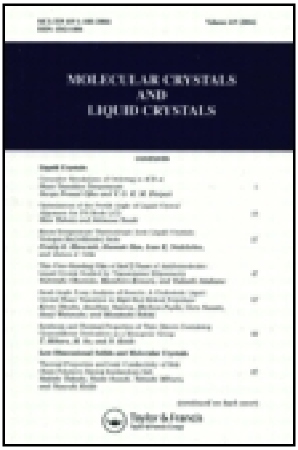

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A Study of the Norrish Type II Reaction in the Solid State[1]

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A STUDY OF THE NORRISH TYPE II REACTION IN THE SOLID STATE[1]

JOHN R. SCHEFFER,* JAMES TROTTER,* NALAMASU OMKARAM, STEPHEN V. EVANS and SARA ARIEL
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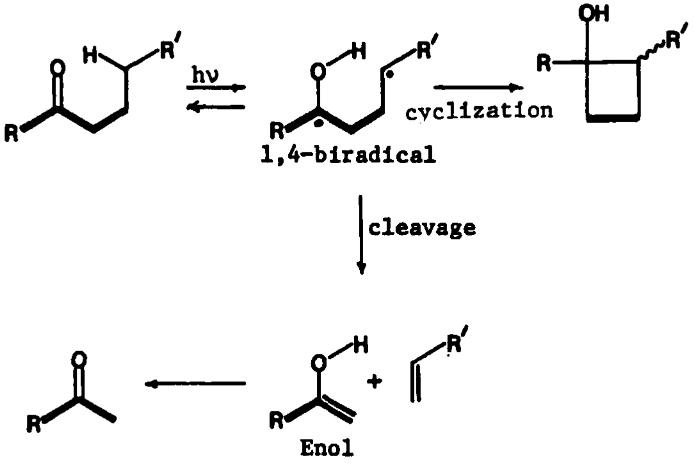
Abstract The solid state photochemistry of six α-cycloalkyl-p-chloroacetophenone derivatives (cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, exo-2-norbornyl and 1-adamantyl) is reported. All six undergo smooth type II photochemistry in the crystalline phase. The cyclization-to-cleavage ratios and the cis-to-trans cyclobutanol ratios are tabulated for each ketone, and the results are compared with the corresponding data from the solution photolyses. In general, the solid state medium was found to exert a relatively small effect on the product ratios. The γ-hydrogen atom to carbonyl oxygen abstraction distances, as well as the angular relationships between these two atoms, were determined from the X-ray crystal structure data for each ketone. The data showed that (1) six atom abstraction geometries other than chairlike can be accommodated, (2) abstraction can occur over distances much longer than previously supposed (up to 3.10 Å), and (3) there is no strict requirement that the hydrogen undergoing abstraction be

in the plane of the carbonyl oxygen n-orbital. Attempts were made to correlate the solid state structural data with the rate constants for hydrogen atom abstraction as determined in solution from Stern-Volmer quenching plots. The lack of any such correlation is interpreted as indicating a significant contribution to reaction in solution from non-minimum energy ketone conformations.

INTRODUCTION

The Norrish type II photochemical reaction (Scheme I) consists of intramolecular γ-hydrogen atom abstraction by an excited carbonyl oxygen atom to produce a 1,4-biradical which has three fates:

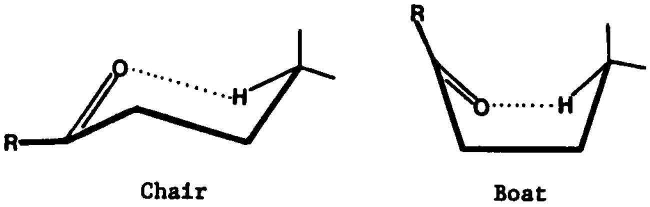
Scheme I. The Norrish Type II Reaction.



closure (cyclobutanol formation), cleavage to an alkene and an enol (isolated as the corresponding keto compound), and reverse hydrogen transfer to regenerate the ground state ketone.[2] The reaction is of great importance for several reasons. Used frequently to prepare unusual strained ring compounds,[3] it is also responsible for much of our current knowledge of the properties of 1,4-biradicals[4] and enols.[5] In addition, it has been implicated as an important contributor to polymer photodegradation.[6]

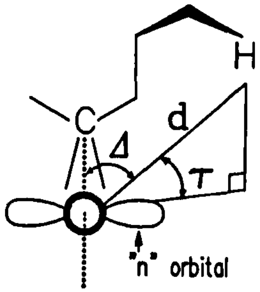
One of the major unresolved questions about the Norrish type II reaction which we hoped to answer with our solid state studies concerns the preferred geometry of the initial, rate-determining γ-hydrogen abstraction process. In terms of overall conformation, is the six-membered transition state best described as chairlike, boatlike, or perhaps twist boatlike(Scheme II)?

<u>Scheme II</u>. Chair vs Boat Abstraction Geometries.



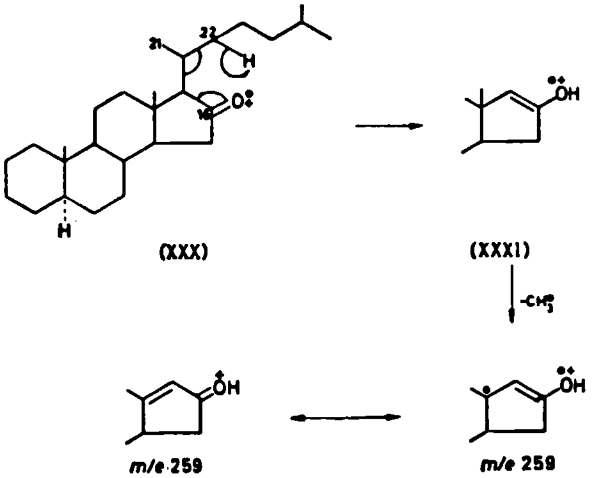
Looking at the abstraction geometry in more detail (Scheme III), we can define three parameters which characterize the geometric relationship between the abstracting oxygen atom and the hydrogen atom being abstracted. These are $\underline{d}$, the oxygen to hydrogen distance, τ, the angle defined by the oxygen···hydrogen vector and its projection on the mean plane of the carbonyl group (which contains the oxygen n-orbital), and Δ, the angle between the carbonyl carbon, the carbonyl oxygen, and the target hydrogen atom. Since all available evidence indicates that it is the oxygen n-orbital which is responsible for hydrogen atom abstraction,[2] we may define "ideal" values for τ and Δ of 0° and 90°, respectively. Similarly, abstraction should be least favorable when $\tau = 90°$ and $\Delta = 0°$ or $180°$. These parameters suggest that the rate constant for hydrogen atom abstraction may have a $\cos^2\tau$ and a $\sin^2\Delta$ dependence.

<u>Scheme III</u>. Definition of Geometric Parameters.



Existing notions about the geometry likely to be preferred in the Norrish type II reaction have been derived largely from studies on its mass spectrometric counterpart, the McLafferty rearrangement. The often quoted upper limit to the abstraction distance, *d*, of 1.8 Å stems from Djerassi's work on steroidal ketones (Scheme IV).

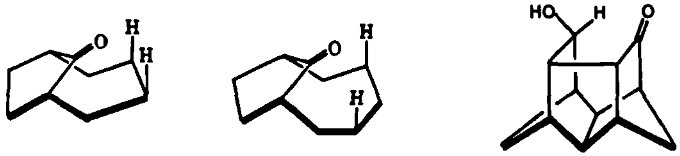
Scheme IV. McLafferty Rearrangement in Steroids.



Djerassi and co-workers found that the McLafferty rearrangement does not occur in these systems when *d* > 1.8 Å, *d* in this case being defined as the minimum oxygen···hydrogen distance as estimated from molecular models.[7] With regard to the angle τ, Henion and Kingston[8] interpreted the lack of

McLafferty rearrangement for ketone 2 (Scheme V) as being due to an unfavorable τ angle of 80°. By way of comparison, ketone 1, with a τ angle of 50°, did undergo the McLafferty rearrangement. In both cases, d was estimated to be 1.6 Å. As before, the values of d and τ were measured at the position of closest approach of H to O using molecular models. A final example is found in the work of Aoyama et al.[9] These authors observed that keto-alcohol 3 (Scheme V) does not undergo observable chemical change upon irradiation despite a very close γ-hydrogen/ketone oxygen contact. This was interpreted as being due to the fact that the γ-hydrogen atom lies almost precisely in the n-orbital nodal plane ($\tau = 90^\circ$), although other factors may contribute to the observed lack of reactivity.

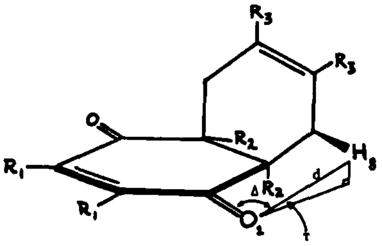
Scheme V.



1 2 3

Recent work from our laboratory has shed some light on the stereoelectronic requirements for five-membered transition state or β-hydrogen atom abstraction.[10] We found that photolysis of ene-diones of general structure 4 (Scheme VI) leads to O(1)···H(8) allylic β-hydrogen atom abstraction, both in solution and the solid state. X-ray crystallography of seven variously substituted ene-diones showed that the abstraction distances varied between 2.26 Å and 2.58 Å and that τ and Δ were close to ideal (0° to 8° for τ and 81° to 86° for Δ). On the basis of this and related work,[11] we suggested an approximate upper limit for hydrogen atom abstraction by oxygen of 2.7 Å, the sum of the van der Waals radii of these two atoms.

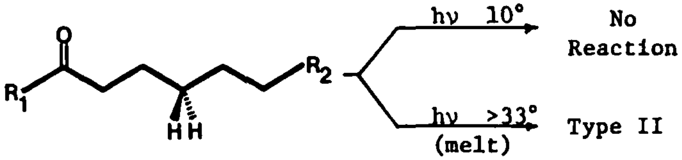
<u>Scheme VI</u>. β-Hydrogen Abstraction Geometry.



4

The study of organic reactions in the solid state has proved to be a very powerful tool in the establishment of structure-reactivity relationships. This stems from the fact that (1) reactions in crystals tend to occur with a minimum of atomic and molecular motion (the "topochemical principle")[12] and (2) the environment and the minimum energy conformation of the reacting molecules can be determined by X-ray crystallography and solid state ^{13}C NMR spectroscopy. We thus decided to initiate a study of the Norrish type II reaction from this point of view. In addition to providing evidence on the preferred geometry of hydrogen atom abstraction, the study was expected to yield interesting information on the effect that immobilization within a crystal lattice has on the partitioning of the intermediate 1,4-biradical.

Reports of Norrish type II reactions in the solid state, some lacking accompanying crystallographic studies, have appeared from time to time.[13] One such, due to Slivinskas and Guillet,[14] described the lack of type II reactivity of crystalline 7-tridecanone (5, Scheme VII). The fact that molten 7-tridecanone or solutions of 7-tridecanone do undergo smooth type II photochemistry was interpreted by the authors as indicating a requirement for chain rotational mobility which is lacking in the solid state. Specifically, we may interpret these results as being due to an extended ketone conformation in the solid state which places the γ-hydrogen atoms on the "wrong" side of the carbonyl group in a position too remote for abstraction. If this interpretation is correct, Scheme VII. Photoreactivity of 7-Tridecanone.



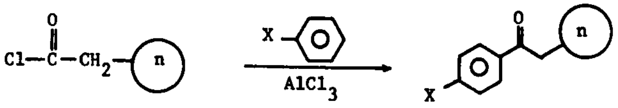
5 $R_1 = n\text{-}C_6H_{13}$
$R_2 = n\text{-}C_{18}H_{37}$
mp = 33°

what is required for solid state type II reactivity in simple ketones is branching at the β-carbon atom such that regardless of the hydrocarbon chain conformation adopted, at least one γ-hydrogen atom is in reasonable proximity to the carbonyl group.

COMPOUNDS STUDIED

α-Cycloalkylacetophenone derivatives (6, Scheme VIII) nicely fulfill the requirements of both β-branching and crystallinity. To date we have prepared over 30 such compounds, of which approximately half have had their X-ray crystal structures determined. Because of space limitations, this paper will discuss only those ketones in which the aromatic ring bears a p-chloro substituent. Table I gives the structure of each compound studied, along with its melting point, space group, and crystallographic R factor. Each ketone was prepared via Friedel-Crafts acylation of chlorobenzene using the appropriate acid chloride.

Scheme VIII. Starting Material Synthesis.

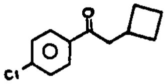
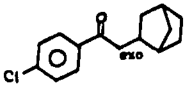
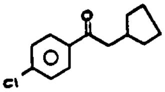
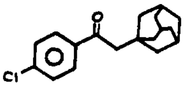
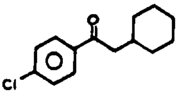
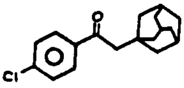
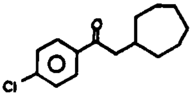


6

n = 4, 5, 6, 7, 1-adamantyl and exo-2-bicyclo[2.2.1]heptyl

X = H, Me, tert-Butyl, F, Cl, CN, COOH, COOMe, OMe and CF_3

Table I. Compounds Studied.

7		50-51° C2/c R = 0.035	11		55-56° $P2_1/a$ R = 0.037
8		60-61° $P2_1/a$ R = 0.061	12	 plates ($EtOH-H_2O$)	72-73° C2/c R = 0.042
9		63-64° $P2_1/a$ R = 0.053	13	 needles (hexane)	73-74° $P2_1/n$ R = 0.039
10		42-43° $P2_1/a$ R = 0.042			

PHOTOCHEMICAL RESULTS

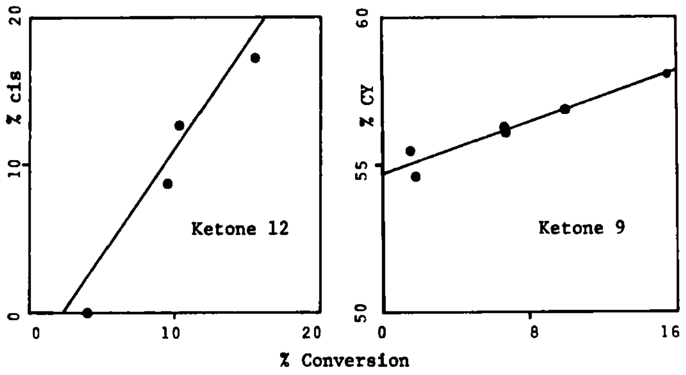
Table II summarizes the quantum yields and photoproduct ratios obtained for each ketone when photolyzed in pure benzene (0.1 M), in acetonitrile containing 2% water (also 0.1 M) and in the solid state. The samples were sealed under

Table II. Quantum Yields[a] and Product Ratios.[b]

Ketone	Φ benzene acetonitrile solid state	$\frac{CY}{CL}$[c] benzene acetonitrile solid state	$\frac{cis}{trans}$[d] benzene acetonitrile solid state
7	0.20	10:90	f
	0.49	12:88	f
	e	8:92	f
8	0.29	8:92	38:62
	0.62	8:92	40:60
	e	8:92	34:66
9	0.35	65:35	34:66
	1.0	69:31	49:51
	e	55:45	47:53
10	0.25	36:64	32:68
	0.76	35:65	41:59
	e	31:69	23:77
11	0.33	12:88	f
	0.56	12:88	f
	e	14:86	f
12	0.05	100:0	27:73
	0.25	100:0	36:64
	e	100:0	1:99
13	g	g	g
	g	g	g
	e	100:0	26:74

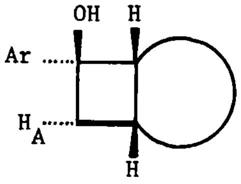
[a] Determined at 313 nm in a merry-go-round apparatus using valerophenone as the actinometer. [b] The photoproduct ratios were determined by capillary GC assuming identical detector response for each photoproduct. This assumption was found to be valid for the products from ketones 9 and 12. Each number represents the average of at least three separate photolyses at a given temperature with a minimum of three chromatographic analyses per photolysis. The estimated error is 5%. The solution conversions were kept below 20%, and the solid state conversions were < 5%. [c] Sum of cyclobutanol photoproduct yield divided by p-chloroacetophenone yield. [d] Cis cyclobutanol to trans cyclobutanol ratio. See text for definitions of cis and trans. [e] The quantum yields in the solid state were not determined. [f] Not determined because of overlapping peaks on GC. [g] Dimorphs 12 and 13 have identical solution photoreactivity.

nitrogen in 3 mm Pyrex tubes after several freeze-pump-thaw cycles, and the irradiations were conducted at 337 nm using the output from a Molectron UV 22 pulsed nitrogen laser (330 mW average power). In the solid state photolyses, identical results were obtained whether polycrystalline (powdered) samples or single crystals were used. Since all the ketones studied are relatively low melting, it was thought necessary to check the photoproduct ratios at temperatures considerably below room temperature. For compounds 9, 10 and 13, the photoproduct ratios were constant between -40° and +25°, both in acetonitrile and the solid state, indicating that in the latter medium, sample melting with concomitant loss of topochemical control is unimportant. However, significant changes were observed in the solid state photoproduct ratios when the conversion percentages were increased at room temperature. This is illustrated graphically below for ketones 9 and 12. As expected, melting leads to results which are more solution-like.

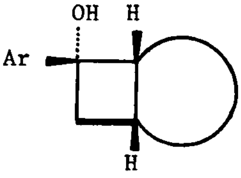


The cyclization (CY) photoproducts have the general structure 14 shown in Scheme IX. The

Scheme IX. Cyclization Photoproduct Structures.



cis-14



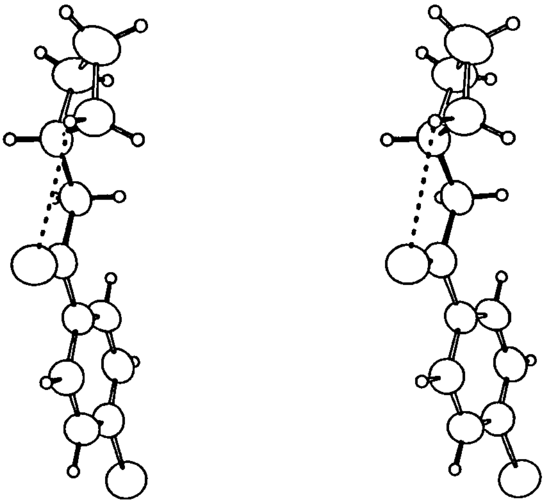
trans-14

designation cis is given to the isomer in which the hydroxyl group is cis to the adjacent ring junction hydrogen atom. Preparative scale solution photolyses permitted isolation of the cyclization products from ketones 9 and 10. The stereochemical assignments are based on a characteristic low field doublet of doublets (δ = 2.8 ppm, J = 6.5 and 4 Hz) in the cis isomer, attributable 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 cycloalkane CH_2). Based on our experience with a large number of analogous 2-aryl-2-hydroxybicyclo[n.2.0]alkane cyclization products, it is found that the trans isomers invariably have shorter GC retention times than the corresponding cis isomers, and this serves as our stereochemical marker for the cyclobutanols derived from the other ketones studied. A similar trend was observed by Wagner et al.[15]

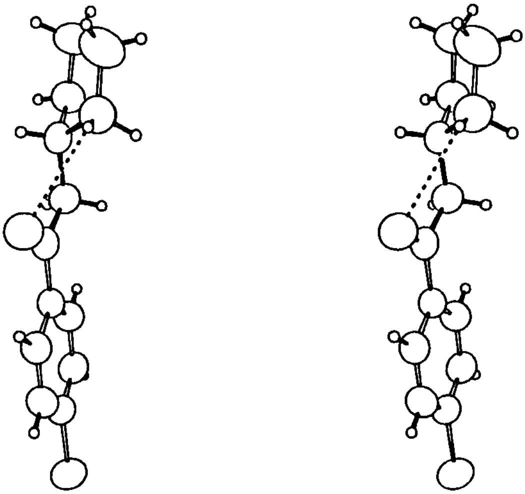
One of the cleavage (CL) photoproducts, p-chloroacetophenone, is constant throughout the series. It was isolated and identified by comparison with an authentic sample. The other cleavage photoproducts are the corresponding cycloalkenes in each case (cyclobutene, cyclopentene, cyclohexene, cycloheptene and norbornene). These had retention times too short to be detected under our normal GC conditions. No p-chloroacetophenone could be detected from photolysis of the α-adamantyl ketone 12 (or 13). This is attributable to the prohibitive strain energy of adamantene and is consistent with previous work on the solution phase photochemistry of α-adamantylacetone[16] and α-adamantylacetophenone.[17]

CRYSTALLOGRAPHIC RESULTS

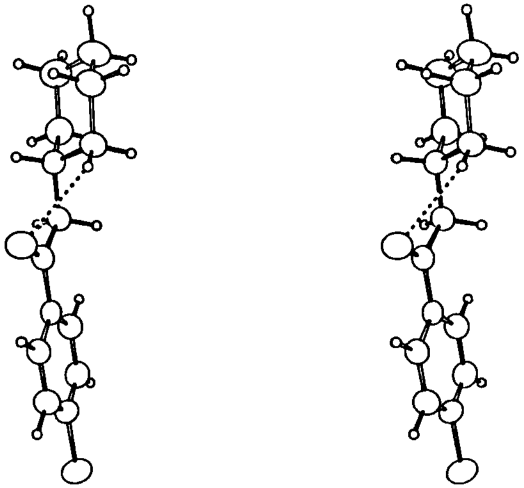
Shown on the succeeding pages are stereodiagrams of the conformations adopted by each of the ketones 7 - 13 in the solid state.[18] The heavy and dotted lines in each case denote the six atom geometry involved in the γ-hydrogen abstraction process. In all but two cases, the choice of which γ-hydrogen atom is abstracted is unequivocal. The equivocal cases are the cyclobutyl ketone 7 and the norbornyl ketone 11. The former has two abstractable γ-hydrogens, one with d = 3.10 Å and the other with d = 3.28 Å. Similarly, ketone 11 has two nearly equidistant γ-hydrogens at 2.98 Å and 3.13 Å. The stereodiagrams illustrate the closer contact in each case. The six atom abstraction geometries found for ketones 7 - 13 may be categorized as belonging to one of three possible types: chair, boat or twist-boat. Ketones 8, 9 and 10 exhibit boatlike abstraction geometries, whereas twist-boatlike geometries are found for ketones 7 and 11. Dimorphs 12 and 13 show chairlike abstraction geometries. This information, along with the values of d, τ, and Δ for each conformation, is summarized in Table III.



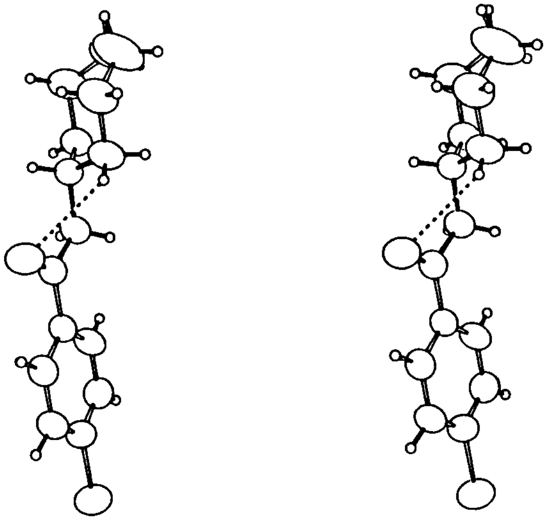
Cyclobutyl Ketone 7



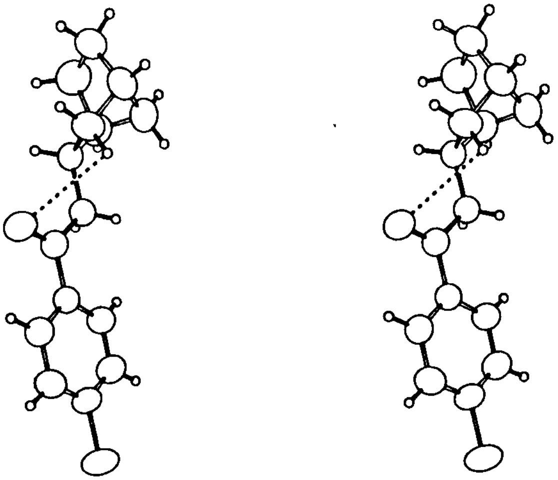
Cyclopentyl Ketone 8



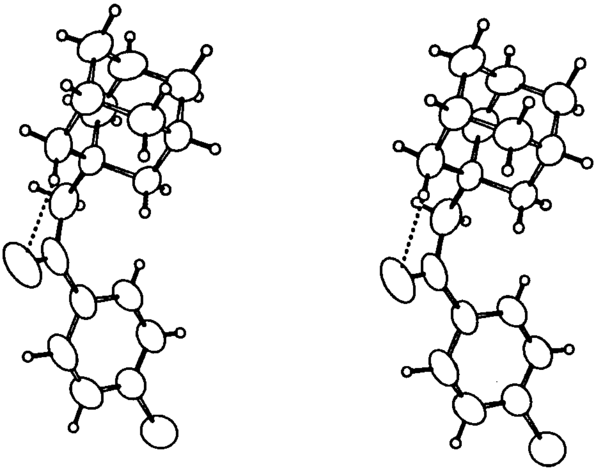
Cyclohexyl Ketone 9



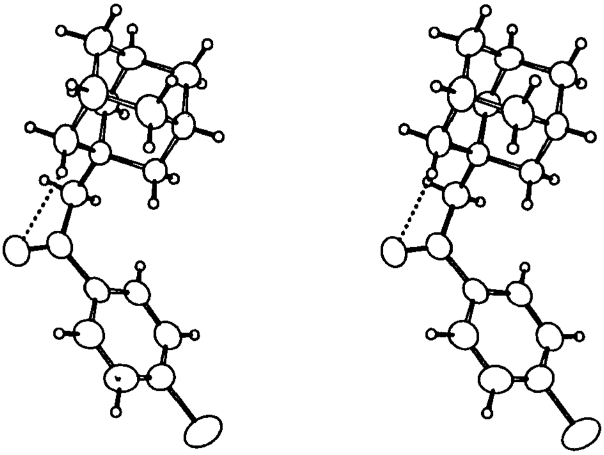
Cycloheptyl Ketone 10



Norbornyl Ketone 11



Adamantyl Ketone 12 (plates)



Adamantyl Ketone 13 (needles)

Table III. Solid State Geometric Data & $k_H(C_6H_6)$.

Ketone	Abstraction Geometry	d(Å)	τ(°)	Δ(°)	k_H(benzene) x 10^8 sec^{-1}
7	twist-boat	3.10	22.8	100.6	0.3
8	boat	2.80	31.0	96.0	1.2
9	boat	2.60	42.0	90.1	1.2
10	boat	2.71	41.8	82.4	5.7
11	twist-boat	2.98	44.2	74.8	0.4
12	chair	2.53	43.3	92.0	1.2
13	chair	2.78	62.3	76.6	1.2

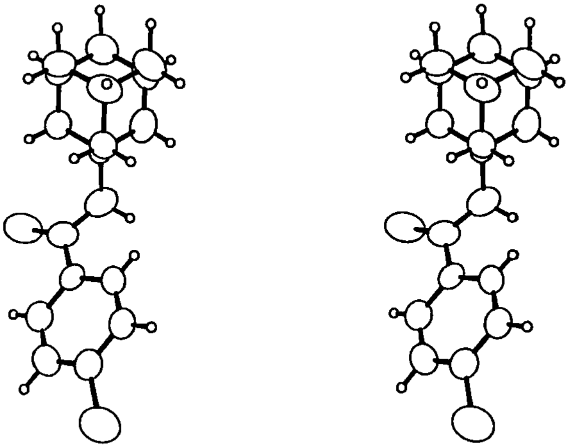
DISCUSSION

Turning first to the cyclization/cleavage (CY/CL) photoproduct ratios, it is apparent from Table II that for the p-chloro substituted acetophenone derivatives 7 - 13, the results in solution are not much different from those observed in the solid state. Only the cyclohexyl compound 9 exhibits a significantly different cyclization to cleavage ratio in the two media, the difference being a modest increase in the amount of cleavage in the crystalline phase. Ketones analogous to those in Table I but with other p-substituents show this trend as well. For example, p-methoxy-9 gives a 75:25 CY:CL ratio upon photolysis in acetonitrile which changes to 51:49 in the solid state.[19] Studies of the Norrish type II reaction in organized media other than the pure crystalline phase have noted similar increases in the amount of cleavage,[20] and we have argued[1] that this reflects a topochemical restriction of the motions necessary for cyclization by the more ordered medium.

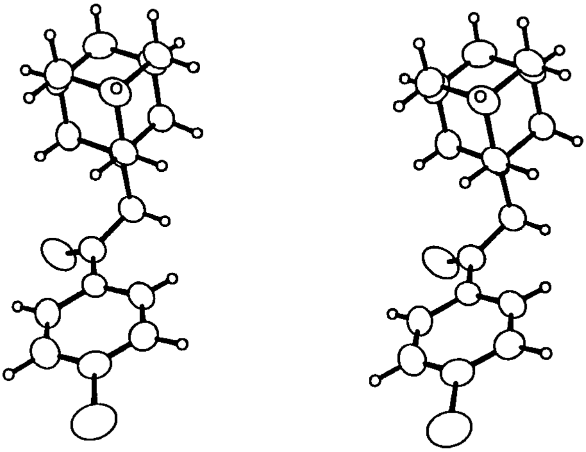
With regard to the cis-to-trans cyclobutanol ratios summarized in Table I, a general increase is noted in proceeding from the less polar solvent benzene to the more polar medium, moist acetonitrile. Similar findings have been reported for valerophenone and related compounds,[2] and have been explained as reflecting, in the polar solvent, the increased bulk of the hydrogen-bonded hydroxyl group as the 1,4-biradical undergoes closure. Hydrogen bonding of solvent to the hydroxyl group of the biradical intermediate has also been invoked to explain the increase in type II quantum yield which typically accompanies an increase in solvent polarity.[2] This effect, which is evident in our quantum yields, is thought to operate through retardation of the energy-wasting reverse hydrogen transfer step (Scheme 1).

The effect of the solid state medium on the cis/trans ratios appears to be variable for ketones 7 - 13. Most interesting is the different solid state photochemical behavior observed for the dimorphic ketones 12 (plates) and 13 (needles). Examples of such changes in <u>unimolecular</u> photoreactivity accompanying changes in packing arrangement are extremely rare.[21] However, in the case of 12 and 13, we feel that it is not the packing arrangement, but rather the conformational differences between the constituent molecules, which are responsible for the experimental results. Scheme X shows the solid state conformations involved; one significant difference between them lies in the "pitch" of the aromatic rings. In ketone 12, which affords only the trans cyclobutanol upon irradiation, one

Scheme X. Stereodiagrams of Dimorphs 12 and 13.



Dimorph 12 (plates)



Dimorph 13 (needles)

of the <u>ortho</u> aromatic hydrogen atoms is wedged between an adamantyl methylene hydrogen (2.48 Å) and one of the methylene hydrogen atoms adjacent to the carbonyl group (2.21 Å). Rotation of the aromatic ring is thus retarded, and attempted formation of the cis cyclobutanol photoproduct from this conformation would drive the <u>ortho</u> hydrogen into the adamantane ring, an impossible steric situation. In contrast, the pitch of the aromatic ring of ketone 13 is 40° removed from that of ketone 12, and the steric interaction with the ortho hydrogen is avoided. During biradical closure, the aromatic ring of 13 exposes its face rather than its edge to the adamantane moiety, and some cis cyclobutanol (24%) is formed. α-Adamantyl-p-methoxyacetophenone crystallizes in a conformation which is intermediate between those of ketones 12 and 13, and due to a packing arrangement which disfavors formation of the trans isomer, it actually gives a predominance of cis cyclobutanol upon irradiation in the solid state.[22]

Turning next to a discussion of the geometry of γ-hydrogen atom abstraction, it is apparent from our results that a chairlike six atom ground state geometry is not a strict requirement for the Norrish type II reaction. This conclusion is very likely valid for the excited states of ketones 7 - 13 as well, because as we have discussed elsewhere,[10] the $n \rightarrow \pi^*$ states of aryl ketones are not greatly distorted from their ground state geometries. A second general conclusion that can be drawn from the geometric data is that abstraction distances substantially in excess of 1.8 Å can still lead to type II reaction. In view of the results with ketones 7, 8, 11 and 13, it appears that our previous suggestion[10,11] of an upper limit of ca. 2.7 Å for hydrogen atom abstraction by oxygen will have to be revised upwards. Finally we see that both Δ and τ, particularly the latter, can vary quite considerably from their optimum values of 90° and 0°, respectively and still permit hydrogen abstraction.

With very few exceptions, organic molecules crystallize in their lowest energy conformations. Thus the solid state geometric data reported in Table III should be valid for the predominant conformer in solution as well. If the Norrish type II reaction in solution occurs from this minimum energy conformation, we might expect to see a correlation between the solution phase hydrogen abstraction rate constants and the geometric data, i.e., k_H should increase as $\underline{d}$ decreases and as τ and Δ more closely approach their optimum values. To test this idea, the hydrogen abstraction rate constants for ketones 7 - 13 were determined in benzene solution using standard Stern-Volmer quenching techniques; they are listed in Table III.

The data in Table III reveal no obvious relationship between k_H and $\underline{d}$, τ, or Δ. For example, ketones 8 and 9 have identical hydrogen abstraction rate constants but have structural parameters which differ markedly. Ketone 10 reacts nearly five times as rapidly as ketone 9 but has somewhat less favorable geometric parameters. As discussed in the INTRODUCTION section, we tested for correlations between k_H and $\cos^2 \tau$ and $\sin^2 \Delta$. We also sought a correlation between k_H and S, where S is the Slater overlap integral for the interaction between a hydrogen 1s and an oxygen 2p atomic orbital.[23] All attempted correlations, including various combinations of the above mentioned functions, were unsuccessful. Our interpretation[24] of these results is that in solution, a substantial amount of abstraction is taking place from non-minimum energy conformers which have geometries more favorable for abstraction than those determined by crystallography. Space does not permit a detailed discussion of this conclusion. We make one final point only. The relative rate of <u>bimolecular</u> free radical hydrogen atom abstraction from the cycloalkane homologous series is in the order cycloheptane > cyclohexane ~ cyclopentane > cyclobutane.[25] The fact that ketones 7 - 11 exhibit the same relative reactivity order argues convincingly for a process in solution in which the reacting molecules are able to explore many abstraction geometries during their excited state lifetimes.

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