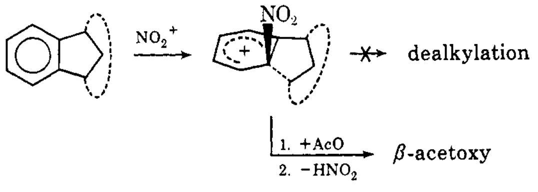
Scheme II



of nitrodeisopropylation of *p*-cymene or *p*-diisopropylbenzene[1] is reasonable; the isopropyl group should have no difficulty achieving a conformation in which the breaking C–C bond can approach a parallel alignment with adjacent p orbitals of the π system, and thereby obtain maximum transition state stabilization.

Further tests of the hypotheses presented here are in progress; we continue to extend our knowledge of structure–reactivity patterns in *ipso* nitration.

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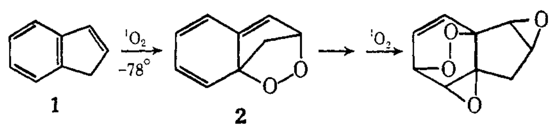
Chemistry of Singlet Oxygen. XIX. Dioxetanes from Indene Derivatives[1]

Sir:

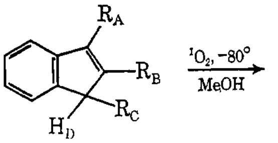
Singlet oxygen undergoes a 1,2-cycloaddition reaction with certain olefins.[2–4] In most cases, dioxetanes have only been isolated from reactions involving electron-rich olefins such as vinyl ethers;[2] usually the proposed dioxetane intermediates undergo cleavage to form two carbonyl fragments.[5] In only a few instances have dioxetanes been isolated from less electron-rich olefins such as adamantylideneadamantane[3] and 2,5-dimethyl-2,4-hexadiene[4] using singlet oxygen; other alkyl-substituted dioxetanes[6] have been prepared only by cyclization of halohydroperoxide compounds (Kopecky's[6a] method).

We previously reported that indenes (1) undergo an initial 1,4-cycloaddition to give usual rearrangement products (3) when the photooxygenation is carried out at −78° in acetone solution.[7] However, while the reaction of indene in aprotic solvents at room temperature is very slow,[8] the reaction in methanol proceeds rapidly with the formation of products apparently derived from dioxetanes.[5d,7,8]

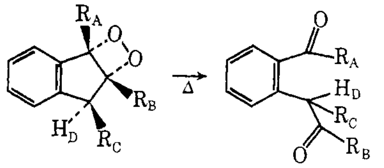


1 2 3

We have now isolated dioxetanes in good yield by low-temperature photooxygenation of indenes in methanol. Compounds **4a–d**, 400–500 mg in 50–100 ml of methanol (50% methanol–acetone in the case of **4a** and **b**), were photooxygenated at −78° (Rose Bengal sensitizer). To avoid photolysis of the dioxetanes by lamp uv[9] (Sylvania DWY), the solutions were irradiated through aqueous $CuCl_2$–$CaCl_2$ (cutoff 450 nm).[10,11]



4a, $R_A = R_B = C_6H_5$; $R_C = H$
b, $R_A = CH_3$; $R_B = C_6H_5$; $R_C = H$
c, $R_A = i\text{-}C_3H_7$; $R_B = R_C = H$
d, $R_A = CH_3$; $R_B = H$; $R_C = t\text{-}C_4H_9$



5 **6**

After vacuum evaporation (<0°), the reaction mixtures were chromatographed on silica gel with $CHCl_3$; the dioxetanes appear as a yellow band.[12] The residues crystallized from cold ether–pentane to give dioxetanes **5a–d** as pale yellow crystals (Table I).

Table I. Dioxetanes from Indenes

Cpd	Yield (%)[a]	Mp, °C
5a[b]	55	47–51 dec
5b	54	69–70 dec
5c[c]	31	49.5–51 dec
5d[c]	32	56–58 dec

[a] After two crystallizations. [b] Incorporates solvent. [c] Not run to completion; yield based on O_2 uptake; unreacted starting material recovered.

The reaction of **4b** also produced "ene" product **7** (in ~3% yield by nmr); "ene" products were not seen

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(1) Paper XVIII: C. S. Foote, T.-Y. Ching, and G. G. Geller, *Photochem. Photobiol.*, submitted. Supported by National Science Foundation Grant No. GP 37165X and Public Health Service Grant No. 20080-01.

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(7) C. S. Foote, S. Mazur, P. A. Burns, and D. Lerdal, *J. Amer. Chem. Soc.*, **95**, 586 (1973).

(8) S. Mazur, Doctoral Thesis, UCLA, 1971, p 41.

(9) Preliminary experiments showed this to be a problem.

(10) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 739.

(11) On a 50 mg scale (without the uv filter), **4b** reacted in less than 10 min, **4a** and **d** in 30 min, and **4c** in 60 min (dye bleaching); since the reaction times were substantially slower using the filter, the larger scale reactions of **4c** and **d** were not run to completion.

(12) Work-up was carried out under minimum natural lighting to avoid photolysis by uv from fluorescent lights.

with **4c** or **d**, nor were products of reaction with 2 mol of oxygen (**3**) observed (by nmr) under these conditions. Dioxetanes **5a–d** chemiluminesce when $CHCl_3$ solutions are warmed with 9,10-diphenylanthracene or 9,10-dibromoanthracene. They decompose explosively above their melting points on rapid heating. The nmr spectra of **5a–d** and **6a–d** are shown in Table II.

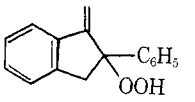
Table II. Chemical Shifts of the Protons of **5** and **6** (δ, TMS, $CDCl_3$, 60 MHz)[a]

Cpd	H_B	H_C	H_D	CH_3	*i*-PrCH	*t*-C_4H_9
5a		3.64	3.64			
5b		3.54	3.54	1.64		
5c	5.88[b]	3.0[c]	3.2	0.69[d] 1.33[d]	2.44	
5d	5.88		3.08[e]	1.81		0.87
6a		4.56	4.56			
6b		4.52	4.52	2.53		
6c	9.71[f]	3.84	3.84	1.15	3.47	
6d	9.91[g]		4.62	2.55		1.00

[a] Aromatic protons omitted for clarity. [b] X portion of ABX spectrum: $J_{BC} = 3.8$ Hz, $J_{BD} = 1.5$ Hz (coupling with the isopropyl CH ($J = 0.7$ Hz). [c] Assigned as H_C based on the larger value of J_{BC} (3.8 *vs.* 1.5 Hz); $J_{CD} = 18$ Hz. [d] Two equivalent doublets ($J = 7.5$ Hz) due to center of asymmmetry. [e] Expected stereochemistry based on the hindrance of the *tert*-butyl group, in agreement with the lack of observed coupling with H_B. [f] $J_{B(CD)} = 1.7$ Hz. [g] $J_{BD} = 2.2$ Hz.

The dioxetanes cleave smoothly to dicarbonyl products **6a–d**, which were used for their further characterization. A preliminary determination of the rate of decomposition of **4a** by nmr gives $k_d = 3.1 \times 10^{-5}$ sec^{-1} at 35° in $CDCl_3$. This rate is faster than that for tetramethyl-1,2-dioxetane by a factor of 10.[13]

The products (**6**) were isolated and gave characteristic ir bands for the carbonyl groups: **6a** (neat), 1689 and 1662 cm^{-1}; **6b** (KBr), 1682 cm^{-1}; **6c** (neat), 1683 and 1730 cm^{-1}; **6d** (neat), 1690 and 1725 cm^{-1}; **6c** and **6d** each had two bands characteristic of an aldehyde CH stretching vibration at 2768 and 2874 and 2740 and 2860 cm^{-1}, respectively. The mass spectra of **6a–d** were in agreement with the assigned structures. Compound **6b**, mp 103–104°, gave a satisfactory analysis. Crystalline pyrylium perchlorate salts were prepared from **6a**, **c**, and **d** (which were liquids); **8a**, orange, mp 244–245° dec (lit.[14] 244–245° dec). Both **8c**, pale yellow, mp 133.5–134.5° dec, and **8d**, pale yellow, mp 195.5– 196.5° dec, gave satisfactory microanalyses.



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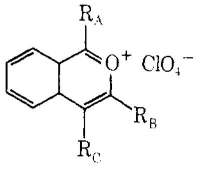

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These results provide a useful synthetic approach to at least some indene-derived dioxetanes. It is not known whether these dioxetanes are formed from a methanol-promoted rearrangement of an endoperoxide intermediate (**2**), a possibility which is suggested by the work of Le Roux and Basselier[15] and Rigaudy *et al.*,[16] or from a solvent-dependent reaction involving a perepoxide intermediate, as proposed by Hasty and Kearns.[4] The role of solvent in these processes is still obscure. It is known that polar solvents increase the ratio of dioxetane formation to ene reaction in at least one case,[17] but it is likely that this is not related to the present findings.

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Fluorescence Detected Circular Dichroism

Sir:

Circular dichroism (CD) is a powerful technique for investigating molecular structure. The local structure near a chromophore in a macromolecule can be studied, if the CD of the chromophore can be isolated. We report here a new method, fluorescence detected circular dichroism (FDCD), which is capable of measuring the CD spectrum of a single chromophore in a macromolecule, provided the chromophore is fluorescent. Preliminary experimental results are given which show good agreement with theory for simple model systems.

The method is based on the usually valid assumption that the excitation spectrum of a fluorescent chromophore parallels its absorption spectrum.[1] This is generally true for systems in which energy transfer is negligible. In FDCD, the difference in absorption for left and right circularly polarized light is obtained by measuring the difference in fluorescence intensity for left and right circularly polarized excitation.[2] A schematic of the experimental arrangement is shown in Figure 1. The detection system of a Cary 60 spectropolarimeter with Model 6001 CD attachment is modified by placing a 5-cm diameter Hamamatsu R375 photomultiplier at 90° to the excitation beam. This photomultiplier is followed by a preamplifier and the resultant signal is processed by the Cary 60 electronics and displayed on the recorder chart. The pen position is digitized and smoothed in a manner described previously.[4] A colored glass filter is used to discriminate against scattered excitation light, and a standard quartz fluorescence cell is employed. In order to collect more fluorescence, the wall of the cell holder opposite the photomultiplier is made highly reflecting. Baselines are recorded by placing an optically inactive, fluorescent solution in the cell. For compounds with a large FDCD, sodium fluorescein proved adequate. However, for compounds with a small FDCD it is necessary for the baseline solution to approximate the fluorescent characteristics of the solution being measured. This is because the baseline seems to shift a small amount for different fluorescent species. The reasons for this

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