peaked at 128 meV. The vibrational spectrum due to the addition of both H_2 and O_2 to the oxygen-titrated surface is illustrated in Figure 1c by the difference spectrum, i.e., the H_2/O_2-dosed surface minus the O_2-titrated surface spectrum. Similar to Figure 1b, the reaction of the H_2 and O_2 on the Pt surface yields additional scattering intensity peaked at 128 meV. The position of this spectral feature is in excellent agreement with the EELS value of 128 meV reported for the δ_{M-OH} (i.e., bending) mode of OH on Pt(111) by Fisher and Sexton.[1] Extension of the IINS spectra above 200 meV yielded no additional scattering intensity at the expected position of the H–O–H scissor mode at 202 meV for adsorbed H_2O on $Pt^{1,15}$ suggesting that the Pt black surfaces represented by Figure 1 (parts b and c) do not possess any significant amount of adsorbed H_2O species. Hence, based on the comparison with the reported EELS results, the neutron scattering feature at 128 meV is assigned to the Pt–O–H bending mode of adsorbed OH species present as the dominant hydrogenous species on the Pt black surface for O:H ratios of unity.

(15) Thiel, P. A.; Madey, T. E. *Surf. Sci. Rep.* **1987**, *7*, 211–385.

The Generation of 1,4-Biradicals in Rigid Media: Crystal Structure–Solid State Reactivity Correlations

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Received March 9, 1988

It is now well established that the crystalline phase provides a reaction medium in which reactants, intermediates, and final products have an enforced geometrical similarity, thereby enabling the development of detailed crystal structure–reactivity relationships.[1] In this communication we report an investigation of the type II photochemistry of the homologous ketones 1a–e (Scheme I), both in the solid state and in solution. The photochemical results, along with the crystal and molecular structures of all five ketones, provide the basis for an increased general understanding of the reactivity of the intermediate 1,4-hydroxybiradicals in terms of structure.

Ketones 1a–e were prepared by Friedel–Crafts acylation of chlorobenzene by using the appropriate acid chloride.[2] Each ketone was photolyzed (nitrogen laser, 337 nm) at 0 °C in its crystalline state as well as in a 0.1 M benzene solution at room temperature; conversions were kept low (<5% in the solid state; <20% in solution). Visual inspection of irradiated single crystals revealed retention of crystallinity with uniform reaction throughout, and the product ratios were not sensitive to attempts to increase surface area or introduce defect sites by, e.g., grinding. Table I summarizes the general finding that, as the cycloalkyl group is varied from cyclobutyl to cyclooctyl, there is a dramatic (if irregular) decrease in the extent of Norrish type II cleavage and a corresponding increase in the amount of cyclobutanol formation.

Separation difficulties and low yields prevented isolation of the cyclobutanol photoproducts from ketones 1a and 1b, but cyclobutanols 5c–e, 6c–e, 7c, and 8c could be isolated and their structures assigned. The assignments rest on the X-ray crystal structures of cyclobutanols 5c and 5e, which clearly show the trans

Scheme I
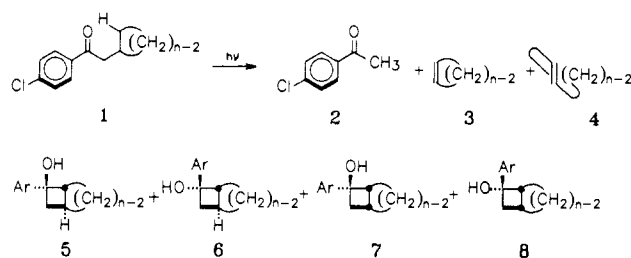
(a) n = 4, (b) n = 5, (c) n = 6, (d) n = 7, (e) n = 8

Table I. Photoproduct Ratios and Crystallographic Data for α-Cycloalkyl-*p*-chloroacetophenones

| | | | % cleavage | | dihedral angles[b] | |
ketone	mp (°C)	R^c	crystal	benzene $(\Phi)^d$	ϕ_1^e (deg)	ϕ_4^f (deg)
1a (n = 4)	50–51	0.035	92	90 (0.20)	+90	−45
1b (n = 5)	60–61	0.061	92	92 (0.29)	+90	−65
1c (n = 6)	63–64	0.053	40	39 (0.35)	+85	−88
1d (n = 7)	42–43	0.042	61	55 (0.25)	+85	−100
1e (n = 8)	48–49	0.039	18	25 (0.16)	+84	−135

^{a}Determined by quantitative GC analysis of the amount of *p*-chloroacetophenone produced; the % cyclization is given by (100 − % cleavage). ^{b}Defined with reference to structure **10**, Scheme II. The mirror image of **10**, which is present in equal amounts (racemic space groups), has the signs of ϕ_1 and ϕ_4 reversed. ^{c}Crystallographic discrepancy factor (*R* factor). ^{d}Solution quantum yields were determined at 313 nm in a merry-go-round apparatus by using valerophenone as the actinometer. ^{e}Dihedral angle between top lope of p-orbital at C(1) and C(2)–C(3) bond. ^{f}Dihedral angle between the top lobe of the hypothetical p-orbital at C(4) (assumed to lie perpendicular to the C-(3)–C(4)–C(5) plane) and the C(2)–C(3) bond.

ring junction stereochemistry. With these compounds as reference points, the remaining structural assignments were made by using 400 MHz ^{1}H NMR spectroscopy.[2] This revealed that the trans-fused cyclobutanols 5 and 6 are the major photoproducts from ketones 1c–e; GC peaks attributable to the cis-fused cyclobutanols 7 and 8 constitute less than 20% of the total cyclobutanols in each case, both in the solid state and solution.[3] For ketone 1c, the 5c:6c:7c:8c ratios are 24:31:3:3 (benzene) and 23:30:4:3 (crystal). For the other four cyclobutanols that were characterized, the ratios are 5d:6d = 6:34 (benzene), 7:29 (crystal) and 5e:6e = 12:49 (benzene), 12:65 (crystal).

Another key aspect of photoproduct structure concerns the geometry of the cycloalkenes formed by cleavage. By using authentic samples of *cis*- and *trans*-cyclooctene for comparison purposes,[4] capillary GC analysis of the reaction mixture from photolysis of ketone 1e revealed that both isomers are formed. The cis:trans ratios (extrapolated to 0% conversion owing to isomerization under the reaction conditions) were 90:10 (benzene) and 72:28 (crystal). Experiments designed to provide evidence for the formation of *trans*-cycloheptene by trapping with acidic methanol[5] were unsuccessful; no attempts were made to detect *trans*-cycloalkenes from photolysis of ketones 1a–c.

A mainstay of the interpretation of solution phase 1,4-biradical reactivity over the years has been the idea that, in order for efficient cleavage to occur, the radical-containing p-orbitals should be parallel to the carbon–carbon bond undergoing scission (0,0 geometry).[6] It seems likely that cyclization, which requires

(1) For two recent review articles on organic photochemistry in the solid state, see: (a) Scheffer, J. R.; Garcia-Garibay, M.; Nalamasu, O. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1987; Vol. 8, Chapter 4. (b) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433.

(2) Details of the characterization of all reactants and photoproducts will be presented in a full paper.

(3) In an earlier communication on portions of this work (Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1983**, *105*, 6959), the two major cyclobutanols from ketone 1c were mistakenly assumed to have the cis ring junction stereochemistry.
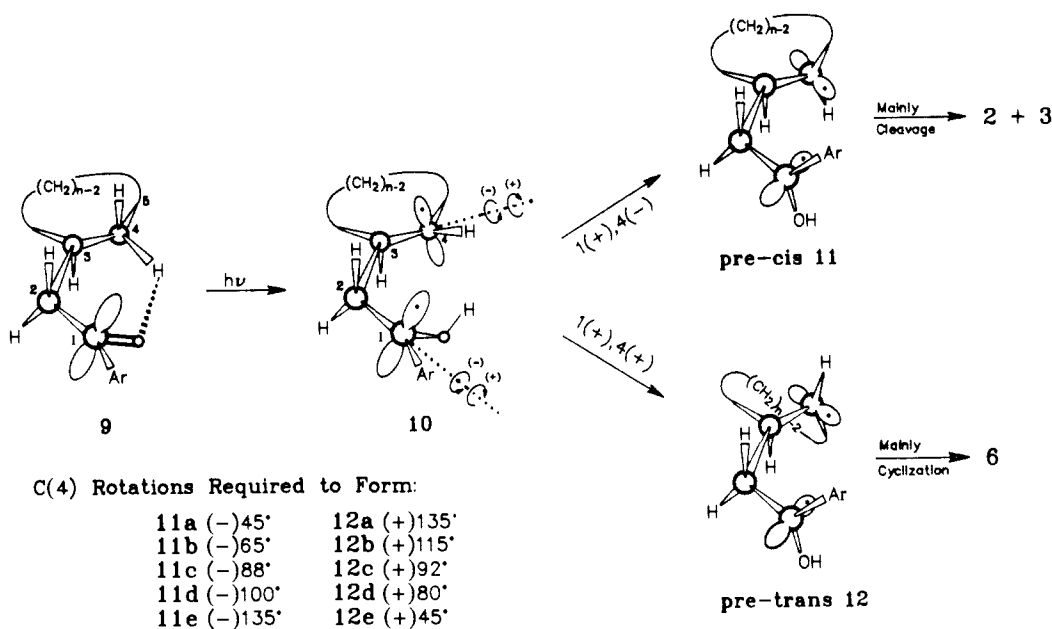
(4) *trans*-Cyclooctene was prepared by the method of Inoue et al. (Inoue, Y.; Takamuku, S.; Kunitomi, Y.; Sakurai, H. *J. Chem. Soc., Perkin Trans. II* **1980**, 1672).

(5) Inoue, Y.; Ueoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1981**, 1031.

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Communications to the Editor

Scheme II

9

10

pre–cis 11

pre–trans 12

C(4) Rotations Required to Form:

11a	(−)45°	12a	(+)135°
11b	(−)65°	12b	(+)115°
11c	(−)88°	12c	(+)92°
11d	(−)100°	12d	(+)80°
11e	(−)135°	12e	(+)45°

through-space overlap of these same p-orbitals, will also prefer a biradical geometry close to 0,0, provided that the radical centers are gauche (or better); cleavage, on the other hand, presumably can occur from both gauche and anti 0,0 conformations.[7]

By using the crystal structure data for ketones 1a–e, determined by direct methods,[8] we can calculate a set of σ–π orbital alignments for biradicals 10a–e assuming that they have the same basic shape as their ketonic precursors. Table I lists the relevant angles ϕ_1 and ϕ_4, which are defined as the torsion angles formed between the C(2)–C(3) σ bond and the top lobes of the p-orbitals at C(1) and C(4), respectively (the hypothetical p-orbital at C(4) was taken as lying perpendicular to the C(3)–C(4)–C(5) plane). The results indicate that all five biradicals, while gauche, are far from the 0,0 geometry preferred for cyclization or cleavage. They are, in fact, in some cases almost perfectly *misaligned* (e.g., 10c).

The directions and magnitudes of the rotations required to align the p-orbitals in the 0,0 geometry are summarized in Scheme II. A (+) rotation at C(1) and a (−) rotation at C(4) lead to biradical 11, and 1(+),4(+) rotations afford biradical 12. A second pair of biradicals (not shown) is formed by 1(−),4(−) and 1(−),4(+) rotations. As the cycloalkyl ring size is increased from cyclobutyl to cyclooctyl, progressively greater (−) rotations are required at C(4) to form biradical 11, whereas the (+) rotations required at C(4) to produce 12 are progressively reduced; at C(1), on the other hand, the rotations necessary to achieve coplanarity between the p-orbital and the C(2)–C(3) bond remain approximately constant at (+) $\approx$ (−) $\approx$ 90°.

As is evident from its structure, biradical 11 can give only *cis*-cycloalkene or cis-fused cyclobutanols, and biradical 12 is capable only of trans photoproduct formation. *A key tenet of our interpretation of the photochemical results is that pre-cis biradical 11 undergoes mainly cleavage and that the pre-trans biradical 12 mainly cyclizes.* This very neatly explains the seeming paradox that photolysis of ketones 1c–e affords predominantly trans-fused cyclization products on the one hand and mainly *cis*-cycloalkene

cleavage products on the other.[9] It also correlates well with the observed % cleavage results. According to the well-known topochemical principle, which states that reactions in crystals occur with a minimum of atomic and molecular motion,[10] biradicals 10a and 10b are clearly predicted to undergo preferential (−) rotation at C(4) resulting in cleavage; biradicals 10c and 10d, with only slight differences between the (+) and (−) rotations, should give mixtures of cleavage and cyclization, and, finally, biradical 10e is predicted to undergo preferential (+) rotation at C(4) and cyclization. These motions minimize eclipsing interactions during rotation and should have lower intrinsic (solution phase) barriers as well. In each case, the prediction is in good agreement with the experimental result.[11]

Are the reactivity differences postulated for biradicals 11 and 12 in fact reasonable? We believe so. Pre-cis biradical 11, a relatively unstrained species, behaves normally in its preference for cleavage.[6] The question then becomes why biradical 12 might behave abnormally, that is, prefer cyclization to cleavage. There are at least two reasons that come to mind. First, cleavage of 12 would form a *trans*-cycloalkene, and this may tip the scales in favor of cyclization. Second, because of ring restraints, biradical 10 very likely cannot rotate to a full 0,0 conformation, a geometry that may be more strictly required for cleavage than for cyclization.[12] Finally, we note that these ideas have a bearing on the formation of trans-fused products in the [2 + 2] photocycloaddition of olefins to cyclohexenones.[13] Gauche pre-trans biradicals that cyclize and pre-cis biradicals that revert to enone plus olefin explain the results without requiring the intermediacy of *trans*-cyclohexenones.

(6) (a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. (b) Wagner, P. J. In *Molecular Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Wiley-Interscience: New York, 1980; Chapter 20. (c) Scaiano, J. C.; Lissi, E. A.; Encina, M. V. *Rev. Chem. Intermed.* **1978**, *2*, 139.

(7) Our results indicate that cleavage is not limited to anti 0,0 biradicals as has sometimes been assumed: Zimmerman, R. G.; Liu, J. H.; Weiss, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 5264.

(8) Ketone 1b: Ariel, S.; Trotter, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 1166. Ketone 1c: Ariel, S.; Trotter, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 446. Ketones 1a, 1d, and 1e: Evans, S. V.; Trotter, J. *Acta Crystallogr., Sect. B: Structural Science*, **1988**, *B44*, 63.

(9) These ideas also nicely explain the predominant formation of trans-fused bicyclo[4.2.0]octane Norrish type II cyclobutanols as recently observed by Paquette and Sugimura (Paquette, L. A.; Sugimura, T. *J. Am. Chem. Soc.* **1986**, *108*, 3841).

(10) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.

(11) The model also explains the 6/5 > 1 cyclobutanol ratios. Closure of 12 to give 6 involves an Ar···H interaction, whereas closure of the biradical (not shown) leading to 5 involves a more severe Ar···CH₂ interaction.

(12) Lewis and Hilliard (Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 6672) have suggested that, in biradicals containing bulky substituents at C(2), cyclization occurs from non-0,0 geometries in which 1,2-eclipsing interactions are minimized.

(13) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.