

A FREE-ROTOR EFFECT IN β,γ -UNSATURATED KETONE PHOTOCHEMISTRY. THE DIVERGING SINGLET AND TRIPLET REACTIONS OF 3-ETHYLIDENE-2,2,5,5-TETRAMETHYLCYCLOHEXANONE

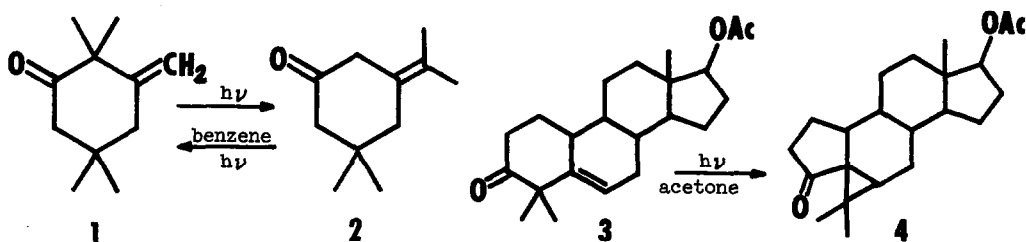
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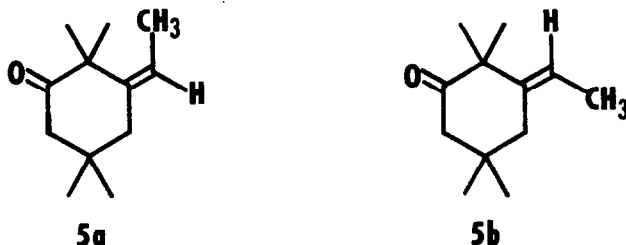
We recently reported the singlet-state photochemical rearrangement of 3-methylene-2,2,5,5-tetramethylcyclohexanone (1) via a 1,3-sigmatropic acyl shift to 3,3-dimethyl-5-isopropylidene-cyclohexanone (2).^{3,4} However, 17 β -acetoxy-4,4-dimethyl-19-norandrost-5-en-3-one (3) is known to undergo a triplet-state 1,2-acyl shift to the cyclopropylketone steroid (4).⁵ As a partial



explanation for the differing reactivities of 1 and 3, despite their essentially isosteric β,γ -unsaturated ketone chromophores, we suggested that the lowest triplet state of 1 was only apparently unreactive, dissipating its energy in an undetected cis-trans isomerization. Such a characteristic $\pi-\pi^*$ process would have been consistent with our finding that the phosphorescent triplet of 1 at 77°K was of the $\pi-\pi^*$ configuration (mean lifetime 0.21 sec⁶).

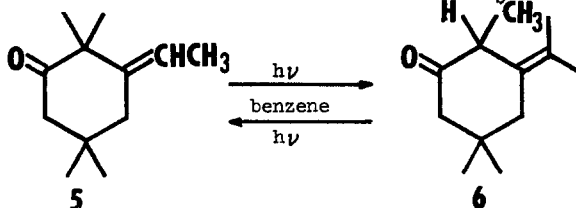
Since our communication, preliminary support of our contention was provided by the fact that although no discernible reaction of 1 could be photosensitized, addition of 1 did indeed quench both the phosphorescence of acetophenone in ethanol glass and the photoreduction of acetophenone in isopropyl alcohol at 3500 Å. Accordingly, we chose to examine the photoreactivity of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone (5). Synthesis by Wittig reaction of 2,2,5,5-

tetramethylcyclohexane-1,3-dione with 1.4 equivalents of ethylidetriphenylphosphorane in dimethylsulfoxide at 50°C gave a 60% yield of 5 as a 85:15 mixture of the two geometric isomers 5a and 5b.



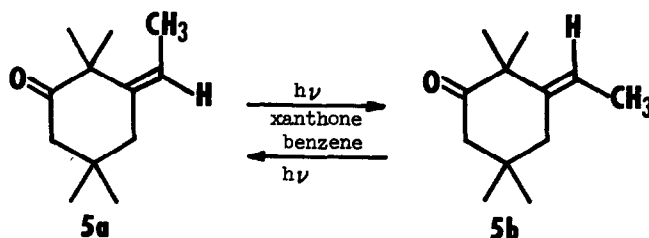
The major isomer 5a was determined to be the one in which the allylic methyl was syn to the C₂ geminal dimethyls on the basis of its 100-MHz nmr spectrum (CCl₄): δ0.92 (6H, singlet, 5,5-dimethyl), 1.26 (6H, singlet, 2,2-dimethyl), 1.70 (3H_a, doublet of triplets, J_{ab}=7Hz, J_{ac}=1Hz, allylic methyl), 2.04 (2H_c, broad singlet, allylic methylene), 2.13 (2H, singlet, -CH₂-C=O), 5.26 (1H_b, quartet, J_{ab}=7Hz, vinyl). The anti arrangement of the allylic and C₂ geminal methyls in the minor isomer 5b is also based on the 100-MHz nmr spectrum (CCl₄): δ0.89 (6H, singlet, 5,5-dimethyl), 1.14 (6H, singlet, 2,2-dimethyl), 1.58 (3H_a, doublet, J_{ab}=7Hz, allylic methyl), 2.18 (2H, singlet, -CH₂-C=O), 2.27 (2H, broad singlet, allylic methylene), 5.41 (1H_b, quartet, J_{ab}=7Hz, vinyl). These assignments are consistent with previously noted deshielding by proximal methyls⁷ and with more pronounced homoallylic coupling in transoid arrangements.⁸

Irradiation through a corex filter of a 0.1 M deoxygenated solution of the 5ab mixture⁹ in benzene resulted in the formation of a single photoproduct 6 in 30% yield, which could be isolated by evaporation of solvent at reduced pressure and preparative gas chromatography on a 3-ft. by 1/4-in. BDS (10% on Chromosorb P) column at 65°. The identity of 6 was established as 3-isopropylidene-2,5,5-trimethylcyclohexanone by ozonolysis to acetone and 2,5,5-trimethylcyclohexane-1,3-dione, and by its 60-MHz nmr spectrum (CCl₄): δ0.78 and 1.08 (two 3H singlets, C₅ methyls), 1.14 (3H_a doublet, J_{ab}=7Hz, C₂ methyl), 1.68 and 1.72 (two 3H singlets, allylic methyls), 2.24 (4H multiplet, -CH₂-C=O and -CH₂-C=C-), 3.27 (1H_b quartet, J_{ab}=7Hz, C₂ methine).



The quantum yield for the conversion of 5 to 6 is 0.20.¹⁰ As is generally the case for photochemical 1,3-acyl shifts of β,γ -unsaturated ketones, the transformation is reversible, with 68% of 5 and 32% of 6 present at a photostationary state. The predominance of 5 in the steady-state mixture may simply reflect the higher $n-\pi^*$ molar absorptivity of 6 (113 at λ_{\max} 299 nm for 6, vs. 61 at λ_{\max} 298 nm¹³ for 5ab) since quantum efficiency is about the same in either direction. Thus, the singlet-state photochemistry of 5 closely parallels the behavior of the methylene analog 1.

However, in contrast to the deceptive apparent inertness of the triplet state of 1, photosensitization of a 5ab mixture at 3500 Å produces a discernible reaction. The reaction observed is not, however, the 1,2-acyl shift commonly observed in cyclic β,γ -unsaturated ketones such as 3, but rather cis-trans isomerization of 5a to 5b. Ketone sensitizers with triplet energies in



the range of 74 (xanthone, acetophenone) to 65 kcal/mole (10-thioxanthone) were all effective. That the triplet reaction product from photosensitization of 5a was indeed 5b, and vice versa, was confirmed by quantitative (ca. 95%) ozonolysis of the product mixture to acetaldehyde and 2,2,5,5-tetramethylcyclohexane-1,3-dione. A $\pi-\pi^*$ configuration is probable for the reactive triplet states of 5a and 5b in the room-temperature geometrical isomerization, but not certain. At 77°K, however, a broad phosphorescence spectrum (both ethanol and isopentane glasses) was recorded, with an approximate (0-0 band) triplet energy of 69 ± 2 kcal/mole and mean lifetime of 0.16 sec, clearly indicative of a $\pi-\pi^*$ triplet state.

Thus, our findings clearly demonstrate that two virtually isosteric β,γ -unsaturated ketones such as 3 and 5 differ in their photochemical reactivity largely because of the presence (in 3) or lack (in 5) of a steric constraint to geometric isomerization. When no such restraint is present, the olefinic moiety is capable of acting as a "free rotor," thereby dissipating triplet energy. When free rotation is impaired, the cyclopropylketone-producing 1,2-acyl shift may be a triplet reaction pathway of last resort. Since 3 and 5 both have triplet states accessible by singlet $n-\pi^*$ excitation and subsequent intersystem crossing, the reactivity differences cannot

de due solely to the singlet-state partitioning ratio of α -cleavage to intersystem crossing, although this may be a contributing factor.^{14,15} Further studies are in progress to assess the degree of steric restraint that must be applied to eliminate the free-rotor effect.¹⁶

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9. Although distinct nmr signals could be discerned and assigned unequivocally for the two isomers, the mixture proved physically unresolvable in our hands, even on a 500-ft. by 0.03-in. i.d. stainless steel capillary column coated with a 20:1 SF96(50): Igepal mixture.
10. The potassium ferrioxalate actinometer of Hatchard and Parker¹¹ was employed, using uranyl oxalate actinometry¹² for standardization.
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13. This is the molar absorptivity of the 85:15 5a:5b mixture used in the irradiations. Individual ϵ values are ca. 54 for 5a (298 nm) and 103 for 5b (298 nm).
14. J. R. Williams and G. M. Sarkisian, Chem. Commun., 1564 (1971).
15. The configuration of the triplet state is also not the source of the difference: K. G. Hancock and R. O. Grider, unpublished results.
16. Potential structural limitations to the free-rotor effect have also been recognized by Z. Goldschmidt and A. S. Kende, Tetrahedron Letters, 4625 (1971), in the sensitized di- π -methane rearrangement of 2-methylene-6,7-benzobicyclo[3.2.2]nona-3,6,8-triene; however, the uncertain extent of involvement of that exocyclic 2-methylene in the di- π -methane reaction obscures its relationship to a β,γ -unsaturated ketone in which an exocyclic methylene is an integral part of the chromophore.