

## The Importance of Non-minimum Energy Reactant Conformations in the Norrish Type II Reaction

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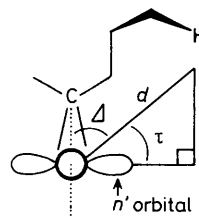
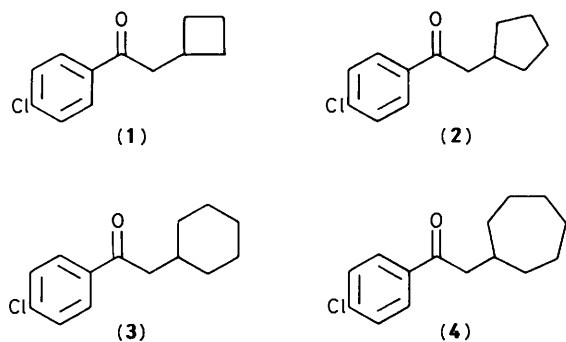
The Norrish type II  $\gamma$ -hydrogen atom abstraction rate constants in solution for the ketone homologous series (1)—(4) do not correlate with the abstraction geometries as determined by X-ray crystallography, but follow instead the well established bimolecular free radical hydrogen abstraction reactivity pattern cycloheptane > cyclopentane ~cyclohexane > cyclobutane; this is interpreted as being due to rapid hydrogen atom abstraction from non-minimum energy reactant conformations.

For Norrish type II systems in which conformational equilibrium is established prior to hydrogen abstraction, it has been suggested, equation (1), that the rate of  $\gamma$ -hydrogen atom abstraction is the sum of the rates for each favourable conformation,  $f$ , times the equilibrium percentage of mole-

cules in that conformation,  $X_f$ .<sup>1</sup> In this communication we report experimental evidence for this hypothesis.

$$k_{\text{H}}(\text{obs.}) = \sum_f X_f k_{\text{H}}(f) \quad (1)$$

If reaction were to occur predominantly from the lowest



**Figure 1.** Representation of  $d$  ( $O \cdots H$  distance),  $\tau$  (angle between  $O \cdots H$  vector and its projection on plane of carbonyl group), and  $\Delta$  ( $C-O \cdots H$  angle).

**Table 1.** Quantum yield, kinetic, and structural data for ketones (1)–(4).

Compound	$\Phi$ C <sub>6</sub> H <sub>6</sub> $\Phi$ MeCN	$k_H(\text{obs.})/$ s <sup>-1</sup>	$d/\text{\AA}$	$\tau^\circ$	$\Delta^\circ$
(1)	0.20 0.49	$0.3 \times 10^8$	3.10	22.8	100.6
(2)	0.29 0.62	$1.2 \times 10^8$	2.80	31.0	96.0
(3)	0.35 1.0	$1.2 \times 10^8$	2.60	42.0	90.1
(4)	0.25 0.76	$5.7 \times 10^8$	2.71	41.8	82.4

energy conformational isomer of a given molecule,  $X_f$  should approach unity and  $k_H(\text{obs.})$  would reflect the intrinsic reactivity of that conformer; intrinsic reactivity depends in turn on the distance and angular relationship between the  $\gamma$ -hydrogen and the carbonyl oxygen. The rate of hydrogen abstraction is expected to decrease as the distance  $d$  increases and as the angles  $\tau$  and  $\Delta$  (*cf.* Figure 1) deviate from their optimum values of  $0^\circ$  and  $90^\circ$ , respectively.<sup>2</sup> Previous work from our laboratory<sup>2,3</sup> has suggested an approximate upper limit for  $d$  of 2.7 Å, the sum of the van der Waals radii for oxygen and hydrogen.

It is well established that, with few exceptions, organic molecules crystallize in their lowest energy conformations.<sup>4</sup> Thus, using *X*-ray crystallography, the values of  $d$ ,  $\tau$ , and  $\Delta$  characteristic of the most stable conformational isomers of a series of homologous ketones can be determined. By comparing these structural data with the values of  $k_H(\text{obs.})$  measured in solution for each of the ketones, and recalling that the  $n \rightarrow \pi^*$  excited state geometry of conjugated ketones is not significantly different from the ground state geometry,<sup>2</sup> the presence or absence of a structure–reactivity relationship can be ascertained. In this communication we report the absence of such a correlation for the ketones (1)–(4) (Table 1); we interpret this as indicating reaction from non-minimum energy conformations with geometries which are more favourable for the type II process than the minimum energy conformers.

The ketones (1)–(4) were synthesized by conventional procedures† and their crystal and molecular structures deter-

mined by direct method *X*-ray diffraction studies.‡ Table 1 gives the values of  $d$ ,  $\tau$ , and  $\Delta$  for each of the ketones; the values listed are those for the  $\gamma$ -hydrogen closest to the carbonyl oxygen atom.

Concomitant with the crystallographic studies, the type II quantum yields in benzene as well as 2% water–acetonitrile solution were determined for each ketone. Stern–Volmer quenching studies in benzene using 2,5-dimethylhexa-2,4-diene as the triplet energy quencher gave excellent straight line plots from which the values of  $k_H(\text{obs.})$  (assumed to be the inverse of the triplet lifetime) were calculated. The quantum yield and kinetic data are summarized in Table 1.

The data in Table 1 reveal no obvious relationship between  $k_H(\text{obs.})$  and  $d$ ,  $\tau$ , or  $\Delta$ . For example, ketones (2) and (3) have identical hydrogen abstraction rate constants but have structural parameters which differ markedly. Ketone (1), which has the longest  $\gamma$ -hydrogen–oxygen contact at 3.10 Å, still has a hydrogen abstraction rate constant which is the same as that for *p*-chlorovalerophenone ( $0.3 \times 10^8$  s<sup>-1</sup>).<sup>7§</sup> Ketone (4) reacts nearly five times as rapidly as ketone (3), but has considerably less favourable geometric parameters. We thus conclude that a substantial portion of the  $\gamma$ -hydrogen atom abstraction in these systems, particularly ketones (1) and (2), occurs from higher energy conformational isomers with more favourable abstraction geometries. Preliminary calculations reveal that rotation about the  $\alpha, \beta$  carbon–carbon bond is most efficacious in reducing  $d$  and improving  $\tau$  and  $\Delta$ . Ring inversions and rotation around the carbonyl carbon to  $\alpha$ -carbon bond have smaller effects.

‡ Ketone (1): m.p. 50–51 °C, monoclinic, space group *C2/c*,  $a = 26.403(9)$ ,  $b = 10.903(4)$ ,  $c = 7.800(2)$  Å,  $\beta = 103.94(2)^\circ$ ,  $Z = 8$ ,  $R = 0.035$  for 727 reflections with  $I \geq 3\sigma(I)$ ; ketone (2): m.p. 60–61 °C, monoclinic, space group *P2<sub>1</sub>/a*,  $a = 7.936(2)$ ,  $b = 10.741(3)$ ,  $c = 14.001(4)$  Å,  $\beta = 101.52^\circ$ ,  $Z = 4$ ,  $R = 0.061$  for 1342 reflections with  $F \geq 3\sigma(F)$ ; ketone (3): m.p. 63–64 °C, monoclinic, space group *P2<sub>1</sub>/a*,  $a = 7.944(1)$ ,  $b = 10.789(1)$ ,  $c = 14.898(2)$  Å,  $\beta = 95.81(1)^\circ$ ,  $Z = 4$ ,  $R = 0.053$  for 1749 reflections with  $F \geq 3\sigma(F)$ ; ketone (4): m.p. 42–43 °C, monoclinic, space group *P2<sub>1</sub>/a*,  $a = 8.085(3)$ ,  $b = 10.916(3)$ ,  $c = 15.280(5)$  Å,  $\beta = 92.18(2)^\circ$ ,  $Z = 4$ ,  $R = 0.044$  for 1019 reflections with  $I \geq 3\sigma(I)$ .

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The finding that ketone (1) and *p*-chlorovalerophenone have identical hydrogen abstraction rate constants can be attributed to offsetting entropy and radical stability effects. Lewis, Johnson, and Kory<sup>8</sup> have shown that as the number of freely rotating bonds between the carbonyl carbon and the  $\gamma$ -carbon is reduced,  $k_H(\text{obs.})$  increases by a factor of 5 to 10. This effect should be constant throughout the series (1)–(4). The relative reactivity of these ketones [(4) > (3) = (2) > (1)] is in the same order as the relative rate of free radical bimolecular hydrogen atom abstraction from the cycloalkane homologous series (cycloheptane > cyclopentane ~ cyclohexane > cyclobutane), attributed to I-strain effects.<sup>9</sup>

† Compounds (1)–(4) gave satisfactory elemental analyses and exhibited spectra completely in accord with their assigned structures.

In summary,  $\gamma$ -hydrogen atom abstraction in the case of ketones (1)—(4) in solution appears to occur through a number of rotational isomers, each possessing a unique hydrogen abstraction rate constant. This results in a composite  $k_{\text{H}}(\text{obs.})$  which is larger than that expected on the basis of the abstraction geometry present in the lowest energy conformer. Because bond rotations are eliminated in the solid state, we are engaged currently in trying to correlate the crystalline phase reactivity of ketones (1)—(4) with the structural data.

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