Communications to the Editor

Norrish Type II Reaction in the Solid State: Involvement of a Boatlike Reactant Conformation

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Received June 29, 1983

The light-induced cleaveage and/or cyclization of organic carbonyl compounds possessing favorably oriented γ-hydrogen atoms, termed the Norrish type II reaction, is the most ubiquitous of all organic photorearrangements and remains the object of much current mechanistic and synthetic interest.[1] One unresolved point concerns the preferred transition-state geometry for the primary hydrogen-abstraction process itself. For conformationally mobile systems, Wagner has suggested that the well-known preference for 1,5 over 1,4 and 1,6 hydrogen atom shifts reflects a strain-free, chairlike, cyclic six-atom reactant conformation.[2]

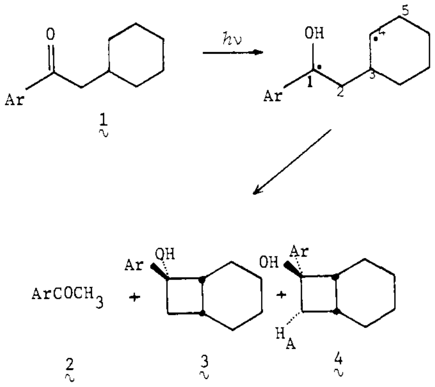
We decided to test this reasonable hypothesis by studying the type II reaction in the crystalline state where the reactant geometry is fixed and determinable by X-ray diffraction methods. In addition, the study was expected to provide interesting information on the effect that immobilization within a crystal lattice has on the partitioning of the intermediate 1,4-hydroxybiradical.[3] In the present communication, we report that in the solid state, a *boatlike* rather than a chairlike reactant conformation is utilized and that the proportion of 1,4-biradical closure (cyclobutanol formation) is less than in solution.

The compounds chosen for study were the crystalline α-cyclohexylacetophenones **1a–c** (Scheme I).[4] Irradiation of these compounds in solution with the output from a Molectron UV 22 pulsed nitrogen laser (337 nm, 330-mW average power) afforded the corresponding para-substituted acetophenones **2a–c**, cyclohexene (not isolated), and the cyclobutanols **3a–c** and **4a–c**. The cyclobutanols were characterized by mass spectrometry and 400-MHz NMR spectroscopy.[5]

Table I summarizes the photoproduct ratios in the solvent acetonitrile (wet or anhydrous). A previous literature report on the photolysis of compound **1a** in pentane and ethanol makes no mention of cyclobutanol products.[4] We find them to be the major photoproducts in all solvents tested including cyclohexane, benzene, and ethanol. In contrast, when crystalline samples of ketones **1a–c** were photolyzed with the nitrogen laser, much less cyclobutanol formation was observed (Table I), the cyclization/cleavage ratio **(3 + 4)/2** in each case being slightly greater than unity.[6] The solid-state results were obtained at conversions of less than 3%, and the photoproduct ratios were constant between −10 and +25 °C indicating that sample melting with concomitant loss of topochemical control is unimportant. Significantly, the ratios in which the cyclobutanols **3** and **4** are formed in the solid state are identical within experimental error with the solution values.

Accompanying the photochemical studies, the X-ray crystal structures of ketones **1a–c** were determined.[7] All three crystallize in a common conformation in which the carbonyl-containing side chain is equatorial with respect to the chair-shaped cyclohexane

Scheme I[a]



[a] a, Ar = *p*-tolyl; b, Ar = *p*-chlorophenyl; c, Ar = *p*-methoxyphenyl.

Table I. Product Ratios in Photolysis of Compounds 1a–c[a]

medium	(3a + 4a)/2a	3a/4a	(3b + 4b)/2b	3b/4b	(3c + 4c)/2c	3c/4c
acetonitrile[b]	3.5	1.5	2.7	1.3	2.2	2.4
solid state[c]	1.1	1.7	1.1	1.4	1.2	2.3

[a] Determined by capillary gas chromatography assuming identical detector response for each photoproduct. Each number represents the average of at least three separate photolyses at a given temperature with a minimum of two chromatographic analyses per photolysis. The estimated error is 10%. [b] Conversion 10–15%. Ratios constant within experimental error between +25 and −25 °C. [c] Conversion ≤ 3%. Ratios constant within experimental error between +25 and −10 °C.

Table II. Solid-State Hydrogen-Abstraction Distances and Angles[a]

ketone	O···H$_e$, Å	τ_e, deg	O···H$_a$, Å	τ_a, deg	O···H$_\beta$, Å	τ_β, deg
1a	2.60	49.6	3.83	38.4	2.57	6.8
1b	2.60	42.0	3.83	35.7	2.59	12.7
1c	2.61	42.5	3.82	37.0	2.64	11.6

[a] The angle τ is the degree by which the hydrogen in question lies outside the mean plane of the carbonyl group.

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(1) For review articles on the Norrish type II reaction, see: (a) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1–52. (b) Wagner, P. J. In "Molecular Rearrangements in the Ground and Excited States"; de Mayo P., Ed.; Wiley-Interscience: New York, 1980; Chapter 20, pp 381–444. (c) Scaiano, J. C.; Lissi, E. A.; Encina, M. V. *Rev. Chem. Intermed.* **1978**, *2*, 139–196. (d) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252–258. (e) Wagner, P. J. *Ibid.* **1971**, *4*, 168–177.

(2) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7500–7506.

(3) For previous instances of type II processes in the crystalline state, see: Mohr, S. *Tetrahedron Lett.* **1979**, 3139–3140. Aoyama, H.; Hasegawa, T.; Omote, Y. *J. Am. Chem. Soc.* **1979**, *101*, 5343–5347. The Norrish type II reaction has also been investigated in polymeric systems. Guillet, J. E. *Pure Appl. Chem.* **1977**, *49*, 249–258.

(4) Compound **1a** was prepared by the procedure of: Wamser, C. C.; Wagner, W. R. *J. Am. Chem. Soc.* **1981**, *103*, 7232–7234. Ketones **1b** and **1c** were prepared similarly. Details will be presented in a full paper.

(5) The stereochemical assignments are based on a characteristic low-field (δ ~2.8) doublet of doublets (J = 6.5 and 4 Hz) in **4a–c** attributed to the proton H$_A$, which lies within the deshielding region of the adjacent aryl group as the result of the latter's restricted rotation (cis to cyclohexane CH$_2$). We also note that the *trans*-cyclobutanols **3a–c** have shorter GC retention times than the corresponding cis isomers **4a–c**. A similar trend was observed by: Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506–7512.

(6) Future studies will investigate the interesting question of the mechanism of enol ketonization in the solid state. Direct observation of enol intermediates in the present study by IR spectroscopy of irradiated KBr pellets was hampered by the presence of cyclobutanol hydroxyl absorption.

(7) Compound **1a**: mp 45 °C, $P2_1/c$, R = 0.06. Compound **1b**: mp 63–64 °C, $P2_1/a$, R = 0.05. Compound **1c**: mp 40 °C, $P\bar{1}$, R = 0.05. Full details will be published separately: Ariel, S.; Trotter, J. *Acta Crystallogr.*, manuscript in preparation.

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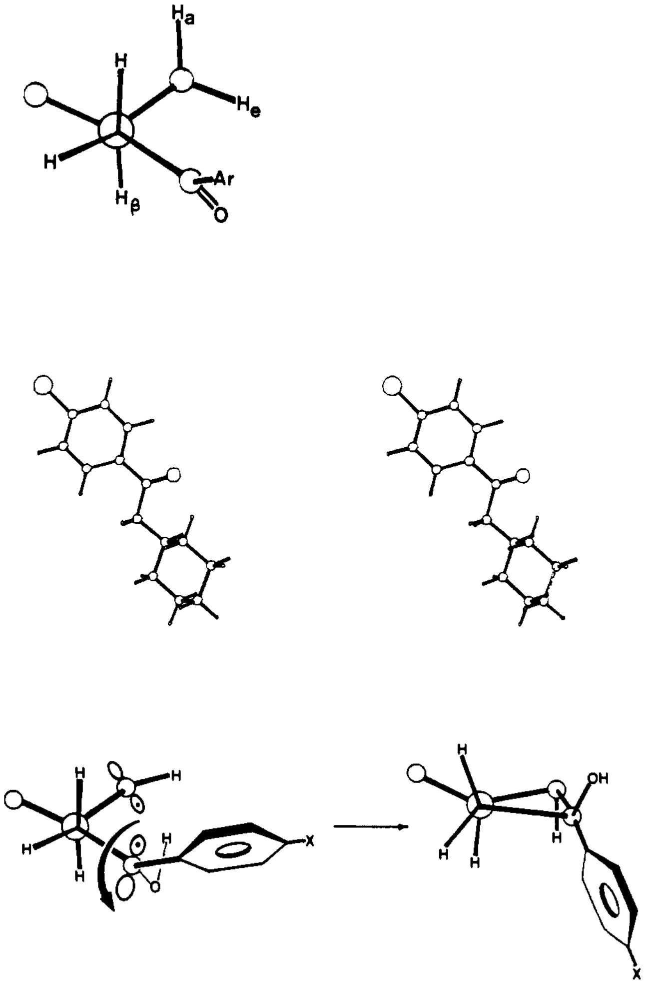

Figure 1. Newman projection down equatorial carbon–carbon bond of ketones **1a–c** (top), stereodiagram of ketone **1b** (middle), and motions involved in formation of *trans*-cyclobutanols **3a–c** (bottom).

ring. A Newman projection down the equatorial carbon–carbon bond is shown in Figure 1. Also shown in Figure 1 is a stereoview of ketone **1b**. This conformation clearly indicates that it is the equatorial hydrogen H_e that is abstracted in the solid state through a boatlike six-atom geometry. This conclusion is borne out quantitatively by the abstraction distances and angles in Table II. The carbonyl oxygen is much closer to H_e (2.6 Å) than to H_a (3.8 Å). This hydrogen abstraction distance of 2.6 Å is consistent with our suggested[8] upper limit of 2.72 Å (van der Waals radii sum) for this type of process.

Turning to the angle τ, the degree to which the hydrogen being abstracted lies outside the mean plane of the carbonyl group, Wagner has clearly pointed out that coplanar ($\tau = 0°$) hydrogen abstraction is not a strict requirement for the type II process.[1a] He has suggested a $\cos^2 \tau$ dependence for abstraction, which, in our case, would reduce the relative reactivity of H_e ($\tau \sim 45°$) by a factor of only two.

Table II also indicates that H_β is in a position favorable for abstraction through a five-membered transition state and in fact is more nearly coplanar with the abstracting oxygen n orbital ($\tau = 7$–$13°$) than is H_e; the tertiary nature of H_β should also facilitate its abstraction.[1] Nevertheless, no products corresponding to abstraction of H_β could be detected either in solution or the solid state. Reversible β-hydrogen abstraction is of course a possibility.

A final point of discussion concerns the difference in cyclization/cleavage ratios in the two media. It is widely accepted[1] that efficient cleavage requires a 1,4-biradical conformation in which both singly occupied p orbitals can overlap significantly with the central σ bond being broken; failing this, cyclization predominates. In the solid state, the 1,4-hydroxybiradical will have the same basic conformation as its ketonic precursor (Figure 1). We suggest that this is the predominant conformation in solution as well. This conclusion is based on the fact, noted previously, that the cyclization stereoselectivity in the solid state is identical with that observed in solution (Table I).

This biradical conformation is very poorly aligned for cleavage. In fact, as indicated by the crystal structure data, it is almost perfectly misaligned, with both singly occupied p orbitals oriented essentially at right angles to the central σ bond.[9] Thus extensive C(1)–C(2) and C(3)–C(4) bond rotations are required for cleavage. The latter motion is of course impeded by ring restraints, hence the preference for cyclization in solution. The reduced amount of cyclization in the solid state can then be ascribed not to enhanced cleavage in this medium but to crystal lattice restriction of cyclization. The product cyclobutanols **3** and **4** bear little structural resemblance to their biradical precursor, and their formation requires extensive molecular and atomic motion, most notably a large permanent displacement of the bulky aryl groups from their original position (Figure 1). This motion sweeps the aryl and hydroxyl groups through a large volume and would be expected to be topochemically disfavored in the solid state relative to the "less-motion" pathway required for cleavage.[10]

Extensions of these concepts to other type II systems and to other organized media are in progress.

Acknowledgment. Support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. 1a, 79650-21-8; **1a** biradical, 87482-76-6; **1b**, 87482-75-5; **1b** biradical, 87482-77-7; **1c**, 58987-23-8; **1c** biradical, 87482-78-8; **3a**, 87482-79-9; **3b**, 87482-80-2; **3c**, 87482-81-3; **4a**, 87508-65-4; **4b**, 87508-66-5; **4c**, 87508-67-6.

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[8] (a) Scheffer, J. R.; Dzakpasu, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 2163–2173. (b) Scheffer, J. R. *Acc. Chem. Res.* **1980**, *13*, 283–290. (c) Appel, W. K.; Jiang, Z. Q.; Scheffer, J. R.; Walsh, L. *J. Am. Chem. Soc.* **1983**, *105*, 5354–5364.

[9] The p orbital at C(4) was assumed to lie normal to the C(3)–C(4)–C(5) plane. The actual angles for compounds **1a**, **1b** and **1c** respectively were θ_1 = 100.7°, 94.9°, and 96.7° and θ_4 = 86.6°, 88.2°, and 88.6°.

[10] For additional examples of crystal lattice control of biradical behavior, see: Appel, W. K.; Greenhough, T. J.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1979**, *101*, 213–215. Quinkert, G.; Tabata, T.; Hickmann, E. A. J.; Dobrat, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 199–200.

Kinetics of Free Radical Brominations. Effect of Ring Substitution on the Strength of Benzyl C-H Bonds

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Received February 14, 1983

Kistiakowsky and his students pioneered the use of kinetic measurements of gas-phase free radical brominations of hydrocarbons to establish bond dissociation energies (BDE).[1] The first reliable value for methane[2] was followed by measurements on ethane,[3] neopentane,[4] and toluene.[5] The toluene work has been criticized both for concluding that termination occurs by Br·

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[1] George B. Kistiakowsky, 1900–1982, in whose memory this work is dedicated.

[2] Kistiakowsky, G. B.; VanArtsdalen, E. R. *J. Chem. Phys.* **1944**, *12*, 469–478.

[3] Andersen, H. C.; VanArtsdalen, E. R. *J. Chem. Phys.* **1944**, 12, 479–483.

[4] Hormats, E. I.; VanArtsdalen, E. R. *J. Chem. Soc.* **1951**, *19*, 778–783.

[5] Anderson, H. R.; Scheraga, H. A.; VanArtsdalen, E. R. *J. Chem. Phys.* **1953**, *21*, 1258–1267.

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