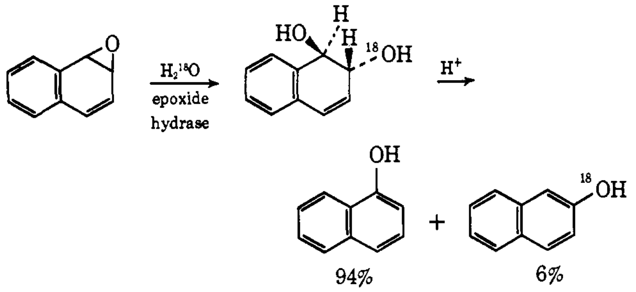

tinguishable from the conjugate obtained directly from naphthalene with microsomes, supernatant, and glutathione. The opening of the oxide II by glutathione also occurs nonenzymatically, but at a much slower rate. During these incubations the oxide also undergoes spontaneous isomerization to 1-naphthol. Likewise, the phenol formed from naphthalene by microsomes is also 1-naphthol.

When the glutathione-conjugating system and increasing amounts of glutathione are added to liver microsomal perparations, III and IV decrease as more and more of the oxide is trapped as V. This experiment suggests that 1,2-naphthalene oxide is the *obligatory intermediate* in the enzymatic hydroxylation of naphthalene. That arene oxides are in general intermediates on the pathway of the hydroxylation of aromatic substrates becomes now an attractive assumption.

The current view on microsomal mixed-function oxygenation favors an oxygen atom transfer reaction[8] rather than endoperoxide intermediates.[9,10] Complete biochemical details will be published elsewhere.

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(8) *Cf.* V. Ullrich and H. J. Staudinger in "Biological and Chemical Aspects of Oxygenases," K. Bloch and O. Hayaishi, Ed., Maruzen Co., Ltd., Tokyo, 1966, p 235; *Physiol. Chem.*, **349**, 85 (1968).

(9) A. H. Soloway, *J. Theoret. Biol.*, **13**, 100 (1966).

(10) J. E. Baldwin, H. H. Basson, and H. Krauss, *Chem. Commun.*, 984 (1968).

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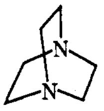
Quenching of Singlet Oxygen by Tertiary Aliphatic Amines. Effect of DABCO

Sir:

While studying the reactions of amines with singlet oxygen ($^1O_2$) generated by an electrodeless radiofrequency discharge,[1] we observed that tertiary aliphatic amines not only yield no reaction products, but act as inhibitors of the oxidation of known reactive acceptors of singlet oxygen. Thus, no reaction product could be detected[2] after treating 2 mmol of 1,4-diazabicyclo[2.2.2]octane (DABCO, **1**) in 25 ml of bromobenzene with $^1O_2$ during 2 hr at 0°. Yet when a small amount of DABCO was added to a solution of 1,3-diphenylisobenzofuran (**2**), the complete oxidation[3] of **2** took much longer than in the absence of DABCO. The oxidation of dibenzyl sulfide and rubrene was also inhibited (see Table Ia). This inhibitory property is not limited to that tertiary aliphatic amine. All those tried, ethyldiisopropylamine, N,N′-tetramethylethylenediamine, and N-allylpiperidine, were also found to be apparently unreactive toward $^1O_2$, yet to retard the oxidation of **2**.



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It therefore seemed interesting to find out if an actual quenching of singlet oxygen took place. Indeed, reactions involving $^1O_2$ generated by entirely different techniques were found to be retarded or suppressed by DABCO. In its presence, not only was the rate of rubrene photooxidation[4] reduced (Table Ib), but a correspondingly smaller volume of oxygen was absorbed by the solution. If the quenching of the rubrene photooxidation had been due to the competitive faster oxidation of the quencher, the rate of oxygen intake would have been unchanged or increased by DABCO. Thus the DABCO is not oxidized. Chemically generated singlet oxygen in aqueous solution is also quenched by DABCO. 2,5-Dimethylfuran, one of Foote's most efficient acceptors,[5] was chosen for this test (Table Ic).

Quenching of $^1O_2$ by DABCO must be very efficient since it affects the rate of oxidation of **2**, the most reactive substrate known,[6] when **2** and DABCO are present at concentrations of the same order. A gas-phase experiment supports this conclusion. A small amount of DABCO was sublimed into a stream of oxygen rich in $^1O_2$ (at a total pressure of 6 torr), while the intensity of the emission band at 635 mμ[7] which is proportional to the square of the concentration of $O_2(^1\Delta_g)$[8] was being monitored downstream. At an estimated flow rate of $\sim 4.5 \times 10^{-3}$ mol/min, the gradual introduction of $<3 \times 10^{-4}$ mol of DABCO into the gas stream resulted in >100-fold decrease in the intensity of the 635-mμ band, lasting 15 min, suggesting that each molecule of DABCO is able to deactivate several molecules of $O_2(^1\Delta_g)$.[9] This nonreactive quenching of $O_2(^1\Delta_g)$ is remarkable in view of its known stability;[10a] for comparison, naphthalene, water, pyridine, and bromobenzene, introduced in the oxygen stream in the same manner as DABCO, caused no or negligible quenching of $O_2(^1\Delta_g)$ (the 635-mμ band).

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(1) E. J. Corey and W. C. Taylor, *J. Am. Chem. Soc.*, **86**, 3881 (1964). In the present experiments, a mixture of 10% oxygen in helium, at a total pressure of 50 torr, passed through the discharge tube, then bubbled through the reacting solution in a vessel with a reflux condenser at Dry Ice temperature.

(2) By nmr, ir, and tlc.

(3) Indicated by the discoloration of **2**.

(4) At 540 mμ DABCO does not interfere with light absorption by the rubrene. Besides, DABCO had no measurable quenching effect on the fluorescence of rubrene, even at a concentration of 4×10^{-2} *M*, greater than in the oxidation experiments. (No effort was made to remove oxygen in the fluorescence measurements, because of the obvious presence of oxygen in the oxidation experiments.)

(5) C. S. Foote, M. T. Wuesthoff, S. Wexler, I. G. Burstain, R. Denny, G. O. Schenck, and K. H. Schulte-Elte, *Tetrahedron*, **23**, 2583 (1967).

(6) T. Wilson, *J. Am. Chem. Soc.*, **88**, 2898 (1966).

(7) Through a Baird-Atomic interference filter, Standard Visible Type B-3, with peak wavelength at 6350 Å, by means of an EMI 9558B photomultiplier tube.

(8) L. W. Bader and E. A. Ogryzlo, *Discussions Faraday Soc.*, **37**, 46 (1964); S. H. Whitlow and F. D. Findlay, *Can. J. Chem.*, **45**, 2087 (1967).

(9) Assuming that about 10% of the oxygen is in the $^1\Delta_g$ stage. See L. Elias, E. A. Ogryzlo, and H. I. Schiff, *ibid.*, **37**, 1680 (1959).

Table I. Effect of DABCO on Oxidation Reactions *via* $^1O_2$

		Initial concn × 10^3 *M*		
Source of $^1O_2$	Substrate	Substrate	DABCO	Results
a. Electric discharge	2[a]	8	36	100% oxidn after 45 min
		8	0	100% oxidn after 6 min
	Dibenzyl sulfide[a]	40	160	No detectable product after 3.5 hr
		40	0	75% oxidn after 3.5 hr
	Rubrene[b]	0.72	43	14% rubrene oxidized in 1 min[f]
		0.72	16	20% rubrene oxidized in 1 min
		0.72	0	84% rubrene oxidized in 1 min
b. Photochemical	Rubrene[c]	3.9	13	10% rubrene oxidized in 16 min
		3.9	3.4	40% rubrene oxidized in 16 min
		3.9	0	100% rubrene oxidized in 16 min
	Rubrene[d]	3.6	13	12% rubrene oxidized in 6 min
		3.6	0	100% rubrene oxidized in 6 min
c. Chemical (H_2O_2 + NaOCl)	2,5-Dimethylfuran[e]	130	400	25 mg of hydroperoxide[g]
		130	0	400 mg of hydroperoxide[h]

[a] In bromobenzene. [b] In *o*-dichlorobenzene. [c] In pyridine. [d] In toluene. [e] In methanol and water (initial amount of substrate 1 g). [f] Calculated from initial and final concentrations of rubrene measured photometrically. [g] 2-Methoxy-5-hydroperoxy-2,5-dimethyldihydrofuran. [h] In excellent agreement with the yield reported by Foote.[13]

DABCO also completely suppresses the red luminescence from a stream of $^1O_2$ bubbled into a solution of violanthrone in bromobenzene. This emission corresponds to the violanthrone fluorescence and depends on the square of the concentration of $O_2(^1\Delta_g)$.[10]

This quenching by DABCO may provide a useful test of involvement of singlet oxygen. Exploratory experiments show, for example, that the rate of autoxidation of tetralin,[11] a well-established free-radical chain reaction, is only negligibly reduced by DABCO, even at a concentration 0.1 *M*, far greater than that at which it markedly inhibits singlet oxygen reactions.[12]

The observations reported here throw no light on the mechanism of the deactivation of singlet oxygen by DABCO. No permanent chemical reaction takes place, and the existence of a low-lying triplet state of DABCO (below 22.5 kcal) to which $O_2(^1\Delta_g)$ could transfer its energy seems unlikely. The availability of the lone electron pairs of DABCO suggests that the quenching of $^1O_2$ may occur through a charge-transfer process.[14]

Acknowledgments. We are grateful to Professors P. D. Bartlett and E. J. Corey for helpful discussions. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, and by a grant from the Milton Fund of Harvard University.

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[10] (a) E. A. Ogryzlo, International Oxidation Symposium, San Francisco, Calif., Aug 1967; Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press. (b) E. A. Ogryzlo and A. E. Pearson, *J. Phys. Chem.*, **72**, 2913 (1968). A preprint is gratefully acknowledged. Although it was noted that the quenching of the fluorescence of violanthrone, *i.e.*, its singlet state, was too small (only a factor of $\sim$3) to account for the effect of DABCO on the luminescence caused by $^1O_2$ (a factor of $\sim 10^3$), one cannot rule out a more effective quenching by DABCO of the violanthrone triplet state, which appears to be involved in the luminescence.

[11] Initiated by azobisisobutyronitrile at 60° in *o*-dichlorobenzene.

[12] 2,6-Di-*t*-butylphenol, 0.04 *M*, stops the autoxidation. Conversely, this free-radical inhibitor does not suppress singlet oxygen oxygenation, according to Foote,[13] although it does seem to have a small inhibitory effect (at high concentration: 0.3 *M*) on the photooxidation of rubrene.

[13] C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Letters*, 4111 (1965).

[14] *Cf.* quenching of the fluorescence of perylene by amines: H. Leonhardt and A. Weller in "Luminescence of Organic and Inorganic Materials," H. P. Kallmann and G. M Spruch, Ed., John Wiley & Sons, New York, N. Y., 1962, p 74; W. R. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968).

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Substituents and Bridgehead Carbonium Ion Reactivities. Inductive and Steric Effects of Alkyl Groups in Saturated Systems

Sir:

Although it is well accepted that alkyl groups are electron releasing when attached to multiply bonded carbon atoms,[1] the direction and the magnitude of alkyl inductive effects in saturated systems have been the subject of considerable debate.[2–13] The Taft

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 70; E. Heilbronner, *Tetrahedron Suppl.*, **2**, 289 (1963).

[2] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 13.

[3] R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

[4] C. D. Ritchie, *J. Phys. Chem.*, **65**, 2091 (1961).