

Photochemical Reaction of Benzophenones with Allylic Silanes

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Synopsis. Photocycloaddition and hydrogen abstraction reactions between benzophenones and allylic silanes have been investigated. The high regioselective oxetane formations were explained in terms of an additional stability due to the $\sigma_{\text{Si-C}}-\text{p}_{\pi}$ hyperconjugation of β -silyl radicals in diradical intermediates. Allyl radical substituted by a trimethylsilyl group, which was generated from a hydrogen abstraction reaction, recombined with benzophenone ketyl radical at the γ position. No electron transfer products were observed in the reactions.

Although a photochemical reaction of allylic silanes has been recently developed, most of them are focused on a photoinduced electron-transfer reaction between allylic silanes and electron acceptors such as iminium salts,¹⁾ cyano aromatics,²⁾ and imides,³⁾ in which a cation radical generated by an electron transfer from allylic silanes readily undergoes desilylation; the resulting allyl radical attacks the substrates to afford allylated products. However, little is known about the reactivity of allylic silanes as an olefin⁴⁾ to the photoexcited carbonyl group. In this paper we wish to describe the Paterno-Büchi reaction and the hydrogen abstraction reaction between benzophenones and allylic silanes.

Results and Discussion

Irradiation of a N_2 -purged acetonitrile solution of benzophenone (**1a**, 1 equiv) and allyltrimethylsilane (**2a**, 6 equiv) with a high-pressure Hg lamp through a Pyrex filter afforded a regioisomeric mixture of oxetanes (**3a** and **4a**, 41%) and (*E*)-1,1-diphenyl-4-trimethylsilyl-3-buten-1-ol (**5a**, 26%), and benzopinacol (**6a**, 15%). These products were separated by preparative thin-layer chromatography on silica gel. Each regioisomer of oxetanes could be separated into **3a** and **4a** by medium-pressure liquid chromatography. The structural identification of these isolated products was elucidated by spectral analyses

and chemical transformation.

The configuration of the oxetanes, **3a** and **4a**, was determined by ^1H NMR (270 MHz): the signals at δ 3.85 (m), 4.38 (dd, $J=5.1$ and 5.4 Hz), and 4.82 (dd, $J=5.4$ and 8.3 Hz) were assignable, respectively, to Ha and Hb or Hc of 2,2-diphenyl-3-(trimethylsilylmethyl)oxetane (**3a**), whereas 2,2-diphenyl-4-(trimethylsilylmethyl)oxetane (**4a**) showed the signals at δ 2.94 (dd, $J=7.6$ and 9.9 Hz, Hb' or Hc'), 3.32 (dd, $J=6.7$ and 9.9 Hz, Hb' or Hc'), and 4.98 (m, Ha'). The isomeric distribution of the oxetanes was estimated by integrations of these signals before separation. The catalytic hydrogenation of the hydrogen abstraction product (**5a**) gave 1,1-diphenyl-4-trimethylsilyl-1-butanol. The *E* configuration of **5a** was confirmed by the coupling constant ($J=18$ Hz) between the olefinic protons. The irradiation of other benzophenones with **2a** under similar conditions afforded **3–6**; the results are summarized in Table 1.

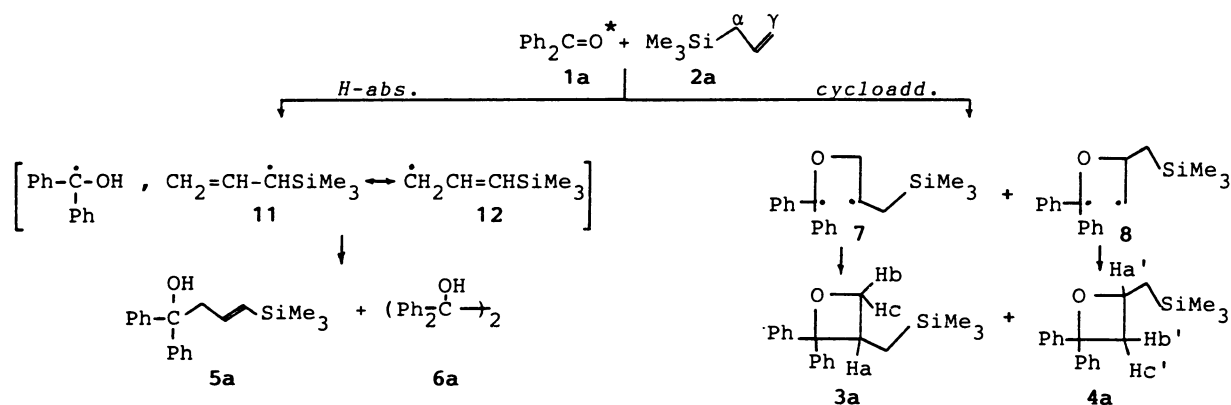
Unsymmetrical allylic silane, (3-methyl-2-butenyl)-trimethylsilane (**2b**) also reacted with the benzophenones to afford oxetanes, hydrogen abstraction product, and benzopinacol (see Table 1).

It is well-known⁵⁾ that electronically excited benzophenones in the triplet state react with olefins to yield [2+2]cycloadducts (oxetanes) and, in fewer cases, allyl alcohols (reduction products), formed by the abstraction of an allylic hydrogen from the olefin by photoexcited benzophenone and a recombination of the two resulting radicals. This reaction pattern also holds for the present reactions, as shown in Scheme 1.

An extremely high regioselectivity of oxetane formation was observed in a reaction of **1** with **2a** (**3**:**4**=24–32:1, see Table 1); this is noteworthy. The regioselectivity of oxetane formation is usually predicted in terms of stability of diradical intermediates.⁵⁾ However these high regioselectivities in the present reactions could not be simply explained on the

Table 1. Photochemical Reaction of Benzophenones with Allyl- and (3-Methyl-2-butenyl)trimethylsilanes

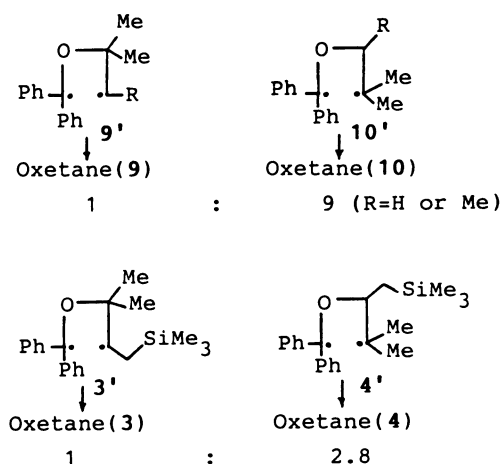
Benzophenone	Allylic silane	Yield of products/%			
		3 + 4	[3 : 4]	5	6
1a ($\text{R}^1 = \text{Ph}$)	2a ($\text{R}^2 = \text{H}$)	3a + 4a (41)	[24 : 1]	5a (26)	6a (15)
1b ($\text{R}^1 = p\text{-ClC}_6\text{H}_4$)	2a	3b + 4b (38)	[32 : 1]	5b (14)	6b (16)
1c ($\text{R}^1 = p\text{-CH}_3\text{C}_6\text{H}_4$)	2a	3c + 4c (36)	[24 : 1]	5c (27)	6c (13)
1a	2b ($\text{R}^2 = \text{CH}_3$)	3d + 4d (54)	[1 : 2.8]	5d (14)	6a (13)
1c	2b	3e + 4e (45)	[1 : 2.8]	5e (16)	6c (11)



Scheme 1.

basis of the stability differences of primary and secondary radicals, because Yang et al.⁶ reported that 1:9 mixtures of oxetanes (**9**:**10**) were produced in the photocycloaddition of benzophenone with isobutene or 3-methyl-2-butene. The diradical **7** could be more stabilized than expected, probably due to a $\sigma_{\text{Si-C}}-\text{p}\pi$ hyperconjugation.⁷

This additional stabilizing effect by the $\sigma_{\text{Si-C}}-\text{p}\pi$ conjugation was further supported by the isomeric distribution of oxetanes formed in the reaction with **2b**. Although isomer **4** predominates, the selectivity (**3**:**4**=1:2.8, see Table 1) is less than that which we had expected (1:9)⁶ from the results of oxetane formation between **1** and isobutene. This also clearly indicates that the diradical **3'** is more stable than the diradical **9'** (**R**=H) owing to the $\sigma_{\text{Si-C}}-\text{p}\pi$ conjugation of β -silyl radical.



A 1-(trimethylsilyl)-2-propenyl radical formed by an H-abstraction of **1a** from **2a** recombined exclusively at the γ position with ketyl radical to give **5a**; nevertheless, radical **11** can be expected to be more stable than radical **12**. This suggests that the coupling at the α position is strongly hindered by a steric interaction between the trimethylsilyl and phenyl groups. 1-(Trimethylsilyl)-3-methyl-2-butenyl radical generated from **2b** also coupled at the γ position with a ketyl radical.

We recently reported a photoinduced electron-

transfer reaction between benzophenones and allylic stannanes,⁸ however, no electron-transfer reaction products (homoallyl alcohols) could be detected in the present reactions. This is understandable on the bases of the endothermicity of the present reactions, since the free energy changes calculated by Rehm-Weller equation⁹ for an electron transfer from allylsilane to photoexcited triplet benzophenones were estimated to be positive (+0.88—+1.21 eV).

Experimental

¹H NMR spectra were recorded on a JEOL MH-100 or GX-270 spectrometer using TMS or chloroform as the internal standard in deuteriochloroform. Infrared spectra were taken with a Hitachi 260-50 spectrometer. Medium-pressure liquid chromatography was performed on a Yamazen FFCL-254 chromatograph equipped with a Lobar column (Merck Si-60). Mass spectra were recorded with a ESCO EMD-05A spectrometer. Elemental analyses were carried out using a Yanaco MT-2 CHN coder. Benzophenones and allyltrimethylsilane were commercially available and used after recrystallization or distillation. (3-Methyl-2-butenyl)trimethylsilane was prepared by a method described in the literature.¹⁰

General Procedure. After a N₂-purged acetonitrile or benzene solution (15 ml) of a benzophenone (0.5 mmol) and allylic silane (3 mmol) was irradiated with a high-pressure Hg lamp through a Pyrex filter for 15 h, the solvent was evaporated, and products were separated by preparative TLC (ether-hexane). The isomeric mixture of oxetanes could be separated into each isomer by liquid chromatography. The yields of the products are shown in Table 1. Benzopinacols (**6a**—**6c**) gave satisfactory spectroscopic data.

Identification of the Products. 2,2-Diphenyl-3-(trimethylsilylmethyl)oxetane (3a): Oil; ¹H NMR δ =−0.03 (s, 9H), 0.41 (t, 1H, J =14 Hz), 0.65 (dd, 1H, J =3 and 14 Hz), 3.85 (m, 1H), 4.38 (dd, 1H, J =5.1 and 5.4 Hz), 4.82 (dd, 1H, J =5.4 and 8.3 Hz), and 7.25—7.43 (m, 10H); IR (CCl₄) 2945, 2853, 1487, 1442, 1245, 980, 860, 840, and 700 cm^{−1}; MS m/z 296 (M⁺). Found: C, 76.59; H, 8.22%. Calcd for C₁₉H₂₄OSi: C, 76.97; H, 8.16%.

2,2-Diphenyl-4-(trimethylsilylmethyl)oxetane (4a): Oil; ¹H NMR δ =0.01 (s, 9H), 1.18 (dd, 1H, J =10.5 and 13.5 Hz), 1.32 (dd, 1H, J =5.4 and 13.5 Hz), 2.94 (dd, 1H, J =7.6 and 9.9 Hz), 3.32 (dd, 1H, J =6.7 and 9.9 Hz), 4.98 (m, 1H), and 7.16—7.49 (m, 10H); IR (CCl₄) 2945, 2905, 1490, 1445, 1245, 940, 860, 838, and 700 cm^{−1}; MS m/z 296 (M⁺). Found: C, 76.81; H, 7.79%. Calcd for C₁₉H₂₄OSi: C, 76.97; H, 8.16%.

(E)-1,1-Diphenyl-4-trimethylsilyl-3-buten-1-ol (5a): Oil; ^1H NMR $\delta=0.01$ (s, SiMe_3), 2.54 (s, OH), 3.14 (t, CH_2 , $J=2.7$ Hz), 5.87 (m, $\text{CH}=\text{CH}$), and 7.22–7.46 (m, aromatic protons); IR (CHCl_3) 3550, 2997, 2945, 1605, 1440, and 1245 cm^{-1} . Found: C, 77.12; H, 8.03%. Calcd for $\text{C}_{19}\text{H}_{24}\text{OSi}$: C, 76.97; H, 8.16%. The alcohol (24 mg, 0.08 mmol) was hydrogenated in methanol (5 ml) in the presence of 5% Pd–C (3 mg) to give 1,1-diphenyl-4-trimethylsilyl-1-butanol: oil (63%); ^1H NMR $\delta=0.00$ (s, SiMe_3), 0.60 (t, CH_2 , $J=8.3$ Hz), 1.38 (m, CH_2), 2.19 (s, OH), 2.36 (t, CH_2 , $J=8.8$ Hz), and 7.25–7.49 (m, aromatic protons); IR (CHCl_3) 3600, 3010, 2950, 1450, and 1250 cm^{-1} ; MS m/z 298 (M^+).

2,2-Bis-(*p*-chlorophenyl)-3-(trimethylsilylmethyl)oxetane (3b): Oil; ^1H NMR $\delta=-0.05$ (s, 9H), 0.38 (t, 1H, $J=14$ Hz), 0.55 (dd, 1H, $J=4.6$ and 14 Hz), 3.66 (m, 1H), 4.24 (t, 1H, $J=5.9$ Hz), 4.70 (dd, 1H, $J=5.9$ and 8.2 Hz), and 7.30 (8H); MS m/z 365 (M^+). Found: C, 62.66; H, 5.70%. Calcd for $\text{C}_{19}\text{H}_{22}\text{OCl}_2\text{Si}$: C, 62.46; H, 6.07%.

2,2-Bis(*p*-chlorophenyl)-4-(trimethylsilylmethyl)oxetane (4b): Oil; ^1H NMR $\delta=0.01$ (s, 9H), 1.20 (dd, 1H, $J=9.3$ and 14 Hz), 1.37 (dd, 1H, $J=4.7$ and 14 Hz), 2.83 (dd, 1H, $J=8.4$ and 10.2 Hz), 3.23 (dd, 1H, $J=8.4$ and 11.2 Hz), 5.20 (m, 1H), and 7.33 (8H); MS m/z 365 (M^+).

(E)-1,1-Bis(*p*-chlorophenyl)-4-trimethylsilyl-3-buten-1-ol (5b): Oil; ^1H NMR $\delta=-0.01$ (s, SiMe_3), 2.51 (s, OH), 3.04 (d, CH_2 , $J=6$ Hz), 5.77 (dt, $\text{C}=\text{CH}=\text{C}$, $J=6$ and 18 Hz), 5.89 (d, $\text{C}=\text{CH}-\text{Si}$, $J=18$ Hz), and 7.21–7.46 (m, aromatic protons); MS m/z 365 (M^+). Found: C, 62.22; H, 5.91%. Calcd for $\text{C}_{19}\text{H}_{22}\text{OCl}_2\text{Si}$: C, 62.46; H, 6.07%.

2,2-Di-*p*-tolyl-3-(trimethylsilylmethyl)oxetane (3c): Oil; ^1H NMR $\delta=-0.02$ (s, 9H), 0.44 (t, 1H, $J=14$ Hz), 0.64 (dd, 1H, $J=2.9$ and 14 Hz), 2.36 (s, 6H), 3.74 (m, 1H), 4.30 (dd, 1H, $J=5.5$ and 7.8 Hz), 4.73 (dd, 1H, $J=5.5$ and 8.3 Hz), and 7.18–7.26 (m, 8H); MS m/z 324 (M^+). Found: C, 78.00; H, 8.77%. Calcd for $\text{C}_{21}\text{H}_{28}\text{OSi}$: C, 77.72; H, 8.70%.

2,2-Di-*p*-tolyl-4-(trimethylsilylmethyl)oxetane (4c): Oil; ^1H NMR $\delta=0.03$ (s, 9H), 1.22 (dd, 1H, $J=10.3$ and 13.5 Hz), 1.38 (dd, 1H, $J=5.3$ and 13.5 Hz), 2.36 (s, 6H), 2.85 (dd, 1H, $J=7.4$ and 11.2 Hz), 3.23 (dd, 1H, $J=7.4$ and 11.2 Hz), 4.96 (m, 1H), and 7.15–7.26 (m, 8H); MS m/z 324 (M^+).

1,1-Di-*p*-tolyl-4-trimethylsilyl-3-buten-1-ol (5c): Oil; ^1H NMR $\delta=0.07$ (s, SiMe_3), 2.38 (s, Me), 2.55 (s, OH), 3.16 (br.s, CH_2), 5.95 (br.s, $\text{CH}=\text{CH}$), and 7.17 (d, 4H, $J=8.3$ Hz), and 7.37 (d, 4H, $J=8.3$ Hz); IR (CHCl_3) 3550, 3000, 2955, 2925, 1613, 1508, 1250, 860, and 837 cm^{-1} ; MS m/z 324 (M^+). Found: C, 77.96; H, 9.00%. Calcd for $\text{C}_{21}\text{H}_{28}\text{OSi}$: C, 77.72; H, 8.70%.

2,2-Dimethyl-4,4-diphenyl-3-(trimethylsilylmethyl)oxetane (3d): Oil; ^1H NMR $\delta=0.04$ (s, 9H), 0.45 (dd, 1H, $J=12$ and 15 Hz), 0.52 (dd, 1H, $J=4$ and 15 Hz), 1.26 (s, 3H), 1.35 (s, 3H), 3.38 (dd, 1H, $J=4$ and 12 Hz), and 7.09–7.36 (m, 10H); IR (CHCl_3) 2995, 2950, 1445, 1370, 1250, 1000, 875, and 860 cm^{-1} ; MS m/z 324 (M^+). Found: C, 77.54; H, 8.87%. Calcd for $\text{C}_{21}\text{H}_{28}\text{OSi}$: C, 77.72; H, 8.70%.

3,3-Dimethyl-2,2-diphenyl-4-(trimethylsilylmethyl)oxetane (4d): Needles from methanol; mp 88°C ^1H NMR $\delta=0.13$ (s, 9H) 0.69 (dd, 1H, $J=5.4$ and 14.2 Hz), 0.99 (s, 3H), 1.00 (s, 3H), 1.02 (dd, 1H, $J=10.3$ and 14.2 Hz), 4.51 (dd, 1H, $J=5.4$ and 10.3 Hz), and 7.11–7.63 (m, 10H); IR (KBr) 2950, 1490, 1460, 1445, 1245, 1000, 940, 860, and 710 cm^{-1} ; MS m/z 324 (M^+). Found: C, 77.59; H, 8.86%. Calcd for $\text{C}_{21}\text{H}_{28}\text{OSi}$: C, 77.72; H, 8.70%.

2,2-Dimethyl-2,2-diphenyl-4-trimethylsilyl-3-buten-1-ol (5d): Oil; ^1H NMR $\delta=0.07$ (s, SiMe_3), 1.17 (s, Me), 2.46 (s, OH), 5.84 (d, $\text{C}=\text{CH}=\text{C}$, $J=19.3$ Hz), 6.34 (d, $\text{C}=\text{CHSi}$, $J=19.3$ Hz), and 7.21–7.55 (m, aromatic protons); IR (CHCl_3) 3600,

2955, 1605, 1495, 1450 1255 870, and 842 cm^{-1} . Found: C, 77.46; H, 8.99%. Calcd for $\text{C}_{21}\text{H}_{28}\text{OSi}$: C, 77.72; H, 8.70%.

2,2-Dimethyl-4,4-di-*p*-tolyl-3-(trimethylsilylmethyl)oxetane (3e): Oil; ^1H NMR $\delta=-0.03$ (s, 9H), 0.47 (dd, 1H, $J=12$ and 15 Hz), 0.54 (dd, 1H, $J=4$ and 15 Hz), 1.30 (s, 3H), 1.40 (s, 3H), 2.37 (s, 6H), 3.40 (dd, 1H, $J=4$ and 12 Hz), and 7.05–7.33 (m, 8H); IR (CHCl_3) 2980, 2950, 1370, 1245, 1155, 1005, and 860 cm^{-1} ; MS m/z 352 (M^+). Found: C, 78.39; H, 8.88%. Calcd for $\text{C}_{23}\text{H}_{32}\text{OSi}$: C, 78.35; H, 9.15%.

3,3-Dimethyl-2,2-di-*p*-tolyl-4-(trimethylsilylmethyl)oxetane (4e): Prisms; mp $79-80^\circ\text{C}$; ^1H NMR $\delta=0.13$ (s, 9H), 0.71 (dd, 1H, $J=4.9$ and 14 Hz), 1.00 (s, 6H), 1.01 (dd, 1H, $J=10$ and 14 Hz), 2.28 (s, 3H), 2.29 (s, 3H), 4.50 (dd, 1H, $J=5.1$ and 10 Hz), and 7.06–7.49 (m, 8H); IR (KBr) 2945, 2910, 1605, 1460, 1245, 993, 945, 860, and 815 cm^{-1} ; MS m/z 352 (M^+). Found: C, 78.60; H, 9.00%. Calcd for $\text{C}_{23}\text{H}_{32}\text{OSi}$: C, 78.35; H, 9.15%.

2,2-Dimethyl-2,2-di-*p*-tolyl-4-trimethylsilyl-3-buten-1-ol (5e): Oil; ^1H NMR $\delta=0.10$ (s, SiMe_3), 1.20 (s, Me), 2.23 (s, Me), 2.38 (s, OH), 5.80 (d, $\text{C}=\text{CH}-\text{Si}$, $J=19$ Hz), 6.45 (d, $\text{C}=\text{CH}=\text{C}$, $J=19$ Hz), and 7.05–7.40 (m, aromatic protons); IR (CHCl_3) 3590, 2990, 2945, 1605, 1500, 1245, 863, and 840 cm^{-1} ; MS m/z 352 (M^+). Found: C, 78.21; H, 9.46%. Calcd for $\text{C}_{23}\text{H}_{32}\text{OSi}$: C, 78.35; H, 9.15%.

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