Tetrahedron Letters No.55, pp. 5795-5798, 1968. Pergamon Press. Printed in Great Britain.

DEUTERIUM ISOTOPE EFFECTS IN THE NORRISH TYPE II ELIMINATION OF A KETONE WITH MULTIPLE AVAILABLE SITES.

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(Received in USA 13 August 1968; received in UK for publication 15 October 1968)

Recent studies on the Norrish Type II photoelimination have provided considerable insight into the nature of the carbonyl excited state. (1) The present evidence suggests that abstraction of the γ-hydrogen is reversible and can occur from either the first excited singlet state or from the triplet state. (2-4) Substitution of the γ-hydrogen with deuterium is known to exert a profound effect on the photoelimination. (5-7) Coulson and Yang (7) have pointed out that the enhanced quantum yield and triplet lifetime of 2-hexanone-5,5-d_2 over 2-hexanone can be interpreted by assuming that deuterium either (a) enhances the intersystem crossing efficiency (b) causes a reduction in the rate of radiationless decay (c) retards the significant return of the biradical formed by γ-abstraction to the ground state of starting ketone. We recently reported that the differences in product distribution arising from specific deuterium substitution in the photolysis of aroylazetidines to be most satisfactorily explained by the prominent reversibility of the hydrogen abstraction step. (8) In connection with these studies we found it desirable to examine the influence of γ-deuterium substitution on the quantum efficiency and distribution of photoproducts from 5-decanone (I) and 5-decanone-2,2-d_2 (II). In this communication we describe results pertaining to deuterium isotope effects in the Norrish Type II photoelimination.

The labeled 5-decanone-2,2-d_2 was synthesized by the cuprous catalyzed addition of ethyl magnesium iodide-1,1-d_2 to 1-octen-3-one and purified for use by preparative vpc. It was assayed for >97% d_2 by mass spectral analysis. Degassed pentane solutions of I and II (0.0266 M) and various concentrations of cis-1,2-dicloroethylene were photolyzed to 6% conversion using 300 mu radiation. The progress of reaction and quantum yields of formation

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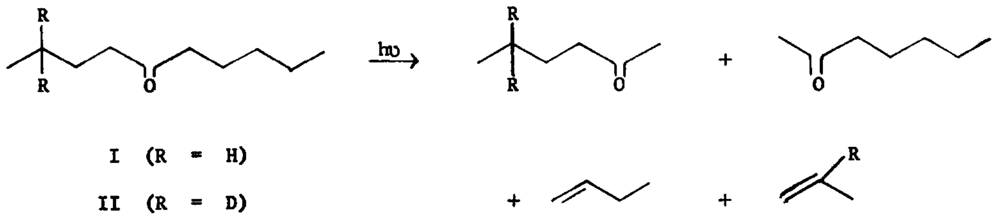
of products were followed by vpc.



I (R = H)

II (R = D)

In both cases the sum of the ketones (2-hexanone and 2-heptanone) and corresponding olefins accounted for 90% of the products. Peaks attributed to cyclobutanols also appeared in the vapor chromatograms of reaction mixtures and accounted for the remaining 10% of the reaction. A simple Stern-Volmer relationship is not followed in either system. However, by taking the quantum yield in 8 M <u>cis</u>-1,2-dichloroethylene as a measure of the amount of singlet reaction, Stern-Volmer plots for the triplet reaction can be determined. The amount of nonquenchable reaction (62% for I, 49% for II) may reasonably be attributed to reaction through the excited $n\text{-}\pi^*$ singlet state with the remainder of the photoelimination occurring through the excited $n\text{-}\pi^*$ triplet state (Table I).

TABLE I.

Quantum Yields for Appearance of 2-Hexanone and 2-Heptanone[a,b]

	2-Hexanone			2-Heptanone		
Starting Ketone	Φ_o[c]	Φ_s[d]	Φ_t	Φ_o	Φ_s	Φ_t
5-Decanone (I)	.079	.049	.030	.088	.055	.033
5-Decanone-2,2-d_2 (II)	.104	.050	.054	.024	.014	.010

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[a] $[\text{Ketone}]_o$ = 0.026 M in pentane, 300 mu

[b] Quantum yields were determined with the aid of a 2-hexanone secondary actinometer

[c] Quantum yield with no added quencher

[d] Quantum yield in 8 M <u>cis</u>-1,2-dichloroethylene, $\Phi_o - \Phi_s = \Phi_t$

The molar ratio of 2-hexanone/2-heptanone derived from I was 0.895 ± 0.02 and from II 4.45 ± 0.02. It was possible to partition the product ratio of II into that derived from the singlet state, 3.6 ± 0.2, and that from the triplet, 5.2 ± 0.2, by quenching the latter reaction with *cis*-1,2-dichloroethylene. These results verify that a γ-hydrogen is considerably more reactive than a γ-deuterium in the type II process of aliphatic ketones. (6,7) The fact that the deuterium isotope effect for the n-π^* singlet state differs from that of the n-π^* triplet implies that these configurationally related states have slightly different chemical reactivity. (9)

In contrast to the 2-hexanone system, (7) the 5-decanone system has a decreased overall quantum yield and appears to be much more of a singlet state reaction. The effects in the latter system, although similar to the former, tend to be less pronounced. It seems that the additional hydrogens available to the excited carbonyl tend to promote both product formation and internal conversion from the singlet state. While the overall quantum yield for ketone disappearance decreases with deuterium substitution, the qunatum yield from the triplet state increases slightly. This lends support to the contention that deuterium substitution enhances intersystem crossing to the more efficient triplet. From the relative ratios of the Stern-Volmer slopes the relative lifetime of the triplet state of II can be estimated to be about two times longer than that of I. The enhancement of the triplet lifetime with deuterium substitution may be caused by factors such as those involved in the deuterium-enhanced biacetyl excited state lifetime. (10)

Acknowledgement: We wish to thank the National Science Foundation (Grant GP-6511) and the Publich Health Service (Grant GM 13990-02) for generous support of this research.

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