The enormous rate-enhancing influence of the five-membered ring in II is reminiscent of the behavior of related phosphate esters.[9] Undoubtedly, steric strain in II is an important contributing factor since the O-P-O bond angle in II is known to be 97°,[10] a significant decrease from the preferred angle of 102-104° in most phosphazenes.[11] However, the apparent over-all preference for cleavage of the phosphazene rather than the dioxyphosphole ring of II cannot be readily explained by the phenomenon of pseudorotation of a simple pentacoordinate intermediate, and this provides a contrast to phosphate ester hydrolysis.[9] Thus, in a pentacoordinate transition state, the N-P-N bonds must be equatorial to maintain the preferred 120° phosphazene ring angle,[11] and the O-P-O bonds must occupy axial and equatorial positions to maintain a ~90° benzodioxyphosphole ring angle. Pseudorotation of this structure is sterically inhibited. However, if hydrogen migration to a ring nitrogen occurs to form a phosphazane structure, pseudorotation would be more feasible. Attack by hydroxyl anion on carbon has been ruled out by the absence of $H_2{}^{18}O$ exchange with the ring oxygen atoms of II. Further work is continuing in an attempt to clarify the mechanism.

Acknowledgments. We are indebted to the Public Health Service (P.H.S. Research Grant No. HE 11418-01, National Heart Institute) for the support of this work, and to the National Science Foundation for an Institutional Fellowship to E. J. W.

[9] F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968), and references therein.

[10] L. H. Siegel and J. H. van den Hende, *J. Chem. Soc., A*, 817 (1967).

[11] H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N. Y., 1967, Appendix II and references therein.

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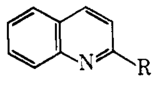
McLafferty Rearrangement and Type II Photocleavage Comparisons in a New System. 2-Substituted Quinolines[1]

Sir:

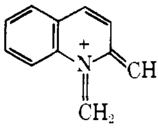
Some correlations of electron-impact fragmentation with photochemical reactivity have recently been reported, nearly all of which deal with molecules containing a carbonyl function. We wish to report some interesting comparisons in a new system.



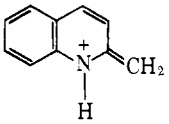
I, R = CH_2CH_3 IV, R = CH_2CH_2OH
II, R = $CH_2CH_2CH_2CH_3$ VII, R = CH_2CH_2OD
III, R = CH_3 IX, R = $CH_2CH_2OCH_3$

Irradiation[2] of 2-ethylquinoline (I) for 60 hr resulted in no reaction, and I was recovered quantitatively. Irradiation[2] of 2-*n*-butylquinoline (II) for 58 hr resulted in 45% conversion ($k = 2.5 \times 10^{-6}$ sec^{-1}) to 2-methylquinoline (III) and propylene (trapped as the dibromide). Irradiation[2] of 2-(2-hydroxyethyl)quinoline (IV) for 18 hr resulted in 73% conversion ($k = 2.3 \times 10^{-5}$ sec^{-1}) to III and formaldehyde (trapped as the 2,4-DNP derivative).

The base peak in the mass spectrum[3,4] of 2-ethylquinoline is at *m/e* 156 ($M^+ - 1$) and has been attributed[4] to V. We cannot conceive of a rational photochemical process from I to V, and it is perhaps not surprising that I is stable to light.

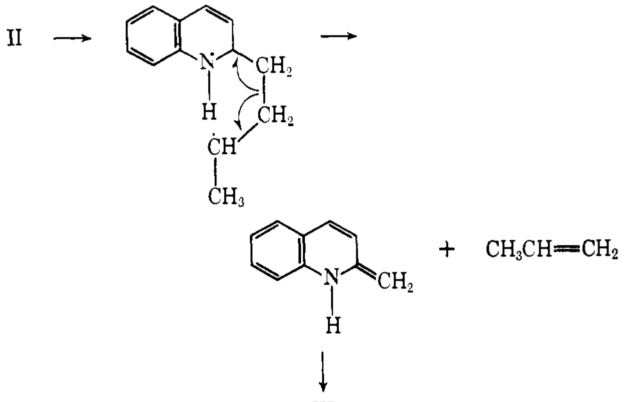


V

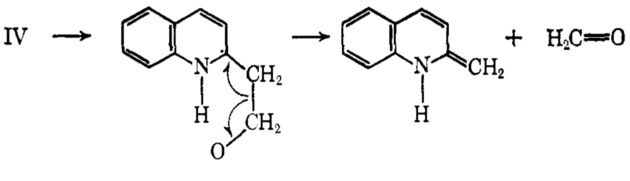


VI

However, the base peak in the mass spectrum[3,4] of II and IV is at *m/e* 143, attributable to VI, and hence, in terms of product formation, a correlation is observed for electron-impact fragmentation and photocleavage. A complete analysis (with deuterium-labeled material) of the mass spectrum of 2-propylquinoline was previously reported,[4] and a McLafferty rearrangement process to VI was proved. Thus, for 2-*n*-butylquinoline photocleavage, it is probably valid to write a process exactly in analogy with ketone "type II" cleavage.



However, for photocleavage of IV abstraction of H from OH must occur if the reaction is to be similarly described. Although this process is unusual, a similar one has been suggested[5] for a 9-substituted isoalloxazine where C═N photoreactivity is also involved. A distinction between the above reaction and abstraction through an unfavored five-membered transition state



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[1] Photochemistry of Aromatic N-Heterocycles. IV. Previous paper in this series: F. R. Stermitz, C. C. Wei, and W. H. Huang, *Chem. Commun.*, 482 (1968). This work was supported in part by Grant GM 14525 from the National Institute of General Medical Sciences, U. S. Public Health Service.

[2] Irradiations were carried out in 10^{-2} *M* benzene solutions (650 ml), under nitrogen, using a Rayonet reactor equipped with 3000-Å lamps. Each of the quinolines had similar absorption spectra with maxima at 273, 302, and 315 nm.

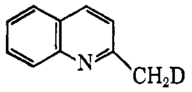
[3] Mass spectra were taken with an AEI MS-12 instrument at 70 eV.

[4] S. D. Sample, D. A. Lightner, O. Burchardt, and C. Djerassi, *J. Org. Chem.*, 32, 997 (1967).

[5] W. M. Moore and C. Baylor, Jr., *J. Am. Chem. Soc.*, 88, 5677 (1966), and private communication (1969).

(but from a far more reactive $-CH_2OH$) was made on the basis of deuterium isotope studies.

Irradiation[2] of VII yielded VIII and formaldehyde. By nmr integration and mass spectrometry no detectable III was present and the formaldehyde was free of CHDO. Thus, the alcoholic hydrogen was specifically



VIII

transferred. Again, the mass spectrum of VII correlated perfectly, with the base peak appearing at m/e 144 instead of m/e 143 as in the case of IV. As further confirmation of the close parallel of these reactions with type II cleavage and the McLafferty rearrangement we found that compound IX was completely stable to irradiation under the same conditions, while its electron impact fragmentation gave a base peak at m/e 155 (vinylquinoline). In IX a six-membered transition state for H abstraction is not possible.

Studies on the excited state(s) involved in these photoreactions are currently under way.

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Variations with Bond Types of the Yields for Deuterium-Atom Abstraction by 2.8-eV Tritium Atoms

Sir:

The reaction yields from the abstraction of hydrogen by energetic tritium atoms from nuclear recoil, as in (1), vary widely with C–H bond type and exhibit a good correlation between higher HT yield and lower bond dissociation energy of the C–H bond for a series of cyclanes and alkanes.[1-4] Subsequent experiments

$$T^* + RH \longrightarrow HT + R \qquad (1)$$

have confirmed the general concept of substantial variations in HT yield with C–H bond type, while demonstrating that the bond dissociation energy correlation must be modified in some cases by allowances for the internal excitation of the residual radical, R.[5,6] Explanations of two general types have been offered to account for the observed sensitivity of HT yield to the nature of the C–H bond, differing most critically in their estimates of the kinetic energy of the reacting tritium atom. One proposal invokes an "energy cut-off" model,[2,3] correlating the yield behavior with the known lower energy thresholds for abstraction from weaker C–H bonds.[7] An alternate mechanistic proposal is the high-energy, "stripping" model,[8,9] which hypothesizes that (a) the hydrogen-abstraction process occurs largely through grazing collisions at relatively high tritium atom energies, and (b) the weaker C–H bonds permit higher yields for such encounters. The energy arguments in support of each model have necessarily been indirect in previous experiments utilizing tritium from nuclear recoil, since all of these atoms are formed with 192,000-eV kinetic energy, and a fraction of them become completely thermalized without reaction, thereby ensuring that all possible energies of reaction are sampled in the experiment.

We have now carried out a series of abstraction reactions from deuterated compounds[10] with 2.8-eV tritium atoms from the 1849-Å photolysis of TBr,[11] and have observed a characteristic, strong dependence of abstraction yield upon the nature of the attacked C–D bond, as shown in Table I. The yields have been expressed as $(DT)_C{}^{2.8}$, the relative yield per C–D bond, from the abstraction of 2.8-eV atoms in excess CH_4.

Table I. Relative Yields of DT from Reactions of 2.8-eV Tritium Atoms with RD

Compound	Relative yields[a,b] $(DT)_C{}^{2.8}$	$(HT)_F{}^{\infty}$, ref 3
CD_4	(1.0)	(1.00)
neo-C_5D_{12}	1.7	1.54 ± 0.03
C_2D_6	2.4	1.84 ± 0.05
c-C_4D_8	2.8	2.77 ± 0.10
C_3D_8	3.4	1.67 ± 0.10
CDF_3	1.3	1.34 ± 0.04
CD_3F	2.7	1.70 ± 0.05

[a] Yields are given as values of $(DT)_C{}^{2.8}$, the relative yield per bond *vs.* yield from C–D of CD_4, as measured in bulk CH_4 with 2.8-eV T atoms: $CH_4/RD \sim 10$; Br_2, 2–7%. [b] The values of $(HT)_F{}^{\infty}$ are the relative yields from RH, as measured in bulk perfluorocyclobutene with 192,000-eV T atoms.

Our measurements have been carried out with CH_4–RD mixtures in a mole ratio of ~10 to ensure that the bulk of the nonreactive collisions have similar energy-loss patterns for all mixtures. The mixtures also contained 2–7% Br_2 as scavenger. This technique is quite similar to that used in the nuclear recoil experiments and has been adopted because of the nearly complete absence of quantitative experimental information concerning energy losses in nonreactive collisions in the 1–20-eV range. Preliminary results indicate that the value of $(DT)_C{}^{2.8}$ is slightly dependent upon Br_2 concentration (~10%), in the pattern of experiments with CH_4,[11] and varies less than 10% with varying mole fractions of CH_4 and RD in the mixture. The variations observed for tritium atoms from nuclear recoil, listed for comparison in Table I, are similar in magnitude to those from the photochemical experiments. The values of $(DT)_C{}^{2.8}$ and $(HT)_F{}^{\infty}$ are not entirely parallel, with the variations for CD_3F and

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(1) W. Breckenridge, J. W. Root, and F. S. Rowland, *J. Chem. Phys.*, **39**, 2372 (1963).

(2) J. W. Root, W. Breckenridge, and F. S. Rowland, *ibid.*, **43**, 3694 (1965).

(3) E. Tachikawa and F. S. Rowland, *J. Am. Chem. Soc.*, **90**, 4767 (1968).

(4) E. Tachikawa, Ph.D. Thesis, University of California, Irvine, 1967.

(5) E. Tachikawa, Y.-N. Tang, and F. S. Rowland, *J. Am. Chem. Soc.*, **90**, 3584 (1968).

(6) E. Tachikawa and F. S. Rowland, *ibid.*, **91**, 559 (1969).

(7) See, for example, A. F. Trotman-Dickenson, *Advan. Free Radical Chem.*, **1**, 1 (1965).

(8) R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965).

(9) R. T. K. Baker and R. Wolfgang, *J. Am. Chem. Soc.*, **90**, 4473 (1968).

(10) Deuterated compounds are technically somewhat easier to use without ambiguity in the photochemical experiments. Much less extensive work has established that the abstraction of deuterium from C–D by tritium atoms from nuclear recoil fits readily into a pattern of variation quite similar to that found for C–H.[2-4]

(11) C. C. Chou and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 2616 (1966); C. C. Chou and F. S. Rowland, *J. Chem. Phys.*, in press.