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THE MECHANISM OF PHOTOREDUCTION OF CYCLOHEXENONES TO CYCLOHEXANONES IN ISOPROPYL ALCOHOL[1]

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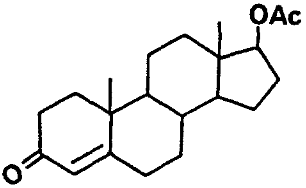
Abstract: The photoreduction of cyclohexenones in 2-propanol is initiated by H-abstraction at C_β of the enone $^3\pi,\pi^*$ state, as shown by the reaction course in deuterated solvents.

Upon excitation in alcohols possessing a hydrogen on the carbinol carbon, 4,4-dialkylcyclohexenones generally undergo three transformations: reduction to 4,4-dialkylcyclohexanones and skeletal rearrangements to form 6,6-dialkylbicyclo[3.1.0]-hexan-2-ones (lumiketones) and 3-substituted 2-cyclopentenones.[2] Several reports suggest that the photoreduction proceeds from the same triplet excited state implicated as the precursor of the rearrangement products,[3-5] postulated to be a $^3\pi,\pi^*$ state, although there are conflicting observations.[2b] If so, the mechanism of the photoreduction should differ in important respects from the more familiar photoreduction of model ketones such as benzophenone and acetone *via* the $^3n,\pi^*$ state, initiated by H-abstraction from the reducing agent by the radical-like oxygen of the excited carbonyl group.[6]

The course of photoreduction of 2-cyclohexenones falls into two general categories: (1) reduction to pinacols and other products attributable to initial H-abstraction by the carbonyl oxygen atom, and (2) reduction of the C=C bond to afford saturated ketones and solvent adducts. The reaction course seems to depend upon structural factors and reaction conditions. Thus, the steroidal enone 1 in ethyl ether gives a pinacol and products of radical addition across the carbonyl group, while in ethanol a complex mixture is obtained including 20% of the saturated ketone.[7] In toluene, the saturated ketone is again formed, in addition to the α-benzyl substituted ketone and the deconjugated β,γ-enone.[3] Similar behavior is shown by octalone 2,[3] while phenanthrone 3 is reported to give pinacol and lumiketone in isopropyl alcohol.[8]

4,4-Dimethylcyclohexenone 4 was reported[9] to give only 4,4-dimethylcyclohexanone 5a and rearrangement products in isopropyl alcohol (IPA), an observation confirmed in the present study. The photolysate contains no trace of the corresponding allylic alcohol 6. Irradiation of 4 in toluene affords 5a as well as 2-benzyl-4,4-dimethylcyclohexanone 7, whose structure was confirmed by direct spectral comparison with an authentic sample prepared independently. This product must be formed by initial H-abstraction from toluene at C_β of the enone, followed by coupling of the resulting enoxyl and benzyl radicals at C_α .



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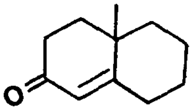

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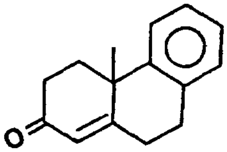

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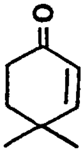

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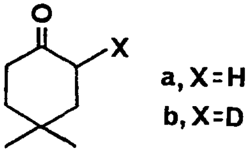

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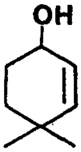

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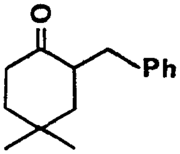

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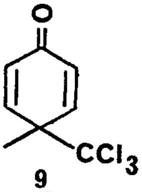

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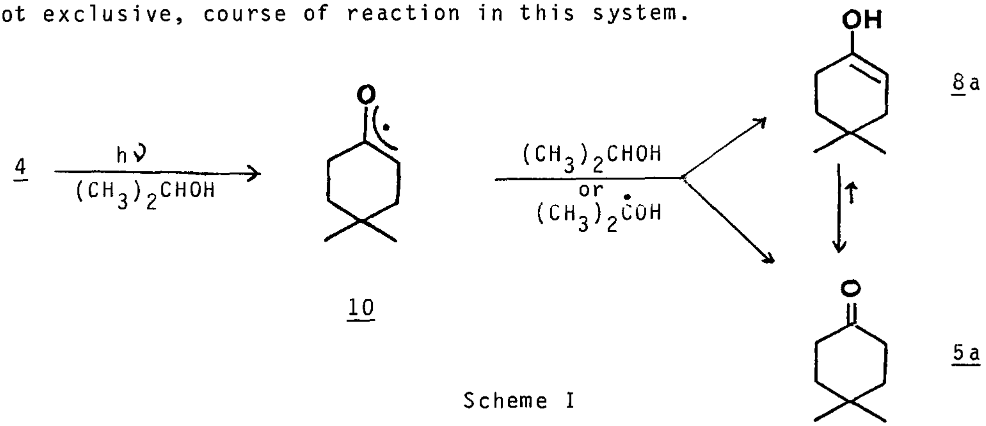
The formation of the saturated ketone 5a in this model system is more problematical, since it could take place by three different mechanisms: (a) initial H-abstraction from $\mathrm{Me_2CHOH}$ at C_α followed by a second H-transfer to C_β from either $\mathrm{Me_2\dot{C}OH}$ or $\mathrm{Me_2CHOH}$; (b) initial H-abstraction at C_β to form an enoxyl radical 10 which obtains a second H-atom from $\mathrm{Me_2\dot{C}OH}$ or $\mathrm{Me_2CHOH}$ to give either 5a directly, or the corresponding enol 8a (Scheme I) which then tautomerizes to 5a; (c) initial H-abstraction at the carbonyl oxygen, followed by a second H-transfer to C_β to afford enol 8a which then gives 5a upon tautomerization. We now present evidence that mechanism (b) is the dominant, if not exclusive, course of reaction in this system.



Scheme I

Experiments were first carried out to determine if a chain reaction analogous to that previously found[10] to operate on irradiation of cyclohexadienone 9, involving H-transfer from Me$_2\dot{C}$OH to the ketone, occurs also with enone 4. No reduction of enone 4 occurred upon thermal decomposition of benzoyl or acetyl peroxide in IPA in the presence of 4 under conditions which led to conversion of 9 to p-cresol. Peroxide decomposition in IPA containing a mixture of 4 and 9 induced rapid reaction of 9 but no consumption of 4. Thus, we must conclude that transfer of hydrogen from Me$_2\dot{C}$OH to 4 does not take place, presumably because the reaction is energetically unfavorable. This result greatly simplified the mechanistic interpretation of the results outlined below from irradiation of 4 in deuterium labeled IPA.

The critical role of the carbinol C-H bond is clearly shown by the greatly reduced yield of 5 on irradiation of 4 in IPA-d_8 compared to the yield of 5 in unlabeled as well as methyl and hydroxyl labeled IPA. The very small yield of 5 in IPA-d_8, corresponding to a very large kinetic isotope effect, precluded determination of the site(s) of deuterium incorporation. Upon irradiation of 4 in IPA-O-d at 254 nm for 16 hr at ambient temperatures, product 5 was found to be ~24% monodeuterated by GC/MS analysis, whereas the recovered starting material was essentially undeuterated. No measurable deuterium incorporation (5a $\longrightarrow$ 5b) could be detected by ^{1}H NMR spectroscopy after 5a stood for 24 hrs in IPA-O-d at 35°C. The photoinduced deuterium incorporation into 5 was entirely at C as shown by the complete loss of the label from 5b upon exchange with KOH in methanol-water.

Assuming only a single mechanism operates, this result is compatible only with mechanism (b), with the percent D incorporated reflecting that portion of 5 (i.e., 5b) formed via enol 8a and subsquent tautomerization. If mechanism (c) were operative, the reduced product would have been generated entirely in its enol form, which would necessarily incorporate deuterium from the solvent (the only proton source present) during tautomerization, resulting in completely deuterated product. The lack of formation of the allylic alcohol 6 also speaks against this mechanism. If mechanism (a) were operative, no deuterium incorporation would be expected, since the enol form of 5 is not a reaction intermediate.

A second experiment using $(CD_3)_2$CHOH under similar irradiation conditions resulted in no deuterium incorporation into the starting material, 5 or the rearrangement products, according to GC/MS analysis of the crude reaction mixture. This result indicates that in-cage H-transfer from the methyl group of Me$_2\dot{C}$OH to the enoxyl radical 10, generating acetone enol and 5 and/or its enol, is unimportant, nor is H-transfer to ground state enone 4, as concluded previously. Such a disproportionation has been shown to occur during the photoreduction of acetone in IPA.[11]

The results from the above experiments in IPA and toluene can be accomodated readily in terms of mechanism (b) involving initial H-abstraction at C_β.

Although the IPA data do not rigorously exclude some contribution of mechanism (a) to the overall result, the failure to detect the 3-benzyl analog of 7 in toluene photolysates argues against the importance of initial H-abstraction at C_α in this system. Similarly, the case against mechanism (c) rests not only on the labeling data, but also on the absence of 6 as well as pinacol in the IPA photolysate. Reactions of α,β-unsaturated enones initiated by H-abstraction at C_β have ample literature precedent in the intramolecular reactions leading to cyclization and disproportionation reported by Agosta and co-workers.[12,13] In a system where there should be no stereochemical or conformational bias between H-transfer to C_α or C_β, initial reaction at C_β was observed,[13] as in the present study. This specificity must be attributed to the electronic character of the reactive triplet excited state, which is consistent with expectations for the behavior of a π,π^* in contrast to an n,π^* triplet.

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