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Further studies on Norrish type II reactions including a reaction in the first excited singlet state and cyclization of 1:4 biradicals

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Abstract

The Norrish type II processes of methyl-2,2-dimethyl- cyclopropyl ketone, α-alkoxy acetones and alkyl pyruvates have been examined using the AM1 semi-empirical molecular orbital method with complete geometry optimization at the partial configuration interaction level in the restricted Hartree–Fock (RHF) frame. The results reveal that the methyl-substituted cyclopropyl ketone has a constrained geometry favourable for hydrogen abstraction from the γ-position relative to the carbonyl group in the excited singlet state. The presence of the ether oxygen atom in the β-position relative to the carbonyl group in alkoxy acetones and alkyl pyruvates leads to increased reactivity relative to alkyl monoketones and diketones respectively. The cyclization of 1:4 biradicals has been studied in the unrestricted Hartree–Fock (UHF) frame, and the results reveal that the 1:4 biradical derived from alkoxy acetones readily cyclizes to form oxetanols. On the other hand, in the 1:4 biradicals derived from methyl-substituted cyclopropyl ketone, the three-membered ring breaks readily to form an enol intermediate. Delocalization of an odd electron in 1:4 biradicals derived from alkyl pyruvates is thought to make cyclization difficult.

Keywords: Norrish type II reactions; Excited singlet state; Cyclization; 1:4 biradicals

1. Introduction

Recently [1,2], we have reported an investigation of the intramolecular γ-hydrogen abstraction (Norrish type II) process in photoexcited alkyl ketones and diketones in their lowest (n,π*) triplet states. In order to achieve hydrogen abstraction, the abstractable hydrogen atom must approach the oxygen atom of the carbonyl group to form a six-membered ring [3]. Scheffer [4] has reported several examples of ketones that undergo efficient intramolecular γ-hydrogen abstraction in the crystalline phase. He suggested that, since the sum of the H and O van der Waals' radii is 2.7 Å, unless the abstractable hydrogen atom approaches to within 2.7 Å of the carbonyl oxygen, reaction cannot occur. Several ketones with separation distances between the H and O atoms of more than 2.7 Å are found to be unreactive [5]. We have observed that, in both systems, the Norrish type II process involves two steps [1,2]. In the first step, the abstractable hydrogen atom is brought close to the carbonyl oxygen (within 2.7 Å) by internal rotation around the β-bond relative to the carbonyl group. This requires a barrier Δ_1 from the equilibrium conformation ($\alpha \approx 180°$, $\beta \approx 180°$, $\gamma \approx 180°$) where α, β and γ are the dihedral angles shown in Fig. 1. Once this reactive conformation is reached, a further barrier Δ_2 is required in the second step to transfer the abstractable hydrogen atom to the carbonyl oxygen of the keto group. Thus the rate constant of the entire process is monitored by $\Delta E^{\ddagger} = \Delta_1 + \Delta_2$ (in our previous papers [1,2], we used the symbol $\Delta G^{\ddagger}$ which is not strictly correct).

If, however, we choose a ketone with a constrained geometry by substitution of a cyclopropane ring adjacent to the carbonyl group (as in methyl-2,2-dimethyl-cyclopropyl ketone (see Fig. 1)), no effort is needed to bring the abstractable hydrogen atom close to the oxygen atom. In such systems, the Norrish type II process can occur more readily than in the ketones with unconstrained side-chains. Marsh et al. [6] studied the photolysis of several cyclopropyl ketones in the vapour phase and observed that the Norrish type II process occurs in methyl-2,2-dimethyl-cyclopropyl ketone presumably in its first excited singlet (n,π*) state. One of our objectives is to study the Norrish type II reaction

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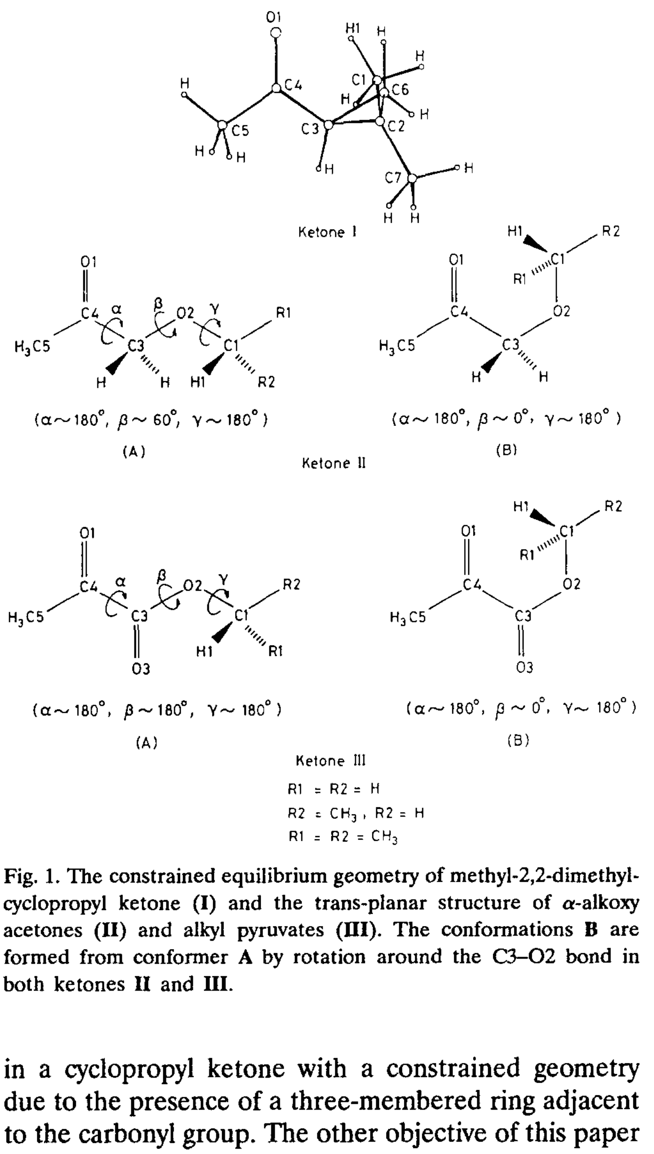


Fig. 1. The constrained equilibrium geometry of methyl-2,2-dimethylcyclopropyl ketone (I) and the trans-planar structure of α-alkoxy acetones (II) and alkyl pyruvates (III). The conformations **B** are formed from conformer **A** by rotation around the C3–O2 bond in both ketones **II** and **III**.

in a cyclopropyl ketone with a constrained geometry due to the presence of a three-membered ring adjacent to the carbonyl group. The other objective of this paper is to examine the type II process in α-alkoxy acetones and alkyl pyruvates. Lewis and Turro [7] observed that the presence of a β-oxygen atom in alkoxy ketones has a strong rate-enhancing effect, while Davidson and Goodwin [8] reported that photofragmentation of alkyl pyruvates takes place via a type II process in the lowest triplet state. We compare the reactivities of α-alkoxy ketones with those of the corresponding alkyl ketones with a view to obtaining an understanding of how an alkoxy group leads to enhanced rate constants in both alkoxy monoketones and alkoxy diketones relative to the corresponding alkyl monoketones and diketones respectively. The Norrish type II reactions generate 1:4 biradicals as intermediates which cyclize to oxetanols from alkoxy ketones [7]. However, there is no evidence of cyclization of the 1:4 biradicals derived from alkyl pyruvates [8]. All of these reactions depend strongly on the electronic structure. Absorption and emission spectroscopy [9] of alkyl pyruvate esters reveals that the dicarbonyl moiety possesses a trans-planar geometry in the lowest triplet state. In order to obtain more detailed information on the electronic structures of alkoxy ketones in their lowest triplet states and the biradicals, we employed the AM1 semi-empirical SCF molecular orbital (MO) method [10] with geometry optimization in both the restricted and unrestricted Hartree–Fock (RHF and UHF) frames.

2. Computational method

Methyl-2,2-dimethyl-cyclopropyl ketone (**I**), α-alkoxy acetones (**II**) and alkyl pyruvates (**III**) are shown in Fig. 1 where the atoms in the main chain are numbered. The oxygens of the two keto groups in diketone are numbered as O1 and O3, while the abstractable hydrogen is always identified as H1 in all ketones. Ketones **II** and **III** can exist in a number of conformations defined by the dihedral angles α, β and γ as shown in Fig. 1. Ketone **I** has a constrained geometry due to the presence of a three-membered ring, with H1 (the abstractable hydrogen) within 2.2 Å from the oxygen O1 in both the ground and the lowest excited $^{1,3}(n,\pi^*)$ states. We performed the semi-empirical SCF MO calculations of the lowest excited $^1(n,\pi^*)$ state for ketone **I** and the lowest excited $^3(n,\pi^*)$ states of ketones **II** and **III** using the AM1 method. Calculations were performed in the RHF frame with configuration interaction (CI) using the program MOPAC (Version 4) [11]. The option CI = 5 was used. Ths means that we have considered all possible configurations arising from excitations from three highest occupied and two lowest unoccupied molecular orbitals. Geometry optimizations for the reactant structures were carried out at the CI level.

The transition state structures for the γ-hydrogen abstraction reaction were also optimized at the CI level using Bartel's method [11] and characterized by only one negative eigenvalue of the force constant matrix. After the transition state structures had been obtained, the O1–H1 distance (see Fig. 1) was reduced and the Broyden–Fletcher–Golgfarb–Shanno [12] optimization process was carried out until a 1:4 biradical was obtained. This was identified by two highest singly occupied MOs which were almost localized on carbons 1 and 4 in the ketones. We found that the singlet and triplet 1:4 biradicals had similar energies and their final optimized structures were similar for a given ketone. For cyclization of the 1:4 biradicals to give stable biradicals, the AM1 method in the UHF frame [10] was used.

3. Results

Our calculations reveal that ketone **I** has a similar conformation in the lowest (n,π*) singlet and triplet states. Both of these states have a favourable conformation for hydrogen abstraction. On the other hand, the preferred conformations of ketones **II** and **III** have the structures defined by $\alpha \approx 180°$, $\beta \approx 60°$, $\gamma \approx 180°$ and $\alpha \approx 180°$, $\beta \approx 180°$, $\gamma \approx 180°$ respectively (Fig. 1). They are denoted as conformers **A** in Fig. 1. In these conformations, the distance between the carbonyl oxygen O1 and the abstractable hydrogen H1 is nearly 4.0 Å, i.e. much greater than the sum of the van der Waals' radii (2.7 Å) of hydrogen and oxygen. For such a separation, hydrogen abstraction is not possible. In order to bring the hydrogen H1 closer to O1, rotation around the β-bond (see Fig. 1) is necessary to reach the favourable conformation where the O1–H1 distance is within 2.3 Å. The energy of this favourable conformer, called conformer **B**, is higher than that of the stable conformer in the lowest triplet state.

Fig. 2 shows the position of the adiabatic (S_A) and vertical (S_V) singlet (n,π^*) excited states of ketone **I**, the transition state for the hydrogen transfer process, the 1:4 biradical and the enol form. The detailed optimized structures are also shown in Fig. 2. Fig. 3 shows the variation with β of the energies relative to the most stable conformer (**A**) in the lowest (n,π^*) triplet state of α-methoxy acetone (i.e. ketone **II**) containing a primary C–H bond in a position γ to the keto group. The conformer **B** ($\alpha \approx 180°$, $\beta \approx 0°$), which is a relevant structure for the hydrogen transfer process, is on the rising part of the potential energy curve and therefore not in equilibrium with conformer **A**. Similar results were obtained for α-alkoxy acetones containing secondary and tertiary C–H bonds in a position γ to the keto group. Using conformer **B** as the reactant, the Norrish type II process was studied with the O1–H1 distance as the reaction coordinate. Calculations were carried out using the AM1 method with CI as outlined in Section 2 for each value of the O1–H1 distance with optimization of all the remaining geometrical parameters in the system. As the O1–H1 distance is decreased to the saddle point, the C4–O1 and C1–H1 distances increase. The saddle point is identified by its force constant matrix with only one negative eigenvalue. Normal coordinate analysis of the transition state structure reveals (corresponding to an imaginary frequency) an asymmetric stretch of the non-linear C1–H1–O1

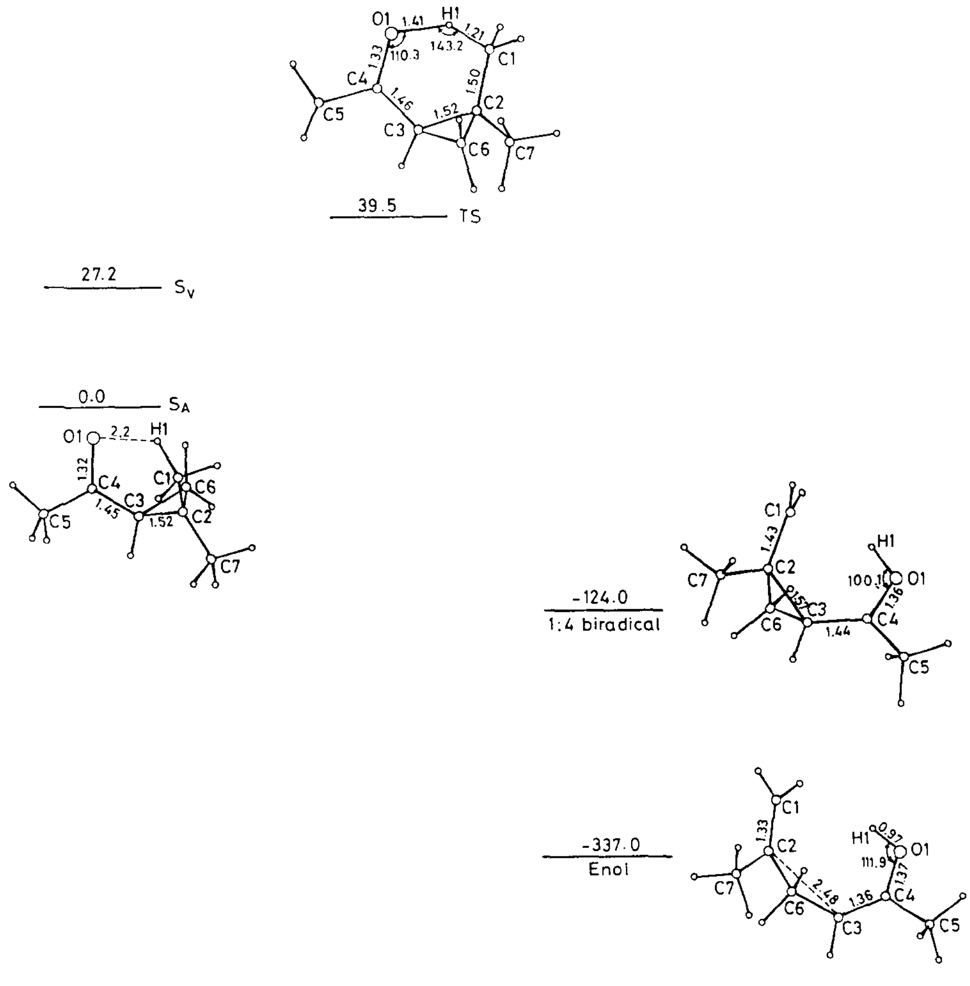


Fig. 2. Energies in kilojoules per mole (relative to S_A) and structures of ketone I, the transition state (TS) for hydrogen abstraction, the 1:4 biradical and the enol intermediate on the first excited singlet surface of ketone I. The bond lengths (Å) and bond angles (°) are also given.

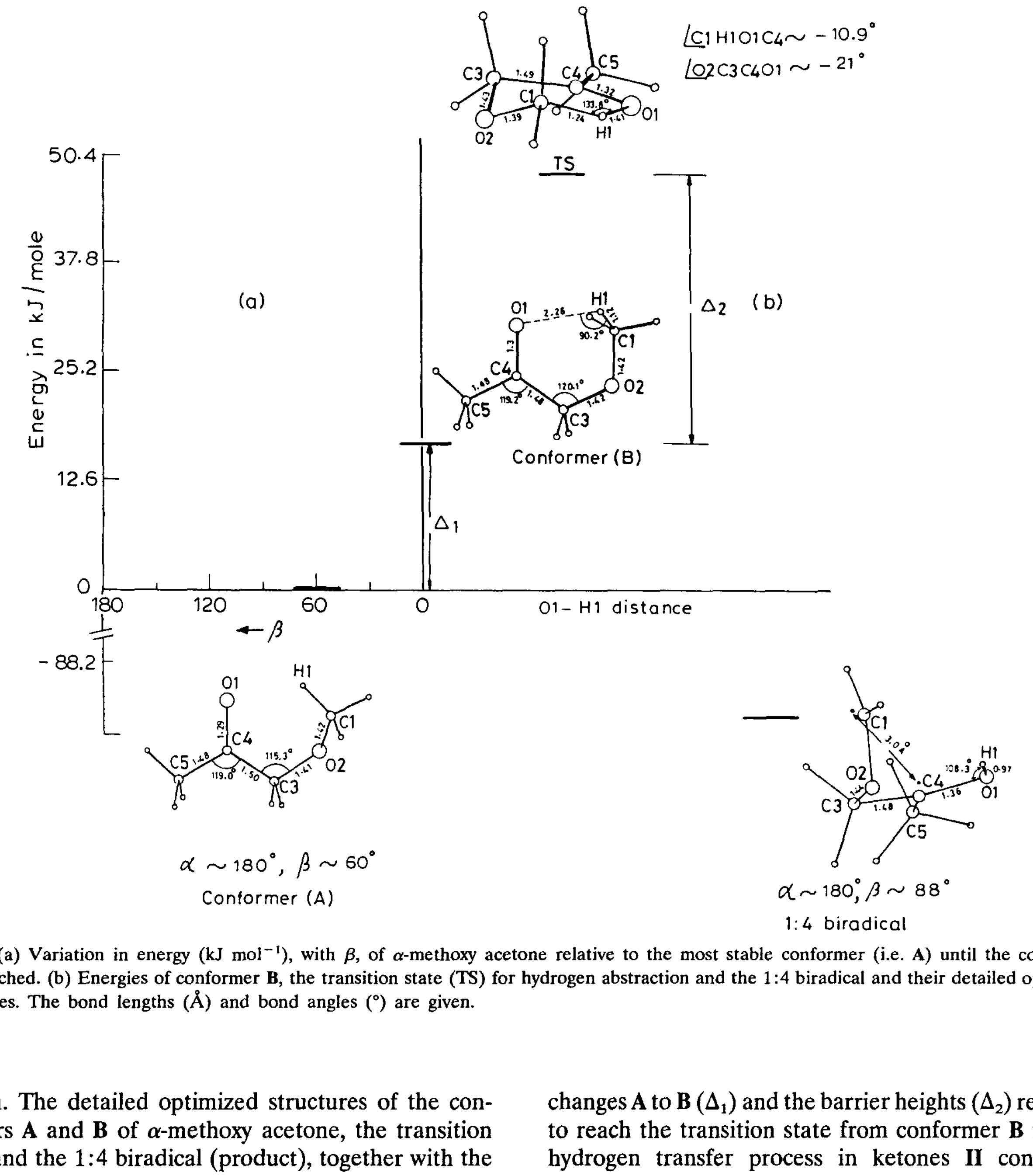


Fig. 3. (a) Variation in energy (kJ mol^{-1}), with β, of α-methoxy acetone relative to the most stable conformer (i.e. **A**) until the conformer **B** is reached. (b) Energies of conformer **B**, the transition state (TS) for hydrogen abstraction and the 1:4 biradical and their detailed optimized structures. The bond lengths (Å) and bond angles (°) are given.

system. The detailed optimized structures of the conformers **A** and **B** of α-methoxy acetone, the transition state and the 1:4 biradical (product), together with the energies relative to that of conformer **A**, are shown in Fig. 3. Table 1 gives the barriers to the conformational changes **A** to **B** (Δ_1) and the barrier heights (Δ_2) required to reach the transition state from conformer **B** for the hydrogen transfer process in ketones **II** containing primary, secondary and tertiary C–H bonds in positions γ to the keto group. Table 1 also lists the magnitudes of ΔH (heat of reaction) for these three alkoxy acetones.

Table 1

Heats of reaction (ΔH), barrier heights for the conformational changes (Δ_1) and the γ-hydrogen abstraction processes ($\Delta 2$) in the lowest triplet states and total free energies of activation ($\Delta E^{\ddagger}$) for α-alkoxy acetones containing primary, secondary and tertiary C–H bonds in γ-positions. Energies are in kilojoules per mole

Bond	ΔH	Δ_1 A→B	Δ_2 B→TS	$\Delta E^{\ddagger}$
Primary	−95	16.6	31.9	48.5
Secondary	−110	20.0	20.0	40.0
Tertiary	−129	20.0	15.0	35.0

For alkyl pyruvates, i.e. ketone **III**, the situation is different. The preferred conformation is conformer **A** (Fig. 1) in the lowest triplet (n,π^*) state; however, variation with β of the energies relative to the stable conformer **A** reveals that conformer **B**, which is the relevant structure for the hydrogen transfer process, also lies on a minimum point on the potential energy surface (Fig. 4). Conformer **B** is therefore in thermodynamic equilibrium with conformer **A**. Similar results were also obtained for other alkoxy diketones containing secondary and tertiary C–H bonds in positions γ to the first keto group (i.e. C1–O1). Using

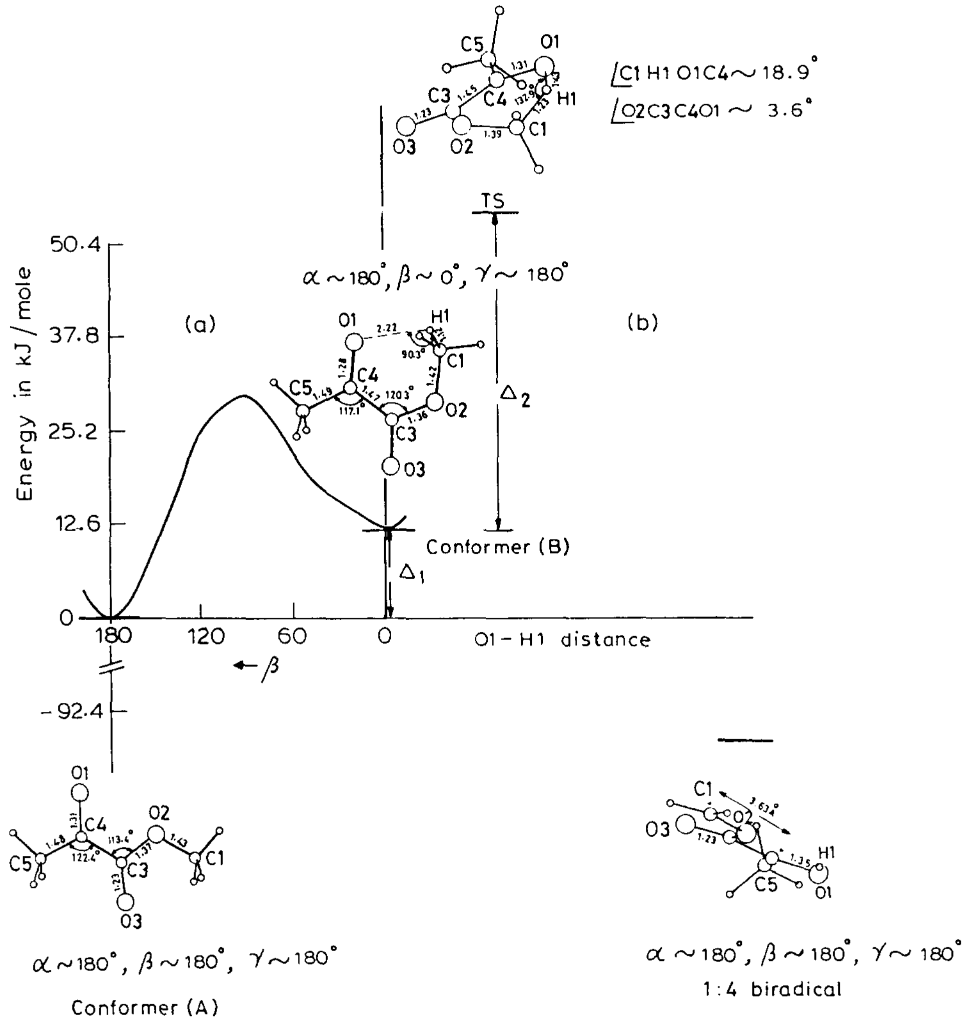


Fig. 4. (a) Variation in energy (in kJ mol^{-1}), with β, of methyl pyruvate relative to the most stable conformer (i.e. A) until the conformer B is reached. (b) Energies of conformer B, the transition state (TS) for hydrogen abstraction and the 1:4 biradical and their detailed optimized structures. The bond lengths (Å) and bond angles (°) are given.

conformer **B** as the reactant, the Norrish type II process was studied with the O1–H1 distance as the reaction coordinate. A further barrier (Δ_2) exists to reach the saddle point. The detailed optimized structures of conformers **A** and **B** of the methyl ester of pyruvic acid, the transition state and the 1:4 biradical (product), together with their energies relative to that of conformer **A**, are shown in Fig. 4. Table 2 gives the magnitude of ΔH and the energy changes involved in the transformations **A**→**B** and **B**→transition state (TS) for the hydrogen transfer process in methyl, ethyl and isopropyl esters of pyruvic acid which contain primary, secondary and tertiary C–H bonds respectively in positions γ to the first keto group. The optimized structures of the transition states of all the ketones studied in this paper reveal slightly puckered six-membered rings with the abstractable hydrogen above the nodal plane of the π electrons of the carbonyl group.

Let us consider the cyclization process of the 1:4 biradicals. The 1:4 biradical derived from ketone **I** has the optimized structure shown in Fig. 2. This biradical is unstable because its C2–C3 bond breaks without any barrier and it is transformed into an enol intermediate whose optimized structure is also shown in Fig. 2. The cyclization process of the 1:4 biradical derived from

Table 2
Heats of reaction (ΔH), energy differences (Δ_1) between the two conformers A and B, barrier height for the γ-hydrogen abstraction processes (Δ_2) in the lowest triplet states and total free energies of activation ($\Delta E^{\ddagger}$) for alkyl pyruvates containing primary, secondary and tertiary C–H bonds in the γ-position with respect to the first keto group (see Fig. 1). Energies are in kilojoules per mode

Bond	ΔH	Δ_1[a] A→B	Δ_2 B→TS	$\Delta E^{\ddagger}$
Primary	−96	12.0	42.0	54.0
Secondary	−106	16.0	34.0	50.0
Tertiary	−122	15.0	29.5	45.0

[a] The barrier heights for this process are higher as shown in Fig. 3.

ketone **II** was studied with the C4–C1 distance as the reaction coordinate on the singlet surface, while optimizing the remaining geometrical parameters using the AM1 method in the UHF frame. Cyclization processes, with their potential for ring strain, steric crowding and a loss of rotational entropy, are expected to produce barriers on the singlet surface. Fig. 5 shows how the energies and structures of the singlet state of the 1:4 biradical derived from α-methoxy acetone change during the cyclization process. The height of the barrier for the cyclization process is estimated to be 53 kJ mol^{-1}. The optimized structures of the transition state and 3-oxetanol (product) reveal that they are almost planar four-membered rings.

The cyclization process of the singlet 1:4 biradical derived from ketone **III** is difficult because of its extended equilibrium structure (see Fig. 4, $\alpha \approx 180°$, $\beta \approx 180°$ and $\gamma \approx 180°$) where the distance of separation between the two radical sites exceeds 3.5 Å. The calculated cyclization barrier is high (72 kJ mol^{-1}). Experimental studies [8] have provided no evidence of cyclization, but reveal that alkyl pyruvates fragment from the triplet state via a type II process.

Table 3 shows the free valence indices on the oxygen atoms of the keto groups (RHF CI method) and on the radical sites of the 1:4 biradicals derived from ketones **I**, **II** and **III** (UHF method). The methods of calculation of the free valence and bond order indices for the optimized structures have been discussed previously [1,2].

4. Discussion

4.1. Barriers to hydrogen abstraction in methyl-2,2-dimethyl-cyclopropyl ketone

The equilibrium conformation of this ketone in its singlet (n,π*) state is favourable for hydrogen abstraction. No conformational change is required. However, a barrier exists for the abstraction of a hydrogen atom by the carbonyl group from one methyl in gem-dimethyl-substituted cyclopropyl ketone. The calculated barrier from S_A is 37 kJ mol^{-1}, but from S_V it is only 12 kJ mol^{-1} (Fig. 2). This means that the reaction could be fast enough from S_V to compete with the relaxation process. Owing to the relatively short lifetime of S_V, the real time determination of the rate constants requires the development of experimental techniques with a fast time resolution. However, Marsh et al. [6], who studied the photolysis of several cyclopropyl ketones, including ketone **I**, suggest that the Norrish type II process for ketone **I** proceeds in the first excited singlet state. Our results show that hydrogen transfer reactions may be very rapid in the singlet excited state. A similar rapid decomposition of acetyl chloride from its S_V (n,π*) state has been reported recently [13]. However, most Norrish type II processes take place in the lowest triplet state and are slow. Large overall barriers in Norrish type II reactions arise from the barriers to conformational change. Ketone **I** exhibits a very rapid Norrish type II reaction in its singlet excited state as no conformational change is required, and reinforces our earlier assertion [1,2] that the barriers to conformational

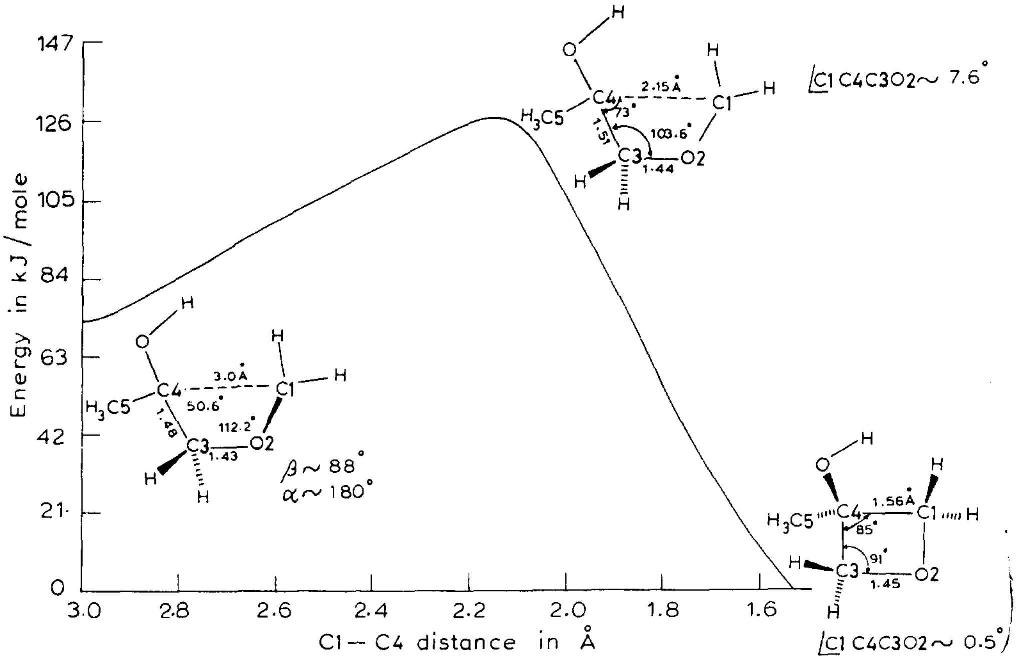


Fig. 5. Energy changes (in kJ mol^{-1}) vs. the C1–C4 distance (Å) during cyclization of the 1:4 biradical derived from α-methoxy acetone on the singlet surface.

Table 3
Free valence indices on the carbonyl oxygen atoms in ketones **I**, **II** and **III** and of the 1:4 biradicals at the C1 and C4 atoms. Ketones **II** and **III** contain primary, secondary and tertiary C–H bonds in the γ-positions (see Fig. 1)

Atom	Ketone **I** (n,π^*)	Ketone **II** $^3(n,\pi^*)$			Ketone **III** $^3(n,\pi^*)$		
O1	9.90	0.85			0.69		
O2	–	–			0.26		
		Primary	Secondary	Tertiary	Primary	Secondary	Tertiary
C1	0.76	0.77	0.72	0.67	0.80	0.75	0.69
C4	0.61	0.65	0.65	0.64	0.52	0.52	0.51

change play an important role in triplet reactions where the process is relatively slow.

4.2. Barrier to hydrogen abstraction via conformational change in α-alkoxy acetones (i.e. ketone II)

In the equilibrium conformation of ketone **II** (i.e. conformer **A**) in its triplet (n,π^*) state, the distance between the abstractable hydrogen H1 and the carbonyl oxygen O1 is about 4.0 Å. In a first step, ketone **II** achieves the favourable conformation (conformer **B**) by internal rotation from the stable conformer **A**. Fig. 3 shows that conformer **A** is not in equilibrium with conformer **B**. In a second step, H1 is brought closer to O1 to form a slightly puckered six-membered ring in the transition state. The results in Table 1 show that $\Delta E^{\ddagger}$ decreases as the C–H bond containing the abstractable hydrogen changes: primary > secondary > tertiary. These results reveal that hydrogen abstraction is easier from a tertiary C–H bond than from a secondary C–H bond which, in turn, is easier than from a primary C–H bond. The exothermic nature of the hydrogen transfer reactions increases in the order: primary < secondary < tertiary. This reflects the fact that the strength of the C–H bond containing the abstractable hydrogen atom decreases from a primary to a tertiary C–H bond via a secondary C–H bond in alkoxy ketones.

If we compare our AM1 results for α-methoxy acetone (Table 1) with those of pentane-2-one [2], we observe that the ΔE values are lower and the ΔH values (heat of reaction) are higher for α-methoxy acetone, suggesting increased rate constants in α-alkoxy acetones. This observation is in agreement with the experimental studies of Lewis and Turro [7]. If we compare the free valence indices on the carbonyl oxygen in the lowest triplet states of α-methoxy acetone (Table 3) and pentane-2-one (Table 2, Ref. [2]), we find that the values are 0.85 and 0.87 respectively, i.e. nearly the same. Thus the ether oxygen in the β-position has no activating influence on the carbonyl oxygen for hydrogen abstraction. The increased rate constants of α-alkoxy acetones relative to aliphatic ketones may be due to a decrease in the bond dissociation energy of C–H homolysis in ethers relative to alkanes. Our RHF CI calculations in the AM1 frame show that C–H homolysis in aliphatic ethers requires about 12–15 kJ mol^{-1} of energy less than in the corresponding alkanes. Thermochemical studies of ethers and alkanes by Benson [14] also support this observation. The decrease in the C–H bond energy in ethers may be explained by the fact that the back lobe of the σ^* orbital of the C–H bond overlaps with one of the two lone pair orbitals on the ether oxygen (Fig. 6) leading to a flow of electrons to the antibonding σ^* orbital of the C–H bond. This should cause a decrease in the C–H bond order of the bond containing the abstractable hydrogen. In agreement with this argument, our RHF CI calculations reveal a slightly lower bond order of the C–H bond in the γ-position in ketone **II** relative to pentane 2-one.

4.3. Barriers to hydrogen abstraction via conformational changes in alkyl pyruvates (i.e. ketone III)

As in α-alkoxy acetones, the γ-hydrogen abstraction in alkyl esters of pyruvic acids (ketones **III**) in the lowest $^3(n,\pi^*)$ state involves a conformational change from the stable form **A** to **B** (see Fig. 4). Unlike ketones **II**, conformer **B** of alkyl pyruvates containing primary, secondary and tertiary C–H bonds is stable and in equilibrium with the corresponding conformer **A** on the triplet surface. In a second step, the abstractable hydrogen atom is brought close to the oxygen atom to form a puckered six-membered ring in the transition state, which then forms a 1:4 biradical as shown in

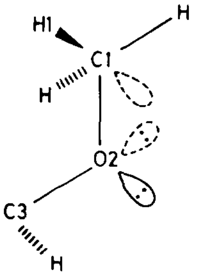


Fig. 6. Overlap of the back lobe of the σ^* orbital of the C1–H1 bond with one of the oxygen lone pair orbitals in ether.

Fig. 4. The kinetic scheme can be written as

$$\mathbf{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{B} \xrightarrow{k_2} 1{:}4 \text{ biradical} \qquad (1)$$

where k_1 and k_{-1} are the rate constants for the transformation from conformer **A** to conformer **B** and the reverse process respectively and k_2 is the rate constant for the formation of the 1:4 biradical from **B**. Using the steady state approximation, the rate constant k_H of the hydrogen abstraction process is given by

$$k_H = (k_1 k_2)/(k_{-1} + k_2) \qquad (2)$$

Since the barrier for the reverse transformation process, i.e. $\mathbf{B} \rightarrow \mathbf{A}$, is about 25 kJ mol^{-1} lower than that for the process $\mathbf{B} \rightarrow 1{:}4$ biradical (see Fig. 4), we expect $k_{-1} > k_2$ and obtain

$$k_H = (k_1 k_2)/k_{-1} \qquad (3)$$

If we assume that the pre-exponential factors for the transformation processes $\mathbf{A} \rightarrow \mathbf{B}$ and $\mathbf{B} \rightarrow \mathbf{A}$ are the same, k_H is given by

$$k_H = A \exp\{-(\Delta_1 + \Delta_2)/RT\} \qquad (4)$$

where A is the pre-exponential factor for the process $\mathbf{B} \rightarrow 1{:}4$ biradical. The meaning of Δ_1 and Δ_2 is indicated in Fig. 4 and their estimated values are given in Table 2, where $\Delta E^{\ddagger} = \Delta_1 + \Delta_2$. Table 2 reveals that the values of $\Delta E^{\ddagger}$ change very little on going from a primary C–H bond to a tertiary C–H bond in alkyl pyruvates. Since the overall barriers for the hydrogen abstraction process in alkyl pyruvates are less than in α-diketones and the exothermic values are greater, the rate is enhanced strongly in alkoxy diketones relative to diketones. Our estimated ratio k_H(alkyl pyruvates)/k_H(α-diketones) $\approx 2.9 \times 10^3$ for the primary hydrogen [15] compares favourably with the observed ratio of 4.8×10^3 at 300 K [8]. However, our results predict a small difference in selectivity for primary vs. secondary vs. tertiary abstraction in alkyl pyruvates relative to that in α-diketones. Our results cannot be compared with the experimental observations of Davidson and Goodwin [8], who measured the rate constants in highly polar solvents which can lead to an increase in the (π,π*) character of the lowest triplet state of alkoxy diketones resulting in a reduced reactivity. The estimated imaginary frequencies at the saddle point lie in the range 1000–1680 cm^{-1} for the hydrogen transfer reactions. The tunnelling corrections according to Wigner's method [16], which is applicable to any form of potential energy curve, are in the range 2–3 at 300 K. Later studies [17] confirmed the validity of Wigner's correction. This quantum correction does not modify our conclusions regarding the hydrogen transfer reactions in α-alkoxy acetones and alkyl pyruvates.

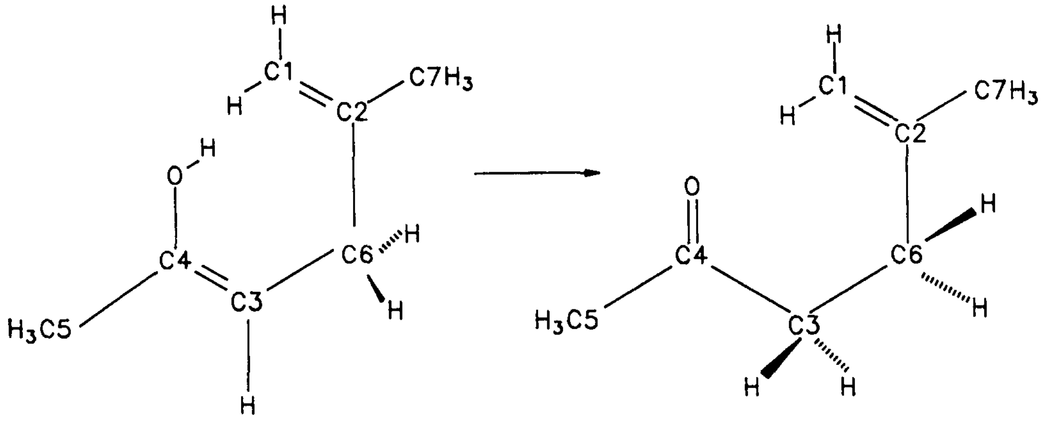
4.4. *Free valence index and reactivity*

The calculated free valence indices on the oxygen atoms of the active carbonyl groups in ketones **I**, **II** and **III** are given in their (n,π*) states in Table 3. They were obtained by the RHF method with CI [2]. The results in Table 3 clearly reveal that the radical-like reactivity is more prominent in monoketones than in diketones. The ether oxygen in ketone **III** has a large deactivating influence on the second keto group. Therefore the second keto group in alkyl pyruvates cannot abstract a hydrogen atom in the lowest triplet state. It should be noted that, in all ketones, the singlet and triplet (n,π*) states have nearly the same free valence indices on the active oxygen of the carbonyl group. The increased activities of ketones **II** and **III**, relative to alkyl monoketones and diketones respectively, towards γ-hydrogen abstraction are due to the decreased bond energy of the C–H bond containing the abstractable hydrogen atom in the γ-position, and not to the increased radical-like property of the carbonyl oxygen.

Tables 1 and 2 show that the exothermic nature and its variation in the hydrogen abstraction process on going from primary to tertiary abstractable hydrogen atoms are similar in α-alkoxy acetones and alkyl pyruvates. This reflects the fact that the strength of the C–H bond containing an abstractable hydrogen atom decreases in the same manner from a primary to a secondary to a tertiary C–H bond in both ketones. The observed decrease in the rate constant of the hydrogen abstraction reaction of alkyl pyruvates (approximately 10^7 s), i.e. ketone **III**, relative to that of α-alkoxy acetones (approximately 10^9 s), i.e. ketone **II**, is due to the overall decrease in the free valence on the carbonyl oxygen in ketone **III** (see Table 3).

4.5. *Cyclization of 1:4 biradicals*

The cyclization of the 1:4 biradical derived from ketone **I** is not observed because of the rapid cleavage of the C2–C3 bond of the cyclopropyl ring. Rice and Teller [18] and Davis and Noyes [19] suggested that a six-membered ring transition state is formed during hydrogen abstraction followed by the formation of an enol intermediate. The optimized structure of the enol intermediate is illustrated in Fig. 2, which shows that the C1–C2 and C4–C3 bond lengths are equal to 1.34 Å, which is close to that of a normal C=C double bond, whereas the C2–C3 separation is increased from 1.57 Å in the intermediate biradical to 2.48 Å in the enol form. Marsh et al. [6] suggested that this enol form isomerizes to 5-methyl-5-hexen-4-one (Scheme 1) which is the final observed product of the photolysis of ketone **I**. Since the enol intermediate is stable, our calculations reveal the presence of a vibrational frequency near 3525 cm^{-1} which can be attributed to the



Scheme 1.

hydroxyl stretch. This theoretical finding is in agreement with the observed 3535 cm^{-1} absorption in a long path length IR cell during the photolysis of ketone **I** [6].

The cyclization process is observed in α-alkoxy acetophenones leading to the formation of 3-oxetanols [7]. Experimental results have not been reported for α-alkoxy acetones. However, our analysis shows that the singlet 1:4 biradical derived from α-methoxy acetone can cyclize readily to form 3-oxetanol. Fig. 5 shows that, in the nascent triplet biradical, the distance between the radical sites is 3.0 Å and the two p orbitals on the carbon atoms at the radical sites are almost perpendicular to each other. This orientation is favourable for spin–orbit coupling [20], but the two-centre spin–orbit coupling is enhanced as the distance between the radical sites decreases. This occurs as the cyclization process progresses. In the transition state, a four-membered ring is formed with a C1–C4 distance of 2.15 Å. This four-membered ring is almost planar. After the saddle point, the singlet surface is stabilized by the developing bond, resulting in the formation of oxetanol with a planar four-membered ring.

In the 1:4 biradical derived from alkyl pyruvates (i.e. ketone **III**), the two half empty p orbitals on the carbon atoms at the radical sites are nearly parallel because of the extended equilibrium structure where the C1–C4 distance is greater than 3.5 Å (see Fig. 4). This results in a very low spin–orbit coupling and the cyclization process leading to the formation of oxetanol is difficult. Indeed, there was no evidence of cyclization in these compounds. Instead, alkyl pyruvates fragment via a type II process [8].

Table 3 shows the free valence indices at the two radical sites in the 1:4 biradicals (singlet state) derived from all the ketones. The results show that, as the γ-carbon atom (i.e. C1) becomes more and more crowded, its free valence index decreases. At the site of the hydroxyl carbon (i.e. C4), the free valence index is significantly less in the 1:4 biradicals derived from alkyl pyruvates than in those derived from ketones **I** and **II**. This may be due to the possible delocalization of the odd electron in the diketone-derived biradicals. A similar observation was reported previously for α-diketones [2]. Our results lead to the conclusion that the cyclization of the 1:4 biradicals derived from alkyl pyruvates is difficult. On the other hand, the 1:4 biradicals derived from α-alkoxy acetones can cyclize readily to form 3-oxetanols.

5. Conclusions

The intramolecular γ-hydrogen abstraction process can take place very rapidly from methyl-2,2-dimethylcyclopropyl ketone in the excited singlet state. This is due to the fact that no conformational change is required to bring the hydrogen atom close to the oxygen atom. The effect of the ether oxygen in a position β to the carbonyl group in ketones **II** and **III** leads to an overall decrease in the energy of activation and an increase in the exothermic nature of the intramolecular γ-hydrogen abstraction process relative to the corresponding alkyl monoketones and diketones. This increased reactivity is not due to the activating influence of the ether oxygen on the carbonyl oxygen that abstracts a hydrogen atom as the free valence indices on the carbonyl oxygen in both alkyl and α-alkoxy ketones are similar. The weaker C–H bonds of the alkoxy group are responsible for the increased reactivity. In ketones **III**, the difference in selectivity for primary vs. secondary vs. tertiary hydrogen abstraction from the γ-position is less than that observed in α-diketones.

The cyclization of the 1:4 biradicals derived from α-alkoxy acetones is possible leading to the formation of oxetanols. The 1:4 biradicals derived from ketones **I** and **III** do not cyclize.

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