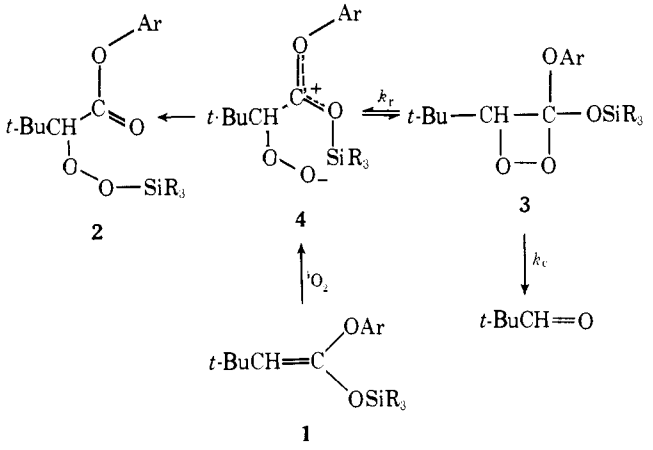
Scheme I



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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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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Table I. Spectra of Mono-COT Thorium Compounds

no.	compound	spectrum
		^{1}H NMR, δ (ppm from Me_4Si)
1a	$C_8H_8ThCl_2$	6.79 (s, ring)[a,b]
		6.6 (s, ring)[c]
1b	n-$C_4H_9C_8H_7ThCl_2$	6.6 (ring)[c]
		3.1, 1.0 (Bu)
1c	1,3,4,7-$Me_4C_8H_4ThCl_2$	6.5 (ring)[c]
		3.1 (Me)
2a	$C_8H_8Th(BH_4)_2$	6.69 (s, 8 H, ring), 3.11 (q, J = 85 Hz, 8 H, BH_4), 3.34, 0.90 (br, 8 H, THF)[a]
		^{13}C NMR, δ (ppm from Me_4Si)
1b		116.5, 104.1, 103.1, 102.7, 101.2 (ring), 49.5, 38.6, 22.8, 14.5 (Bu)[c]
		IR (Nujol), cm^{-1}
2a		2482 (s) (B-H, terminal), 2282 (w), 2220 (s), (B-H, bridging), 2150 (m), 1180 (s), 1163 (s), 722 (sh), 714 (s) (COT)

[a] In C_6D_6. [b] Also showed resonances for THF, 3.69 (t), 13.6 (m); areas for the three resonances are 1:1:1, consistent with $C_8H_8ThCl_2 \cdot 2THF$. [c] In THF-d_8.

we hoped that replacement of chloride by borohydride would result in more volatile complexes. Also of interest is the nature of the bonding of the borohydride groups to the metal center; both tridentate and bidentate bonding to the BH_4 groups are known for actinide compounds.[8] The preparation of $C_8H_8Th(BH_4)_2$ (**2a**) and n-$C_4H_9C_8H_7Th(BH_4)_2$ (**2b**) has been achieved by several routes. Refluxing an equimolar mixture of $Th(BH_4)_4(THF)_2$[9] and di-n-butylthorocene[3] in THF gave **2b** in 67% yield. Because of the low solubility of thorocene, **2a** is more easily prepared by the reaction of equimolar amounts of $Th(BH_4)_4(THF)_2$ and K_2COT in THF at room temperature. We also prepared **2a** by the sequence

$$ThCl_4 + 2LiBH_4 \xrightarrow{THF} \text{“}ThCl_2(BH_4)_2\text{”} \xrightarrow[THF]{K_2COT} C_8H_8Th(BH_4)_2$$
2a

This route is made more complicated, however, by the necessity to remove the LiCl also formed.

2a and **2b** are white microcrystalline products soluble in THF and benzene but not volatile. Satisfactory combustion analyses were not obtained,[10] but the compounds were well characterized by NMR and IR spectra (Table I). The ^{1}H NMR spectrum of **2a** in C_6D_6 shows two molecules of coordinated THF in addition to the COT and two equivalent BH_4 groups. The quartet from the borohydride protons is similar to that in $(C_5H_5)_3ThBH_4$[8a] and indicates fluxional behavior among these protons. At −80 °C the quartet collapses to a broad singlet at δ 3.0 and, as noted by Marks and Shimp,[11] probably indicates a temperature-dependent loss of B-H coupling rather than a slowing of the fluxional process. The IR spectrum is in accord with tridentate binding to borohydride. The 2500-2100-cm^{-1} region is similar to that for $Th[N(SiMe_3)_2]_3BH_4$ for which tridentate geometry has been established by crystal structure determination.[12] The strong band at ~715 cm^{-1} (15 cm^{-1} higher than a band in thorocene) appears to be characteristic of the mono-ring or “half-sandwich” structure.

All of these compounds are air and moisture sensitive. The further chemistry of these compounds is being studied.

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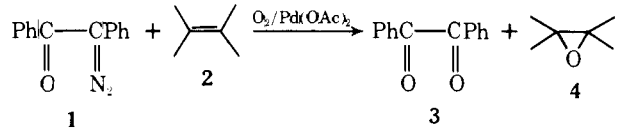
Olefin Epoxidation by an Intermediate Formed in the Metal Ion Catalyzed Oxygenation of Azibenzil

Sir:

Many monooxygenase-catalyzed reactions involve a species which transfers an oxygen atom to the substrate. One model for this species is the “oxenoid” intermediate.[1] Much attention has been devoted to the structure and reactivity of carbonyl oxides as model oxenoids, which are proposed to be formed as intermediates in ozonation of alkenes,[3] alkynes,[4] and ketenes.[5] Intermediates in the photooxygenation of diazo compounds[6] and singlet oxygen oxygenation of diazo compounds and ylides[7] are probably similar in structure and can also transfer oxygen to alkanes,[8] alkenes,[9] sulfides,[10] and aromatic substrates.[11] We now report that azibenzil reacts readily with oxygen in the presence of metal ion catalysts to give an intermediate which can transfer an oxygen atom to olefins to give epoxides under very mild conditions.



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