ent slope values are observed for different series of compounds indicates that β_{cc} is an empiric quantity, rather than the constant required by eq II. This is yet another result of the many approximations used in the HMO method.

It is debatable whether Hückel's method can be applied to charged systems.[9] Its use here for a class of very similar compounds can, however, be justified by the linear relation between the HMO energies for the $m \rightarrow m + 1$ transition and the SCF–CI energies for the essentially similar transition observed for the thiapyrylium series.[10]

A more elaborate method is now being applied in the investigation of the electronic transitions of these nine cations.

Registry No.—I, 2567-17-1; II, 2567-18-2; III, 10352-19-9; IV, 2749-61-3; V, 53391-12-1; VI, 53391-14-3; VII, 53391-16-5; VIII, 53391-18-7; IX, 3541-46-6.

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(1) This work has been supported by the National Research Council (CNR).

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Photooxidation of Benzophenone Oxime and Derivatives

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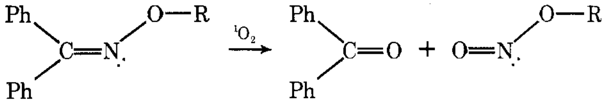
Singlet oxygen, generated by dye photosensitization of ground state triplet oxygen or by chemical reactions, has been shown to undergo a variety of reactions with organic compounds.[2] One of the more interesting of these reactions has been the [2 + 2] cycloaddition of singlet oxygen to electron-rich olefins, giving 1,2-dioxetanes which subsequently cleave to carbonyl products.[2,3] We have found that singlet oxygen reacts with benzophenone oxime and derivatives to give benzophenone and nitrite (Scheme I). To our knowledge, this represents the first report of a reaction of singlet oxygen with a π bond other than a C═C double bond.

Scheme I. Photooxidation of Benzophenone Oxime Derivatives



1a, R = H
b, R = CH_3
c, R = $:^-$

Photooxidations were carried out in methanol solution, using rose bengal as sensitizer, keeping the solution saturated with oxygen, and irradiating with a 500-W projector bulb. Appropriate blank experiments indicated that the dye, the oxygen, and the light were all necessary for the photooxidation reaction. Further evidence that these are singlet oxygen reactions was the observation of specific quenching by 1,4-diazabicyclo[2.2.2]octane (Dabco), a singlet oxygen quencher.[4] Photooxidation of benzophenone oxime (**1a**), benzophenone oxime *O*-methyl ether (**1b**), or benzophenone oximate anion (**1c**) yielded benzophenone as the only product observable by gas chromatography. Benzophenone was isolated and characterized from the photooxidation of **1c**. The presence of nitrite ion was also detected in the photooxidations of **1a** and **1c**.

The addition of 2-methyl-2-butene, a singlet oxygen acceptor, decreased the rate of photooxidations. The rate of disappearance of 2-methyl-2-butene was taken to be 1.3 × 10^6 M^{-1} s^{-1}, using the reported relative reactivity[2] and the reported lifetime of singlet oxygen in methanol.[5] The rate of appearance of benzophenone from **1a**, **1b**, or **1c**, compared to the disappearance of 2-methyl-2-butene, thus allowed the absolute reactivities of the oxime derivatives to be determined (Table I). The order of reactivity is what would be expected for reaction with an electrophilic reagent such as singlet oxygen—reactivity is enhanced by electron donation to the π bond.[2]

Table I. Reaction Rate Constants for Singlet Oxygen Reactions

Substrate	Rate constant, M^{-1} s^{-1}	Substrate	Rate constant, M^{-1} s^{-1}
2-Methyl-2-butene	1.3 × 10^6	**1a**	7.7 × 10^4
1c	3.4 × 10^5	Acetone oxime	<1 × 10^4
1b	2.0 × 10^5		

While we have obtained no direct evidence for a dioxetane intermediate in this reaction, we consider it highly probable, based upon analogies with similar reactions which involve cleavage of an electron-rich π bond by singlet oxygen.[2]

Experimental Section

Materials. Benzophenone oxime (**1a**) was prepared from benzophenone and hydroxylamine hydrochloride, mp 138–141 °C (lit. 142 °C).[6] Benzophenone oximate anion (**1c**) was prepared from **1a** and sodium in ether solution.[7] Benzophenone oxime *O*-methyl ether (**1b**) was prepared by refluxing **1c** with methyl iodide in ether solution, mp 97.5–100 °C (lit. 102 °C).[8] Acetone oxime was prepared from acetone and hydroxylamine hydrochloride, mp 54–57 °C (lit. 60–61 °C).[9] Dabco was from Eastman and was used as received.

Photooxidation Procedure. The light source was a 500-W quartz–iodine projector bulb (G.E. FBG), contained in a water-jacketed well and also cooled by air. A yellow glass filter was used to eliminate short-wavelength light (OD >2 for λ <390 nm). The sample to be irradiated was contained in a test tube cooled in ice in a clear Dewar flask, and was within several inches of the light source. Oxygen was presaturated with solvent and bubbled slowly into the reaction solution. Oxygen bubbling continued for 5 min before the light was turned on.

A typical reaction solution contained 1 × 10^{-4} M rose bengal as sensitizer and 0.1 M substrate in methanol solvent. Aliquots were removed at intervals and analyzed by GC, using a Hewlett-Packard Model 700 with a 6 ft × 0.125 in. column packed with 10% UC-W98. Benzophenone was the only product detectable as the photooxidation proceeded. By temperature programming, the disappearance of the oxime (**1a**) or the *O*-methyl ether (**1b**) could also be observed.

Detection of nitrite ion from the photooxidations of **1a** and **1c** was accomplished by testing with acidic ferrous sulfate;[10] a dark green-brown color indicated the presence of nitrite, even in the presence of the dye. A blank solution including all components of the reaction before irradiation gave no color change. Nitrate ion gave no color change.

Benzophenone was isolated after 7 h of photooxidation of **1c** by evaporating the solvent, washing with water to remove the dye, and recrystallizing the residue, yield 60%, mp 48–49.5 °C. It was identified by GC and mixture melting point comparison with an authentic sample.

Relative reactivities were obtained by inclusion of 0.1 M 2-methyl-2-butene (competitive singlet oxygen acceptor) and 0.1 M cyclohexane (internal standard) in the reaction solution. The appearance rate of the benzophenone and the disappearance rate of the 2-methyl-2-butene were monitored up to 50% conversion, during which time both were linear (zero order). The ratio of the slopes was taken to be the ratio of their absolute rate constants with singlet oxygen. Appropriate blank reactions were run: with oxygen bubbling and no irradiation, with irradiation and nitrogen bubbling, and with irradiation and oxygen bubbling but no dye. These blanks amounted to less than 10% of the photooxidation reaction and were simply subtracted from the reaction rates.

Quenching by Dabco was demonstrated by running two parallel photooxidations, containing 0.1 M **1c**, 0.1 M 2-methyl-2-butene, and 1×10^{-4} M rose bengal in methanol. One solution contained 1×10^{-3} M Dabco. After 3 h of irradiation, the solution with Dabco showed no detectable reaction, while in the other solution both **1c** and 2-methyl-2-butene showed substantial reaction.

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Registry No.—**1a**, 574-66-3; **1b**, 3376-34-9; **1c**, 58074-11-6; 2-methyl-2-butene, 513-35-9; acetone oxime, 127-06-0.

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A Chromium(II)-Promoted Heterolytic Fragmentation Reaction. Application to the Synthesis of 1,5-Dienes[1]

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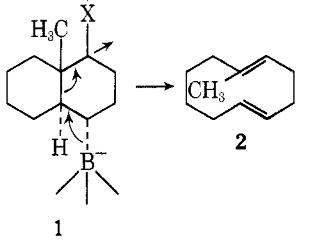
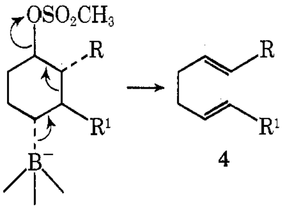
Interest in the stereoselective synthesis of 1,5-dienes has increased markedly in the last decade, as attested by the variety of methods[2] that have been developed for obtaining this class of compounds. Among the important natural products that possess two (or more) double bonds in a 1,5 relationship are a number of medium-ring sesquiterpenes[3] possessing the 1,5-cyclodecadiene skeleton as well as several important acyclic compounds such as squalene, farnesol, and the juvenile hormone of *Hyalophora cecropia*.[4]

One of the more promising approaches to such systems involves the base-promoted heterolytic fragmentation[5] of appropriately substituted decalinboronate derivatives (e.g., **1** in eq 1) for the stereospecific synthesis[3] of 1,5-cyclodecadienes (**2**). Fragmentation of the corresponding cyclohexaneboronate (**3**) has been shown[6] likewise to yield in a stereospecific manner an acyclic 1,5-diene (**4**) (eq 2).



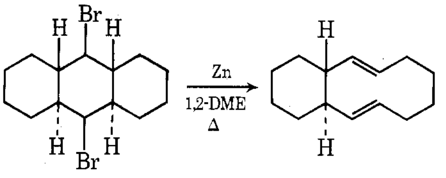
1 **2** (1)

$X = OSO_2CH_3$, Br, etc.

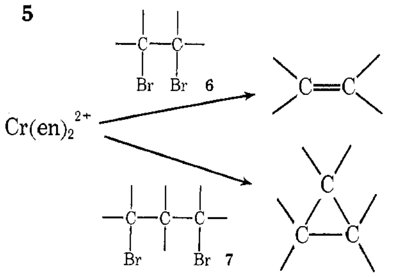


3 **4** (2)

The report[7] of a zinc-initiated fragmentation reaction of a cyclic 1,4-dibromide (**5**) (eq 3), together with studies of Kochi and Singleton[8] involving the reaction of ethylenediaminechromium(II)[9] with 1,2- and 1,3-dibromides (**6** and **7**, respectively) (eq 4), suggests that chromium(II) should also initiate fragmentation of an alicyclic bromide possessing a suitable nucleofugal group at the γ carbon.



5 (3)



(4)

If successful, the use of chromium(II) may be advantageous over that of zinc since fragmentation reactions involving the latter are generally run at elevated temperature, conditions under which a Cope rearrangement of the 1,5-diene products can occur.[10]

The system selected for testing the feasibility of a Cr(II)-promoted fragmentation reaction directed toward the synthesis of 1,5-dienes was bromomesylate **9c**. The preparation of this substrate from the commercially available[11] 2-adamantanol (**8a**) is outlined in Scheme I. Acetylation of alcohol **8a** using acetic anhydride–pyridine afforded the corresponding acetate (**8b**)[12] in 94% yield. Ionic bromination of the latter (**8b**) afforded an undetermined mixture[13]