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SYNTHESIS AND PYROLYSIS OF 1,1-DIMETHYL-2-PHENYL-1-SILACYCLOBUT-2-ENE

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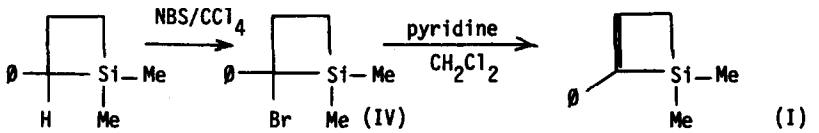
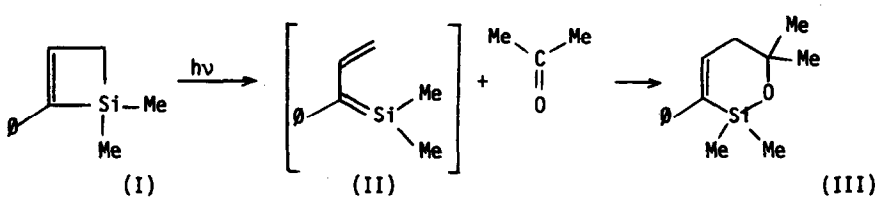
By comparison with the great recent interest in the chemistry of silacyclobutanes,[1,2] little work has been reported[3,4] on silacyclobutenes since two of them were prepared some ten years ago.[5,6] We should like to report a facile synthesis of 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene (I) and an example of its photochemistry which appears to involve 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene (II) as a reactive intermediate.

I was prepared in 60% yield from 1,1-dimethyl-2-phenyl-1-silacyclobutane[7] as follows: benzylic bromination with NBS in CCl_4 quantitatively yields a crude bromide which was dehydrohalogenated by treatment with four equivalents of pyridine in CH_2Cl_2.



Photolysis of an acetone solution of I slowly led to formation of 2,2,6,6-tetramethyl-1-oxa-3-phenyl-2-sila-3-cyclohexene (III) in 83% yield. No reaction was observed in the dark. Formation of III may be economically rationalized as follows: photoexcited I opens to II, which undergoes a 2+4 cycloaddition reaction with acetone to yield III. II would be expected to have some 1,2 and 1,4 zwitterionic character on the basis of the known chemistry of simple carbon-silicon doubly bonded intermediates.[1,8-10] Acetone has been shown to be an efficient trapping agent for 1,4-dipolar species.[11,12] While II has the potential for 2+4 and 2+2 cycloaddition reactions, the fact that II is formed in a cisoid conformation is expected to favor the 2+4 pathways.



Experimental: 2-Bromo-1,1-dimethyl-2-phenyl-1-silacyclobutane (IV) To a dry 250 ml flask equipped with a reflux condenser was added 15 g (0.085 mol) of 1,1-dimethyl-2-phenyl-1-silacyclobutane,[7] 15.2 g (0.085 mol) of NBS, a catalytic amount of benzoyl peroxide, and 100 ml of CCl_4. The

mixture was irradiated at reflux for 0.5 hr using a 275 W GE UV sunlamp. Succinimide was removed by filtration and the CCl_4 solvent was removed by evaporation under reduced pressure. The crude product (21.5 g, 99%) could not be purified due to elimination of HBr on attempted distillation under high vacuuum. It was characterized by nmr:δ 0.11(s,3H), 0.63(s,3H), 1.36(m,2H), 2.83(m,2H), 7.27(m,5H).

1,1-Dimethyl-2-phenyl-1-silacyclobut-2-ene(I) To a dry 500 ml flask equipped with a reflux condenser and a N_2 inlet was added 21.5 g of IV, 300 ml CH_2Cl_2, and 28.0 g of purified pyridine. The mixture was refluxed for 48 hr. The solution was extracted (2 x 50 ml) with cold 1.2 N HCl, dried over anhydrous $MgSO_4$, filtered and the solvent reduced to one quarter of the original volume under reduced pressure. This mixture was added to 200 ml of pentane, stirred, and the solution decanted from a viscous oil which formed. Solvents were removed from the decantate under reduced pressure to yield 8.8 g (58%) of I. An analytical sample was obtained by glpc (0.25" x 4', 20% SE-30 on Chromosorb P, 130°); nmr (CCl_4)δ 0.54(s,6H), 1.60(d,2H) J = 2.2 Hz, 7.28(m,6H); ir(film) Si-CH_3 1242, C=C 1600 cm^{-1}; uv(ethanol) λ_{max} 2570 Å (ε 16,100), λ 2920 Å (ε 1350); mass spectrum at 70 eV parent m/e = 174 (base peak), P-15 m/e = 159 (61.7%); Anal. Calcd; C, 75.79; H, 8.09. Found: C, 75.38; H, 8.02.

Photolysis of I with acetone. To 0.906 g dry acetone in a quartz nmr tube was added 0.318 g of I. The sample was deoxygenated and then irradiated for 48 hr at 10° using a 450 W medium pressure Hanovia Hg lamp. III (83%) was isolated from the reaction mixture by glpc (0.25" x 20", 20% Polyphenylether on Chromosorb P, 180°): nmr(CCl_4) δ 0.20(s,6H), 1.28(s,6H); 2.36(d,2H) J = 5Hz, 6.62 (t,1H) J = 5Hz, 7.14(m,5H); ir(film) Si-CH_3 1247, Si-O and C-O 996, 1013, 1129, and C=C 1595 cm^{-1}; uv(ethanol) λ_{max} 2470 Å (ε 10,420) λ 2930 Å (ε 290); mass spectrum at 70 eV, parent m/e = 232 (50.0%), P-15 m/e = 217 (27.6%). Anal. Calcd: C, 72.35; H, 8.68. Found: C, 72.40; H, 8.69.

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