$CH_3(RC{\equiv}CR')L_2]$ and deactivated toward these reactions by coordination to a relatively electron-rich metal such as I and III.

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Can Molecular Conformation Control Photochemical Behavior?[1]

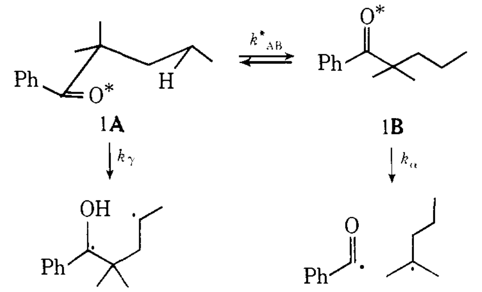
Sir:

The effect of ground-state conformation on photochemical reactivity[2,3] and product composition[4] is a topic of considerable current interest. When two conformers can give rise to different photoproducts (eq 1),

$$\begin{tikzcd}
 & A \arrow[r, shift left, "k_{AB}"] \arrow[d, "h\nu"] & B \arrow[l, shift left] \arrow[d, "h\nu"] & \\
X & A^* \arrow[l, "k_A"'] \arrow[r, shift left, "k^*_{AB}"] & B^* \arrow[l, shift left] \arrow[r, "k_B"] & Y
\end{tikzcd} \qquad (1)$$

two limiting cases should be possible. In case I the energy barrier for excited state conformational isomerization[5] is *lower* than the activation energies for formation of X or Y ($k^*_{AB} \gg k_A, k_B$). In this case the ratio of products will depend on the difference in energy for the transition states leading to X and Y (Curtin–Hammett principle[6]) and the lifetimes of both excited state conformers will be the same ($\tau^*_A = \tau^*_B = (k_A + k_B)^{-1}$).[7] In case II the energy barrier for excited state conformational isomerization is ***higher*** than the activation energy for formation of X or Y ($k^*_{AB} \ll k_A, k_B$). In this case the ratio of products depends upon the relative population of A* and B* and the lifetimes of the excited state conformers need not be the same ($\tau^*_A = k_A^{-1}$, $\tau^*_B = k_B^{-1}$). Since electronic excitation is much faster than nuclear motion (Franck–Condon principle[8]), the initial population of A* and B* will be determined by ground-state conformational populations and extinction coefficients. We wish to present the first quantitative evidence that both case I and case II do occur.

We[2,9] and Wagner and McGrath[10] recently reported that *tert*-alkyl phenyl ketones such as α,α-dimethylvalerophenone (**1**) undergo competitive photochemical α cleavage and γ-hydrogen abstraction (eq 2). γ-Hydrogen abstraction requires a six-membered transition state (**1A**), whereas α cleavage should occur from all conformations (**1A**, **1B**, etc.).[11,12] Since bond rotations for acyclic compounds ($k^*_{AB} \geq 10^{10}$ sec^{-1}) are much more rapid than k_γ for valerophenone (**2**) or k_α for pivalophenone (**3**) (Table I),[13] ketone **1** should provide an example of case I. That this is indeed the case is shown by the observations that (a) Stern–Volmer plots ($\Phi_0/\Phi = 1 + k_q\tau[Q]$) for quenching α cleavage and γ-hydrogen abstraction products have identical slopes ($\tau^*_A = \tau^*_B$) and (b) the ratio of products is roughly similar to the ratio of rate constants for the model compounds **2** and **3**.[9,10,16]



(2)

Table I. Quantum Yields and Kinetic Data[a]

Ketone	Φ_α[b]	Φ_γ[c]	$k_q\tau$,[d] M^{-1}	$1/\tau$[e] $\times 10^{-8}$ sec^{-1}
1[f]	0.06	0.11 0.45[g]	44	1.1
2[f]		0.42	36	1.4
3[f]	0.30		447	0.11
4	0.03	0.19	380[h,i]	0.13[h,i]
5	0.20	0.045 0.21[j]	200[h] 29[i]	0.25[h] 1.7[i]

[a] Benzophenone–benzhydrol actinometry with 313- or 365-nm irradiation. [b] Quantum yield for benzaldehyde formation in degassed benzene containing 10^{-2} *M* dodecanethiol. [c] Total quantum yield for photocyclization and elimination products in degassed benzene. [d] Slope of linear Stern–Volmer plots for naphthalene quenching using 365-nm irradiation. [e] Calculated assuming $k_q = 5 \times 10^9\ M^{-1}$ sec^{-1}. [f] Values from ref 9. [g] Value from ref 10 for 1-propanol solvent. [h] Values for quenching of benzaldehyde formation. [i] Values for quenching bicyclic alcohol formation. [j] Value for 1-propanol solvent.

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[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.

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

[3] A. Padwa and D. Eastman, *ibid.*, **91**, 462 (1969).

[4] (a) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *ibid.*, **87**, 3406 (1965); (b) J. E. Baldwin and S. M. Kruger, *ibid.*, **91**, 6444 (1969); (c) C. W. Spangler and R. P. Hennis, *J. Chem. Soc., Chem. Commun.*, 24 (1972); (d) W. G. Dauben, J. Rabinowitz, N. D. Vietmeyer, and P. H. Wendschuh, *J. Amer. Chem. Soc.*, **94**, 4285 (1972); (e) R. M. Moriarty and R. C. Reardon, *Tetrahedron*, 1379 (1970).

[5] Ground- and excited-state energy barriers for conformational isomerization need not be the same. For the systems studied electronic excitation should not have a large effect on conformational mobility ($k_{AB} \approx k^*_{AB}$). This is probably not the case when the chromophore is part of the conformationally mobile system (*cf.* ref 4).

[6] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 151, 237.

[7] Other excited state processes including nonradiative decay are neglected for the purposes of clarity and simplicity.

[8] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 30.

[9] F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **94**, 3852 (1972).

[10] P. J. Wagner and J. M. McGrath, *ibid.*, **94**, 3849 (1972).

[11] Since γ-hydrogen abstraction from a secondary alkyl center is approximately ten times more rapid than α cleavage of *tert*-alkyl phenyl ketones,[9,10] the simplifying assumption that $k_\gamma > k_\alpha$ when γ-hydrogen abstraction is geometrically feasible will be made.

[12] Walling and Padwa have suggested that the analogous intramolecular hydrogen abstraction and β-cleavage reactions of alkoxy radicals might be faster than alkyl side-chain conformation changes: C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1597 (1963).

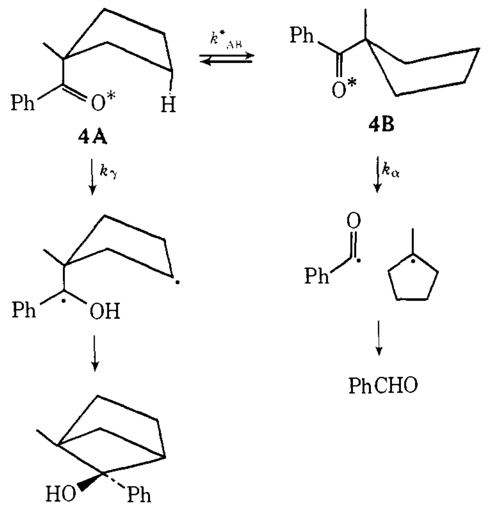
[13] The energy barrier for alkane bond rotation which does not involve alkyl–alkyl eclipsing is ~3.4 kcal/mol.[14] The Arrhenius activation energy for valerophenone γ-hydrogen abstraction is 5–6 kcal/mol.[15] The activation energy for α cleavage of pivalophenone has not been measured, but probably is slightly larger than that for valerophenone γ-hydrogen abstraction.[9]

[14] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, p 9.

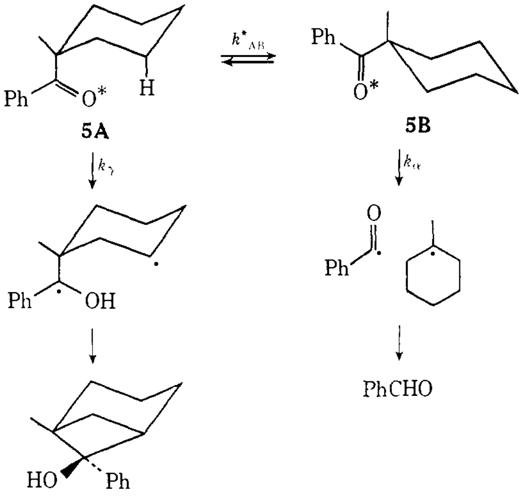
[15] (a) J. C. Scaiano, J. Grotewold, and C. M. Previtali, *Chem. Commun.*, 390 (1972); (b) F. D. Lewis, *Mol. Photochem.*, in press.

[16] Both biradical and radical pair intermediates can revert to ground-state ketone.[2,9,10] Addition of alcohols to the solvent often increases biradical product quantum yields.[10] We have recently observed ~50% cage recombination following α cleavage of an optically active alkyl phenyl ketone (F. D. Lewis and J. G. Magyar, unpublished results). Further discussion of this topic will be deferred to our full paper.

The photochemical behavior of α-methylcyclopentyl phenyl ketone (**4**) provides an example of case I for an alicyclic system. Cyclopentane pseudorotation should be much more rapid ($k^*_{AB} > 10^{10}$ sec^{-1} [17]) than k_α or k_γ. Therefore, even though γ-hydrogen abstraction can only occur from the axial conformation **4A**,[2,3] the lifetimes of **4A** and **4B** must be the same ($\tau_A = \tau_B = (k_\alpha + k_\gamma)^{-1}$). The identical slopes of Stern–Volmer plots for quenching of benzaldehyde and bicyclobutanol formation (Figure 1) support this conclusion.



(3)



(4)

Ketones **1** and **4** belong to case I by virtue of the low energy barriers for alkane bond rotation and cyclopentane pseudorotation. The energy barrier for cyclohexane ring inversion is much larger ($E_A \sim 10$ kcal/mol[18]). Thus the photochemistry of α-methylcyclohexyl phenyl ketone (**5**) might be expected to provide an example of case II ($k^*_{AB} \ll k_A, k_B$). Stern–Volmer plots for quenching of benzaldehyde and bicyclobutanol formation do indeed have markedly different slopes (Figure 1).[19] Values of $1/\tau^*_A = k_\gamma = 1.8 \times 10^8$ sec^{-1} and $1/\tau^*_B = k_\alpha = 2.5 \times 10^7$ sec^{-1} are in good agreement with those for the model compounds **2** and **3** (Table I). If $k^*_{AB} \ll k_\alpha, k_\gamma$, then product quantum yields should depend upon both ground-state conformational populations[20] and the efficiency of product formation from the biradical and radical pair intermediates,[16] but not upon the ratio of rate constants k_α and k_γ. Low-temperature 22.6-MHz ^{13}C nmr spectra of ketone **5** show the equatorial benzoyl conformation to be favored (*A* value = 0.51 kcal/mol, equatorial/axial ratio of 2.7/1 at 25°). The quantum yields for benzaldehyde formation (0.20 *vs.* 0.30 for pivalophenone) and cyclobutanol formation in 1-propanol solution agree quite well with the conformational populations, but not at all with the ratio of rate constants.

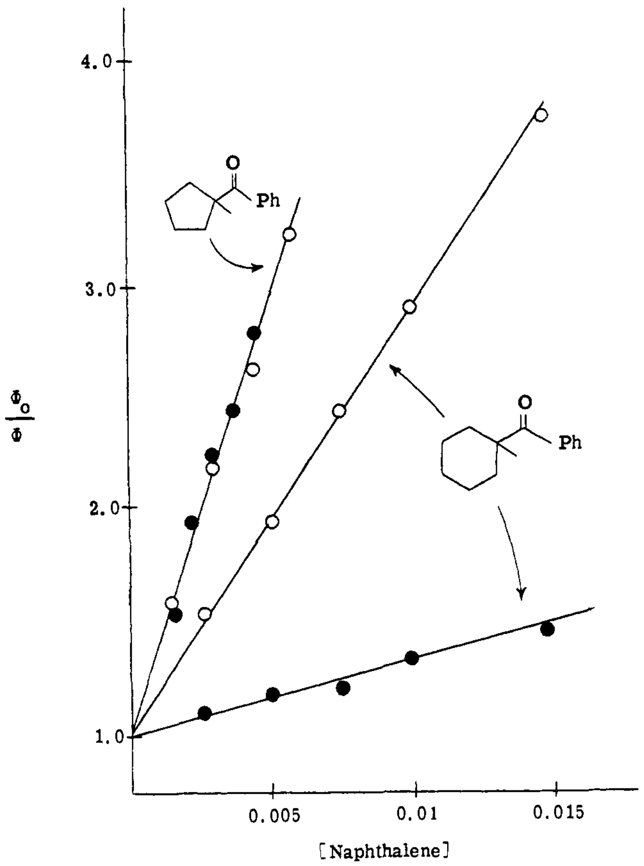


Figure 1. Stern–Volmer plots for quenching of benzaldehyde (○) and bicyclobutanol (●) formation from α-methylcyclopentyl phenyl ketone and α-methylcyclohexyl phenyl ketone.

In conclusion, the Curtin–Hammett principle (case I) applies to some photochemical reactions, but does not need to be considered for others (case II). At least an approximate knowledge of the relative rate constants or activation parameters for excited state reactions and conformational isomerization is necessary in order to predict what effect, if any, ground-state conformation will have on photochemical behavior. It should be noted that the analysis given for reactions which involve two excited state conformations should also apply for any reaction which involves two interconverting excited states or an excited state reactant and product.

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(17) The energy barrier for cyclopentane pseudorotation is <3 kcal/mol; see ref 6, p 248.

(18) The rate constant for inversion of 1,1-dimethylcyclohexane at 25° is $\sim 7 \times 10^4$ sec^{-1}: D. K. Dalling, M. Grant, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 3678 (1971).

(19) α cleavage from both axial and equatorial conformations of ketone **5** might be expected to result in a curved quenching plot. However, axial α cleavage is the minor reaction (~10%)[11] of the minor conformer (~27%, *vide infra*). Thus, <5% of the total α cleavage should occur from the axial conformation. In accord with this, the Stern–Volmer plot is linear to >90% quenching.

(20) The ultraviolet spectra of rigid model compounds show axial and equatorial benzoylcyclohexanes to have nearly identical molar extinction coefficients at 313 nm.

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Hydrogen Transfer from Dioxane to an Olefin Catalyzed by Chlorotris(triphenylphosphine)rhodium(I)

Sir:

In transfer-hydrogenation[1] the donation of hydrogen to olefins by alcohols,[2] cyclohexene,[3] and partially hydrogenated aromatic compounds containing nitrogen atoms[4] has been observed. However, with the exception of alcohols there have been very few reports of double hydrogen abstraction by soluble complexes.[5]

We wish to report here that, with $RhCl(PPh_3)_3$[6] as a catalyst, a saturated cyclic ether, 1,4-dioxane, donated hydrogen to an olefin to give stoichiometric amounts of dioxene.

When a dioxane solution of cyclopentene (0.5 *M*) and the catalyst (0.02 *M*) was sealed in a Pyrex glass tube under vacuum (10^{-2} mm) and heated at 180° for 1 hr,[7] the formation of 0.43 *M* dioxene and 0.42 *M* cyclopentane in addition to the survival of 0.08 *M* cyclopentene[8] was shown by gas chromatographic analysis of the reaction mixture. Dioxene was identified by comparison with an authentic sample.[9] The following observations indicate that the reduction proceeded by hydrogen transfer from dioxane rather than by disproportionation. (1) The amount of the dioxene was almost equal to that of the cyclopentane.[10] (2) The total amount of the cyclopentane and the cyclopentene was equal to the amount of the charged cyclopentene. (3) Only a negligible amount of cyclopentadiene or the products of Diels–Alder reactions involving the diene was detected. (4) The reduction did not proceed in toluene without dioxane.[11]

The hydrogenation proceeded almost quantitatively and the observed initial rate of the formation of cyclopentane or of the consumption of cyclopentene was 1.2×10^{-2} mol l.$^{-1}$ min^{-1} at 180°, 6.2×10^{-3} at 170°, 3.7×10^{-3} at 160°, and 2.0×10^{-3} at 150°.

After the reactions, orange-red needles (A) were isolated by leaving the reaction mixtures at room temperature. The structure of A was inferred as $RhCl(PPh_3)_2(C_4H_8O_2)$, formed by replacing a triphenylphosphine of $RhCl(PPh_3)_3$ by a dioxane. The identification of the structure was based on the following grounds: (1) The value of the elemental analysis of A fitted the calculated value (*Anal.* Calcd for $C_{40}H_{38}ClO_2P_2Rh$: C, 66.72; H, 5.32 Found: C, 66.88; H, 5.16). (2) The ^1H nmr spectrum in $CDCl_3$ has a peak assignable to dioxane (singlet, τ 6.3) and peaks attributable to the aromatic hydrogens of triphenylphosphine (multiplet centered at τ 2.7). The ratio of the area of the former to that of the latter was about 1:4. (3) A was obtained also by dissolving $RhCl(PPh_3)_3$ in dioxane on warming and then cooling the solution. (4) Though $RhCl(PPh_3)_3$ has been reported to give the dimer, $[RhCl(PPh_3)_2]_2$ on heating in solvents such as toluene and ethanol,[6] the infrared spectrum of A is different from that of the dimer and has peaks attributable to coordinated dioxane at 870 and 890 cm^{-1}.

By analogy to the hydrogenation by molecular hydrogen[5,6,12] and the isomerization of olefins,[13] we should like to propose the following reaction scheme: $RhCl(PPh_3)_2(C_4H_8O_2) \rightleftarrows RhClH(C_4H_7O_2)(PPh_3)_2 \rightleftarrows RhClH_2(PPh_3)_2(C_4H_6O_2)$ (− dioxene) (+ olefin) $\rightleftarrows$ $RhClH_2(PPh_3)_2(\text{olefin}) \rightleftarrows RhClH(\text{alkyl})(PPh_3)_2$ (+ dioxane) $\rightleftarrows RhCl(PPh_3)_2\text{-}(C_4H_8O_2)$ + paraffin. The rate-determining step of the reaction is inferred to be the dehydrogenation step, that is, the formation of the monohydrido complex, $RhClH(C_4H_7O_2)(PPh_3)_2$ or $RhClH(C_4H_7O_2)(PPh_3)_2(S)$ (S = dioxane or olefin), by the oxidative addition of dioxane by the cleavage of a C–H bond, on the following grounds:[14] (1) The kinetic isotope effect at 180° was $k_H/k_D = 3.0$.[15] This value shows that a hydrogen transfer step is rate determining and exhibits a clear contrast to the reduction by molecular hydrogen in which the isotope effect is 0.78–

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[1] T. Nishiguchi and K. Fukuzumi, *Bull. Chem. Soc. Jap.*, **45**, 1656 (1972).

[2] (a) K. Sakai, T. Ito, and K. Watanabe, *ibid.*, **39**, 2230 (1966); (b) H. N. Basu and M. M. Chakrabarty, *J. Amer. Oil Chem. Soc.*, **43**, 119 (1966); (c) J. C. Bailar, Jr., and H. Itatani, *J. Amer. Chem. Soc.*, **89**, 1592 (1967); (d) S. Nanya, M. Hanai, and K. Fukuzumi, *Kogyo Kagaku Zasshi*, **72**, 2005 (1969).

[3] E. A. Braude, R. P. Linstead, and P. W. D. Mitchell, *J. Chem. Soc.*, 3578 (1954).

[4] L. M. Jackman, *Advan. Org. Chem.*, **2**, 329 (1960).

[5] (a) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972); (b) G. N. Schrauzer, "Transition Metals in Homogeneous Catalysis," Marcel Dekker, New York, N. Y., 1971, pp 33, 41.

[6] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

[7] This concentration of the olefin and the catalyst was used in every instance, unless otherwise noted.

[8] When cyclopentene and the catalyst (0.01 *M*) were heated for 1 hr at 180° in isopropyl alcohol, 0.18 *M* cyclopentane was obtained along with acetone.

[9] R. K. Summerbell and R. R. Umhoefer, *J. Amer. Chem. Soc.*, **61**, 3016 (1939).

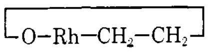
[10] Though the amount of dioxane was a little more than that of cyclopentane, the difference seems to be within experimental error.

[11] In this reaction, $[RhCl(PPh_3)_2]_2$ was isolated.

[12] F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1574 (1967).

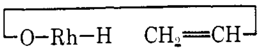
[13] (a) J. F. Biellmann and M. J. Jung, *J. Amer. Chem. Soc.*, **90**, 1673 (1968); (b) A. S. Hussey and Y. Takeuchi, *ibid.*, **91**, 672 (1969); (c) G. C. Bond and R. A. Hillyare, *Discuss. Faraday Soc.*, **46**, 20 (1968); (d) R. L. Augustine and J. F. V. Peppen, *J. Amer. Oil Chem. Soc.*, **47**, 478 (1970); (e) C. H. Heathcock and S. R. Poulter, *Tetrahedron Lett.*, 2755 (1969).

[14] A referee suggested another route instead of the C–H insertion. This is a C–O insertion to give



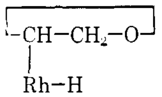
$$\text{O–Rh–CH}_2\text{–CH}_2$$

followed by Rh–H elimination to give



$$\text{O–Rh–H}\quad \text{CH}_2\text{=CH}$$

An insertion of O–Rh to give



$$\underset{\text{Rh–H}}{\text{CH}}\text{–CH}_2\text{–O}$$

followed by a second Rh–H elimination would give $RhClH_2(PPh_3)_2\text{-}(C_4H_6O_2)$. According to this mechanism, the rate-determining step must be one of the Rh–H elimination steps from the observed isotope effect. We should like to point out the resemblance of the two steps to the steps involved in the isomerization of olefins under hydrogen which occurs under milder conditions.

[15] The initial rate of the reduction in which cyclopentene (0.25 *M*), dioxane (2.0 *M*), and the catalyst (0.02 *M*) in toluene were heated at 180[11] was 2.1×10^{-3} mol l.$^{-1}$ min^{-1}, while that of the one in which octadeuteriodioxane was used instead of dioxane was 6.9×10^{-4}.