limit to either pressure or intensity where selective reactions can take place. However, the energy of activation of the reaction studied in this paper is very high. By the use of laser light at shorter wavelength for reactions having lower energy of activation, lower light intensities may be used at higher pressures.

These results have some implications also to photochemical reactions in electronic excited states. Ordinarily, electronically excited molecules are initially formed in vibrationally excited states, and the rate of radiative decay of excited singlets may exceed the rate of complete thermalization of these vibrational states in the gas phase at low pressure. Double resonance experiments may be designed to control the vibrational temperature of electronically excited states. This subject will be discussed separately.

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[24] Taken in part from the Ph.D. thesis of R. M. J. Loewenstein-Benmair, to be submitted to the Feinberg Graduate School of the Weizmann Institute of Science.

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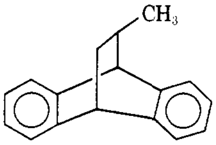
Bridged Polycyclic Compounds. LXXIX. Steric Acceleration in Free-Radical Bromination Reactions[1]

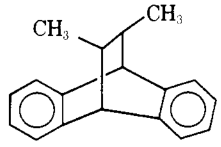
Sir:

Although steric factors have been invoked to rationalize the effects of ortho substituents on the equilibrium between triarylmethyl radicals and their dimers[2] and on the rates of decomposition of trans azo compounds,[4] steric acceleration of rate by back-strain relief[5] has received little attention. Russell and Brown[6] did not observe steric acceleration in their investigation of the chlorination of a number of highly branched hydrocarbons. On the other hand, in the only case we have noted in the literature, Simamura,[7a] quoting the results described in the thesis of one of his students,[7b] reported that the tertiary equatorial hydrogen in 1,1,3,5-tetramethylcyclohexane reacts with alkylperoxy radicals 4.2 times as rapidly as the equivalent atom in *trans*-1,3,5-trimethylcyclohexane, a result which he ascribed to relief of 1,3 interaction in the radical abstraction reaction (methyl–methyl greater than methyl–hydrogen).

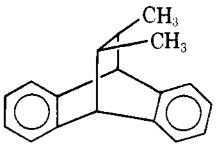
Rate enhancement might be anticipated[5,6] when the radical formed allows two groups compressed in the initial state to move farther apart, and, as it may be assumed that the angles between groups in these radicals will be greater than tetrahedral,[8] will be noted when the transition state is sufficiently advanced along the reaction coordinate. We wish now to report relative reactivities for light-promoted bromination of compounds **1–4**, which react only at the tertiary bridge positions and which provide excellent evidence for steric acceleration.



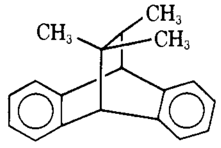
1



2



3



4

Relative bromination rates will give relative hydrogen abstraction rates only if the reaction in eq 1 is irreversible, or if k_{-1}/k_2 is identical for each alkyl radical, which seems highly unlikely except for closely analogous radicals. The high reactivity of the radicals from **3** with hydrogen bromide compared with bromine may be noted from the fact that treatment of **3** with 1 mol of bromine in 60 mol of CCl_4 gave a mixture of 54% 7,8-dimethyl-7-bromodibenzobicyclo[2.2.2]octadienes (cis and trans), 8–11% of **3**, and 31–33% of the trans isomer **2**.[9] The isomerization of **3** to **2** could be cut substantially when 4–6% of the solvent was replaced by a hydrogen bromide scavenger, 2,3-epoxy-2,3-dimethylbutane,[11] and almost completely eliminated when ratios of 1 mol of **3**, 1 mol of Br_2, 50 mol of CCl_4, and 21 mol of epoxide were used (at 50% bromination, the hydrocarbon mixture gave a ratio of 3% of **2** and 97% of **3**).

$$\mathrm{R{-}H} + \mathrm{Br}\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{R}\cdot + \mathrm{HBr} \tag{1}$$

$$\mathrm{R}\cdot + \mathrm{Br_2} \xrightarrow{k_2} \mathrm{RBr} + \mathrm{Br}\cdot \tag{2}$$

Relative rates of disappearance of **1**,[12] **2**,[13] **3**,[14] and **4**[14] were measured at 10–11°, using ratios of 0.5 to 1.0 mol of Br_2 to one of hydrocarbon mixture, 36 of CCl_4, and 21 of epoxide. After irradiation, solvents were removed by rotary evaporation, petroleum ether was added, and oxygen-containing products were extracted with 85% H_3PO_4. Analysis was by pmr and/or glc. The reactivity ratios were compared in pairs, as generally done.[15] Typical data and results are given in Table I, and we estimate that relative reactivities are reproducible to ±25%.

When the data in Table I are corrected for the num-

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[1] Paper LXXVIII: S. J. Cristol, A. A. Roberts, and T. E. McEntee, *J. Org. Chem.*, in press.

[2] C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 530; G. W. Wheland, "Advanced Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1960, p 785. In this argument, it was assumed that the dimers were hexaarylethanes. This may now be assumed to be in doubt.[3]

[3] H. Lankamp, W. T. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968).

[4] E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1952, p 148.

[5] H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *J. Amer. Chem. Soc.*, **66**, 435 (1944).

[6] G. A. Russell and H. C. Brown, *ibid.*, **77**, 4031 (1955).

[7] (a) O. Simamura, *Top. Stereochem.*, **4**, 1 (1969); (b) S. Mayajima, D.Sc. Thesis, Tokyo University, Tokyo, Japan, 1967.

[8] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 30.

[9] This result is clearly different from that reported for the 1-bromo-2-methyl-2-butyl radical, which is reported to react with bromine much faster than with hydrogen bromide.[10]

[10] K. J. Shea and P. S. Skell, *J. Amer. Chem. Soc.*, **95**, 283 (1973).

[11] N. Prileschajeff, *J. Russ. Phys. Chem. Soc.*, **42**, 1387 (1910).

[12] E. I. Snyder and R. A. Clement, *J. Amer. Chem. Soc.*, **82**, 1424 (1960).

[13] H. M. Walborsky, *Helv. Chim. Acta*, **36**, 1255 (1953). We have also prepared **2** and **3** from the corresponding butenes and anthracene.[14]

[14] H. W. Mueller, Ph.D. dissertation, University of Colorado, 1973.

[15] W. A. Thaler, *Methods Free-Rad. Chem.*, **2**, 121 (1969).

Table I. Typical Data and Results on Photobromination in a Carbon Tetrachloride–2,3-Dimethyl-2,3-epoxybutane Mixture

	Mol ratios		Recovered substrates,[a] % of aromatic peaks	
Run	Substrates	Br_2		Rel react.
1	**3**, 0.63; **2**, 0.37	0.70	**3**, 6.4; **2**, 34.6	**3**:**2** = 34:1
2	**2**, 0.52; **4**, 0.48	0.70	**2**, 48.2; **4**, 16.1	**4**:**2** = 14:1
3	**2**, 0.55; **1**, 0.45	0.50	**2**, 45.0; **1**, 35.6	**1**:**2** = 1.2:1

[a] Mixtures of bromides were also present.

ber of tertiary hydrogen sites, it becomes evident that **1** and **2** have a reactivity ratio of about 2, while **3** and **4** are about equal in reactivity. These pairs differ in having a methyl group which might provide interference with the attacking bromine atom; this effect is small or negligible. On the other hand the reactivities of **3** and **4** compared with **1** and **2** (factors of 15–30) show the relatively large rate enhancement caused by the additional eclipsed methyl group remote from the site of attack. We see no simple explanation of these results other than steric acceleration due to back-strain relief.

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