Tetrahedron Letters No. 13, pp 1173 - 1176, 1975. Pergamon Press. Printed in Great Britain.

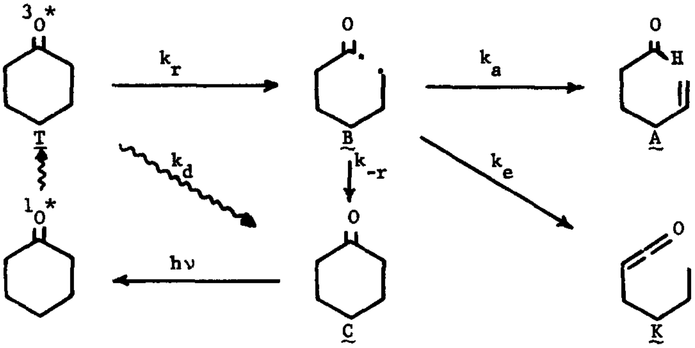
Photochemistry of Cyclic Ketones. II.
Deuterium Isotope Effects on Product Formation.

Willis B. Hammond* & T.S. Yeung

Department of Chemistry, Yale University
New Haven, Connecticut 06520

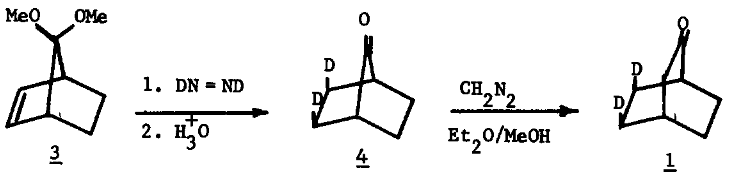
(Received in USA 2 December 1974; received in UK for publication 25 February 1975)

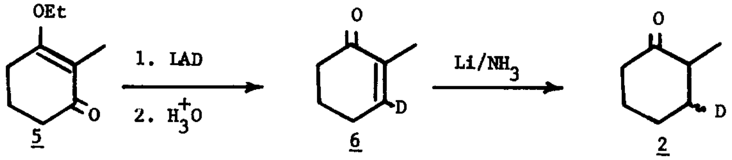
In a previous paper we have shown that deuterium substitution can effect the product distribution from the biradical intermediate (B) produced in the photolysis of cyclohexanone [1]



We were able to evaluate the isotope effect on the rates of formation of aldehyde (A) and ketene (K isolated as its methyl ester). An isotope effect of $k_e^H/k_e^D = 1.09$ for disproportionation to give ester and $k_a^H/k_a^D = 1.18$ for disproportionation to give aldehyde were reported. These numbers appear unusually small compared to other results in the literature for radical disproportionation reactions which range from 1.4 to 2.0[2-5]

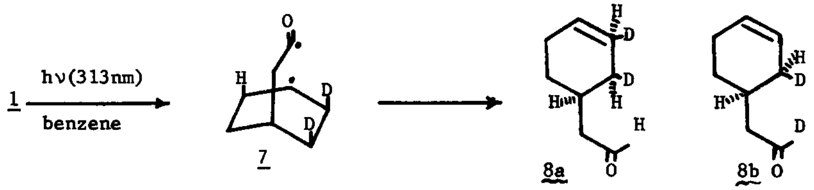
Ketones 1 and 2 were selected as model systems which might provide further information on the importance of primary isotope effects on intramolecular disproportionation. Their syntheses are outlined below.[6] Ketal 3 was reduced with dideuterodiimide[7] and hydrolyzed to give 4. Treatment of 4 with ethereal CH_2N_2 containing 10% methanol[8] produced 1 in high yield. Mass spectral analysis of 1 at 15 e.V. indicated 0 3% d_0, 4.9% d_1 and 94.8% d_2 NMR analysis of 4 using Eu(fod)$_3$ shift reagent indicated >95% cis-exo reduction as expected.[9] Reduction[10] of 5 with lithium aluminum deuteride (LAD) to give 6 and further reduction[11] with lithium in liquid ammonia gave 2 in good yield after purification by g.c. The method of synthesis of 2





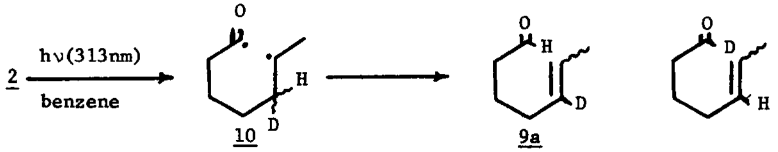
should give equal amounts of equatorial and axial deuterium at the 3-position. Mass spectral analysis at 15 e.V. indicated 98 3% d_1 and 1 7% d_0.

Photolysis of 1 in benzene proceeded in high yield to give 8 isolated by prep. g.c [12]



NMR integration of the aldehyde peak for 8 at δ 9.68 and the olefin peak at δ 5.59 gave a ratio of 8a/8b = k^H/k^D = 1.07 ± 0.02 (average of three separate photolyses) [13]

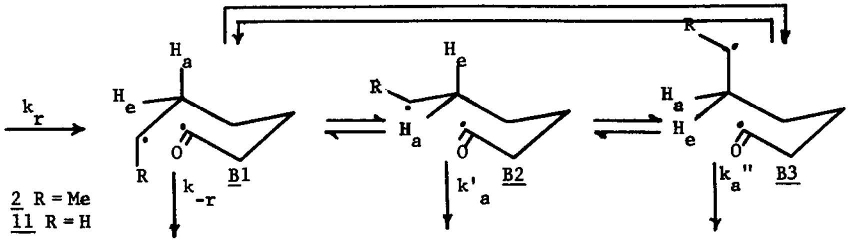
In like manner photolysis of 2 in benzene and nmr analysis of the resulting mixture of cis & trans aldehydes isolated by prep. g c. gave a ratio of 9a/9b = k^H/k^D = 1.24 ± 0 05.[13]



The primary isotope effects observed in this work are of the same order of magnitude as we reported earlier[1] but are smaller than values reported in the literature [2-5] This suggests that either the activation energy for disproportionation of a 1,6-biradical is smaller than the activation energy for disproportionation of two separate radicals or that disproportionation may not be rate determining.

For compound 1, the high quantum yield for product (Φ_{ald} = 0.62)[12] requires that recombination of the biradical (k_{-r}) is inefficient relative to product formation. The small isotope effect (1.07) suggests that the acyl radical abstracts the first hydrogen or deuterium that it encounters with nearly unit efficiency

Φ_{ald} from cyclohexanone is determined by the rate of rotation of the biradical conformation B1 to B2 and B3, conformations favorable for disproportionation, compared to the rate of recombination from B1 [1,14] Rotation from B1 to B2 should be favored over rotation to B3 and conformation B2 should be more stable than B3.[15] Agosta[16] has reported that two-thirds of the aldehydic hydrogen is abstracted from the 3-axial position of 4-methylcyclohexanone. This can be explained as kinetic or thermodynamic, either abstraction from B2 occurs faster than equilibration with B3 or abstraction occurs from the more densely populated conformer B2 For 3,3,5,5-d_4-cyclohexanone Φ_{ald} is decreased relative to cyclohexanone by a decrease in k_a (k_a^H/k_a^D = 1.18)[1] and B2 and B3 must return to B1 in competition with product formation. For 2 k_{-r} should be reduced relative to k_{-r} for 11[17,18] and thus less competitive with k_a The larger intramolecular isotope effect for 2 (k^H/k^D = 1 24) suggests that interchange of B2 and B3 must occur on a time scale at least comparable to the rate of disproportionation If $k_a > k_{B2 \rightleftarrows B3}$ no isotope effect would be observed.



2 R = Me
11 R = H

Acknowledgement. We are grateful to the Petroleum Research Fund administered by the American Chemical Society for financial support of this work.

References

1. Willis B Hammond & T.S. Yeung, Tet. Let. 0000 (1975).
2 K.W. Watkins and H.C. Moser, J. Phys. Chem., 69, 1040 (1965)
3. P J Boddy & E.W.R. Steacie, Can. J. Chem., 38, 1576 (1960).
4. M.J. Gibian & R.C. Corley, J. Am. Chem. Soc., 94, 4178 (1972).
5. J M. McBride, ibid., 93, 6302 (1971)
6. All compounds have spectra properties consistant with their assigned structures.
7. J.A. Berson, M.S. Poonian and W.J. Libbey, J. Am. Chem. Soc., 91, 5567 (1969). Diimide

reduction of 7-nornornenone produced a high yield of 7-norbornanone azine apparently by reaction of 7-norbornanone with hydrazine produced by disproportionation of diimide.

8. R.S. Bly, F. Bartow Culp, Jr., and R.I. Bly, *J. Org Chem.*, **35**, 2235 (1970).

9. W.C. Baird, Jr., B. Franzus, and J.H. Surridge, *J. Am. Chem. Soc.*, **89**, 410 (1967).

10. W.F. Gannon and H.O. House, *Org. Syn.*, **40**, 14 (1960).

11. H.A. Smith, B.J. Huff, W.J. Powers and D. Caine, *J. Org. Chem.*, **32**, 2851 (1967).

12. Sr. D. Heidrick, Masters Thesis, University of Kansas, reports that aldehyde *8* is the only product detected on irradiation of *1* ($\Phi_{ald} = 0.62$). We thank Prof. R.S. Givens for communicating this information to us. We have synthesized *8* from 3-cyclohexene-1-carboxyaldehyde and methoxymethyltriphenyl phosphonium ylid followed by treatment with dilute perchloric acid to cleave the enol ether.

13. These values are not corrected for the small amount of undeuterated material in each sample.

14. C.C. Badcock, M.J. Perona, G.O. Pritchard and B. Rickborn, *ibid.*, **91**, 543 (1969), J.D. Coyle, *J. Chem. Soc.* (*B*), 1736 (1971).

15. Using butane as a model conversion of *B1* to *B2* and interconversion of *B2* and *B3* should show activation energies of about 3 kcals per mole. The conversion of *B1* directly to *B3* goes through an eclipsed butane ($E_a \approx 5$-6 kcal/mole). The *anti*-conformer *B2* should be of lower energy than the *gauche*-conformer *B3*.

16. W. Agosta and W.L. Schrieber, *J. Am. Chem. Soc.*, **93**, 3947 (1971).

17. Substitution at the alkyl radical center should reduce the rate of recombination but have little effect on the rate of rotation from *B1* to *B2* and *B3*. This is supported by the increased quantum yield for aldehyde observed for *2* (Φ_{ald}(*2*) = 0.28, Φ_{ald}(*11*) = 0.07)

18. P.J. Wagner and R.W. Spouke, *ibid.*, **91**, 4437 (1969).