December, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *56*, *3853—3854 (1983)* 3853

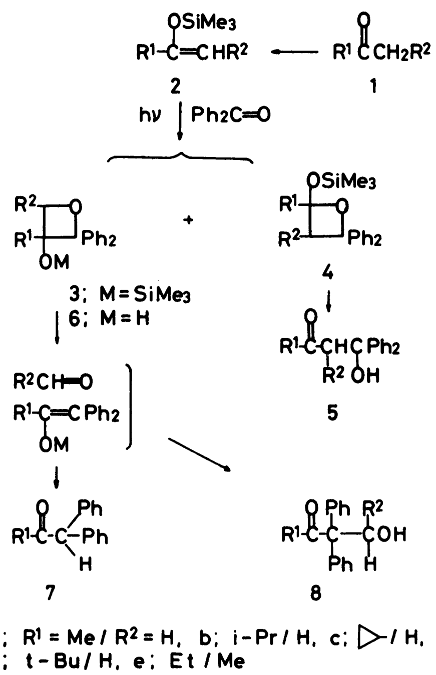
Synthesis of 2,2-Diphenyl-3-oxetanol Derivatives and Their Thermal or Acid-catalyzed Decomposition

Nobujiro SHIMIZU,* Shintaro YAMAOKA, and Yuho TSUNO
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812

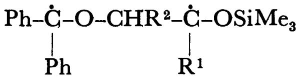
(Received June 27, 1983)

Synopsis. A series of five different 2,2-diphenyl-3-oxetanols was synthesized by photocycloaddition of benzophenone and enol trimethylsilyl ethers followed by protolysis of the resultant 3-trimethylsiloxyoxetanes. Thermal cleavage and acid-catalyzed rearrangement of these oxetanes are described.

Synthesis of 3-oxetanols has been accomplished by only a very limited number of methods.[1,2] A cycloaddition reaction of a carbonyl group and an enol would provide another simple synthetic route. The present work deals with the photocycloaddition of benzophenone and enol trimethylsilyl ethers of aliphatic ketones **1**, and subsequent regioselective decomposition of the resultant 3-siloxy and hydrxyoxetanes.



On irradiation through a Pyrex filter (10—15 °C, 4 h), benzophenone reacted with2-trimethylsiloxypropene (**2a**, 1.5 equiv) in benzene to give a mixture of two isomeric oxetanes **3a** and **4a** (94 : 6). Chromatography of the mixture separated the abundant isomer in 73% yield as colorless crystals; the other one was labile and inevitably afforded a hydrolysis product **5a** (4%) on chromatography. The photocycloaddition with other enol ethers **2b**—**e** also occurred regioselectively to yield the corresponding oxetanes **3b**—**e** as the principal product in each case.[3] The results are shown in Table 1. The efficiency for the oxetane formation appears extremely low from **2d** compared to the other enol ethers. This is presumably ascribed to a rapid decay of an intermediate diradical going back to the starting materials, since a cyclization process must be sterically very unfavorable especially when $R^1=t\text{-Bu}$.



$$\underset{\displaystyle\text{Ph}}{\text{Ph-}\dot{\text{C}}}\text{-O-CHR}^2\text{-}\underset{\displaystyle\text{R}^1}{\dot{\text{C}}}\text{-OSiMe}_3$$

The oxetanes **3** except **3d** were readily converted to the corresponding alcohols **6** by treatment with methanol saturated with potassium carbonate (rt, 1 d). **3d** was surprisingly stable under these conditions; however, acidic methanol using *p*-toluenesulfonic acid effected the desilylation.

The oxetanols **6** cleanly underwent a regioselective decomposition on heating (200 °C, 1 h) in the presence of a catalytic amount of carbon tetrachloride to give the corresponding *α*,*α*-diphenyl ketones **7** in excellent yields.[4] **6c**, for example, gave cyclopropyl diphenylmethyl ketone in 94% yield without cleavage of the cyclopropane ring. The overall reaction therefore corresponds to a transformation of an aliphatic ketone **1** to an arylated ketone **7** *via* a metathesis between benzophenone and an enol silyl ether of **1**.

Thermally, the siloxyoxetane **3a** was stable (240 °C, 4 h) but it rapidly decomposed when treated with boron trifluoride etherate(4 equiv) in dichloromethane to give a rearranged product **8a** in 81% yield after aqueous workup. Two successive reactions both catalyzed by a Lewis acid may account for this rearrangement—regioselective ring cleavage and subsequent recombination of the two fragments, formaldehyde and an enol silyl ether of 1,1-diphenyl-2-propanone. The same rearrangement also occurred smoothly from **3b** and **3c**, but **3d** and **3e** furnished only poor results. **3e** afforded mainly **7e**, although the use of titanium tetrachloride in place of boron trifluoride brought a significant increase in the yield of **8e**, whereas **3d** gave a complicated mixture of products in which neither **7d** nor **8d** was detectable.[5] These results are included in Table 1.

TABLE 1. SYNTHESIS AND REACTIONS OF **3** AND **6**

R^1	R^2	Yield/%[a)]			
		3	**6**	**7**	**8**
Me	H	73	87	87[b)]	81
i-Pr	H	78	92	90[b)]	78[b)]
▷	H	80	90	94[b)]	53[b)]
t-Bu	H	8, 86[c)]	51	90[b)]	0
Et	Me	57	80	92[b)]	27[b,d)]

a) Isolated yield unless otherwise noted. b) Determined by GLC. c) Based on benzophenone consumed. d) Titanium tetrachloride was used in place of BF_3.

Experimental

NMR spectra were determined in carbon tetrachloride with a Hitachi R-20B spectrometer. Enol trimethylsilyl ethers **2a**—**e** were prepared by a conventional method.[6]

2,2-Diphenyl-3-trimethylsiloxyoxetanes (3). The following procedure for the preparation of **3a** was representative. A benzene solution (200 ml) of **2a** (3.1 g, 24 mmol) and benzophenone (2.89 g, 16 mmol) was irradiated through a Pyrex filter by a 450 W mercury lamp at 10—15 °C for 4 h under nitrogen. Solvent and excess **2a** were removed on a rotary evaporator. The yellow residue was chromatographed over alumina eluting with hexane–benzene to give **3a** (3.23 g, 73%) and **5a** (245 mg) in order of elution. **3a**: mp 40—41 °C; IR 1260, 985, 850, and 710 cm^{-1}; NMR $\delta=-0.11$ (9H, s), 1.35 3H, s), 4.15 and 4.49 (both 1H, d, $J=5.6$ Hz), and 6.9—7.8 (10H, m). Found: C, 73.24; H, 7.67%. Calcd for $C_{19}H_{24}O_2Si$: C, 73.03; H, 7.74%.

Related Oxetanes: **3b**: Mp 83—84 °C (Found: 73.92; H, 8.21%), **3c**: mp 70—72 °C (Found: 74.39; H, 7.71%), **3d**: Mp 95—96 °C (Found: C, 74.55; H, 8.54%), and **3e** (a mixture of stereoisomers) showed similar spectral data: IR near 1260, 1000, 850, and 710 cm^{-1}; NMR near $\delta=-0.2$ ($SiMe_3$) and the following characteristic signals of the C_4 protons: 4.45 and 4.63 (both 1H, d, $J=7.5$ Hz) for **3b**; 4.20 and 4.60 (both 1H, d, $J=6$ Hz) for **3c**; 4.30 and 4.77 (both 1H, d, $J=7$ Hz) for **3d**; 4.58 (1H, m) for **3e**.

2,2-Diphenyl-3-oxetanols (6). *A*: A solution of **3a** (3.29 g) in methanol saturated by potassium carbonate was stirred for 1 d at room temperature. A crude product obtained after workup was recrystallized from hexane to give **6a** (2.21 g): mp 111—113 °C; IR 3530, 3450, 980, and 715 cm^{-1}; NMR $\delta=1.27$ (3H, s), 2.02 (1H, s), 4.14 and 4.42 (both 1H, d, $J=6.4$ Hz), and 7.1—7.7 (10H, m). Found: C, 79.81; H, 6.68%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%. Similarly, **3b**, **3c**, and **3e** were respectively converted to **6b**: mp 143—145 °C (Found: C, 80.21; H, 7.46%), **6c**: mp 102—104 °C (Found: C, 81.05; H, 6.80%), and **6e**: mp 132—137 °C. These oxetanes showed IR bands near 3450 and 980 cm^{-1}, and NMR signals characteristic of the C_4 protons: 4.1 and 4.63 (both 1H, d, $J=6.5$ Hz) for **6b**, 4.26 and 4.45 (both 1H, d, $J=6$ Hz) for **6c**, and 4.68 (1H, q, $J=6.5$ Hz) for **6e**.

B: Into a solution of **3d** (650 mg) in carbon tetrachloride (20 ml) was added methanol containing *p*-toluenesulfonic acid (15 mg) and the mixture was allowed to stand for 1 d at room temperature. Workup followed by chromatography gave **6d** (260 mg): mp 150—152 °C; IR 3480 and 985 cm^{-1}; NMR $\delta=0.86$ (9H, s), 4.02 and 4.77 (both 1H, d, $J=7$ Hz), and 7.1—7.8 (10H, m); (Found: C, 80.62; H, 7.80%).

Thermal Decomposition of 6. A mixture of **6** (*ca.* 50 mg), carbon tetrachloride (1 μl), and diphenylmethane (20 mg) was heated at 200 °C for 1 h in a glass ampoule and analyzed directly by GLC. Ketones **7a**—**e** were characterized by their spectral data.

BF_3-Catalyzed Decomposition of 3. A solution of **3a** (510 mg) in dichloromethane (10 ml) was cooled to −75 °C and boron trifluoride etherate (617 μl) was added. The mixture was stirred for 2 h at −75 °C, then for 1 h at 0 °C and quenched with aq sodium carbonate. A crude oil obtained after workup was chromatographed over alumina to give **8a** (314 mg): IR 3450 and 1705 cm^{-1}; NMR $\delta=2.02$ (3H, s), 2.65 (1H, t), 4.12 (2H, d, $J=7$ Hz), 7.27 (10H, s). Found: C, 79.74; H, 6.70%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

8b: Mp 72—74 °C, **8c**, and **8e** were obtained by the same procedure. **8b**: IR 3490 and 1705 cm^{-1}; NMR $\delta=0.78$ (6H, d, $J=6.6$ Hz), 2.93 (1H, m), 4.18 (2H, broad d, $J=6$ Hz), 7.27 (10H, s); (Found: C, 80.40; H, 7.48%). **8c**: IR 3450 and 1705 cm^{-1}; NMR $\delta=0.5$—2.8 (5H, m), 4.15 (2H, s), 7.27 (10H, s). **8e**: IR 3500 and 1705 cm^{-1}; NMR $\delta=0.85$ (3H, t, $J=7.3$ Hz), 0.90 (3H, d, $J=6.5$ Hz), 2.26 (2H, m), 4.95 (1H, q, $J=6.5$ Hz), 7.28 (10H, s).

References

1) J. A. Wojtowicz and R. J. Polak, *J. Org. Chem.*, **38**, 2061 (1973); H. G. Richey, Jr., and D. V. Kinsman, *Tetrahedron Lett.*, **1969**, 2505; P. Yates and A. G. Szabo, *ibid.*, **1965**, 485.

2) 3-Alkoxyoxetanes have been prepared photochemically: S. H. Schroeter and C. M. Orlando, Jr., *J. Org. Chem.*, **34**, 1180 (1969).

3) Regioselective formation of **3** (the ratio **3**/**4** was more than 16 for **2a**—**d** and 4.3 for **2e**) is consistent with a conventional mechanism involving diradical intermediates: D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968).

4) Regioselective decomposition of 2-aryloxetanes has been reported: N. Shimizu, M. Ishikawa, K. Ishikura, and S. Nishida, *J. Am. Chem. Soc.*, **96**, 6465 (1974).

5) One of the products was assignable to 3,3-dimethyl-1-diphenylmethoxy-2-butanone.

6) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).