Table I. Proton Affinities of Methyl Derivatives (**2, 4, 6,** and **8**)[a]

Compd	Proton affinity,[a] kcal mol^{-1}	Reference base used[b]
2	215.8	Pyridine; **2** is 0.9 kcal mol^{-1} weaker
4	217.9	tert-Butylamine; **4** is 1.0 kcal mol^{-1} stronger
6	214.9	Isopropylamine; **6** is 0.3 kcal mol^{-1} stronger
8	224.6	Diisopropylamine; **8** is 0.3 kcal mol^{-1} weaker

[a] Based upon PA(NH$_3$) = 201.0 ± 2 kcal mol^{-1} (ref 8 and 10); relative values are precise to ±0.2 kcal mol^{-1}; cf. ref 7 and 8. [b] Values given are $\Delta G°$ from direct equilibrium constant determinations.

the experimental $\Delta H° = -0.3$ kcal mol^{-1} obtained by Beak suggests that in the present series the differential methylation effect is in reasonable accord with the above figures,[9] i.e., ~2.4 kcal mol^{-1}.

For the corresponding tetrahydro compounds we find that **8** is more basic than **6** by 9.7 kcal mol^{-1}; correcting this for the differential effect of O- vs. N-methylation indicates 7.3 kcal mol^{-1} as the difference between **5** and **7**, in reasonable agreement with the value of 6.7 kcal mol^{-1} deduced by Beak.

We believe that gas-phase basicities will be of considerable interest in the elucidation of prototropic equilibria in the gas phase, particularly in heavily biased cases.

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References and Notes

(1) Tautomeric Pyridines. Part 19. For part 18, see ref 3.
(2) For a survey see (a) J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, *Adv. Heterocycl. Chem.*, Supplement 1 (1976); (b) A. R. Katritzky and J. M. Lagowski, *Adv. Heterocycl. Chem.*, 1, 311 (1963).
(3) M. J. Cook, A. R. Katritzky, L. G. Hepler, and T. Matsui, *Tetrahedron Lett.*, 2685 (1976).
(4) (a) P. Beak and F. S. Fry, Jr., *J. Am. Chem. Soc.*, 95, 1700 (1973); (b) P. Beak, F. S. Fry, Jr., J. Lee, and F. Steele, *ibid.*, 98, 171 (1976).
(5) P. Beak, J. Bonham, and J. T. Lee, Jr., *J. Am. Chem. Soc.*, 90, 1569 (1968).
(6) (a) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, 93, 4314 (1971); (b) R. T. McIver, Jr., *Rev. Sci. Instrum.*, 41, 555 (1970); (c) T. B. McMahon and J. L. Beauchamp, *ibid.*, 43, 509 (1972); (d) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, 94, 4728 (1972).
(7) For a review, cf. R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975, p 31.
(8) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, submitted for publication.
(9) Unpublished results suggest that other groups may be more suitable than the methyl group in minimizing differential effects between oxygen and nitrogen. This matter is under further investigation.
(10) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, 98, 1320 (1976).

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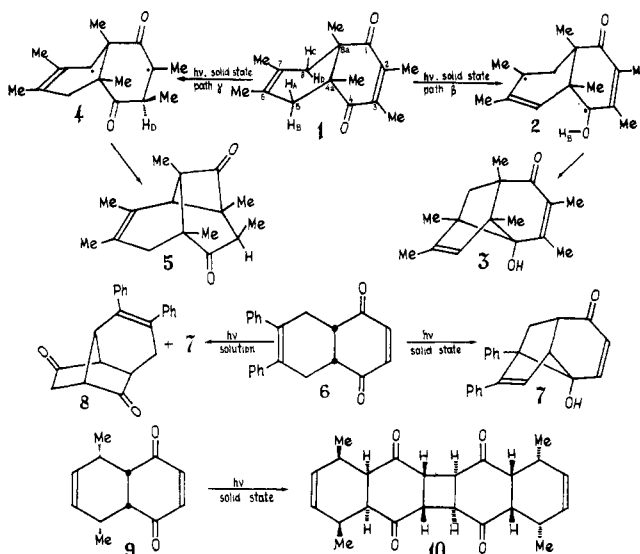*Department of Chemistry, University of California*
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Intramolecular Photochemical Hydrogen Abstraction Reactions in the Solid State. Correlation with X-Ray Crystal Structure Data[1]

Sir:

The correlation of solid state chemical reactivity with x-ray crystal structure data has provided valuable insight into a va-

Scheme I

Table I. Selected Angles and Nonbonded Distances in Adducts **1, 6,** and **9** (Refer to Structure **1**)[a]

Compound	Angles (deg)[b]			Distances (Å)	
	α	β	τ	H$_B$ to O$_4$	H$_D$ to C$_3$
1	60.0 (6)	61.4 (5)	0	2.47 (6)	2.89 (6)
6	62 (2)	67.9 (2)	3	2.46 (3)	3.05 (3)
9	61 (2)	72.8 (1)	c	c	d

[a] The values in parentheses represent the standard deviation in the data. [b] α = Dihedral angle CH$_3$-C$_{4a}$-C$_{8a}$-CH$_3$ or H-C$_{4a}$-C$_{8a}$-H; β = dihedral angle C$_4$-C$_{4a}$-C$_{8a}$-C$_8$; τ = angle subtended by the O to H$_B$ vector and its projection on the plane of the C$_4$ carbonyl group; cf. ref 8a. [c] Hydrogen B replaced by methyl. [d] Hydrogen D replaced by methyl.

riety of organic reaction types including (among others) 2 + 2 photodimerizations,[2] base-induced dehydrohalogenations,[3] thermal rearrangements,[4] azoalkane and diacyl peroxide photodecompositions,[5] and the reaction of carboxylic acids with amines.[6]

In this paper we report the initial development of solid state structure–reactivity relationships in a class of organic reactions not yet studied in this way, namely, those involving intramolecular photochemical hydrogen atom abstractions. A study of this type was expected to provide evidence on five main points: (1) Over what distances can abstraction occur? (2) What is the preferred geometry for abstraction? (3) Can abstraction be facilitated relative to competing processes by "freezing" a reactant molecule in a favorable solid state conformation?[7] (4) Will the products of such reactions in the solid state differ in type or amount from those obtained in solution due to crystal lattice restriction of rotation of the diradical intermediates involved? (5) Will changes in reaction molecularity be observed in going from studies in dilute solution to those in the solid state? We believe our results provide preliminary evidence on all five of these questions. In addition, the results are of relevance to the intramolecular hydrogen abstraction processes observed for carbonyl compounds upon electron impact (McLafferty rearrangement[8]) and anodic oxidation.[9]

The substrates chosen for study were the crystalline Diels–Alder adducts **1, 6,** and **9** (Scheme I) whose solution phase photochemistry has recently been elucidated.[1,10] In solution, two main reaction courses were identified as exemplified by the photoisomerization of **1** to **3** and **5**. These were (path β)
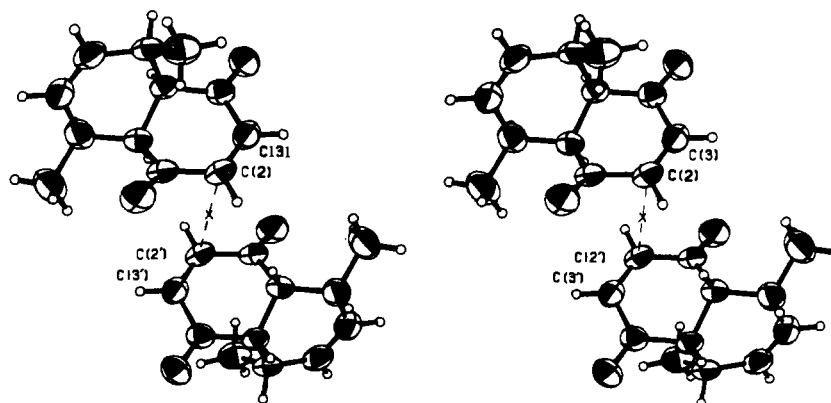
Figure 1. Stereo diagram showing the relationship between nearest neighbor molecules of 9 in the crystal.

abstraction of an allylic (C_5) hydrogen atom by the adjacent oxygen through a five-membered transition state, and (path γ) transfer of an allylic C_8 hydrogen to C_3 via a six-membered transition state. Collapse of the resulting diradical species 2 and 4 then accounts for the novel tricyclic products 3 and 5, respectively.

We now report that irradiation ($\lambda >355$ nm) of 1 in the crystalline state at -30 °C gives rise to near-quantitative yields of the same two photoproducts, 3 and 5, in a ratio of 1:1.6.[11] *This result is beautifully consistent with the conformation of 1 in the solid state as shown by x-ray crystallography.*

The crystal structure of 1, as well as the structures of 6 and 9, were determined by single crystal direct methods and refined to conventional R values of 0.088, 0.053, and 0.045, respectively. The molecular conformations correspond, in all three instances, to "twist" conformation 1 with small differences in the torsion angles and bond lengths.[12] Table I summarizes the values of certain structural parameters for the three systems. Particularly to be noted is the near-coplanar arrangement of H_B and the plane of the C_4 carbonyl group in compounds 1 and 6 as well as the close approach possible in compound 1 between the C_4 oxygen atom and H_B (2.47 Å) and between the C_3 carbon and H_D (2.89 Å). These are precisely the atoms involved in hydrogen abstraction processsess β and γ which are suggested to give rise to photoproducts 3 and 5. The fact that these distances are very close in each case to the sum of the van der Waals radii of the atoms involved[13] renders the postulated hydrogen transfers eminently reasonable.[14]

Equally important to the success of the solid state reactions is the fact that the diradical intermediates 2 and 4 are formed in conformations favorable for collapse to stable products. Alternative modes of closure (i.e., C_2-C_7 or C_2-C_5 bonding for 2 and C_2-C_6 bonding for 4) require ring flipping of 2 and 4 which is prevented by lattice restraints in the solid state. Further evidence for this comes from the solid state irradiation of adduct 6[15] at -10 °C which gives only the photoproduct 7 analogous to 3.[16] In solution, irradiation of 6 gives 7 plus 8, the latter being formed via C_2-C_5 bonding in a ring flipped form of a diradical analogous to 2.

Finally we provide an example of a change in molecularity in proceeding from a reaction in solution to a reaction in the solid state. In solution, adduct 9 reacts exclusively in an intramolecular fashion to give products resulting from internal γ-hydrogen abstraction by oxygen.[10] In contrast, irradiation of crystalline samples of 9 at -1 °C leads stereospecifically to the *intermolecular* dimer 10 (12 chiral centers!), mp 265 °C dec, whose structure was determined by x-ray crystallography ($R = 0.050$).[12] The reason for this can be seen from Figure 1 which is a drawing showing the relationship between nearest neighbor molecules of 9 in the crystal. As can be seen, the ene-dione double bonds of adjacent molecules are nearly

ideally situated for dimerization, being related by a center of symmetry with a distance (C_2 to $C_{2'}$) across this center of 3.624 (3) Å. The photodimerization is thus topochemically controlled since C_2-$C_{3'}$ and C_3-$C_{2'}$ bonding leads to dimer 10. Dimerization is unimportant for 1 and 6 because there are no intermolecular double bond contacts shorter than 6.0 and 4.1 Å, respectively.[17]

We are engaged in the extension of these solid state studies to other photochemical hydrogen abstraction processes, in particular, the Norrish type II reaction.

References and Notes

(1) Paper 17 in our series on organic photochemistry. For paper 16, see J. R. Scheffer, B. M. Jennings, and J. P. Louwerens, *J. Am. Chem. Soc.*, in press.
(2) (a) L. Addadl, M. D. Cohen, and M. Lahav, *J. Chem. Soc., Chem. Commun.*, 471–473 (1975); (b) M. D. Cohen, *Angew. Chem., Int. Ed. Engl.*, 14, 386–393 (1975); (c) M. D. Cohen and B. S. Green, *Chem. Brit.*, 9, 490–497 (1973); (d) G. M. J. Schmidt, *Pure Appl. Chem.*, 27, 647–678 (1971); and (e) G. M. J. Schmidt in "Reactivity of the Photoexcited Organic Molecule", Interscience, New York, N.Y., 1967, pp 227–288.
(3) (a) G. Friedman, M. Lahav, and G. M. J. Schmidt, *J. Chem. Soc., Perkin Trans. 2*, 428–432 (1974); (b) H. W. Kaufman, D. Rabinovich, and G. M. J. Schmidt, *ibid.*, 433–435 (1974).
(4) (a) I. C. Paul and D. Y. Curtin, *Acc. Chem. Res.*, 6, 217–225 (1973); (b) C. N. Sukenik, J. A. P. Bonapace, N. S. Mandel, R. G. Bergman, P-Y. Lau, and G. Wood, *J. Am. Chem. Soc.*, 97, 5290–5291 (1975).
(5) (a) A. B. Jaffe, K. J. Skinner, and J. M. McBride, *J. Am. Chem. Soc.*, 94, 8510–8514 (1972); (b) A. B. Jaffe, D. S. Malament, E. P. Slisz, and J. M. McBride, *ibid.*, 94, 8515–8521 (1972); (c) N. J. Karch, E. T. Koh, B. L. Whitsel, and J. M. McBride, *ibid.*, 97, 6729–6743 (1975).
(6) (a) R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Am. Chem. Soc.*, 96, 6329–6334 (1974); (b) R. S. Miller, I. C. Paul, and D. Y. Curtin, *ibid.*, 96, 6334–6339 (1974); (c) R. S. Miller, D. Y. Curtin, and I. C. Paul, *ibid.*, 96, 6340–6349 (1974).
(7) F. D. Lewis, R. W. Johnson, and D. R. Kory, *J. Am. Chem. Soc.*, 96, 6100–6107 (1974), have shown that, in solution, conformationally restricted systems exhibit enhanced rates in γ-hydrogen abstractions relative to mobile systems due to favorable transition state entropy effects.
(8) (a) J. D. Henion and D. G. I. Kingston, *J. Am. Chem. Soc.*, 96, 2532–2536 (1974); (b) D. G. I. Kingston, M. M. Bursey, and J. T. Bursey, *Chem. Rev.*, 74, 215–242 (1974).
(9) J. Y. Becker, L. R. Byrd, L. I. Miller, and Y-H. So, *J. Am. Chem. Soc.*, 97, 853–856 (1975).
(10) J. R. Scheffer, K. S. Bhandari, R. E. Gayler, and R. A. Wostradowski, *J. Am. Chem. Soc.*, 97, 2178–2189 (1975).
(11) The 3:5 ratio in ether at -30 °C was 1:2.2. The solid state reaction was carried out in vacuo in a specially designed variable temperature apparatus which will be described in our full paper. The temperature of -30 °C was chosen so as to be below the eutectic temperature of the three-component (1, 3, and 5) mixture which was determined to be -16 °C by differential scanning calorimetry. Similar precautions were taken in the irradiations of 6 and 9.
(12) S. E. V. Phillips and J. Trotter, *Acta Crystallogr.*, in press.
(13) J. T. Edward, *J. Chem. Educ.*, 47, 261 (1970).
(14) In view of the fact that organic molecules generally crystallize in confor-

mations in which they are most stable in solution, we have suggested[1] that the formation of **3** and **5** upon irradiation in solution also occurs through conformation **1**.

(15) Adduct **6**, mp 163 °C, was prepared according to the procedure of C. F. H. Allen, C. G. Eliot, and A. Bell, *Can. J. Res.*, **17**, 75–88 (1939). The characterization of **7** and **8** will be discussed in our full paper.

(16) Invariably, cyclobutanone-containing products (e.g., **5**) are not formed from the irradiation, either in solution or in the solid state, of Diels–Alder adducts which lack C_2 and C_3 methyl substitution.[1,10] The source of this effect is not clear at the present time, but is likely[1] related to the requirement for a low-lying $(\pi,\pi^*)^3$ state (favored by ene–dione methyl substitution) in process γ which leads to **5**.

(17) The Diels–Alder adducts formed between *p*-benzoquinone and butadiene and 2,3-dimethylbutadiene also undergo solid state photodimerization in preference to the intramolecular processes (hydrogen abstraction[10]) observed in solution. Preliminary results indicate topochemical control in these cases as well. The competing effects of an intramolecular and intermolecular solid state reaction, albeit of the same type (photodimerization), have been described by J. K. Frank and I. C. Paul, *J. Am. Chem. Soc.*, **95**, 2324 (1973).

(18) Commonwealth Predoctoral Fellow, 1974–present.

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Thermally Induced Decarbonylation of Cage Ketones[1]

Sir:

Recently much attention has been focused on edge participation of the cyclobutane vs. cyclopropane ring in thermally induced extrusion reactions.[2] In the decarbonylation of bridged ketones, the contribution of a cyclopropyl σ-bond has been well documented,[3] but as to cyclobutyl edge participation the situation is not well understood.[4] In this connection, we wish to report the first example of the thermally induced decarbonylations of cage ketones **1**, in which a concomitant cleavage of the strained cyclobutyl σ-bond (C_2–C_3) occurred to give tricyclic dienes **2**. In addition, it was found that the irradiation of **2** led to the quantitative formation of cage compounds **3**. Thus, this reaction series offers an advantageous route to strained cage molecules **3**.

Starting ketones **1** were synthesized[5] by the irradiation of tricyclic dienones **4** which were obtained by Cope rearrangement of the cycloadducts of the corresponding dienes and 2,5-dimethyl-3,4-diphenylcyclopentadienone.[6,7] When a benzene solution of **1** was passed through a quartz column preheated at 450 °C for **1b** or 320 °C for **1c–e**, tricyclic dienes, **2b**, mp 55–56 °C, **2c**, mp 80–81 °C, **2d**, mp 113–114 °C, and **2e**, oil, were obtained in nearly quantitative yields. Contrary to **1b–e**, **1a** was completely stable at 420 °C, but it decomposed at 480 °C without decarbonylation affording an isomeric ketone in 30% yield which may be formed by the cleavage of the C_3–C_4 bond followed by complex rearrangements.[8] The structures of **2** were deduced on the basis of the spectroscopic data[9] along with chemical evidence. Particularly, the fact that the dienes, e.g., **2b** or **2d**, upon irradiation, provided a quantitative yield of the cage compounds, **3b**, mp 63–64 °C, or **3d**, mp 78–79 °C, which reverted to **2b** or **2d** by heating at 80 °C supports the structure of **2** and **3**. On the other hand, the irradiation of the ketones, e.g., **1b** or **1d**, resulted in inefficient decarbonylation to give the corresponding cage compounds, **3b** or **3d** in 16 or 17% yield, respectively. The thermal decarbonylations of **1** to **2** involving a cyclobutane ring cleavage are novel ones, and are in sharp contrast with the thermal decarbonylation of pentacyclodecanone **5** which is the only report in the thermolysis of pentacyclic ketones.[10]

In order to clarify the mechanism and the relationship between the ease of decarbonylation and the structure of the cage ketones, the decarbonylation rates of **1b**, **1c**, and **1e** were de-

Compd	Temp, °C	$10^5 k$, s^{-1}	E_a,[a] kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate[b]	M$^+$/ (M − CO),[c] %
1a	...	...	...	...	...	37
1b	230.0	2.60	44.3 ± 1.1	5.7 ± 2.2	1	6
1c	184.5	11.2	39.1 ± 0.6	6.0 ± 1.2	214	1
1e	185.0	5.07	39.2 ± 1.1	4.6 ± 2.4	95.6	...

[a] Kinetic study was carried out in *o*-dichlorobenzene in the temperature range 220–250 °C for **1b**, 175–205 °C for **1c**, and 180–205 °C for **1e**. [b] At 230 °C. [c] The M − CO peaks were base peaks in all cases.
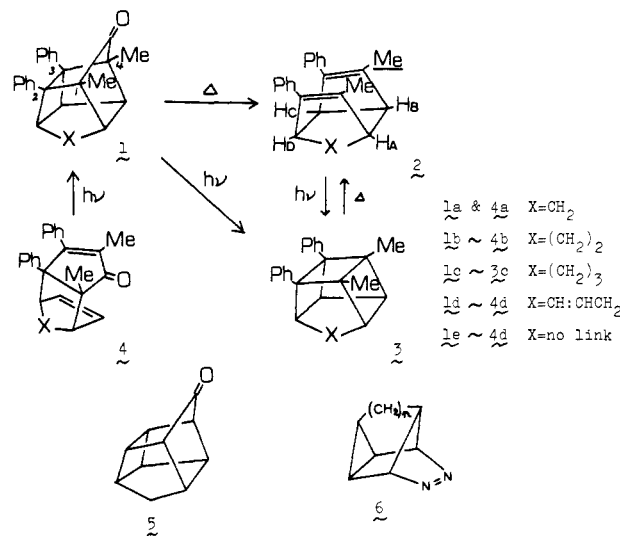
termined by measuring the depletion of their methyl signals in the NMR spectrum. Good first-order kinetics were observed and the rate and activation parameters are summarized in Table I. It is revealed that the rate of decarbonylation strongly depends on the length of the carbon bridge, increasing as the bridge becomes longer. This same trend is observed in the mass spectrometer, where the relative intensity of the M − CO peak increases as the length of the carbon bridge increases. A similar structural influence was observed for an extrusion reaction involving the elimination of nitrogen from cyclic azo compounds **6**.[11]

Inspection of the molecular models of the ketones reveals that the cyclobutyl C_2–C_3 bond becomes strained and bends towards the ketonic group when the number of carbons in the chain (X) increases or when there is no bridge, while the C_3–C_4 bond is rather strained in **1a**. The magnitude of the strain of the C_2–C_3 bond is well correlated with the reactivity of the ketones **1**, i.e., the more strained, the easier the decarbonylation. Two pathways for the decarbonylation can be postulated; one is a concerted path in which the σ-bonds of the ketonic group interact with the cyclobutyl C_2–C_3 bond in the transition state **7**, six electrons being involved; the other is a stepwise path in which an initial cleavage of the cyclobutyl bond gives the diradical intermediate **8**, which, in turn, leads to **2**. The E_a values seem a little high for concerted reactions, but they are lower than those for the ring cleavage of 1,2-diphenylcyclobutanes.[12] The $\Delta S^{\ddagger}$ values are comparable to those reported for the cheletropic decarbonylation of tricyclo[3.2.1.0^{2,4}]-octan-8-ones.[13] Furthermore, the ethylene ketal of **1b**, **9**, which would be expected to decompose if a diradical like **8** is initially formed,[14] was found to be stable under a pyrolyzing condition at 550 °C. The formation of ring opening products such as **10** was not observed in the decomposition of **1b–e**. These facts