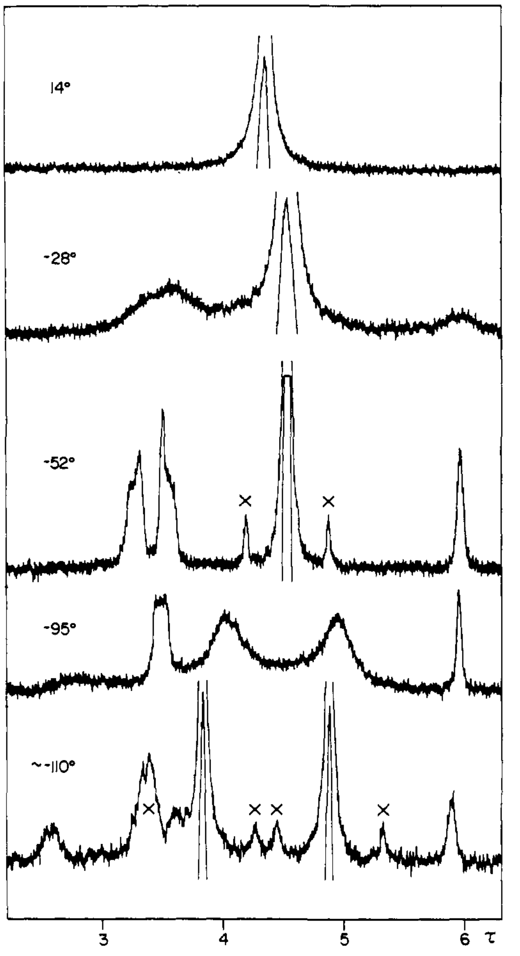

Figure 1. Nmr spectra illustrating the more critical changes which occur between +25 and ~−110°. The gain varies from trace to trace. Bands marked × are spinning side bands (spectra recorded at 60 Mc; ~0.2 *M* solution in CS_2).

(4) One possible instantaneous structure has an h^5-C_5H_5 ring and an h^3-C_5H_5 ring which at −110° is still undergoing eccentric rotation rapidly enough to average the environments of its five protons. The (h^5-C_5H_5)(h^3-C_5H_5)(NO)Mo group would then be dissymmetric and nonequivalence of the A and A′ as well as of the B and B′ protons of the h^1-C_5H_5 ring would be mandatory regardless of the rate of internal rotation, although the magnitude of the difference might be enhanced by conformational effects. This interpretation is in accord with the conventional assumptions about metal–nitrosyl and metal–C_5H_5 bonding. Thus, if NO is assumed to be a three-electron (NO^+) donor, if it is further accepted that there is one h^1-C_5H_5 ring (which is hardly debatable on the evidence), and if it is also *assumed* that the total number of ligand electrons donated to Mo must be 12, the remaining rings must jointly denote eight electrons. This suggests an h^5-C_5H_5 and an h^3-C_5H_5 ring.

(5) However, the reported experimental results do *not, in themselves*, demand this interpretation. It is entirely possible that there is one h^1-C_5H_5 ring and two others which do not differ in their intrinsic relation to the metal atom. The changes in the nmr spectrum between −52 and −110° *could* then be due to a freezing in of a particular orientation of the h^1-C_5H_5 ring such that the other two rings experience different degrees of shielding by the diamagnetically anisotropic h^1-C_5H_5 group.

Further studies of this and related molecules will be required in order to reach a decision between these, and perhaps other, possibilities for the instantaneous structure of the molecule.

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Received July 16, 1968

Chemistry of Singlet Oxygen. VII. Quenching by β-Carotene[1]

Sir:

The detrimental effects of photosensitizing dyes, light, and oxygen upon various organisms, including the human, are well known. These effects are referred to as "photodynamic action," and are the result of photosensitized oxidation of certain cell constituents.[2] Photosensitized oxygenation of olefins, dienes, and heterocyclic compounds is believed to proceed *via* the intermediacy of singlet oxygen, formed by energy transfer from triplet sensitizer.[3,4] Chlorophyll is among the most effective sensitizers for dye-sensitized photooxygenations of organic substrates.[4] Photosynthetic organisms, however, are protected from the lethal effects of their own chlorophyll by carotenoids; mutants lacking certain carotenoids are readily killed by light and oxygen; carotenoids also protect organisms against the effects of exogenous photosensitizers such as methylene blue.[5] The mechanism of this protective action has not been established, although it is known that carotenes quench triplet sensitizers efficiently.[6]

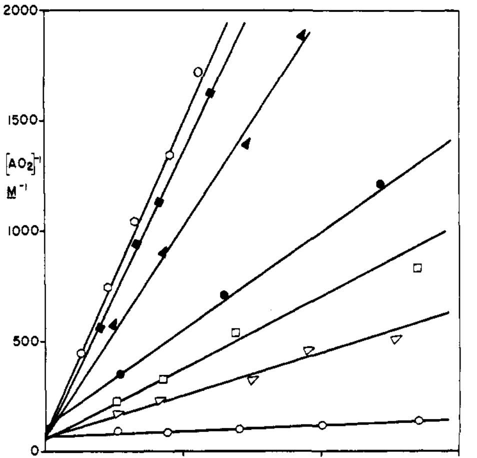

Figure 1. Methylene blue photosensitized oxygenation. β-Carotene concentrations: ○, 0.0 *M;* △, 3.10 × 10^{-5} *M;* ●, 3.54 × 10^{-5} *M;* □, 6.11 × 10-5 *M;* ▲, 8.61 × 10^{-5} *M;* ■, 8.95 × 10^{-5} *M;* ○, 9.90 × 10^{-5} *M.*

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[1] Supported by National Science Foundation Grants GP-5835 and GP-8293.

[2] J. D. Spikes and R. Straight, *Ann. Rev. Phys. Chem.*, **18**, 409 (1967).

[3] C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

[4] K. Gollnick, *Advan. Photochem.*, in press.

[5] R. Y. Stanier, *Brookhaven Symp. Biol.*, **11**, 143 (1959); W. A. Maxwell, J. D. Macmillan, and C. O. Chichester, *Photochem. Photobiol.*, **5**, 567 (1966); M. M. Mathews, *Nature*, **203**, 1092 (1964).

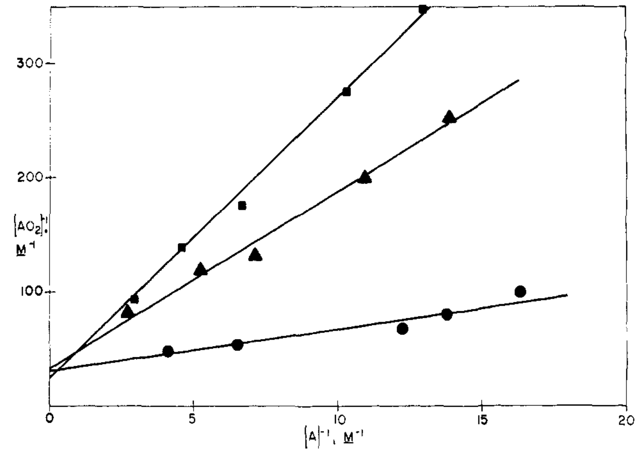

Figure 2. OCl^-–H_2O_2 oxygenation. β-Carotene concentrations: ●, 0.0 *M*; ▲, 4.50 × 10^{-5} *M*; ■, 9.31 × 10^{-5} *M*.

However, since oxygen also quenches triplet sensitizers at a diffusion-controlled rate (to give singlet oxygen),[4] quenching of triplet chlorophyll by carotenes cannot be responsible for the protective effects unless the local concentration of carotenes greatly exceeds that of oxygen.

We wish to report that singlet oxygen (generated by methylene blue photosensitization or by reaction of NaOCl and H_2O_2)[3] is quenched very effectively by low concentrations of β-carotene; 95% of the photooxygenation of 0.1 *M* 2-methyl-2-pentene is inhibited by 10^{-4} *M* β-carotene.

Solutions in benzene–methanol (4:1, v:v) containing *ca.* 4 × 10^{-5} *M* methylene blue (MB), various amounts of β-carotene (C), and various amounts of 2-methyl-2-pentene (A) were irradiated in an immersion irradiation apparatus at 25° for a known time. The resulting mixture of hydroperoxides (AO_2) was reduced, and the total amount of product alcohols was determined gas chromatographically using an internal standard.[7] Results are shown in Figure 1.

Chemical oxygenations were carried out on 100-ml solutions in 1:1:1 methanol–benzene–diglyme (the latter added for solubility) 0.26 *M* in H_2O_2, containing various amounts of A. To these solutions were added 7.2 × 10^{-3} equiv of aqueous 22% NaOCl. The solutions were reduced and analyzed as above; the results are shown in Figure 2.

Both methods give results which fit the following scheme

$$\begin{tikzcd}
{}^3O_2 & {}^1O_2 \arrow[l, "k_d"'] \arrow[r, "A", "k_A"'] \arrow[d, "C"', "k_C"] & AO_2 \\
 & {}^3O_2 &
\end{tikzcd}$$

in which

$$[AO_2]^{-1} = \text{constant}\left(1 + \left[\frac{k_d}{k_A} + \frac{k_C}{k_A}[C]\right]\frac{1}{[A]}\right)$$

The best fit of the data to this equation gives k_C/k_A = 1.6 × 10^4 and 0.7 × 10^4 for the photochemical and nonphotochemical oxygenations, respectively. Because these values depend critically on the values of the intercepts of each of the lines in Figures 1 and 2, and since these intercepts are difficult to determine accurately, the values of k_C/k_A are subject to an uncertainty of at least a factor of two. However, the following conclusions can be drawn. (1) The inhibitory effect of β-carotene in the photochemical reaction is *not* caused by quenching of triplet sensitizer, since the intercepts of the lines in Figure 1 are constant within the experimental uncertainty. (Light absorption by β-carotene resulting in a "shadowing effect" is also ruled out by this observation, as well as by the fact that the absorption spectra of β-carotene and methylene blue do not overlap.) (2) The values of k_C/k_A for the two methods are in reasonable agreement, allowing for the difference in reaction conditions and the uncertainty. As a further check, a second series of experiments was carried out in which solutions containing a constant amount of A were oxygenated at different carotene concentrations; plots of $[AO_2]^{-1}$ *vs.* [C] gave straight lines from which the values of k_C/k_A = 2.2 × 10^4 and 2.9 × 10^4 for the two methods were determined. These methods would be subject to error if quenching of triplet sensitizer were occurring in the photochemical case or if production of singlet oxygen were being inhibited by β-carotene in the chemical case (since "constant" in the above expression would vary); however, the fact that constant intercepts were obtained in Figures 1 and 2 makes this unlikely. The best value of k_C/k_A is therefore probably around 2 × 10^4. In none of these experiments was there appreciable consumption of β-carotene; in fact, one molecule of β-carotene must quench as many as 250 molecules of singlet oxygen in some runs.

An attractive mechanism for the quenching of singlet oxygen by β-carotene would involve energy transfer in a process which is the reverse of the reaction which produces singlet oxygen by energy transfer from triplet sensitizer to oxygen.[3] This mechanism is tenable

$$ {}^1O_2 + C \longrightarrow {}^3C + {}^3O_2 $$

only if the triplet energy of β-carotene is below or near that of singlet oxygen (the ${}^1\Delta_g$ state is at 22.5 kcal). Unfortunately, the triplet energy does not seem to be known, but such a low energy would not be unreasonable. However, other mechanisms for the quenching which do not involve consumption of β-carotene cannot be excluded.

From the large value of k_C/k_A, it is seen that the quenching is very efficient. If k_C is taken to be the diffusion-controlled rate, roughly 5 × 10^9 M^{-1} sec^{-1},[8] then the decay rate of singlet oxygen in solution, k_d, can be calculated to be about 10^4 sec^{-1}, from the fact that k_d/k_A is 0.07 *M*, as determined from Figures 1 and 2. This value of k_d is an upper limit and is considerably lower than that estimated by Schenck and Koch by an indirect method for the reactive intermediate in the photooxygenation.[9]

From the results reported here, it is evident that quenching of singlet oxygen by β-carotene may be an important protective mechanism in plant biochemistry. How relevant these results are to *in vivo* systems will

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(6) M. Chessin, R. Livingston, and T. G. Truscott, *Trans. Faraday Soc.*, **62**, 1519 (1966); E. Fujimori and R. Livingston, *Nature*, **180**, 1036 (1957).

(7) R. Higgins, C. S. Foote, and H. Cheng, International Oxidation Symposium, San Francisco, Calif., 1967; Advances in Chemistry Series, No. 77, American Chemical Society, Washington, D. C., in press.

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(9) G. O. Schenck and E. Koch, *Z. Electrochem.*, **64**, 170 (1960); see also C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Am. Chem. Soc.*, **90**, 975 (1968).

require further study. It will also be of interest to see what other quenchers for singlet oxygen can be found.[10]

[10] G. O. Schenck and K. Gollnick, *Angew. Chem.*, 70, 509 (1958), report nicotine quenches the reactive intermediate (presumably singlet oxygen) in photosensitized oxygenations. See also ref 4 for some other possible cases.

[11] John Simon Guggenheim Fellow, 1967–1968.

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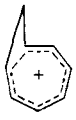
Received August 19, 1968

A New Dibenzohomotropylium Cation[1]

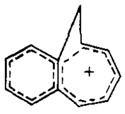
Sir:

The homotropylium cation I, the benzohomotropylium cation II, and the dibenzohomotropylium cation III have been described by Pettit[2,3] and Winstein[4] and their coworkers.

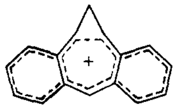
In this communication we wish to report the generation and characterization of a new dibenzohomotropylium ion IV, an isomer of III. The precursors V and VI used for the generation of IV in the strong acid media have been prepared by Nenitzescu and his collaborators during the investigation of the dibenzocycloheptane–dibenzocyclooctane rearrangement.[5,6]



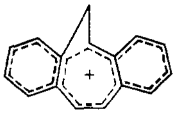
I



II

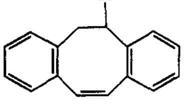


III



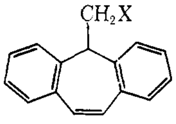
IV

X



V, X = OH

CH$_2$X



VIa, X = OH
b, X = Cl
c, X = Br
d, X = OTs

When a sulfur dioxide solution of the alcohol V is added with vigorous stirring to a FSO_3H–SbF_5 (1:1) solution in sulfur dioxide at −60° the dibenzohomotropylium cation IV is formed *via* the protonated species VII and the unstable secondary cation VIII. The same cation (IV) is obtained from the primary halides VIb and VIc in SbF_5–SO_2 solution at −60°. The unstable primary cation IX is initially formed but undergoes, with aryl participation, an instantaneous rearrangement to the relatively more stable eight-membered ring secondary cation VIII. The final homoaromatic stabilization to IV is easily accomplished by the participation of the double bond.

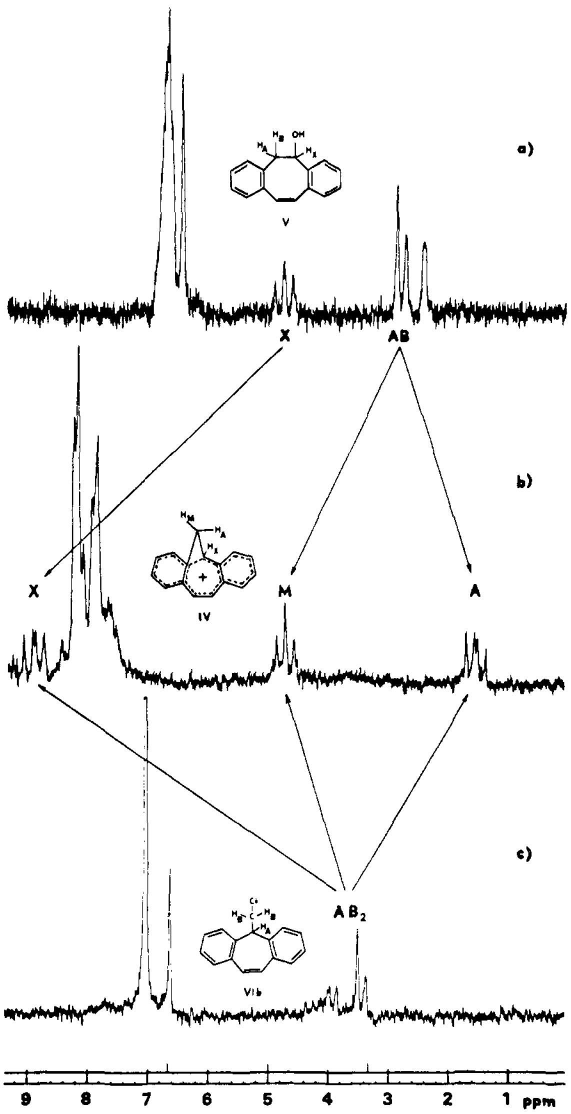


Figure 1. Nmr spectra (60 MHz) of V in liquid SO_2 (a), IV in FSO_3H–SbF_5–SO_2 (b), and VIb in liquid SO_2 (c), all recorded at −60°. No change was observed by raising the temperature to −18°.

Ion IV could also be detected in FSO_3H–SbF_5 solutions of VIa, VIb, VIc, and VId; however, only poor nmr spectra could be obtained probably due to secondary reactions.

The protonation of the dibenzocyclooctatetraene X in FSO_3H–SO_2 also leads to the formation of the dibenzohomotropylium cation IV. Evidence of the homoaromatic nature of the cation IV is provided by its nmr spectrum shown in Figure 1 in comparison with those of the precursors V and VIb. The nmr spectrum of V in liquid sulfur dioxide (Figure 1a) presents a relatively narrow multiplet at δ 6.70 for the eight aromatic protons and a single slightly broadened line at 6.40 for the two olefinic protons. The hydroxylic proton absorbs at δ 2.38. The remaining three protons H_A, H_B, and H_X form an ABX spectrum with an X quadruplet centered at δ 4.70 and an unresolved AB

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[1] (a) Support of the research by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged; (b) considered as Stable Carbonium Ions. LXXVII.

[2] J. L. von Rosenberg, Jr., J. E. Mahler, and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 2842 (1962).

[3] W. Merk and R. Pettit, *ibid.*, **90**, 814 (1968), and references cited therein.

[4] R. F. Childs and S. Winstein, *ibid.*, **89**, 6348 (1967).

[5] E. Cioranescu, A. Bucur, M. Banciu, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **10**, 141 (1965); *Chem. Abstr.*, **63**, 11456*g* (1965).

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