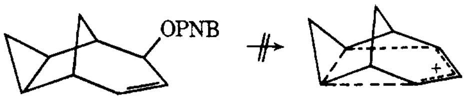
more than 4 Å removed from the site of initial ionization. The remarkable longevity of this cation, which permits the weakly nucleophilic leaving group to compete with water in the product-forming step, suggests a greater stability than one would attribute to an isolated secondary cation, **5**. In addition, such a cation could not reasonably be expected to yield **2a** or **2b** with the high stereospecificity observed; in fact, one would expect capture of this cation to lead to a predominance of product epimeric with **2**. In light of these considerations, the σ–π delocalized structure **6** presents an attractive alternative.

To the best of our knowledge, this represents the first demonstration that a remote cyclopropane ring is capable of nucleophilic attack on a carbon–carbon double bond or that such interaction can lead to an extensively delocalized, stabilized, cationic intermediate. The results reported here lend added credence to the explanation recently offered to explain the failure to observe such participation and stabilization in a closely related system, **7**; namely, that participation in that case would lead to an antiaromatic delocalized cation **8**.[9]



7 8

PNB = *p*-nitrobenzoyl

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yields exclusively *endo*-2-tricyclo[3.3.0.0^{4,6}]octanol, *i.e.*, the product of exo attack by hydride.[6] Inspection of a model clearly demonstrates that the presence of the vinyl substituent at C-5 would not significantly shield exo attack at C-2 of cation **5**.

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[10] National Science Foundation Undergraduate Research Participant.

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An α-Peroxy Lactone. Synthesis and Chemiluminescence[1]

Sir:

The suggestion of α-peroxy lactones as intermediates in bioluminescence and chemiluminescence has been amply documented in recent years.[2,3] Among the extensively studied biological substrates we mention the luminescence observed for the *Cypridina hilgendorfii*,[4a,b] the latia neritoides,[5] and the firefly luciferin.[6a–d] In the latter case, detailed oxygen-18 labeling experiments seriously question the α-peroxy lactone intermediacy, at least in the enzymatic oxidation.[6e,6f] Yet, very convincing arguments have been put forward on the involvement of α-peroxy lactones in the chemiluminescence observed in the reaction of acridinium salts with hydrogen peroxide[7] and in the reaction of ketenes with singlet oxygen.[8] However, to the best of our knowledge the synthesis and characterization of an authentic α-peroxy lactone derivative has not been reported so far. Our success in preparing β-peroxy lactones[9] and γ-peroxy lactones[10] encouraged us to undertake the synthetic challenge inherent with the α-peroxy lactone structure. We now report on the synthesis of 4-*tert*-butyl-1,2-dioxetan-3-one (**4**), the first α-peroxy lactone to be prepared and characterized.

Among the initial, obvious approaches to the preparation of α-peroxy lactones, we attempted the base-catalyzed cyclization of α-haloperoxy acids, but decomposition of the α-halo percarboxylate anion prevailed over the desired intramolecular cyclization.[11] Attempts to add singlet oxygen, chemically as well as photochemically,[12] to bis(trifluoromethyl)ketene and bis(*tert*-butyl)ketene failed; both ketenes were recovered unchanged. The addition of singlet oxygen to ketene dithioketals proceeded smoothly to give the respective 1,2-dioxetanes, but the latter fragmented even at Dry Ice temperatures.[13]

After these numerous failures we decided to mimic the biological systems[2,3] by preparing first an authentic α-hydroperoxy acid and attempting to cyclize it to the α-peroxy lactone, employing one of the various cyclants that have proved useful for the preparation of β-lactones from β-hydroxy acids.[14] Although α-hydroperoxy esters are readily available *via* base-catalyzed autoxidation of the corresponding esters,[15] attempts to hydrolyze these met with failure due to facile decarboxylative fragmentation of the intermediary α-hydroperoxy acids under basic as well as acidic conditions.[16] α-Lactones can be efficiently trapped by methanol in the form of α-methoxy acids.[17] Analogous photodecarboxylation of an ether solution of di-*n*-butylmalonoyl peroxide in the presence of concentrated hydrogen peroxide resulted in the desired α-hydroperoxy acid, but all efforts to obtain a pure sample met with failure. However, photooxidation of the ketene bis(trimethylsilyl)ketal (**1**),

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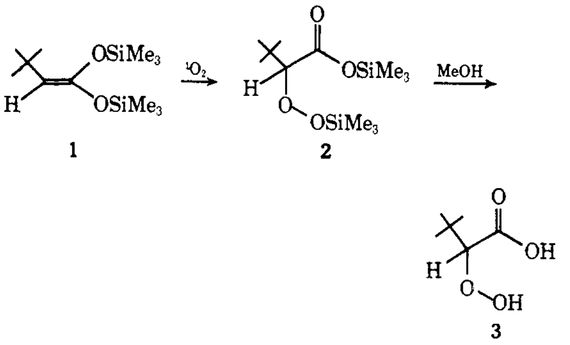
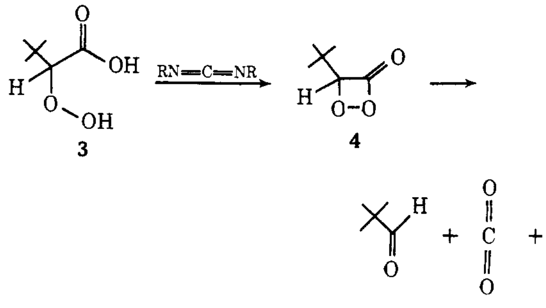
readily available by silylation of the α-lithio carboxylate,[18] gave quantitatively the α-silyl peroxy ester **2** (eq 1):



(1)

bp 67–69° (0.2 mm); 99 ± 1% pure by iodometric titration; ir (cm^{-1}, CCl_4) 1730 and 1710 (C═O), 1365 (*tert*-butyl), and 1245 (Si–O); nmr (60 MHz) δ (TMS, CCl_4) 0.30 (s, 9, OOSi-*Me*₃), 0.20 (s, 9, CO_2SiMe_3), 0.98 (s, 9, C*Me*), and 3.97 (s, 1, $\gg$C*H*). This novel ene reaction involving migration of a trimethylsilyl group was anticipated, since in the photooxidation of trimethylsilyl enol ethers a similar migration was observed.[19] Hydrolysis of the silyl ester **2** with methanol at 5–10° afforded the desired α-hydroperoxy acid **3** essentially quantitatively, which on recrystallization from anhydrous ether-pentane mixture gave white needles: mp 69–70°; 99.5 ± 0.5 % pure by iodometric titration; ir (cm^{-1}, CCl_4) 3510–3450 (OOH), 1715 (C═O), and 1365 (*tert*-butyl); nmr (60 MHz) δ (TMS, CCl_4) 1.05 (s, 9, CMe_3), 4.30 (s, 1, $\gg$C*H*), and 9.52 (s, 2, OO*H* and CO_2H). Catalytic reduction over platinum gave the α-hydroxy acid quantitatively, mp 85–87° (lit.[20] mp 87–88°).

The cyclization of the α-hydroperoxy acid **3** into the α-peroxy lactone **4** (eq 2) was most effectively achieved by stirring equimolar quantities of **3** and dicyclohexylcarbodiimide in CCl_4 below −10° for 30 min. Flash distillation of the reaction mixture at −10° permitted separation of the unreacted starting materials and the dicyclohexylurea, affording a clean solution of the α-peroxy lactone **4** in CCl_4, whose ir exhibited a strong carbonyl band at 1875 cm^{-1} (for comparison, α-lactones[21] absorb at 1900 cm^{-1} and β-lactones at 1830 cm^{-1}) and the characteristic *tert*-butyl at 1365, while the nmr spectrum showed singlet proton resonances at δ 1.10 (*tert*-butyl) and 5.48 ($\gg$CH). However, the infrared and nmr spectra quickly changed (the approximate lifetime of the α-peroxy lactone is 5–8 min at room temperature) to that of pivalaldehyde under vivid evolution of CO_2. The presence of pivalaldehyde, the exclusive decomposition product, was confirmed by comparison of glpc retention times and ir and nmr spectra with the authentic material. Warming of a sample to room temperature in the dark clearly displayed the expected luminescence, which could be significantly enhanced by addition of 9,10-diphenylanthracene as the photoreceptor.[8]



(2)

Efforts to isolate the α-peroxy lactone **4** in pure form have failed, since it readily codistills with CCl_4, and efforts to crystallize the compound have not succeeded. Presently we are exploring substitution patterns which should help stabilize the α-peroxy lactone structure and at the same time incorporate desirable physical properties to permit isolation. Measurements of luminescence quantum yields, the luminescence spectrum, and activation parameters, as well as synthetic utilization of this novel peroxide heterocycle, are in progress.

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[22] Taken in part from the Doctoral Dissertation of J. C. Liu to be submitted to the University of Puerto Rico in partial fulfillment of the requirements of the Ph.D. degree.

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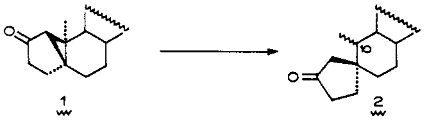
Stereochemistry of the Lithium–Ammonia Reduction of *cis*-1,7-Dimethyltricyclo[4.4.0.0^{2,6}]decan-3-one and Related Compounds

Sir:

The alkali metal–ammonia reduction of conjugated cyclopropyl ketones is now a well-known process[1–5] and has considerable synthetic potential. It has been established[1] that, in general, the cyclopropyl bond which cleaves is the one possessing the greater overlap with the π orbital system of the carbonyl group. However, one interesting and potentially useful facet of this reaction which has not yet received investigative attention is the stereochemical fate of the β carbon atom. For example, although lumicholestenone (**1**) has been reduced with lithium in liquid ammonia,[1] the stereochemistry at C_{10} in the product **2** was not determined.



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