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

Source of $^1O_2$	Substrate	Initial concn × 10^3 *M*		Results
		Substrate	DABCO	
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 ~3) to account for the effect of DABCO on the luminescence caused by $^1O_2$ (a factor of ~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).

(15) Chargée de Recherches au C.N.R.S., Paris.

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Received July 29, 1968

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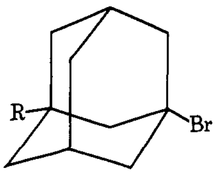
(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 70; E. Heilbronner, *Tetrahedron Suppl.*, **2**, 289 (1963).

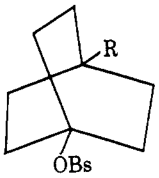
(2) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 13.

(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).

Table I. Solvolysis Rates of Substituted Bridged Ring Systems[a]





R	Solvolysis in 80% aq ethanol, 75° 10^5k, sec^{-1}	k_R/k_H	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu	Solvolysis in acetic acid, 75° 10^5k, sec^{-1}	k_R/k_H	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
H	13.8	1.00	22.9	−10.8	11.3	1.00[b]	26.2	−1.7
t-C_4H_9	29.0	2.10	24.5	−4.7	6.24	0.55[b]	27.1	−0.3
i-C_3H_7	19.3	1.40	24.5	−5.5	4.75	0.43	26.8	−1.6
C_2H_5	13.4	0.97	23.3	−9.6	4.04	0.36	26.9	−1.6
CH_3	9.76	0.71	24.0	−8.2	3.38	0.30	27.4	−0.6
C_6H_5	2.39	0.174	24.3	−10.1	0.814	0.072	27.6	−2.9
COOR	0.115	0.00834	25.7	−12.3	0.0789	0.0070	27.1	−8.9
CN	0.00241	0.000175	24.7	−22.5	0.0025	0.000221	29.1	−10.1

[a] Some of the data for adamantyl derivatives was taken from ref 8. [b] Solvolysis of the corresponding bromides in 80% ethanol at 125° gave practically identical relative rates (R. C. Bingham, unpublished observations).

Table II. Summary of $\sigma^*_{CH_2}$ Correlations

Reaction or process	$\rho^*_{CH_2}$	Correlation coefficient	Ref
Solvolysis of 3-substituted 1-adamantyl bromides, 80% EtOH, 75°	−2.70	0.996	Table I
Solvolysis of 4-substituted 1-bicyclo[2.2.2]octyl brosylates, HOAc, 75°	−2.32 (−2.25)[a]	0.981 (0.999)[c]	Table I
Bridgehead adamantane H atom abstractions, $CCl_3\cdot$, 40°	−0.40	0.980	12
pK_a of 4-substituted bicyclo[2.2.2]octanecarboxylic acids, 50% EtOH, 25°	+0.70	0.994	5
pK_a of 3-substituted 1-adamantanecarboxylic acids, 50% EtOH, 25°	+0.68 (+0.71)[b]	0.950 (0.987)[d]	*c*
Displacement of 4-substituted bicyclo[2.2.2]oct-1-yl carbinyl tosylates with sodium thiophenoxide, EtOH, 75.3°	+0.25	0.8	*d*

[a] Point for H omitted. [b] Points for OH and OCH_3 omitted. [c] H. Stetter and J. Mayer, *Ber.*, **95**, 667 (1962); R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964). [d] H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **87**, 2404 (1965).

σ^{*}[2] (and the related σ_I)[3] constants indicate that methyl and other alkyl groups should be electron releasing relative to hydrogen.[12,13] However, it has been argued from an analysis of these constants that alkyl groups and hydrogen may well exhibit no significant differences in polar properties,[4] and there is some experimental support for this contention.[5] In contrast, other evidence suggests that methyl groups can act as if they were electron withdrawing relative to hydrogen;[6–11] thus, all possibilities are represented.

Bridged ring carboxylic acids have been favored substrates for the study of substituent effects in saturated systems.[5,13,14] The use of a carboxyl group suffers from the disadvantage that the charge is located rather far from the substituent, and polar effects are attenuated. Generation of a carbonium ion directly upon the molecular framework has seemed to be a worthwhile alternative, and the first applications of this approach gave surprising results.[8–11] Bridgehead methyl substituents were found to decrease the solvolysis rates of 1-adamantyl bromide, but ethyl groups had little effect and isopropyl derivatives actually had enhanced rates.[8–11] In order to test the generality of this behavior, we have determined the solvolysis rates of a number of 4-substituted bicyclo[2.2.2]oct-1-yl brosylates and extended the bromoadamantane series by including more polar substituents (Table I).[15]

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(5) H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **86**, 5188 (1964); F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, **89**, 5677 (1967).

(6) V. W. Laurie and J. S. Muenter, *ibid.*, **88**, 2883 (1966).

(7) H. Kwart and L. J. Miller, *ibid.*, **83**, 4552 (1961); H. Kwart and T. Takeshita, *ibid.*, **86**, 1161 (1964).

(8) R. C. Fort, Jr., and P. von R. Schleyer, *ibid.*, **86**, 4194 (1964); R. C. Fort, Jr., Ph.D. Thesis, Princeton University, 1964.

(9) C. A. Grob, W. Schwarz, and H. P. Fischer, *Helv. Chim. Acta*, **47**, 1385 (1964).

(10) R. C. Fort, Jr. and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

(11) K. Bott, *Ber.*, **101**, 564 (1968).

(12) P. H. Owens, G. J. Gleicher, and L. M. Smith, Jr., *J. Am. Chem. Soc.*, **90**, 4122 (1968).

(13) J. Weber, Dissertation, Technische Hochschule, Aachen, 1966. We are indebted to Professor H. Stetter for making this information available to us.

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(15) All new compounds showed satisfactory spectral properties and carbon–hydrogen analyses. Synthetic details, to be published at a later date, may be found in the Ph.D. Thesis of C. W. W., Princeton University, 1968. Key references for the preparation of compounds include: H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **86**, 5183 (1964); J. Colonge and R. Vuillemet, *Bull. Soc. Chim. France*, 2235 (1961); H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **64**, 2850 (1942); J. C. Kauer, Netherlands Patent 6,507,929; *Chem. Abstr.*, **64**, 15772 (1966) (we thank Dr. Kauer for his assistance); J. D. Roberts, W. T. Moreland, Jr., and W. Frazer, *J. Am. Chem. Soc.*, **75**, 637 (1953); C. W. Woodworth, V. Buss, and P. von R. Schleyer, *Chem. Commun.*, 569 (1968); H. Stetter and J. Mayer, *Ber.*, **95**, 667 (1962).

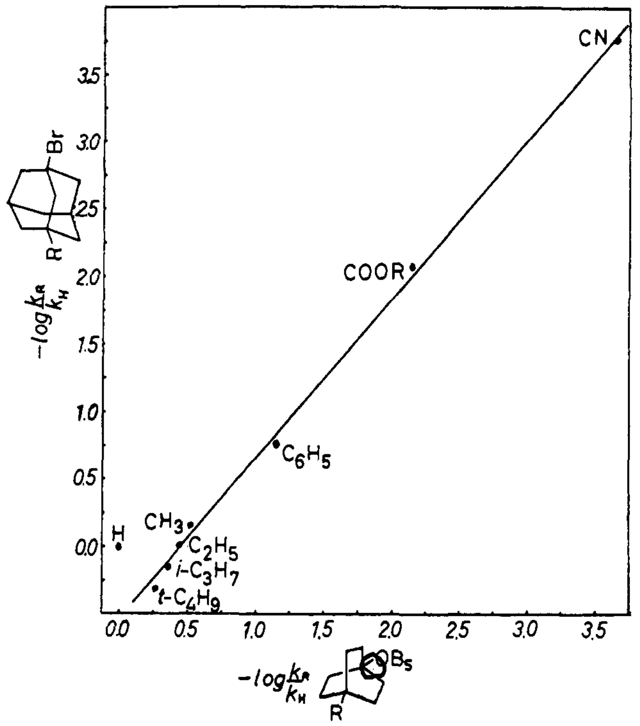

Figure 1. Log relative acetolysis rates of 4-substituted 1-bicyclo[2.2.2]octyl brosylates at 75° plotted against the log relative 80% ethanolysis rates of 3-substituted 1-adamantyl bromides, also at 75°. Data from Table I.

The introduction of a 4-methyl group in the bicyclooctyl system produces an unexpectedly large threefold reduction in solvolysis rate. Although there is a regular rate increase along the series methyl, ethyl, isopropyl, *t*-butyl, all of these substituents produce a rate diminution relative to hydrogen. In this respect, the behavior of the bicyclo[2.2.2]octyl system differs from the adamantyl, where hydrogen occupies an intermediate position in relation to the alkyl series (Table I).

The anomalous position of hydrogen is emphasized in Figure 1, a linear free energy plot of the adamantyl and the bicyclooctyl data. Included are points for a number of electron-withdrawing substituents, which help define the correlation line (slope 1.19, correlation coefficient 0.999, point for H omitted).

Excellent results are also obtained when the data from each polycyclic system are plotted separately against $\sigma^*_{CH_2}$ constants.[3,4] Table II summarizes the results and provides a comparison with recent literature observations. As expected, the sensitivity toward substituents is much more pronounced for carbonium ion solvolysis (ρ −2.7) than for free radical (ρ −0.4), carboxylic acid dissociation (ρ +0.7), or S_N2 displacement (ρ +0.25) processes.

The nonhydrogen substituents have similar effects on both adamantyl and bicyclooctyl solvolyses (Figure 1), effects very probably largely inductive in origin. This conclusion is reinforced by the excellent correlation with $\sigma^*_{CH_2}$ constants (Table II).

The failure of hydrogen to maintain a constant position in the rate order of the two systems (Table I and Figure 1) indicates that the difference between the nonhydrogen substituents and hydrogen cannot be entirely inductive in origin. We believe that steric effects are responsible for these deviations of hydrogen.

Deviations from strict tetrahedral geometry are the rule rather than the exception in organic compounds.[16] When hydrogen is replaced by a methyl group or other carbon-based substituent, a small but significant change in geometry is produced (*e.g.*, isobutane ∠CCC 111.15°[17] *vs.* neopentane ∠CCC 109.5°). Replacement of hydrogen by methyl in the system we have studied should also produce a change in structure which would be reflected in the solvolysis rates. In our compounds *both* the substituents and the leaving groups are attached directly to the rigid polycyclic ring systems and, hence, steric effects should be more pronounced than in cases (*e.g.*, those involving carboxylic acid pK_a's)[5] where the reaction sites are farther removed or where smaller structural changes during reaction would be anticipated.[2]

Although the adamantyl and the bicyclooctyl systems would be expected to respond similarly to substituent inductive effects, they should respond differently to substituent steric effects, because of variation in the intervening connective structures. The greatest steric effect should be observed when hydrogen is replaced by a carbon atom. For this reason, the position of hydrogen in a rate-order series may be variable, and may depend critically on the nature of systems involved (Table I and Figure 1).

We interpret our results to show that alkyl groups in saturated systems *do have* an inductive order of electron release increasing from methyl through *t*-butyl. The behavior of hydrogen as a substituent is variable, evidently due to differences in steric effects from system to system.[7] Until the magnitude of these steric effects can be evaluated accurately, or their absence ensured, conclusions regarding the direction of inductive effects of alkyl groups relative to hydrogens should be reserved. In particular, it probably is unwise to interpret the rate depressions produced by methyl substitution[7-11] as firm evidence for the "electron-withdrawing" nature of such groups in saturated systems.

Acknowledgment. This research was supported by grants from the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, administered by the American Chemical Society.

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[17] D. R. Lide, Jr., *J. Chem. Phys.*, 33, 1519 (1960).

[18] National Institutes of Health Predoctoral Fellow, 1965–1968.

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Received July 29, 1968

Causes for the Low Efficiency of Thymine and Uracil Photodimerization in Solution

Sir:

A vast amount of research[1] has implicated dimerization of pyrimidine bases as being responsible for photodeactivation of the nucleic acids. Such photodimerizations in DNA[2] or in frozen aqueous thymine solutions[3]

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[1] R. B. Setlow and W. L. Carrier, *J. Mol. Biol.*, 17, 237 (1966), and references cited therein.

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[3] J. Eisinger and R. G. Shulman, *Proc. Natl. Acad. Sci. U. S.*, 58, 895 (1967).