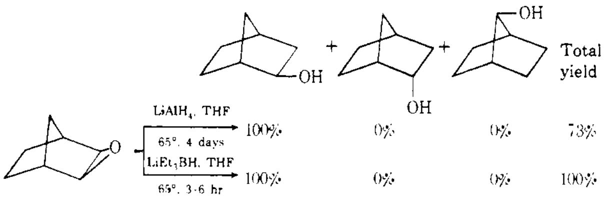
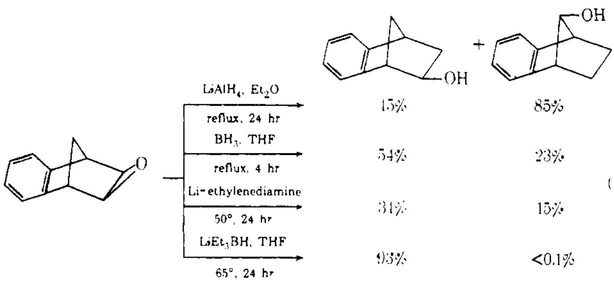


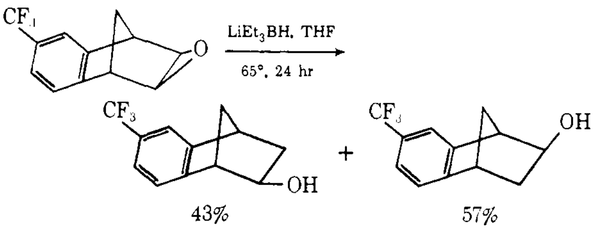
(5)

(eq 6). However, lithium triethylborohydride achieved



(6)

the clean reduction of this derivative to give 93% of *exo*-benzonorbornenol in >99.9% isomeric purity. Similar results were realized with the epoxide derived from 6-trifluoromethylbenzonorbornadiene (eq 7).



(7)

The following procedure for the reduction of 1-methylcyclohexene oxide is representative. An oven-dried 200-ml flask equipped with a side arm fitted with a Silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was cooled to room temperature under dry nitrogen. The flask was immersed in a water bath at 25°; then 25 ml of a 1.5 *M* solution in THF of $LiEt_3BH$ (37.5 mmol) was introduced into the reaction flask, followed by 3.1 ml (2.8 g, 25 mmol) of 1-methylcyclohexene oxide. The reaction mixture was stirred vigorously. After 2 min, glpc analysis of the reaction mixture indicated the completion of >99.5% reaction. The mixture was hydrolyzed and the organoborane oxidized. The aqueous phase was saturated with anhydrous potassium carbonate, the organic phase separated, and the aqueous phase extracted with two 20-ml portions of ether. The combined extracts were dried (K_2CO_3) and the solvents removed on a rotary evaporator. Upon distillation there was obtained 2.34 g (82%) of 1-methylcyclohexanol, bp 67° (21 mm), $n^{20}D$ 1.4604 [lit.[7] bp 53-54° (7 mm), $n^{20}D$ 1.4610].

In conclusion it should be emphasized that $LiEt_3BH$ provides a range of applicability far broader than the reducing agents previously available for such synthetic transformations. First, the reaction is rapid, clean, and gives excellent yields for a wide variety of epoxides. Second, the high regiospecificity and stereospecificity of the reaction, especially with the labile bicyclic epoxides, enable us to use this reaction as a chemical tool to determine precisely the stereochemistry of epoxidation of such bicyclic olefins.[8] The present results make it clear that not only is lithium triethylborohydride an exceptionally powerful nucleophile in reductions but it is likewise remarkably free of electrophilic characteristics that sometimes complicate reduction by lithium aluminum hydride or other reagents.[9] We are continuing our active exploration in this area.[10]

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(7) F. K. Signaigo and P. L. Cramer, *J. Amer. Chem. Soc.*, **55**, 3326 (1933).

(8) R. M. Schubert, Ph.D. Thesis, Purdue University, 1972.

(9) (a) L. W. Trevoy and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 1675 (1949); (b) E. L. Eliel and M. N. Rerick, *ibid.*, **82**, 1362 (1960); (c) M. N. Rerick and E. L. Eliel, *ibid.*, **84**, 2356 (1962); (d) E. C. Ashby and J. Prather, *ibid.*, **88**, 729 (1966); (e) D. K. Murphy, R. L. Alumbaugh, and B. Rickborn, *ibid.*, **91**, 2649 (1969), and the references cited therein; (f) H. C. Brown, P. M. Weissman, and N. M. Yoon, *ibid.*, **88**, 1458 (1966).

(10) Research in progress with Dr. S. Krishnamurthy and Mr. S. C. Kim.

(11) Postdoctoral Research Associate on Grant No. DA-ARO(D)-31-124-73-G1 supported by the U. S. Army Research Office (Durham).

(12) National Institutes of Health Predoctoral Fellow, 1967–1972.

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Photochemistry in the Electronic Ground State. II. Selective Decomposition of *trans*-2-Butene by Pulsed Carbon Dioxide Laser

Sir:

The possibility to disturb the Boltzmann energy distribution by infrared (ir) lasers and thus control chemical reactions has already been discussed in the literature.[1-7] In all the cases which have been reported,[7-10] the interruption of chemical equilibrium by ir light was studied with compounds in which the energy of activation was equal to or smaller than the energy per einstein of the ir light beam. The most important problem in reactions induced by ir lasers is the competition between excitation and energy relaxation. In the past it was speculated that total redistribution of energy is expected within ten collisions in molecules with a number of atoms larger than ten. This assumption was based on shock-wave experiments.[11,12] Recently, it was shown in our laboratory by ir–ultraviolet (uv) double resonance experiments that thermal equilibrium was not reached within 10^{-5} sec at pressures in the

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(1) A. Yogev, R. M. J. Loewenstein, and D. Amar, *J. Amer. Chem. Soc.*, **94**, 1091 (1972).

(2) K. L. Kompa, *Z. Naturforsch. B*, **27**, 89 (1972).

(3) F. V. Bunkin, R. V. Karapetyan, and A. M. Prokhorov, *Sov. Phys. JETP*, **20**, 145 (1965).

(4) N. D. Artamonova, V. T. Platonenko, and P. V. Khokhlov, *Sov. Phys. JETP*, **31**, 1185 (1970).

(5) R. V. Ambartzumian, V. S. Letokhov, G. N. Makarov, and A. A. Puretzkiy, *Chem. Phys. Lett.*, **16**, 252 (1972).

(6) J. L. Lyman and R. J. Jensen, *J. Phys. Chem.*, **77**, 883 (1973).

(7) M. I. Buchwald, R. McFarlane, and S. H. Bauer, Third Conference on Chemical and Molecular Lasers, St. Louis, Mo., May 1–3, 1972.

(8) R. T. Hall and G. C. Pimentel, *J. Chem. Phys.*, **38**, 1889 (1963).

(9) S. W. Mayer, M. A. Kwok, R. W. F. Gross, and D. J. Spencer, *Appl. Phys. Lett.*, **17**, 516 (1970).

(10) T. J. Odiore, P. R. Brooks, and J. V. V. Kasper, *J. Chem. Phys.*, **55**, 1980 (1971).

(11) T. C. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworth, London, 1961.

(12) J. D. Lambert, *J. Chem. Soc., Faraday Trans.*, **68**, 364 (1972).

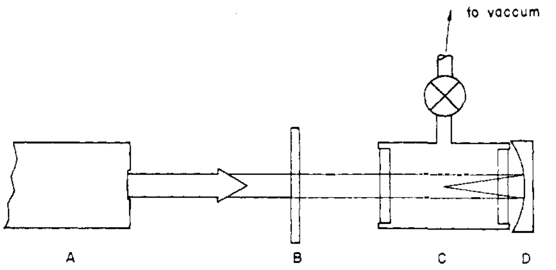

Figure 1. Scheme of the experimental apparatus: A, TEA laser; B, attenuator; C, irradiation cell equipped with two NaCl windows and vacuum valve; D, focusing mirror.

range of 1–40 Torr.[13] This time corresponds, approximately, to 10^3 collisions. It is expected on the basis of the data from this experiment that with lasers of sufficient intensity it will be possible to induce specific chemical reactions in the electronic ground state with molar energy of activation larger than the energy per einstein of the laser light.

We have studied the reaction of 2-butene in the gas phase induced by a CO_2 laser (R-35 TEA laser, Israel Electro-Optical Industry Ltd., Rehovot, Israel) with a typical 0.1 μsec pulse width and 10 MW peak power at 10.6 μ. The experimental device is shown in Figure 1. No products were obtained when the light was not focused. After focusing the main products obtained by the irradiation of *trans*-2-butene were identified as methane, ethylene, propene, *cis*-2-butene, and butadiene. After 3600 pulses 16% conversion was attained. The distribution of products and relative rates of conversion were only slightly dependent on pressure (Table I). The same was observed when inert gases like nitrogen, helium, or argon were added. At total pressures above 30 Torr, dielectric breakdown occurred. When *cis*-2-butene was irradiated under the same conditions, the same products were formed and similarly some conversion to the trans isomer was observed; however, the rate of conversion was fivefold smaller than that of the trans isomer under the same conditions. The preferred decomposition of the trans isomer can be attributed to its greater absorption coefficient [$\epsilon_{\text{trans}(\text{Torr}^{-1}\text{ cm}^{-1})}$ 15×10^{-4}, $\epsilon_{\text{cis}(\text{Torr}^{-1}\text{ cm}^{-1})}$ 1.3×10^{-4}]. It is not expected that there will be a considerable difference in the energy of activation for the decomposition of both isomers. When a 1:1 mixture of both isomers was irradiated under the same conditions and at a total pressure of 14 Torr, there was no significant change in the ratio of both isomers after irradiation. This result is significant for complete redistribution of energy after light absorption and prior to decomposition. However, when a similar experiment was carried out at a pressure of 4 Torr, a 15% enrichment of the mixture by the cis isomer was observed. The change of composition occurred partially by direct isomerization and partially by selective decomposition of the trans isomer. The equilibrium between *trans*- and *cis*-2-butene was extensively studied,[14,15] and it was found that in none of the experiments did the amount of cis isomer exceed the amount of the trans isomer. Therefore in our experiment, redistribution of energy did not occur before the reaction took place. There are no precise figures for the energy of activation for the decomposition of 2-butene, but, since the decomposition occurs at temperatures much higher than the temperature where significant cis–trans isomerization takes place, it may be assumed that the energy of activation for decomposition is higher.[16] The energy of activation of cis–trans isomerization was estimated to be 62 kcal/mol,[16–22] namely 20 times more than the energy per einstein in the laser light.

Table I. Relative Conversion of *trans*-2-Butene to Products after 3600 Pulses at Different Pressures

Pressure (Torr) of *trans*-2-butene	% *trans*-2-butene after reaction	% products: Methane	Ethylene	Propene	*cis*-2-Butene	Butadiene
3	84		3	3	5	3
9	81	2	2	4	5	4
18	87		2	2	4	5

Three different mechanisms may be responsible for the effect: (1) multiphoton absorption, (2) cascade excitation, (3) specific energy transfer by collisions.

There is not sufficient experimental evidence for the choice of the right mechanism. Mechanism 1 cannot be responsible alone for the reaction, since there is a pressure dependence of the selectivity of the reaction. Cascade excitation is more probable since, during the pulse time, complete thermalization of energy cannot occur. Mechanism 3 alone cannot account by itself for all the observations. Absorption of a single photon will raise the temperature after thermalization by about 30°. Multiplying the energy in intermediate steps by collision of excited molecules will not raise the energy sufficiently for any of the observed reactions. However, multiplying of energy by collisions of molecules which have absorbed several photons by either mechanism 1 or 2 may contribute to the effect.

At pressures about 30 Torr or by increasing the light intensity at lower pressures, breakdown takes place. The main product of the breakdown is acetylene. Formation of acetylene does not change the ratio of components in any mixture of hydrocarbons tested by us and is independent of the absorption coefficient of the different hydrocarbons. Formation of acetylene occurs at intermediate light intensities before emission of light can be observed. Whenever acetylene is formed the selectivity is lost, and we assume that inverse bremsstrahlung is responsible for acetylene formation and hence cannot be selective. This effect puts a higher

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(13) A. Yogev and Y. Haas, *Chem. Phys. Lett.*, in press.

(14) G. B. Kistiakowsky and W. R. Smit, *J. Amer. Chem. Soc.*, **58**, 766 (1936).

(15) H. H. Voge and N. C. May, *J. Amer. Chem. Soc.*, **68**, 550 (1946).

(16) A. Lifshitz, S. H. Bauer, and E. L. Resler, Jr., *J. Chem. Phys.*, **38**, 2056 (1963).

(17) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

(18) V. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968).

(19) W. F. Anderson, J. A. Bell, J. M. Diamond, and K. R. Wilson, *J. Amer. Chem. Soc.*, **80**, 2384 (1958).

(20) B. S. Rabinovitch and K. W. Michel, *J. Amer. Chem. Soc.*, **81**, 5056 (1959).

(21) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **57**, 1936 (1961).

(22) P. M. Jeffers and W. Shaub, *J. Amer. Chem. Soc.*, **91**, 7706 (1969).

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.

(23) C. P. Scott Research Fellow of the Weizmann Institute of Science, Rehovot.

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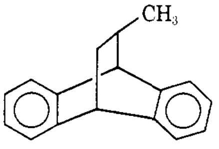
Bridged Polycyclic Compounds. LXXIX. Steric Acceleration in Free-Radical Bromination Reactions[1]

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.



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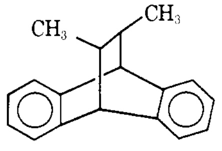

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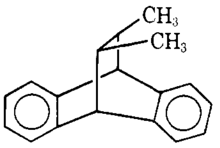

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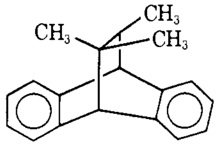

4

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.

$$\text{R–H} + \text{Br}\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R}\cdot + \text{HBr} \qquad (1)$$

$$\text{R}\cdot + \text{Br}_2 \xrightarrow{k_2} \text{RBr} + \text{Br}\cdot \qquad (2)$$

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**).

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).