)-enolates give three aldols, we have prepared mixtures of (E)- and (Z)-enolates of varying composition from ketone 3^5 and allowed these mixtures to react with benzaldehyde. In each case, the erythro/threo ratio is identical within experimental error to the (Z)/(E) ratio.



Our results are explicable in terms of a six-center transition state, depicted in structure I for a (Z)-enolate, in which the