in the presence of solid K_2CO_3 and a catalytic amount of NaI afforded **3** (R^1 = H, R^2 = R^3 = CH_3; Y = COOEt) in 80% yield.
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(14) This aldehyde was trapped as its 2,4-dinitrophenylhydrazone which was purified by column chromatography on silica gel.
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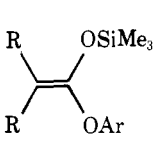
Singlet Oxygenation of Ketene Acetals: Formation of 1,2-Dioxetanes and Their Thermal Rearrangement to α-Peroxy Esters

Sir:

Recently we reported[1] that the photosensitized singlet oxygenation of ketene methyl trimethylsilyl acetals gave the corresponding methyl α-trimethylsilylperoxy esters in high yield. However, when we applied this convenient synthetic utilization of singlet oxygen for the preparation of aryl α-hydroperoxy esters to the corresponding ketene acetals **1,** besides



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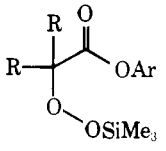

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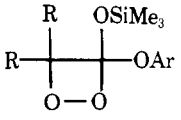

3

the expected α-trimethylsilylperoxy esters **2,** the 1,2-dioxetanes **3** were formed as well.[2] These unexpected results implied the intervention of an intermediate as product branching point in the singlet oxygenation of such electron-rich substrates, a suggestion for which recent evidence has been documented.[3] Still more unusual and mechanistically significant was our observation that the 3-aryloxy-3-trimethylsilyloxy-1,2-dioxetanes **3** rearranged into the α-trimethylsilylperoxy esters **2** on heating. This unprecedented thermal transformation of 1,2-dioxetanes in preserving the peroxide bond is rationalized in terms of heterolytic cleavage of the dioxetane ring at the carbon-oxygen bond leading to a 1,4-dipolar intermediate, which subsequently rearranges via trimethylsilyl migration to afford **2.** The following experimental results substantiate our mechanistic supposition: (i) electron-donating substituents increase while electron-withdrawing substituents decrease the proportion of **3** → **2** rearrangement; (ii) polar solvents enhance rearrangement of dioxetane **3** into α-silylperoxy ester **2** vs. fragmentation into carbonyl products. The experimental results are detailed below.

On tetraphenylporphyrin-sensitized photooxygenation of a 0.05 M solution of *tert*-butylketene phenyl trimethylsilyl acetal (**1a**) in CH_2Cl_2 at −78 °C, irradiating with a 150-W sodium lamp, gave, besides the expected phenyl α-trimethylsilylperoxy-α-*tert*-butylacetate (**2a**) product (characteristic ^1H NMR resonance at δ 4.10 ppm for the α proton), a thermally labile product, exhibiting a characteristic dioxetanyl proton at δ 4.70 ppm. Low-temperature (−78 °C) silylated silica gel chromatography eluting with pentane afforded a 20% yield[4] of the 1,2-dioxetane **3a:** 99% peroxide titer by iodometry; correct elemental composition by combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ (ppm) 0.10 (9 H, s, Me_3Si), 1.15 (9 H, s, *t*-Bu), 4.70 (1 H, s, dioxetanyl), 6.6–7.2 (5 H, m, Ph); no carbonyl absorption in the IR.

Table I. Product Data of the Thermolysis of 1,2-Dioxetanes **3**[a]

dioxetane	solvent	% cleavage[b]	% rearrangement[c]	ratio[d]
3a (H)	C_6H_6	30.4 ± 3.7	69.6 ± 1.0	2.29 ± 0.29
3a (H)	$CDCl_3$	11.8 ± 1.6	88.2 ± 1.0	7.45 ± 0.40
3b (*p*-MeO)	C_6H_6	12.9 ± 1.0	87.0 ± 3.0	6.72 ± 0.23
3c (*p*-Br)	C_6H_6	58.2 ± 4.6	41.8 ± 0.8	0.72 ± 0.10

[a] [3], ~ 0.4 M at 80 °C. [b] *t*-BuCHO product by ^1H NMR integration. [c] α-Silylperoxy esters **2** by ^1H NMR integration. [d] Rearrangement vs. cleavage product ratio for 100% decomposition of the 1,2-dioxetanes **3.**

On heating at 89 °C the dioxetane **3a** decomposed with light emission into the expected *tert*-butylcarboxaldehyde and presumably phenyl trimethylsilyl carbonate (not characterized); however, the major product was the α-peroxy ester **2a** (Table I), isolated by silylated silica gel chromatography at −50 °C and purified by vacuum distillation (bp 75 °C at 0.07 Torr, n^{25}_D 1.4735): 99% peroxide titer by iodometry; correct elemental composition by combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ (ppm) 0.25 (9 H, s, Me_3Si), 1.10 (9 H, s, *t*-Bu), 4.10 (1 H, s, α proton), 6.6–7.2 (5 H, m, Ph); 1780 and 1760 cm^{-1} carbonyl bands in the IR (CCl_4). Methanolysis of the α-peroxy ester **2a** or dioxetane **3a** afforded a 79% yield of phenyl α-*tert*-butyl-α-hydroperoxyacetate: mp 91–93 °C (from hexane); >99% peroxide titer by iodometry; correct elemental composition by combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ (ppm) 1.0 (9 H, s, *t*-Bu), 4.40 (1 H, s, α proton), 6.9–7.3 (5 H, m, Ph), 4.70 (1 H, s, OOH); IR (CCl_4) ν (cm^{-1}) 3550–3200 (OOH), 1780 (C=O), 1385 and 1375 (*gem*-dimethyl).

The rearrangement of dioxetane **3a** into α-silylperoxy ester **2a** represents the first example of a peroxide bond preserving transformation of 1,2-dioxetanes. Usually such energy-rich molecules suffer peroxide bond cleavage to afford electronically excited carbonyl fragments on thermal activation.[5] It was, therefore, surprising that the latter event was the minor course in the thermolysis of the 1,2-dioxetane **3a.** The fact that the rearrangement **3a** → **2a** outweighs the usually facile dioxetane cleavage process intrigued us sufficiently to elucidate the mechanism of this unprecedented reaction.

For this purpose we prepared the *p*-methoxy (**3b**) and *p*-bromo (**3c**) derivatives via singlet oxygenation of the respective ketene acetals. Their isolation, purification, and characterization followed the same procedure as outlined for the parent system **3a.**[6] As with the parent system so also these dioxetanes rearrange into the respective α-silylperoxy esters and cleave into *t*-BuCHO, but the relative amounts depend on the electronic nature of the substituent (Table I). For example, the rearrangement *vs.* cleavage product ratio increases with the electron-donating ability of the para substituent on the aryloxy moiety, i.e., *p*-MeO > H > *p*-Br. In fact, a Hammett plot of the product ratio vs. σ gave a negative ρ (−1.94 ± 0.08), indicating buildup of positive charge at the ketal carbon. These results are rationalized in terms of the 1,4-dipolar intermediate **4** shown in Scheme I.

Additional evidence for the unexpected heterolytic ring opening of the 1,2-dioxetane **3** comes from solvent effects. As Table I reveals, for the dioxetane **3a** in the more polar $CDCl_3$ the rearrangement outweighs the cleavage process by ca. threefold compared with benzene. Consequently, a dipolar transition state is being stabilized by the polar solvent. Attempts to use more polar solvents such as CH_3CN, Me_2SO, or DMF (aprotic) and CH_3OH (protic) were thwarted owing to competing and complex side reactions. The trimethylsilyl-1,2-dioxetanes are extremely susceptible to hydrolysis even by adventitious moisture.

Since 1,4-dipolar intermediates, produced by [2 + 2] cy-

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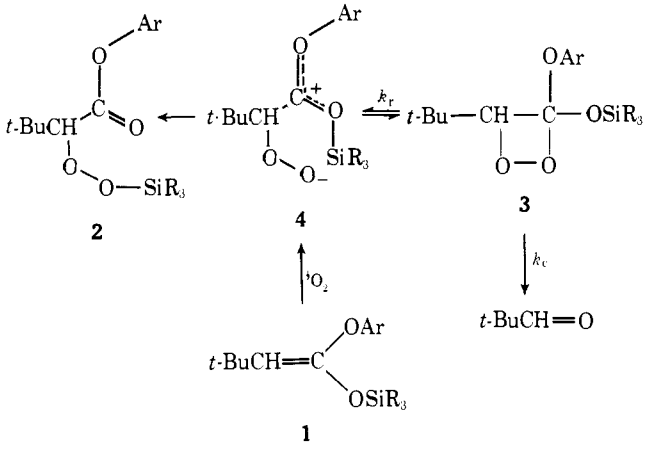
Scheme I



cloaddition, have been trapped by intervention with external dipolarophiles,[7] we attempted such trapping experiments in the hope of providing unequivocal proof for the existence of the postulated 1,4 dipole **4.** On heating of dioxetane **3a** in $CDCl_3$ in the presence of dipolarophiles such as hexafluoroacetone and adamantanone, only rearrangement and cleavage products could be detected.

Huisgen[8] has demonstrated that alcohols serve as efficient dipolarophilic trapping agents in [2 + 2] cycloaddition. Trapping experiment with such protic nucleophiles as ROH was especially encouraged since the formation of α-methoxy peracids in the singlet oxygenation of ketenes in the presence of methanol was rationalized in terms of trapping of dipolar intermediates by the MeOH.[9] However, in view of the hydrolytic lability of the trimethylsilyl derivatives of **3,** it was necessary to prepare the more stable, *tert*-butyldimethylsilyl-1,2-dioxetane **3d** for this purpose.[6] Already in benzene as solvent, **3d** rearranged into the corresponding α-silylperoxy ester **2** and only traces of cleavage product (*t*-BuCHO) could be detected by VPC. Moreover, the corresponding α-silylperoxy ester **2d** is stable toward methanolysis. Thus, the dioxetane **3d** is an ideal substrate for dipolar trapping by CH_3OH because the cleavage reaction is suppressed and the rearrangement product **2d** survives CH_3OH.

In methanol **3d** affords exclusively the rearrangement product **2d** already at room temperature. Had dipolar trapping by CH_3OH taken place, the expected ortho ester should have either survived or should have been methanolized into α-hydroperoxy ester. Apparently the 1,4-dipolar intermediates **4** must undergo silatropic shift faster than being trapped by CH_3OH. Not always is it possible to trap such 1,4 dipoles by alcohols. For example, in the [2 + 2] cycloaddition of TCNE with tetramethoxyethylene, instead of the expected ortho ester, only cyclobutane was formed in the presence of alcohols.[7]

Whether the postulated 1,4 dipole **4** is also the intermediate in the singlet oxygenation of the ketene acetal **1** (Scheme I) is of obvious mechanistic relevance. Singlet oxygenation of the *tert*-butyldimethylsilyl ketene acetal **1d** in methanol gave only the rearrangement product **2d.** Of course, any dioxetane **3d** that may have been formed would have rearranged into **2d** in CH_3OH, as confirmed in the attempted trapping experiments. From our preliminary data we are tempted to suggest that the same 1,4-dipolar **4** intermediate intervenes in the singlet oxygenation of the ketene acetal **1** and the thermal rearrangement of the 1,2-dioxetane **3.** However, further experimentation is in progress to substantiate this mechanistic claim.

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References and Notes

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(2) In this experiment we used a General Electric 150-W sodium street lamp instead of the General Electric 650-W tungsten–halogen lamp. While the sodium lamp was used directly, efficient infrared and ultraviolet filters were necessary for the tungsten–halogen lamp to prevent photodecomposition of the peroxide products. Even with these latter precautions, no dioxetane **3** product was obtained when using the tungsten–halogen lamp. In fact, control experiments revealed that the dioxetanes **3** suffered photofragmentation with the tungsten–halogen lamp, but not with the sodium lamp. The advantage of the sodium vs. the tungsten–halogen lamp as irradiation source in preparative photosensitized oxygenations is clearly evident.
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(4) These 1,2-dioxetanes **3** rearrange partly to the α-peroxy esters **2** during the silica gel chromatography and it is for this reason that the isolated yields are low.
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Half-Sandwich Cyclooctatetraenethorium Compounds

Sir:

Bis(η_8-cyclooctatetraene)actinide(IV) compounds have been known for over a decade[1] and are now known for all of the lower actinides.[2] We now report the first monocyclooctatetraenethorium dichloride and bisborohydride. During reaction of potassium *n*-butylcyclooctatrienediide (K_2BuCOT) with thorium tetrachloride we observed the presence of a NMR signal at δ 6.6 ppm not associated with either the thorocene[3] or K_2BuCOT, and therefore attributed to (BuCOT)$ThCl_2$ (**1b**). From the reaction of thorocene (di-π-cyclooctatetraenethorium) and $ThCl_4$ in THF we isolated a microcrystalline white nonvolatile compound that gave a satisfactory analysis for $C_8H_8ThCl_2 \cdot 2C_4H_8O$.[4] X-ray crystal structure determination showed the compound to have a planar C_8 ring coordinated at the center to a thorium atom that was also coordinated to two chlorines and the oxygens of two tetrahydrofurans.[5]

$$(C_8H_8)_2Th + ThCl_4 \xrightarrow{THF} C_8H_8ThCl_2$$
1a

Related substituted COT compounds are also best prepared by refluxing the appropriate thorocene[3] with excess $ThCl_4$ in THF or DME until the yellow color of the thorocene disappears. The *n*-butylcyclooctatetraene and 1,3,5,7-tetramethylcyclooctatetraene compounds (**1b** and **1c,** respectively), prepared in this way, are characterized by the NMR spectra summarized in Table I. The ^{13}C NMR spectrum for **1b** shows the five resonances of the substituted C_8 ring and the four resonances of the butyl group. The mono-COT·$ThCl_2$ derivatives can also be prepared by reaction of the thorocenes with dry hydrogen chloride.[6]

Based on the volatility of actinide borohydride compounds,[7]

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