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THE SINGLET-STATE PHOTOCHEMISTRY OF 3-METHYLENE-2,2,5,5-TETRAMETHYLCYCLOHEXANONE

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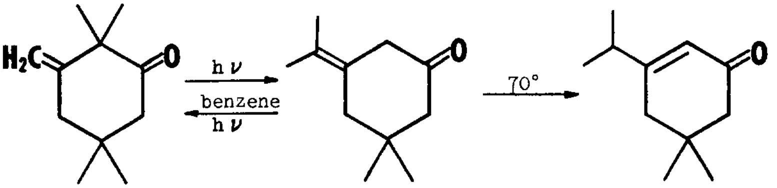
Recent developments in the elucidation of reaction mechanisms for β,γ-unsaturated ketones[2,3] indicate a distinct dichotomy in photoreactivity for such systems. Where multiplicity studies have been reported, the singlet states of β,γ-unsaturated ketones undergo photochemical 1,3-acyl shifts to isomeric 3-en-1-ones whereas triplet ketones undergo the oxa-di-pi-methane transformation to cyclopropyl ketones. However, no definitive correlation of these divergent reaction pathways with reactant structure has been presented. It is this gap in understanding which spurs us to report forthwith our study of the photochemistry and emission spectra of 3-methylene-2,2,5,5-tetramethylcyclohexanone (1), which, taken together, provide a partial rationalization of the dichotomous reactivity of β,γ-unsaturated ketones in terms of steric constraints on the olefinic portion of the chromophore. Additionally, compound 1 is the first example of a photochemically reactive β,γ-unsaturated ketone in which the olefinic moiety is exocyclic, as opposed to endocyclic or acyclic.

Inferring from the available evidence that a "free rotor" effect, similar to that hypothesized for deactivation of flexible di-pi-methane triplets,[4,5] might be operative in β,γ-unsaturated ketone photochemistry as well, we examined the behavior of 3-methylene-2,2,5,5-tetramethylcyclohexanone (1). Synthesis of the title compound (m.p. 25°) was accomplished by Wittig reaction of 2,2,5,5-tetramethylcyclohexane-1,3-dione[6] with methylenetriphenylphosphorane in dimethylsulfoxide at 50°C. The ultraviolet spectrum of 1 revealed modest enhancement of the $n\text{-}\pi^*$ band[7] ($\lambda_{max}^{C_6H_{12}}$ 298 nm, ϵ 72).

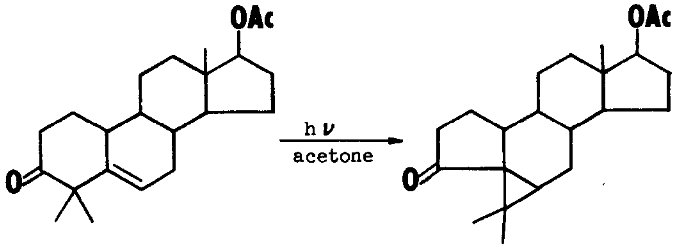


1 2 3

In a typical experiment, 8 g. of 1 in 200 ml. of benzene (or dioxane or methanol) was purged with nitrogen and irradiated 4 hr. with a corex-filtered 450-w. high-pressure mercury lamp. Examination of the photolysate by nmr and/or glpc indicated 50% conversion of 1 to a single photoproduct. The photoproduct 2 was isolated by evaporation of solvent below 40° and chromatography at 50° through a 1.5-ft. x 3/8-in. SE-30 (3% on Chromosorb G) column. It was identified as 3,3-dimethyl-5-isopropylidenecyclohexanone (2) on the basis of spectral and chemical evidence. Distinguishing spectral parameters were: ir absorption at 1712 cm^{-1}(CCl_4); nmr singlets at δ0.90 (6H, ring methyls), 1.68 (6H, allylic methyls), 2.13 (2H, $-CH_2-\overset{|}{C}=C<$), 2.28 (2H, $-CH_2-\overset{|}{C}=O$), and 2.97 (2H, $-C=C-CH_2-C=O$); enhanced n-π* UV absorption ($\lambda_{max}^{C_6H_{12}}$ 298 nm, ϵ 118); and mass spectrum (m/e 166). Additionally, ozonolysis of 2 gave only dimedone and acetone. At temperatures above 70°, 2 rearranged rapidly to 3-isopropyl-5,5-dimethylcyclohex-2-ene-1-one (3).[8]

The photochemical formation of 2 from 1 is reversible. Starting with either ketone, a 50:50 photostationary mixture was obtained. Conversion of 1 to 2 under direct irradiation is clearly a singlet-state process since it is unquenched by even 2.6 M piperylene and cannot be sensitized by acetone, xanthone, acetophenone or benzophenone. The quantum yield for the 1 → 2 transformation is 0.13,[9] indicative of a practicable preparative reaction. The lack of fragmentation or hydrogen-abstraction photoproducts is consistent with, but not demanding of, a symmetry-allowed concerted 1,3-sigmatropic acyl shift.[12]

Rearrangement of 1 to 2 within the singlet manifold is of particular interest when viewed in contrast to the photorearrangement of 17β-acetoxy-4,4-dimethyl-19-norandrost-5-en-3-one (4) to cyclopropyl ketone 5.[13] The latter reaction clearly originates in the triplet state under photosensitization conditions.



4 **5**

Examination of molecular models shows the β,γ-unsaturated ketone moieties of **1** and **4** to be nearly isosteric, the only prominent difference between the two being the geometric inhibition to cis-trans isomerization in steriod **4** caused by enclosing the exocyclic (to ring A) methylene in ring B. Prevented from undergoing a low-energy cis-trans isomerization, the triplet state of **4** must use an alternate reaction pathway — the oxa-di-pi-methane reaction. There is no such restraint on free rotation in the simple exocyclic methylene ketone **1**; having a facile deactivation mechanism, the triplet state of **1** is thus expected to be unreactive.

Supporting this contention are the emission spectra of the methylene ketone **1**. In addition to a room-temperature fluorescence spectrum ($\lambda_{max}^{C_6H_{12}}$ 395 nm; 0-0 band, 343), ketone **1** also displayed strong phosphorescence at 77°K ($\lambda_{max}^{C_6H_{12}}$ 427 nm; 0-0 band, 405), with a mean lifetime of 0.18 sec, characteristic of a π-π^* triplet. It is not unreasonable to presume that the π-π^* triplet which phosphoresces in rigid media at 77°K undergoes rapid cis-trans isomerization (a characteristic π-π^* reaction) as a decay mechanism in fluid solution.

Although the paucity of triplet emission and lifetime data in the literature on β,γ-unsaturated ketones makes any generalization tenuous, we suggest that ketones whose lowest triplets are of the π-π^* type and which are not geometrically prevented from cis-trans isomerization, may generally react via their singlet states to isomeric 3-en-1-ones. Further studies are in progress to determine whether 1,3-acyl shifts are characteristic of ketones with flexible π-π^* lowest triplets and 1,2-acyl shifts characteristic of n-π^* lowest triplets.[14]

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