Tetrahedron Letters, Vol.31, No.9, pp 1245-1248, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

PHOTOOXYGENATION OF 1,2-BIS(SILYLOXY)CYCLOALKENES

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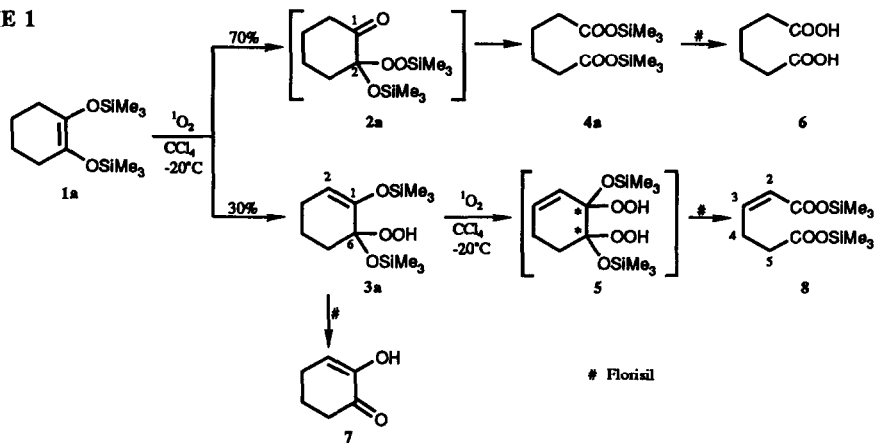
Abstract: The reaction of singlet oxygen with O-silylated cyclic enediols **1a,b** afforded as ene products the hydroperoxy silyl enol ethers **3a,b** and as cleavage products the silyl esters **4a,b**; the latter presumably derived from rearrangement of the intermediary silylperoxy ketones **2a,b**.

Olefins containing allylic hydrogen react with singlet oxygen to produce ene products.[1] If the double bond is substituted with a silyloxy group, also silyl migration takes place, affording α-silylperoxy ketones.[2] In this paper we report on the photooxygenation of 1,2-bis(trimethylsilyloxy)cyclohexene (**1a**) and -cyclopentene (**1b**), showing that both the prototropic (hydrogen shift) and silatropic (silyl shift) ene reactions occur (Schemes 1, 2).

SCHEME 1

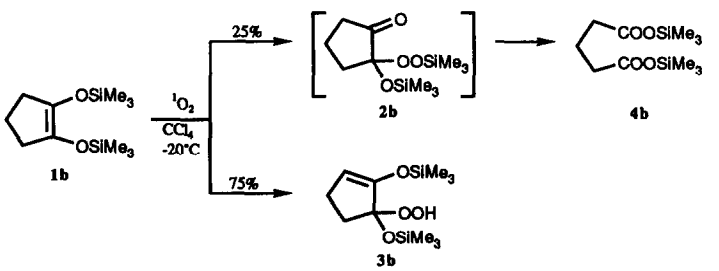


1,2-Bis(trimethylsilyloxy)cyclohexene [3] (**1a**) and $^1O_2$ in CCl_4 with TPP as photosensitizer at -20 °C gave within 50 min the silatropic ene product **2a** [4] [characteristic ^{13}C signals: δ 205.0 (C-1), 104.1 (C-2)] and the prototropic ene product **3a** [5] [characteristic ^{13}C signals: δ 101.7 (C-6), 109.5 (C-2), 147.1 (C-1); characteristic ^1H signals: δ 4.96 [s, 1H, C=CH), 8.6 (s, 1H, OOH)], the **2a** : **3a** ratio being 70 : 30. The α-silylperoxy cyclohexanone **2a** was quite unstable, but could be detected at subambient temperature (-20 °C) by ^1H and ^{13}C NMR. When a sample of the product mixture was warmed up to 20 °C and further monitored by NMR, it was observed that the silatropic ene product **2a** rearranged gradually in a period of 1h completely into the cleavage product bis(trimethylsilyl) adipate (**4a**) [6], as evidenced in the ^{13}C NMR spectrum by the disappearance of the signals at δ 104.1 and 205.0 (specific for **2a**) and the appearance of the signal at δ 173.6 (specific for **4a**). During this period the signals of the prototropic ene product **3a** suffered no change.

On prolonged photooxygenation (ca. 3h, -20 °C) NMR monitoring revealed new proton resonances at δ 5.5, 5.9, 9.0, 9.7, 10.1, and 10.2 (in the approximate relative ratios 2:2:1:1:1:1). These were assigned to the olefinic and hydroperoxy protons of the diastereomeric double ene products **5**. The solvent was removed by rota-evaporation (0 °C, 15 torr) and the residue chromatographed at -40 °C on a Florisil column, eluting with petroleum ether / diethyl ether (9:1) to give as products the silyl adipate **4a**, adipic acid (**6**), the hydroxy-enone **7**, and the disilyl ester **8** in the relative proportion ca. 50 : 20 : 25 : 5, as well as hexamethylsiloxane. The physical constants and spectral data of these products, except those of the disilyl ester **8**, were identical with those of the authentic compounds. Although the ^{1}H NMR data of cleavage product **8** are not known, our spectral data, especially the chemical shifts δ 2.42 (t, $J_{5,4}$=7.1Hz, 2H, 5-H), 2.85 (tdd, $J_{4,3}$=7.4Hz, $J_{4,5}$=7.1Hz, $J_{4,2}$=1.6Hz, 2H, 4-H), 5.74 (dt, $J_{2,3}$=11.4Hz, $J_{2,4}$=1.6Hz, 1H, 2-H), and 6.19 (dt, $J_{3,2}$=11.4Hz, $J_{3,4}$=7.4Hz, 1H, 3-H), support the structure proposed for silyl ester **8**. On-column desilylation of disilyl adipate **4a** is a logical pathway to adipic acid (**6**), while desilylation of the hydroperoxy silyl enol ether **3a**, followed by loss of hydrogen peroxide, is a reasonable route to hydroxy-enone **7**. Disilyl ester **8** presumably arises via rearrangement of the novel double ene product **5** (Scheme 1). During NMR monitoring no dioxetane signals were observed.

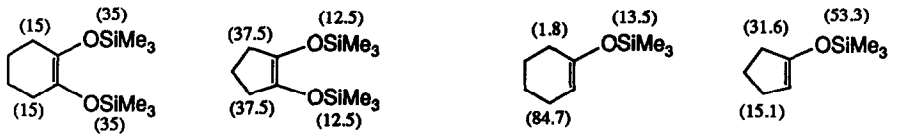
The photooxygenation of the disilyloxycyclopentene **1b** [3] gave under the same conditions as employed for **1a** the bis(trimethylsilyl) glutarate (**4b**) [7] and the hydroperoxy silyl enol ether **3b** [8], as detected by ^{1}H and ^{13}C NMR at -20°C (Scheme 2). The structures of **3b** and **4b** were confirmed by comparison of the ^{1}H and ^{13}C NMR spectra with those of compounds **3a** and **4a**.

SCHEME 2



The differences in the behavior of the cyclopentene substrate **1b** *versus* the cyclohexene derivative **1a** towards singlet oxygen are: i) no silyl peroxy ketone **2b** was observed during NMR monitoring and ii) the proportion of **4b** to **3b** was ca. 25 : 75 compared to 70 : 30 for **4a** to **3a**, indicating that the prototropic ene reaction dominates for the cyclopentene system. Since five-membered ring-annelated 1,2-dioxetanes are more stable than six-membered analogues,[9] it is unlikely that the disilyl diester **4a** arose from cleavage of the corresponding intermediary dioxetane because it should have survived subambient NMR monitoring. Moreover, since the disilyl diester **4a** resulted exclusively from rearrangement of the intermediary silylperoxy ketone **2a** (Scheme 1), it is more probable that also **4b** came from the corresponding silylperoxy ketone **2b**, except that the latter was too labile for NMR detection.

Accepting this hypothesis, it is of interest to compare the present prototropic (hydrogen migration) *versus* silatropic (silyl migration) ene reactivities of the disilyloxycycloalkenes **1a,b** with those reported [2i] for the monosilyloxycycloalkenes **9a,b**. In view of the symmetric nature of the **1a,b** substrates, for better comparison



1a **1b** **9a** **9b**

the observed proto- and silatropic ene reactivities have been divided equally between the two possible sites. Ignoring the regioselectivities exhibited for the ring protons of the unsymmetrical substrates **9a,b**, clearly a pronounced difference exists in the proto- *versus* silatropic ene reactivities between the disilyloxy and monosilyloxy sets **1a,b** and **9a,b**. For the latter, hydrogen migration dominates in the six-membered ring **9a** and silicon migration for the five-membered ring **9b**, while the reverse obtains for **1a,b** , i.e. silatropic ene reactivity is preferred for the six-membered ring **1a** and prototropic for the five-membered ring **1b**. This result is in keeping with the well established *cis*-effect, [10] as examplified by the pronounced exocyclic prototropic ene reaction for 1-methylcyclohexene but overwhelming endocyclic hydrogen abstraction for 1-methylcyclopentene.[11] Conformational control is responsible, in that for the cyclopentene the better perpendicular alignment of the allylic hydrogens relative to the molecular plane provides for a more favorable perepoxide-like complexation, a requirement for the *cis*-effect.[10]

The rearrangement of the intermediary α-silylperoxy ketone **2a** into the cleavage product **4a** (and presumably also of **2b**, which was postulated in the scission of **1b** into **4b** in Scheme 2) is analogous to the Hock-Criegee rearrangement [1, 12] of a variety of peroxides, except that here the silyl group rather than protonation promotes the 1,2-acyl shift. It is significant that such transpositions do not occur for the simpler α-silylperoxy ketones derived from the photooxygenation of the silyl enol ethers **9a,b**.[2i] Apparently the presence of the peroxy ketal moiety at C-2 in **2a** (Scheme 1) is a necessary condition for such rearrangements, as proposed in the enzymatic conversion of analogous catechol derivatives into the corresponding muconic acids by means of dioxygenases.[13,14]

Although our initial goal of preparing the 1,2-dioxetanes of the 1,2-bis(trimethylsilyloxy)cycloalkenes **1a,b** *via* photooxygenation forfeited, and such dioxetanes are still challenging target molecules, novel rearrangements in the reaction of singlet oxygen with disilylated cyclic ene-1,2-diols were uncovered. The fact that silyloxy groups undergo ene reactions with $^1O_2$ opens up interesting possibilities for synthetic applications and mechanistic studies.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft (SFB Nr. 172 "Molekulare Mechanismen Kanzerogener Primärveränderungen"), the Sander-Stiftung and the Fonds der Chemischen Industrie for generous financial support.

References and Notes:

1. (a) Frimer, A. A.; Stephenson, L. M. in Frimer, A. A. (ed.): *Singlet O_2*, CRC Press, Inc., Boca Raton, 1985, Vol. II, Chap. 3, p. 67.
   (b) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359.
2. (a) Adam, W.; Steinmetzer, H. C. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 540.
   (b) Rubottom, G. M.; Lopez Nieves, M. I. *Tetrahedron Lett.* **1972**, *24*, 2423.

(c) Adam, W.; Liu, J-C. *J. Am. Chem. Soc.* **1972**, *94*, 2894.
(d) Jefford, C. W.; Rimbault, C. G.*Tetrahedron Lett.* **1977**, *27*, 2375;
J. Am. Chem. Soc. **1978**, *100*, 6437.
(e) Adam, W.; Alzerreca, A.; Liu, J-C.; Yany, F. *J. Am. Chem. Soc.* **1977**, *99*, 5768.
(f) Friedrich, E.; Lutz, W. *Angew. Chem. Int. Ed. Engl.* **1977**, *89*, 413.
(g) Adam, W.; del Fierro, J. *J. Org. Chem.* **1978**, *43*, 1159.
(h) Adam, W.; del Fierro, J. Quiroz, F.; Yany, F. *J. Am. Chem. Soc.* **1980**, *102*, 2127.
(i) Friedrich, F.; Lutz, W. *Chem. Ber.* **1980**, *113*, 1245.

3. Prepared analogous to Rühlmann, K. *Synthesis*, **1971**, 230.

1a: ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.12(s, 18H), 1.56(m, 4H), 2.01(m, 4H);

^{13}C NMR (50 MHz, $CDCl_3$), δ 0.9(q), 23.2(t), 29.5(t), 132.0(s).

1b: ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.14(s, 18H), 1.73(m, 2H), 2.20(m, 4H);

^{13}C NMR (50 MHz, $CDCl_3$), δ 0.9(q), 16.6(t), 30.0(t), 130.2(s).

4. **2a**: ^{1}H NMR (200 MHz, $CDCl_3$, -20 °C), δ 0.11(s, 9H), 0.17(s, 9H), 1.5 - 2.4(m, 6H), 2.74(m, 2H);

^{13}C NMR (50 MHz, $CDCl_3$, -20 °C), δ -1.0(q), 2.3(q), 22.5(t), 27.5(t), 39.3(t), 39.8(t), 104.1(s), 205.0(s).

5. **3a**: ^{1}H NMR (200 MHz, $CDCl_3$, -20 °C), δ 0.13(s, 9H), 0.19(s, 9H), 1.5 - 2.4(m, 6H), 4.96(t, J =4Hz, 1H), 8.56(s, 1H);

^{13}C NMR (50 MHz, $CDCl_3$, -20°), δ 0.4(q), 1.6(q), 19.7(t), 24.1(t), 33.6(t), 101.7(d), 109.5(s), 147.1(s).

6. **4a**: ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.24(s, 18H), 1.59(m, 4H), 2.28(m, 4H);

^{13}C NMR (50 MHz, $CDCl_3$), δ -0.2(q), 24.4(t), 35.5(t), 173.6(s).

7. **4b**: ^{1}H NMR (200 MHz, $CDCl_3$, -20 °C), δ 0.23(s, 18H), 2.20(m, 2H), 1.75(m, 4H);

^{13}C NMR (50 MHz, $CDCl_3$, -20 °C), δ -0.2(q), 19.6(t), 34.4(t), 173.6(s).

8. **3b**: ^{1}H NMR (200 MHz, $CDCl_3$, -20 °C), δ 0.14(s, 9H), 0.19(s, 9H), 1.84(t, J = 6 Hz, 2H), 2.36(m, 2H), 4.90(t, J = 2 Hz, 1H), 8.9(s, 1H);

^{13}C NMR(50 MHz, $CDCl_3$, -20 °C), δ 0.0(q), 1.6(q), 23.0(t), 33.7(t), 108.2(d), 111.3(s), 150.6(s).

9. Baumstark, A. L.; Wilson, C. *Tetrahedron Lett.* **1981**, *22*, 4363.
10. (a) Schulte-Elte, K.H.; Müller, B.; Rautenstrauch, V. *Helv. Chim. Acta* **1978**, *61*, 2777;
Schulte-Elte, K.H.; Müller, B.; Pamingle, H. *Helv. Chim. Acta* **1979**, *62*, 816;
Schulte-Elte, K.H.; Müller, B.; Ohloff, G. *Nouv. J. Chim.* **1978**, *2*, 427.
(b) Stephenson, L. M. *Acc. Chem. Res.* **1980**, *13*, 419.
(c) Adam, W.; Catalani, L. H.; Griesbeck, A. *J. Org. Chem.* **1986**, *51*, 5494.
11. Schulte-Elte, K. H.; Rautenstrauch, V. *J. Am. Chem. Soc.* **1980**, *102*, 1738.
12. (a) Criegee, R. *Chem. Ber.*, **1944**, *77*, 722.
(b) Criegee, R. *Justus Liebigs Ann. Chem.* **1948**, *560*, 127.
13. Hamilton, G. A. in Hayaishi, O. (ed.): *Molecular Mechanisms of Oxygen Activation*, Academic Press, New York, 1974, p. 443-445.
14. Que, L., Jr.; Lipscomb, J. D.; Münck, E.; Wood, J. M. *Biochimica et Biophysica Acta*, 1977, 485, 60.

(Received in Germany 6 December 1989)