CONFORMATIONAL CONTROL OF PHOTOCHEMICAL BEHAVIOR.

CYCLOHEXYL PHENYL KETONE[1]

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Ground state molecular conformations can influence photochemical behavior in cases where excited state reactions are more rapid than conformational isomerization.[2] Our interest in the role of molecular conformation in photochemistry led us to reexamine the photochemistry of cyclohexyl phenyl ketone (1) and its cis- and trans-4-t-butyl derivatives (2 and 3). Previous investigations of 1 and 2 have revealed inefficient formation of acetophenone,[3] presumably via consecutive type II eliminations (eq 1, 2). The anticipated primary photoproducts 4 and/or 5
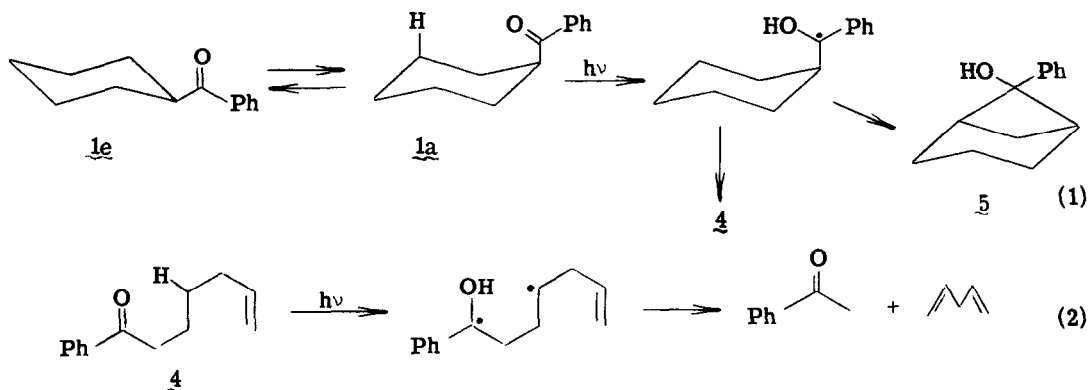
have not been identified. The relative stability of 1 and 2 has been attributed to the inaccessibility of the γ-hydrogen to the carbonyl group in the more stable conformers of 1 (equatorial) and 2 (diequatorial twist boat).[3b] The inefficiency of product formation from 1 seemed surprising for the following reasons· (a) at least several percent of the ground state molecules

should be in conformer 1a and (b) chair-chair interconversion in the excited state should

compete with radiationless decay of conformer 1e. Even more surprising are the reported

results for 2 which we would expect to exist in a highly reactive chair conformation.[4]

The conformational preference of the benzoyl group was determined by base catalyzed

equilibration of 2 and 3 (eq 3) to be 1.79 kcal/mole at 25° C. This value is only slightly larger

$$\text{2} \quad\xrightleftharpoons{\text{OMe}^-}\quad \text{3} \tag{3}$$
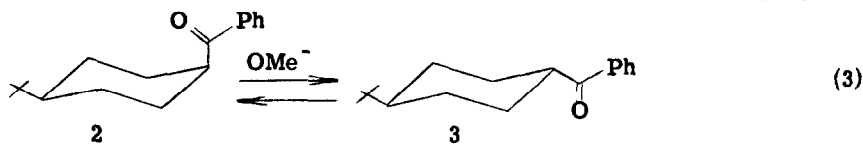
than those for the acetyl (1.52 kcal/mole)[5a] and methyl groups (1.7 kcal/mole).[5b] Thus

there is no reason to expect 2 to have a most stable twist boat conformation.[4]

Irradiation of 2 in degassed benzene solution through pyrex results in the formation of

6 (Φ= 0.024) as the only observed primary photoproduct (eq 4).[6] The low quantum yield could

$$\text{2} \quad\underset{k_r}{\overset{h\nu}{\rightleftharpoons}}\quad \xrightarrow{k_c}\quad \text{6} \tag{4}$$
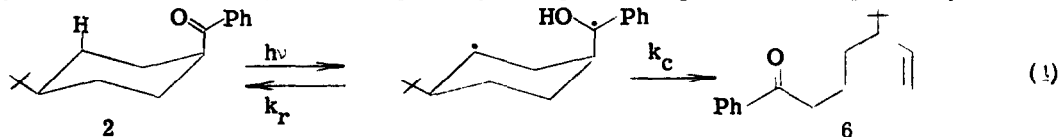
result from inefficient biradical formation and/or reversion of the biradical intermediate to

ground state ketone (k_r). Since alcohol solvents are known to suppress biradical reversion,[7]

the effect of added 1-propanol on the quantum yield was investigated. The quantum yield

increases with 1-propanol concentration to a value of 0.098 in 8.9 M 1-propanol-benzene.[8]

Thus the inefficiency of product formation from 2 is due at least in part to biradical reversion,

as is the case for several bicycloalkyl phenyl ketones with similar rigid geometries.[9] The

excited state lifetime (τ) of 2 was estimated by the usual Stern-Volmer method using 1,3-

pentadiene as the triplet quencher in 4.5 M 1-propanol-benzene solution. The value for $1/\tau$ =

6.8 x 10^9 (Table I) is in good agreement with that for endo-2-benzoylnorbornane (7).[9]

Irradiation of 3 does not lead to the formation of 6; however the quantum yield for

disappearance of 3 (Φ ~ 0.1) is surprisingly high. The products are thermally unstable and

have not been isolated. Stern-Volmer quenching of the disappearance of 3 in degassed benzene

gives a value of $1/\tau$ = 2.1 x 10^7 sec^{-1}. Thus the triplet lifetime of 3 is 300 times that of 2 .

Irradiation of 1 in degassed benzene solution results in the inefficient formation of 4 and

an isomeric alcohol, tentatively identified as 5 (Φ = 0.005).[10] Even at moderate conversions

($<10\%$) 4 is converted to acetophenone as rapidly as it is formed, thus precluding the isolation

of 4 in significant quantities upon irradiation of 1 in benzene. Addition of 1-propanol again

Table I.   Quantum Yield and Kinetic Data for Cyclohexyl Phenyl Ketones

Ketone	$\Phi_{C_6H_6}$	Φ_{PrOH}[a]	k_q[b]	$1/\tau$, sec^{-1}
1a	0.008	0 13	2.9	1 7 x 10^9
1e			765	6 6 x 10^6
2	0.024	0.098	0.74	6 8 x 10^9
3	0.10	--	239	2.1 x 10^7
7[c]	0.10	0.16	0.70	7.1 x 10^9

[a]Quantum yield in 8.9 M 1-propanol-benzene.   [b]Slope of Stern-Volmer plots where k_q is the rate constant for triplet quenching by pentadiene, assumed to be 5 x 10^9 M^{-1} sec^{-1} [c]Data from ref. 9.

results in a marked increase in the quantum yield for 4[3] (Table I), however, no increase in the quantum yield for 5 was observed. Since the ground state population of the axial conformer 1a (4-5%)[11] is significantly less than the quantum yield for biradical formation (Φ 0.13), the excited equatorial conformer 1e* must undergo ring inversion followed by biradical formation in competition with other processes which deactivate the excited state

The formation of 4 upon excitation of both 1a and 1e was confirmed by quenching experiments in 4.5 M 1-propanol-benzene (Figure 1). The two linear portions of the Stern-Volmer plot have markedly different slopes, indicative of product formation from a short lived (1a*) and a long lived (1e*) excited state   Kinetic analysis[12] of the quenching data provides values of $1/\tau$ = 1.7 x 10^9 sec^{-1} for 1a and $1/\tau$ = 6.6 x 10^6 sec^{-1} for 1e. These values are in reasonable accord with those for the model compounds 2 and 3. Approximately 80% of the product results from initial excitation of 1e in 4.5 M 1-propanol-benzene.

In conclusion, the axial conformer of cyclohexyl phenyl ketone (1a) and cis-4-t-butyl-cyclohexyl phenyl ketone (2) have very short triplet lifetimes due to their favorable geometries for -hydrogen abstraction. The short lifetime of 1a   precludes competition of conformational isomerization with -hydrogen abstraction. In contrast, the longer triplet lifetime of 1e' allows ring inversion to compete with radiationless decay processes. The low quantum yields for product formation from 1a and 2 in benzene solution are due at least in part to efficient biradical reversion to ground state ketone. It is interesting to note that conformation-

ally non-mobile excited ketones such as 1a, 2, and 6 which have geometrically accessible

γ-hydrogens, undergo exceptionally rapid γ-hydrogen abstraction. Furthermore, the same

non-mobile conformations which enhance biradical formation also favor biradical reversion to

ground state ketone, resulting in low quantum yields for product formation.
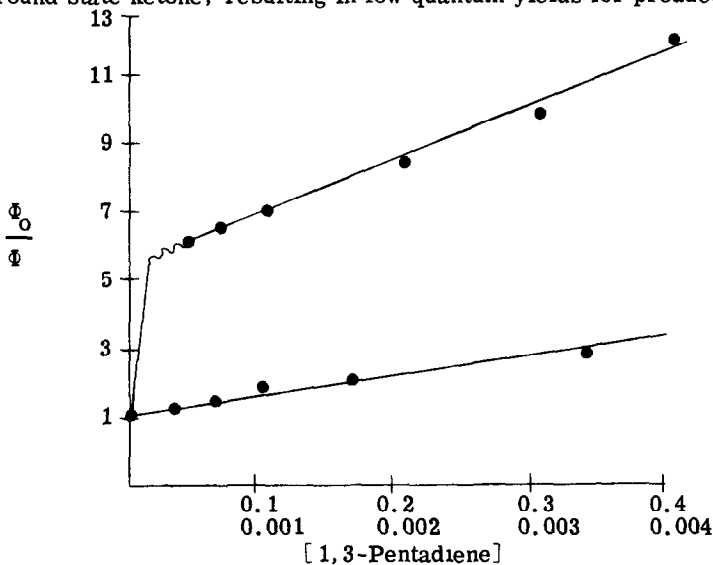

Figure 1. Stern-Volmer plots for quenching of the formation of 4 from 1 using high (upper curve) and low (lower curve) concentrations of 1,3-pentadiene.

References

1. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and PPG Industries for support of this research

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6. Isolated by silica gel chromatography IR (film), 1680 cm^{-1}, nmr (CCl_4) ᵟ 0.83 (s, 9H), 1.1-1.9 (m, 4H), 2 1-2.3 (m, 1H), 2.82 (t, 2H), 4.7-5.4 (m, 3H), 7.4, 7.9 (m, 5H).

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8 The quantum yield is still increasing with added 1-propanol at this concentration

9. F D. Lewis, R. W. Johnson, and R. A. Ruden, J Amer. Chem. Soc , 94, 4292 (1972).

10. Preparative photolysis of 1 in 1-propanol followed by silica gel chromatography gave 4 spectral properties identical to those of an authentic sample prepared by the Grignard reaction of benzonitrile with 4-pentenylmagnesium bromide. Photolysis of 1 in benzene followed by chromatography gave 5 IR (film), 3450 cm^{-1}, nmr (CCl_4) ᵟ 0.8-2.0 (m, 10H), 4.2 (s, 1H), 7.2 (m, 5H). The spectral properties of 5 were not the same as an authentic sample of cyclohexylphenylcarbinol