

Direct Photooxidation of Aryl Substituted Allyl-trimethylsilanes

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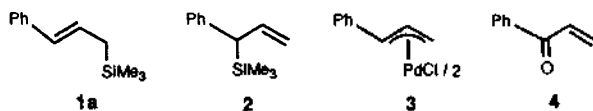
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Allylsilanes have been shown to be versatile intermediates in organic synthesis.¹ Their oxidation² and photochemistry³ have been the subject of a number of publications. Especially, the 1,2-shift and 1,3-shift of trimethylsilyl group of alkyl substituted allyltrimethylsilanes have been studied extensively.⁴

In general, organosilicon compounds are much more stable than other organometallic compounds. However, the C-Si bond is more polarized than the C-H bond, and for this reason, organosilicon compounds are often more reactive than the corresponding hydrocarbons. For example, allylsilanes react very rapidly with palladium chloride or acetate in protic solvents, forming π -allyl complex of palladium and organic splitting products.⁵

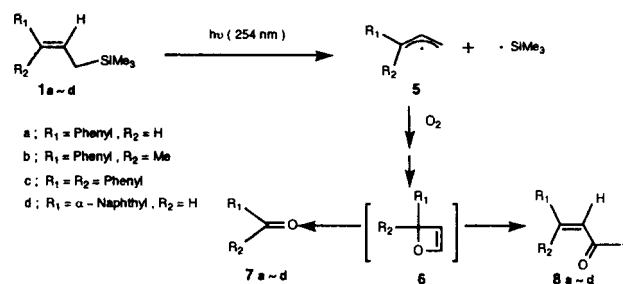
Muzart and his coworkers have been reported that the electrophilic substitution of allylsilanes by Pd(II) salts leads to the splitting of the C-Si bond with formation of η^3 -allylpalladium complex.⁵ They have also shown that photolysis of oxygenated solutions of such complexes provided the corresponding α,β -ethylenic carbonyl compounds.⁵ By further experiments,⁷ however, they have shown that the conversion of **1a**, **2**, and **3** for the palladium-catalyzed photooxidation reactions to cinnamaldehyde (**8a**) only, but no obtained phenyl vinyl ketone (**4**), cinnamyl alcohol, or 1-phenylprop-2-en-1-ol. EPR⁸ and CIDNP⁹ studies have shown the formation of allylic radical intermediates during the coupling reaction of (η^3 -allyl) palladium complexes but have not been decisive in the case of their photochemically mediated oxidation.



For these results, they explained that the intervention of free radicals seemed to be excluded under the palladium-catalyzed conditions because the oxygenations of phenylallyl derivatives carried out either under Pd catalysis or under radical conditions led to different regioselectivities. The observation of the same regioselectivity from either **1a**, **2** plus Pd catalyst or **3** led them to suspect a common (η^3 -allyl)palladium complex intermediate for these three reactions.

Farid and his coworkers have shown that benzyltrimethylsilane undergoes a facile desilylation followed by oxidation.¹⁰ Presumably the radical cation, which is first formed by photooxidation of benzyltrimethylsilane, undergoes the cleavage reaction to benzyl radical and trimethylsilyl cation. However, the mechanism of photooxidation have not been illustrated clearly.

For the purpose of illustration of the direct photooxidation mechanism more clearly, the direct photooxidation of aryl



Scheme 1.

substituted allyltrimethylsilanes was investigated. In a typical experiment, a solution of the aryl substituted allyltrimethylsilanes (**1**)^{10,11} in *n*-hexane or benzene was irradiated at 254 nm in a Rayonet photochemical reactor (Model: RPR-208) under oxygen for about 10 h. Qualitative analyses of the reaction mixture were carried out by HPLC techniques.¹² The products were isolated by column chromatography on silica gel (70-230 mesh, *n*-hexane eluting) and by low-pressure preparative liquid chromatography (LPLC) technique.¹³ The arylketones or aldehydes (**7**) and α,β -unsaturated aldehydes (**8**) were obtained in contrast to the results of palladium-catalyzed photooxidation.⁹ The structures of (**7**), (**8a**) and (**8c**) of the photooxidation products have been confirmed by comparison with those of literatures data as Sadlar and Aldrich.¹⁴ The structures of the other photooxidation products were characterized by the spectroscopic methods.¹⁵

By analysis of photooxidation products, the direct photooxidation of aryl substituted allyltrimethylsilanes has no regioselectivity in contrast to the palladium-catalyzed reaction. This fact indicates that the allyl radical (**5**), which is formed by C-Si bond cleavage on excited state, has no regioselectivity to oxygen. The allyl radical reacts with oxygen and gives the photooxidation products through an unstable spiro-oxetene intermediate (**6**), which is observed in photoaddition reactions of *p*-quinones to alkynes.¹⁶ The intervention of singlet oxygen as reagents for the light-mediated oxygenation of aryl substituted allylsilanes may have been excluded since it is well-known that a monosubstituted olefin is resistant to allylic hydroperoxidation by ¹O₂.¹⁷ That is, if singlet oxygen takes part in this reaction, the formation of **8a** and **8d** seems to be excluded since singlet oxygen would lead to an ene reaction without loss of the silyl group.¹⁸ However, the reaction pathway from **5** to **6** is not well-understood at this moment.

From these results, we proposed the mechanism of the direct photooxidation of aryl substituted allyltrimethylsilanes described in Scheme 1. After promotion of **1** to an excited state, the cleavage of the C-Si bond leads to allyl radical and trimethylsilyl radical. Allyl radical reacts with oxygen to produce the unstable spiro-oxetene (**6**). Spiro-oxetene gives **7** and **8** by ring opening cleavage and rearrangement.

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 - Arylallyltrimethylsilanes were prepared by the reported methods: Seyferth, D.; Wursthorn, K. R.; Lim, T. F. O. *J. Organometal. Chem.* 1979, 181, 293 and see ref. 1b, p. 778 (Preparation of Allylsilanes by Wittig Reaction). In this case, however, arylallylsilanes were only produced by reflux for 15 h at final step.
Spectral data of (E)-1-methyl-1-phenyl-3-(trimethylsilyl)-1-propene (1b); liquid at room temp.; IR (KBr) 3057, 3027, 2955, 1659, 1599, 1493, 1447, 1248, 855, 754, 696 cm^{-1} ; UV (*n*-hexane) λ_{max} 255, 295 nm; ^1H NMR (CDCl_3) δ (ppm) 0.01 (9H, s, $-\text{SiMe}_3$), 1.60 (2H, d, $-\text{SiCH}_2$, $J=ca.$ 8 Hz), 2.00 (3H, s, $-\text{Me}$), 5.90 (1H, t, $=\text{CH}$, $J=ca.$ 8 Hz), 7.30 (5H, m, phenyl); MS (EI) m/e 204 (M^+)
Spectral data of 1,1-diphenyl-3-(trimethylsilyl)-1-propene (1c); liquid at room temp.; IR (KBr) 3057, 3023, 2955, 1620, 1597, 1494, 1445, 1248, 851, 760, 700 cm^{-1} ; UV (*n*-hexane) λ_{max} 258, 298 nm; ^1H NMR (CDCl_3) δ (ppm) 0.01 (9H, s, $-\text{SiMe}_3$), 1.65 (2H, d, $-\text{SiCH}_2$, $J=ca.$ 8 Hz), 6.20 (1H, t, $=\text{CH}$, $J=ca.$ 8 Hz), 7.30 (10H, m, phenyl); MS (EI) m/e 266 (M^+)
Spectral data of (E)-1-(α -naphthyl)-3-(trimethylsilyl)-1-propene (1d); liquid at room temp.; IR (KBr) 3057, 3029, 2955, 1630, 1599, 1504, 1383, 1248, 855, 754, 694 cm^{-1} ; UV (*n*-hexane) λ_{max} 228, 300 nm; ^1H NMR (CDCl_3) δ (ppm) 0.11 (9H, s, $-\text{SiMe}_3$), 1.80 (2H, d, $-\text{SiCH}_2$, $J=ca.$ 8.5 Hz), 6.25 (1H, d of t, $=\text{CH}$, $J=ca.$ 15 Hz and $ca.$ 8.5 Hz), 6.95 (1H, d, $=\text{CH}$ -naphthyl, $J=ca.$ 15 Hz), 7.60 (7H, m, naphthyl); MS (EI) m/e 240 (M^+)
 - HPLC conditions: column, Shodex SIL-5B column; detector, ERMA ERC-7210 UV detector at 280 nm; eluting solvents, *n*-hexane/diethyl ether (100 : 1, v/v); flow rate, 2 mL/min.
 - LPLC conditions: column, Yamazen Co. prepacked Si-25 column; detector, Yamazen Co. Prep. UV-10V detector at 280 nm; eluting solvents, *n*-hexane/diethyl ether (50 : 1, v/v); flow rate, 5 mL/min.
 - 7a** is bezaldehyde, **7b** is acetophenone, **7c** is benzophenone, **7d** is α -naphthaldehyde, **8a** is cinnamaldehyde, and **8c** is β -phenylcinnamaldehyde.
 - Spectral data of (E)- β -methylcinnamaldehyde (8b)**; liquid at room temp.; IR (KBr) 3030, 2950, 2850, 1670, 1150, 1020; 855, 750 cm^{-1} ; UV (*n*-hexane) λ_{max} 275, 283 nm; ^1H NMR (CDCl_3) δ (ppm) 2.00 (3H, s, $-\text{Me}$), 5.90 (1H, d, $=\text{CH}$, $J=12$ Hz), 7.30 (5H, m, phenyl), 9.60 (1H, d, $-\text{CHO}$, $J=12$ Hz); ^{13}C NMR (CDCl_3) δ (ppm) 195.2, 149.6, 138.3, 135.1, 129.9, 129.4, 128.6, 10.9; MS (EI) m/e 146 (M^+), 117 (M^+-CHO)
Spectral data of (E)-3-(α -naphthyl)-2-propenal (8d); liquid at room temp.; ^1H NMR (CDCl_3) δ (ppm) 6.83 (1H, d of d, $=\text{CH}-\text{CO}$, $J=24$ Hz and 12 Hz), 7.40-8.20 (7H, m, naphthyl), 8.32 (1H, d, $=\text{CH}$ -naphthyl, $J=24$ Hz), 9.84 (1H, d, $-\text{CHO}$, $J=12$ Hz); ^{13}C NMR (CDCl_3) δ (ppm) 193.6, 149.3, 133.8, 131.6, 131.2, 130.9, 129.0, 127.3, 126.4, 125.7, 122.8; MS (EI) m/e 182 (M^+), 153 (M^+-CHO)
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Preparation of α -Nosyloxy Carbonyl Compounds Using [Hydroxy(nosyloxy)iodo]benzene

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In recent years, there has been a significant interest in the synthetic utilities of [*p*-nitrophenyl)sulfonyloxy]carbonyl compounds due to their much simpler reactivity than that of the analogous α -halo ketones.^{1,2a} Various kinds of densely functionalized carbon skeletons were prepared from these intermediates.^{2,3} Preparation of synthetically useful α -azido ketones by reaction of α -(nosyloxy)ketones with sodium azide was reported recently.⁴ Conventional methods for preparation of α -(nosyloxy)ketones have been essentially based upon the conversion of enol acetates⁵ and silyl enol ethers⁶ by treatment with *p*-nitrobenzenesulfonyl peroxide (pNBSP).^{2a}