

- 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.
- (12) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.-I.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741.
- (13) Braun, H.; Mayer, N.; Kresze, G. *Justus Liebig's Ann. Chem.* **1972**, *762*, 111.
- (14) This aldehyde was trapped as its 2,4-dinitrophenylhydrazone which was purified by column chromatography on silica gel.
- (15) Address correspondence to the Department of Synthetic Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho 1-33, Chiba 260, Japan.

Katsuyuki Ogura,\*<sup>15</sup> Shigeko Furukawa  
Gen-ichi Tsuchihashi\*

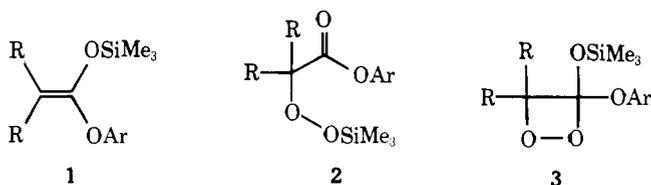
Sagami Chemical Research Center  
Nishi-Ohnuma 4-4-1, Sagami-hara, Kanagawa 229, Japan

Received October 5, 1979

### Singlet Oxygenation of Ketene Acetals: Formation of 1,2-Dioxetanes and Their Thermal Rearrangement to $\alpha$ -Peroxy Esters

Sir:

Recently we reported<sup>1</sup> that the photosensitized singlet oxygenation of ketene methyl trimethylsilyl acetals gave the corresponding methyl  $\alpha$ -trimethylsilylperoxy esters in high yield. However, when we applied this convenient synthetic utilization of singlet oxygen for the preparation of aryl  $\alpha$ -hydroperoxy esters to the corresponding ketene acetals **1**, besides



the expected  $\alpha$ -trimethylsilylperoxy esters **2**, the 1,2-dioxetanes **3** were formed as well.<sup>2</sup> 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.<sup>3</sup> Still more unusual and mechanistically significant was our observation that the 3-aryloxy-3-trimethylsilyloxy-1,2-dioxetanes **3** rearranged into the  $\alpha$ -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**  $\rightarrow$  **2** rearrangement; (ii) polar solvents enhance rearrangement of dioxetane **3** into  $\alpha$ -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  $-78^\circ C$ , irradiating with a 150-W sodium lamp, gave, besides the expected phenyl  $\alpha$ -trimethylsilylperoxy- $\alpha$ -*tert*-butylacetate (**2a**) product (characteristic  $^1H$  NMR resonance at  $\delta$  4.10 ppm for the  $\alpha$  proton), a thermally labile product, exhibiting a characteristic dioxetanyl proton at  $\delta$  4.70 ppm. Low-temperature ( $-78^\circ C$ ) silylated silica gel chromatography eluting with pentane afforded a 20% yield<sup>4</sup> of the 1,2-dioxetane **3a**: 99% peroxide titer by iodometry; correct elemental composition by combustion analysis;  $^1H$  NMR ( $CCl_4, Me_4Si$ )  $\delta$  (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 **3a**

dioxetane	solvent	% cleavage <sup>b</sup>	% rearrangement <sup>c</sup>	ratio <sup>d</sup>
<b>3a</b> (H)	$C_6H_6$	$30.4 \pm 3.7$	$69.6 \pm 1.0$	$2.29 \pm 0.29$
<b>3a</b> (H)	$CDCl_3$	$11.8 \pm 1.6$	$88.2 \pm 1.0$	$7.45 \pm 0.40$
<b>3b</b> ( <i>p</i> -MeO)	$C_6H_6$	$12.9 \pm 1.0$	$87.0 \pm 3.0$	$6.72 \pm 0.23$
<b>3c</b> ( <i>p</i> -Br)	$C_6H_6$	$58.2 \pm 4.6$	$41.8 \pm 0.8$	$0.72 \pm 0.10$

<sup>a</sup> [**3**],  $\sim 0.4$  M at  $80^\circ C$ . <sup>b</sup> *t*-BuCHO product by  $^1H$  NMR integration. <sup>c</sup>  $\alpha$ -Silylperoxy esters **2** by  $^1H$  NMR integration. <sup>d</sup> Rearrangement vs. cleavage product ratio for 100% decomposition of the 1,2-dioxetanes **3**.

On heating at  $89^\circ C$  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  $\alpha$ -peroxy ester **2a** (Table I), isolated by silylated silica gel chromatography at  $-50^\circ C$  and purified by vacuum distillation (bp  $75^\circ C$  at 0.07 Torr,  $n_D^{25}$  1.4735): 99% peroxide titer by iodometry; correct elemental composition by combustion analysis;  $^1H$  NMR ( $CCl_4, Me_4Si$ )  $\delta$  (ppm) 0.25 (9 H, s,  $Me_3Si$ ), 1.10 (9 H, s, *t*-Bu), 4.10 (1 H, s,  $\alpha$  proton), 6.6–7.2 (5 H, m, Ph); 1780 and  $1760\text{ cm}^{-1}$  carbonyl bands in the IR ( $CCl_4$ ). Methanolysis of the  $\alpha$ -peroxy ester **2a** or dioxetane **3a** afforded a 79% yield of phenyl  $\alpha$ -*tert*-butyl- $\alpha$ -hydroperoxyacetate: mp  $91\text{--}93^\circ C$  (from hexane); >99% peroxide titer by iodometry; correct elemental composition by combustion analysis;  $^1H$  NMR ( $CCl_4, Me_4Si$ )  $\delta$  (ppm) 1.0 (9 H, s, *t*-Bu), 4.40 (1 H, s,  $\alpha$  proton), 6.9–7.3 (5 H, m, Ph), 4.70 (1 H, s, OOH); IR ( $CCl_4$ )  $\nu$  ( $\text{cm}^{-1}$ ) 3550–3200 (OOH), 1780 (C=O), 1385 and 1375 (*gem*-dimethyl).

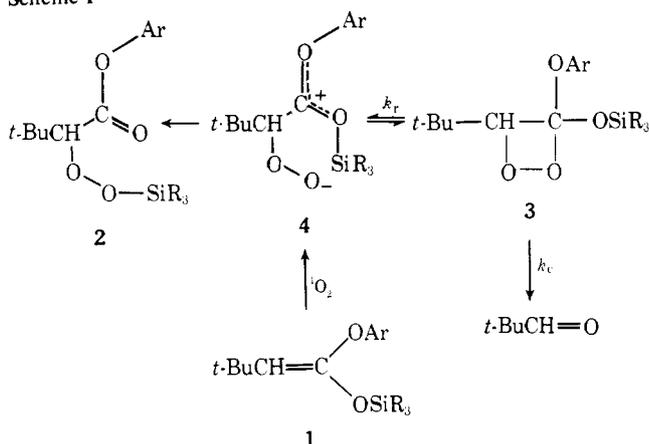
The rearrangement of dioxetane **3a** into  $\alpha$ -silylperoxy ester **2a** represents the first example of a peroxide bond preserving transformation of 1,2-dioxetanes. Usually such energy-rich molecules suffer peroxide bond cleavage to afford electronically excited carbonyl fragments on thermal activation.<sup>5</sup> 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**  $\rightarrow$  **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**.<sup>6</sup> As with the parent system so also these dioxetanes rearrange into the respective  $\alpha$ -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.  $\sigma$  gave a negative  $\rho$  ( $-1.94 \pm 0.08$ ), 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 1.

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-

Scheme I



cloaddition, have been trapped by intervention with external dipolarophiles,<sup>7</sup> 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  $\text{CDCl}_3$  in the presence of dipolarophiles such as hexafluoroacetone and adamantanone, only rearrangement and cleavage products could be detected.

Huisgen<sup>8</sup> 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  $\alpha$ -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.<sup>9</sup> 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.<sup>6</sup> Already in benzene as solvent, **3d** rearranged into the corresponding  $\alpha$ -silylperoxy ester **2d** and only traces of cleavage product (*t*-BuCHO) could be detected by VPC. Moreover, the corresponding  $\alpha$ -silylperoxy ester **2d** is stable toward methanolysis. Thus, the dioxetane **3d** is an ideal substrate for dipolar trapping by  $\text{CH}_3\text{OH}$  because the cleavage reaction is suppressed and the rearrangement product **2d** survives  $\text{CH}_3\text{OH}$ .

In methanol **3d** affords exclusively the rearrangement product **2d** already at room temperature. Had dipolar trapping by  $\text{CH}_3\text{OH}$  taken place, the expected ortho ester should have either survived or should have been methanolized into  $\alpha$ -hydroperoxy ester. Apparently the 1,4-dipolar intermediates **4** must undergo silatropic shift faster than being trapped by  $\text{CH}_3\text{OH}$ . 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.<sup>7</sup>

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  $\text{CH}_3\text{OH}$ , 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.

**Acknowledgments** are made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (Grant No. 78-12621), and the National Institutes of Health (Grant Nos. GM-00141-04 and RR-8102-07) for financial support.

## References and Notes

- (1) Adam, W.; del Fierro, J. *J. Org. Chem.* **1978**, *43*, 1159.
- (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.
- (3) (a) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6437, 6515. (b) Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. *Ibid.* **1977**, *99*, 7977.
- (4) These 1,2-dioxetanes **3** rearrange partly to the  $\alpha$ -peroxy esters **2** during the silica gel chromatography and it is for this reason that the isolated yields are low.
- (5) (a) Adam, W. *Adv. Heterocycl. Chem.* **1977**, *21*, 437. (b) Horn, K. A.; Koo, J.-Y.; Schmidt, S. P.; Schuster, G. B. *Mol. Photochem.* **1978**, *9*, 1.
- (6) The experimental details are reserved for a full paper.
- (7) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 199.
- (8) Huisgen, R.; Schug, R.; Steiner, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 80.
- (9) (a) Turro, N. J.; Ito, Y.; Chow, M. F.; Adam, W.; Rodriguez, O.; Yany, F. *J. Am. Chem. Soc.* **1977**, *99*, 5836. (b) Turro, N. J.; Chow, M.-F.; Ito, Y. *Ibid.* **1978**, *100*, 5580.
- (10) NIH Career Development Awardee (1975-1980).
- (11) (a) Graduate Research Fellow. (b) Undergraduate Research Participant in the Support for University Biomedical Education Program (SUBE) sponsored by NIH-MBS.
- (12) Inter-American University.

Waldemar Adam,<sup>\*10</sup> Javier del Fierro<sup>11a</sup>  
Fernando Quiroz,<sup>11b</sup> Faris Yany<sup>12</sup>

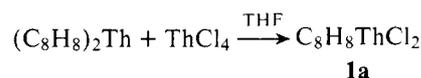
*Department of Chemistry, University of Puerto Rico  
Rio Piedras, Puerto Rico 00931, and  
Department of Chemistry, Inter-American University  
Hato Rey, Puerto Rico 00919*

*Received December 7, 1979*

## Half-Sandwich Cyclooctatetraenethorium Compounds

*Sir:*

Bis( $\eta_8$ -cyclooctatetraene)actinide(IV) compounds have been known for over a decade<sup>1</sup> and are now known for all of the lower actinides.<sup>2</sup> We now report the first monocyclooctatetraenethorium dichloride and bisborohydride. During reaction of potassium *n*-butylcyclooctatrienediide ( $\text{K}_2\text{BuCOT}$ ) with thorium tetrachloride we observed the presence of a NMR signal at  $\delta$  6.6 ppm not associated with either the thorocene<sup>3</sup> or  $\text{K}_2\text{BuCOT}$ , and therefore attributed to  $(\text{BuCOT})\text{ThCl}_2$  (**1b**). From the reaction of thorocene (di- $\pi$ -cyclooctatetraenethorium) and  $\text{ThCl}_4$  in THF we isolated a microcrystalline white nonvolatile compound that gave a satisfactory analysis for  $\text{C}_8\text{H}_8\text{ThCl}_2 \cdot 2\text{C}_4\text{H}_8\text{O}$ .<sup>4</sup> X-ray crystal structure determination showed the compound to have a planar  $\text{C}_8$  ring coordinated at the center to a thorium atom that was also coordinated to two chlorines and the oxygens of two tetrahydrofurans.<sup>5</sup>



Related substituted COT compounds are also best prepared by refluxing the appropriate thorocene<sup>3</sup> with excess  $\text{ThCl}_4$  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 <sup>13</sup>C NMR spectrum for **1b** shows the five resonances of the substituted  $\text{C}_8$  ring and the four resonances of the butyl group. The mono-COT· $\text{ThCl}_2$  derivatives can also be prepared by reaction of the thorocenes with dry hydrogen chloride.<sup>6</sup>

Based on the volatility of actinide borohydride compounds,<sup>7</sup>