

KINETIC PROPERTIES OF THE TRIPLET EXCITED STATE OF A LINEARLY CONJUGATED STEROID DIENONE STUDIED BY LASER FLASH PHOTOLYSIS^{†‡}

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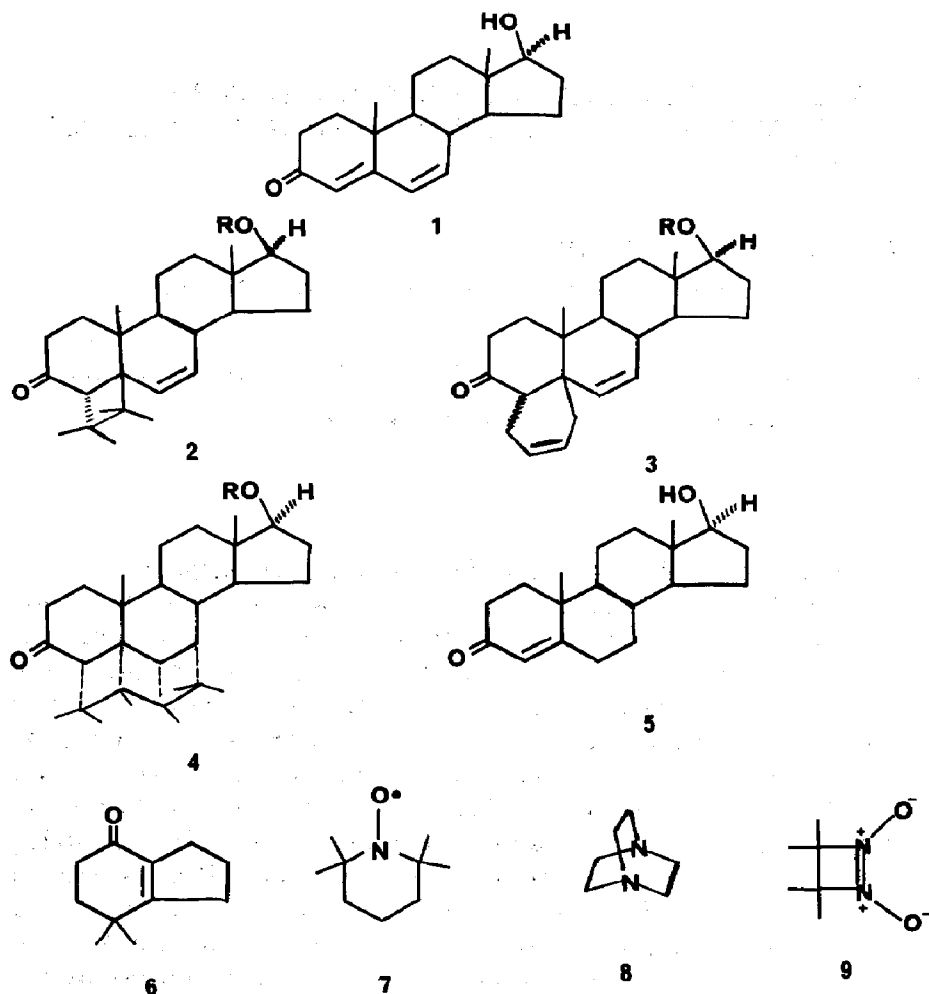
Summary

Laser flash excitation of the steroidal dienone Δ^6 -testosterone at 355 nm in ethanol results in the formation of a transient species absorbing between 300 and 600 nm with a lifetime of about 10 μ s at room temperature. This species is quenched by oxygen, ferrocene, nitroxyl radicals and olefins. By comparison with earlier flash kinetic data on monocyclic and polycyclic enones, it is concluded that this species is a triplet excited state with an excitation energy of 42 - 43 kcal mol⁻¹, which is somewhat lower than that estimated (about 50 kcal mol⁻¹) from the spectroscopic triplet of this compound indicating that some geometric relaxation, probably involving slight twisting around the α,β C=C bond, has occurred. The extent of twisting is suggested to be less than that in the corresponding enone testosterone. These results are compared with data in the literature for the photocycloaddition of olefins to these compounds to give mixtures of *cis*- and *trans*-fused cycloadducts in terms of a mechanism involving the addition of alkenes to twisted triplet excited states of conjugated enones.

We have been engaged in a program of characterization of transient intermediates generated by the laser flash photolysis of a series of cyclohexenone derivatives, and correlation of these kinetic data with the behavior of these systems on continuous irradiation [3]. It was of interest to extend this study to a system containing a linearly conjugated dienone chromophore, which is conveniently provided by the steroid 17- β -hydroxyandrost-4,6-dien-3-one (Δ^6 -testosterone) (1) whose photochemistry has been studied by

[†]Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

[‡]Part 75 of the New York University series on the photochemistry of ketones in solution. Parts 74 and 73 are published as refs. 1 and 2 respectively.



Lenz [4]. This compound readily undergoes photocycloaddition to electron-rich alkenes to give exclusively *trans*-fused [2 + 2] cycloadducts 2, while similar reactions with electron-deficient alkenes give mainly adducts of type 2 in addition to some *cis*-fused cycloadducts. Photocycloaddition of 1 to 1,3-dienes gives a mixture of *cis*- and *trans*-fused [4 + 2] cycloadducts 3 as well as ladder-type [2 + 2 + 2 + 2] adducts 4.

Laser flash excitation of cyclohexenones results in the formation of a transient which absorbs from 250 to 400 nm with a maximum at 280 - 290 nm and whose lifetime varies from about 25 ns for simple cyclohexenones to 450 ns for testosterone (5) and 1.5 - 2.0 μ s for enone (6) [3]. It has been concluded that this species is most likely a twisted triplet π, π^* state. The dependence of the triplet lifetime on the enone structure can be understood in terms of variations in the rates of radiationless decay from the triplet to the ground state potential surface at the relaxed triplet geometry owing to variations in the constraints to twisting around the C=C bond [5]. Twisted triplet states of enones are logical intermediates in the photo-

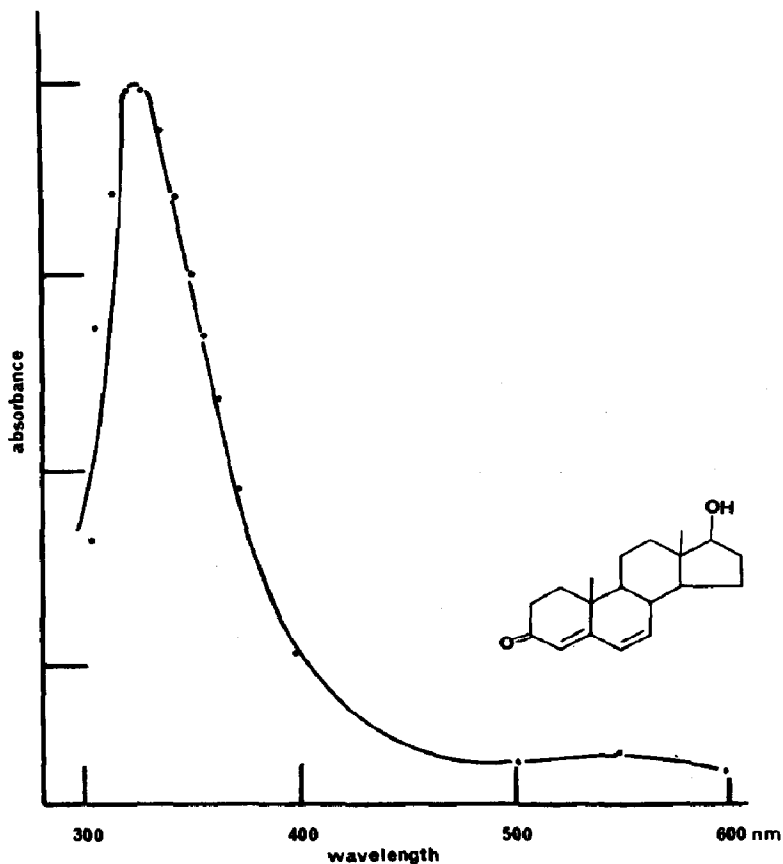


Fig. 1. Transient absorption spectrum of compound 1 in ethanol solution measured 300 ns after laser flash excitation at 266 nm.

chemical rearrangements of cyclohexenones [6] as well as in photocycloaddition to alkenes to give *trans*-fused cycloadducts [7]. Indeed, it has recently been demonstrated that these two reactions proceed from the same triplet excited state in the case of 4,4-dimethyl-2-cyclohexenone [8].

We now report that the laser flash excitation at ambient temperatures of dienone 1 in degassed ethanol at 266 nm using a neodymium-doped yttrium aluminum garnet laser as previously described [5] results in the formation of a long-lived triplet species whose lifetime varies from 4.4 to 10.1 μs depending on the efficacy of the degassing procedure. The absorption spectrum of this transient is shown in Fig. 1. This species is quenched by oxygen, ferrocene, the nitroxyl radical tetramethylpiperidinyloxy (Tempo) (7) and 1,1-dimethoxyethylene with rate constants as given in Table 1. However, it is not quenched by the diamine 1,4-diazabicyclo[2.2.2]octane (Dabco) (8) which is an effective quencher of enone triplets (k_q for quenching testosterone triplets is $(1.0 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [3].

These results are entirely consistent with the proposal that this transient is a low energy stabilized triplet π, π^* state of 1. Lenz [4] has

TABLE 1

Rate constants for the quenching of the transient triplet excited state of the steroidal dienone Δ^6 -testosterone in ethanol^a

Quencher	$k_q (\text{M}^{-1} \text{s}^{-1})$
Oxygen ^b	$1.7 \pm 0.1 \times 10^9$
Tempo (7)	$3.4 \pm 0.1 \times 10^8$
Ferrocene	$4.5 \pm 0.1 \times 10^9$
1,1-Dimethoxyethylene	$1.1 \pm 0.1 \times 10^6$

^aSamples in quartz cuvettes were deoxygenated by passage of nitrogen through the solution for at least 10 min immediately prior to irradiation. The possibility of solvent loss was checked by weighing the sample cuvette before and after this procedure.

^bThree points were utilized corresponding to saturation of the ethanol solution with oxygen, nitrogen or a 1:1 mixture of oxygen and nitrogen.

estimated from spectroscopy data that the π, π^* triplet state T_1 of 1 should have an energy of about 50 kcal mol^{-1} by comparison with the triplet energy E_T of 3,5-heptadienone which is 54 kcal mol^{-1} [9]. The rates of quenching of the observed transient from 1 by oxygen, Tempo and ferrocene ($E_T = 39 \text{ kcal mol}^{-1}$) are as expected for such a species. Quenching of enone triplets by Dabco and other amines in polar solvents has been shown to involve photoinduced electron transfer to give solvated enone radical anions and amine radical cations which can be directly observed in flash experiments [1]. The large difference between the triplet excitation energies of 1 and testosterone ($E_T \approx 72 \text{ kcal mol}^{-1}$ [4]) would cause increased endothermicity for electron transfer in the case of 1 to the extent of about 1 eV, so that it is not surprising that this process is not energetically favorable in the case of 1. The quenching of the long-lived transient of 1 by $(\text{CH}_3\text{O})_2\text{C}=\text{CH}_2$ indicates that this transient is indeed the excited state responsible for the photocycloaddition reactions observed by Lenz [4] and Rubin *et al.* [10]. It is interesting to note that the reaction rate constant is an order of magnitude less than that found for the reaction of this alkene with triplet states of cyclohexenones in steady state [8] as well as flash irradiations [3]. Ullman's triplet quencher 9 quenches the cycloaddition of 1 to 2,3-dimethyl-1,3-butadiene with a Stern-Volmer slope $k_q \tau_T$ of 1450 M^{-1} [4]. When our measured value of $\tau_T \approx 10 \mu\text{s}$ is used, this corresponds to $k_q = 1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which is close to the rate measured for the quenching of anthracene by 9 ($1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [11]). This suggests that the energy of the relaxed triplet of dienone 1 is around $42 - 43 \text{ kcal mol}^{-1}$. The difference between this value and the previous estimate [4] of $50 - 54 \text{ kcal mol}^{-1}$ can be tentatively ascribed to energetic stabilization as a consequence of geometric relaxation, such as twisting around the α, β C=C bond. This is comparable with the difference of $10 - 12 \text{ kcal mol}^{-1}$ found in the case of 5 between the triplet energies determined by low temperature spectroscopy [12] and from quenching of the transient species at room temperature [3].

It is clear from the molecular structure of **1** that twisting around the α,β C=C bond in its triplet state must be severely limited. The values of the quenching rate constants for oxygen, ferrocene and Tempo and the relatively long lifetime of the transient are consistent with a relatively large energy gap between the triplet and ground state potential surfaces and a planar (or nearly planar) structure for this triplet, by analogy with previous studies of planar and twisted triplets of arylethylenes [13]. The 10 μ s lifetime of the dienone triplet is much longer than that of **5** (τ_T is about 440 ns in cyclohexane and 330 ns in acetonitrile [3, 5]), suggesting that the extra double bond in the γ,δ position of **1** is remarkably effective in stabilizing the π,π^* triplet, presumably by lowering the triplet excitation energy and giving a more rigid structure.

Our conclusion that the extent of twisting around the α,β C=C bond in the relaxed triplet state of **1** is probably much less than that in the case of **5** is, however, not consistent with observations from steady state experiments [4, 10]. Photocycloaddition of a number of electron-rich alkenes to **1** results in the exclusive formation of *trans*-fused [2 + 2] cycloadducts, while the addition of such alkenes to **5** invariably results in a mixture of *cis*- and *trans*-fused cycloadducts. The formation of sterically strained *trans*-fused cycloadducts is most readily rationalized in terms of addition of the alkene to a twisted enone moiety [8]. The proposed mechanism for photocycloaddition [4, 7, 8, 14] involves exciplex and biradical intermediates which can decay to the ground state enone and alkene in competition with the formation of cycloadducts. Since the quantum efficiency of these reactions with **1** and **5** has not been determined, it is conceivable that differences between the ratios of the decay to product pathways exist in the two systems and these would markedly affect the observed stereoselectivities. We hope to resolve the conflict between these findings from flash and steady state photochemical studies in progress in our laboratories.

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