Reactivity of n,π^* and π,π^* Triplet Excited States of 4a-Methyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrone[1]

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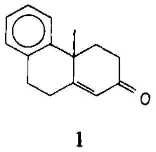
It is well known that 4,4-disubstituted cyclohex-2-enones will undergo photorearrangement to bicyclo[3.1.0]hexan-2-ones and C=C bond reduction via a triplet π,π^* state,[2-6] while reactions involving initial hydrogen abstraction by oxygen or aryl migrations have been ascribed to triplet states with n,π^* character.[3,4,7,8]

We report a reinvestigation of the photochemistry of phenanthrone **I** in isopropyl alcohol (IPA). Employing either naphthalene or phenanthrene as triplet quencher, we find that Stern–Volmer plots for formation of **2** and **3** have clearly distinct slopes (see Figure 1), in conflict with the conclusion of Zimmerman et al.[9] that the ^{3}(n,π^*) state was responsible for the formation of both products.



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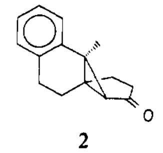

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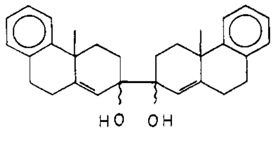

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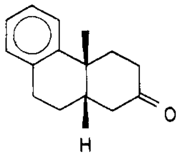
Using a laser flash technique, Bonneau et al.[10] have directly measured the lifetime, τ_0, of a transient triplet excited state of **1** in IPA to be 145 ns and the rate constant, k_q, of quenching of this triplet by naphthalene to be 4×10^8 M^{-1} s^{-1}. Taking this value and the upper slope in Figure 1 (60 M^{-1}),[11] we find τ_0 equals 150 ns. The gratifying agreement of these τ_0 values supports the conclusion that the twisted π,π^* triplet state observed in the flash study[10,12] is indeed the precursor to the lumiketone.[13] The quenching data further indicate that the pinacol is coming from a different triplet state, presumably the n,π^* triplet,[2,7,9] and the two triplet states are not in thermal equilibrium. If quenching of this triplet by naphthalene occurs at close to the diffusion-controlled rate (~5×10^9 M^{-1} s^{-1}),[7] its lifetime would be too short (~4 ns) to be detected in this flash experiment.[10]

The previously undetected products **4**,[14] **5**,[14,15] and **6**[16,17] were isolated and identified by both GC/MS data and coinjection with authentic samples synthesized independently. Compounds **2–6** were formed in approximately the same ratio on direct irradiation and triplet sensitization using acetophenone and *p*-methoxyacetophenone. Stern–Volmer quenching plots for all these products on direct excitation are linear (see Figure 1), indicating that all are derived exclusively from triplet excited states.



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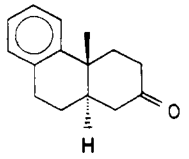

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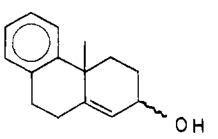

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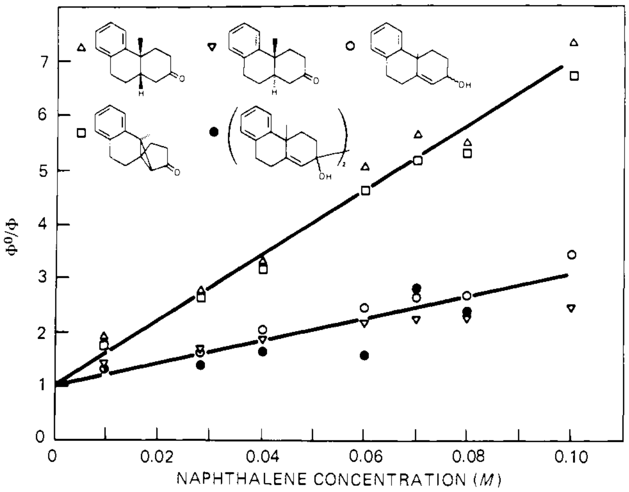
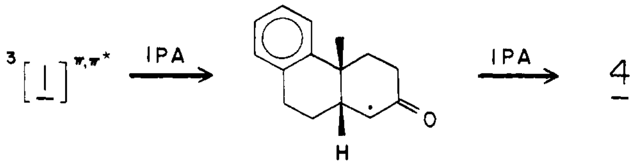


Figure 1. Stern–Volmer plots for quenching by naphthalene of formation of products **2–6** on irradiation of **1** in IPA.

Scheme I



The quenching data indicate that the stereoisomeric saturated ketones **4** and **5** arise from two different triplet excited states. The *cis*-hexahydrophenanthrone **4**, which originates from the $^3(\pi,\pi^*)$ state, presumably arises by a mechanism involving initial H abstraction at C_β (see Scheme I).[3,5] The *trans*-hexahydrophenanthrone **5** originates from the ^{3}(n,π^*) state,[7] presumably via the hydroxyallyl radical, which is also the likely precursor to compounds **3** and **6** (see Scheme II).

This is the first reported observation that reduction of the C=C bond of an α,β-enone can originate from both $^3(\pi,\pi^*)$ and ^{3}(n,π^*) states and that each pathway is stereospecific. It is well established[13,18-20] that α,β-enone $^3(\pi,\pi^*)$ states are stabilized by twisting around the C=C bond, and their lifetimes correlate with the expected ease of such twisting.[10,12,21] When **1** achieves such a twisted conformation (depicted in Figure 2), which is ideal for stereospecific rearrangement,[22] the approach of any H donor at C_β will be seriously hindered from the side opposite to the angular methyl substituent but relatively open on the top face, leading to *cis*-phenanthrone **4**. On the other hand, the allylic radical formed from the ^{3}(n,π^*) state by H abstraction on oxygen will be basically planar in ring A.[12] The angular methyl group will hinder attack at C_β by a H-donating species on the top face of this radical, affording ketone **5** after tautomerization of the first-formed trans-fused enol (see Scheme II).

We therefore conclude that phenanthrone **1** indeed displays characteristic photoreactivity of cyclic enones.[2] The observation

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[1] Photochemistry of Ketones in Solution. 64. 63: Calcaterra, L. T.; Schuster, D. I. *J. Am. Chem. Soc.* **1981**, *103*, 2460.

[2] For a review of the reactions of these enones in their excited states, see: Schuster, D. I. In "Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. III, Essay 17.

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[10] Bonneau, R.; Schuster, D. I.; Rao, J. M., unpublished results.

[11] This value is similar to the $k_q\tau$ (51 M^{-1}) reported by Zimmerman et al.[9]

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[17] Reduction to allylic alcohols is not a commonly observed photoreduction mode of α,β-cyclohexenones. The only other report was by Schaffner (Schaffner, K. *Int. Congr. Pure Appl. Chem., 23rd.* **1971**, p 405).

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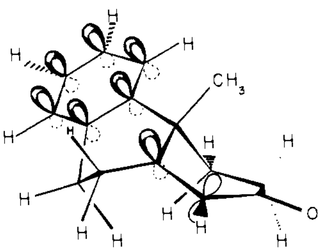
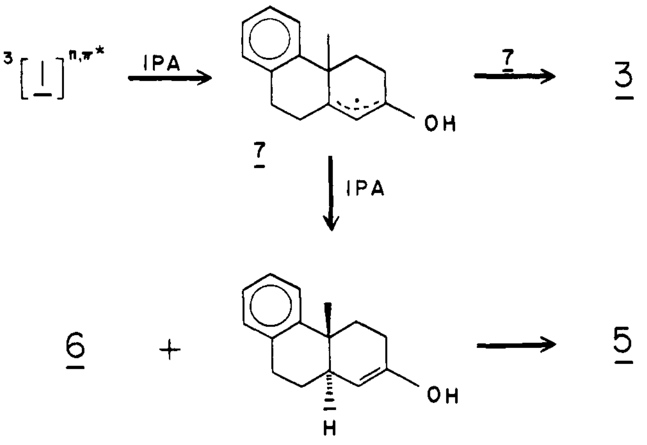


Figure 2. Phenanthrone **1** in its relaxed $^3\pi,\pi^*$ state.

Scheme II



that reduction of the C=C bond of **1** occurs by different mechanisms with opposite stereochemistry from two distinct triplet excited states is unprecedented. The possible generality of this phenomenon will be examined in other enones where the substitution pattern permits elucidation of the stereochemical course of this transformation.

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Registry No. 1, 6606-34-4; **2**, 6606-35-5; **3**, 7363-88-4; **4**, 70524-91-3; **5**, 1686-50-6; **6**, 81457-34-3.

The Methylenoxonium Radical Cation ($CH_2OH_2^{+}\cdot$): A Surprisingly Stable Isomer of the Methanol Radical Cation

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The simplest alcohol, methanol (CH_3OH), is the only low-energy isomer in the CH_4O potential-energy surface.[1] This has also generally been assumed to be the case for the radical cation, most experimental studies of the $CH_4O^{+}\cdot$ system to date having been discussed in terms of the $CH_3OH^{+}\cdot$ structure (**1**).[2] We report in this communication a second $CH_4O^{+}\cdot$ structure, the methylenoxonium radical cation $CH_2OH_2^{+}\cdot$ (**2**), that not only represents an additional stable isomer in the $CH_4O^{+}\cdot$ potential-energy surface but lies lower in energy than $CH_3OH^{+}\cdot$ itself.

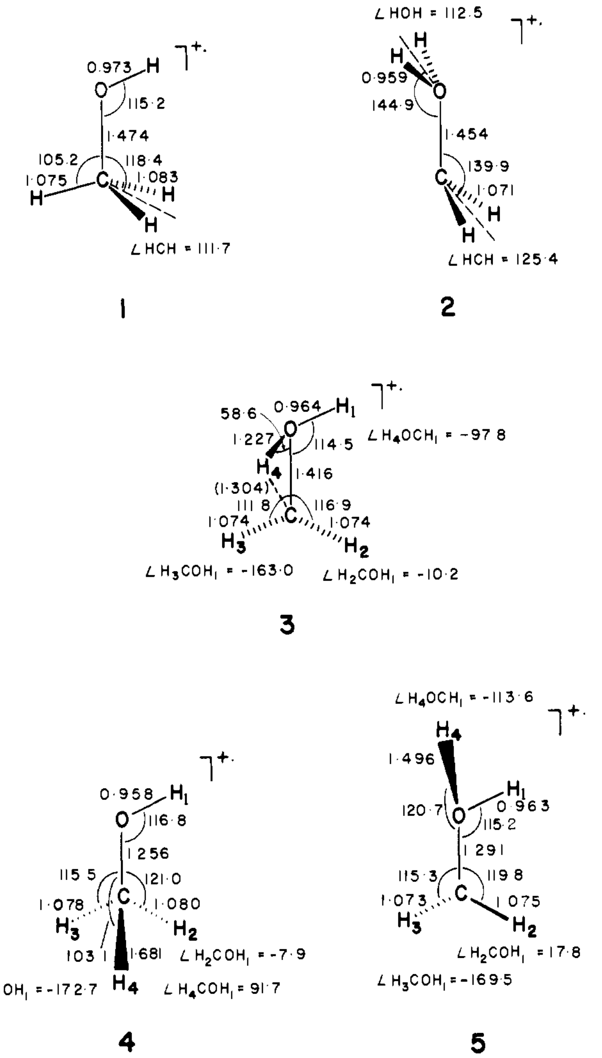

Figure 1. Optimized geometries (HF/6-31G**) of $CH_4O^{+}\cdot$ isomers (**1** and **2**) and transition structures (**3**–**5**).

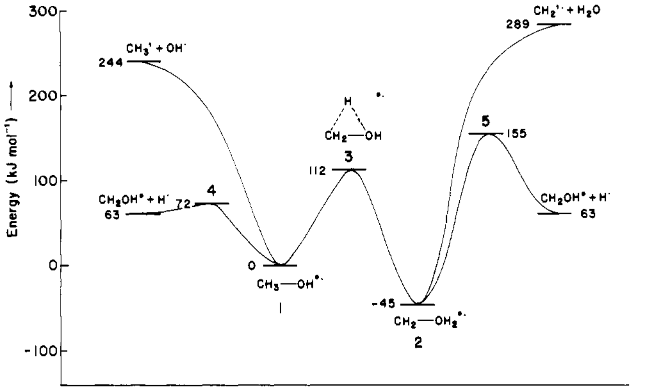

Figure 2. Schematic potential-energy profile for intramolecular and dissociative rearrangements in the $CH_4O^{+}\cdot$ system.

Ab initio molecular orbital calculations with a large basis set and incorporating electron correlation were carried out[3] for **1**, **2**, the transition structure **3** separating these isomers, the transition structures **4** and **5** for loss of H· from **1** and **2**, respectively, and for the dissociation products CH_2OH^+ + H·, CH_3^+ + OH·, and $CH_2^{+}\cdot$ + H_2O. Geometry optimizations utilized analytical gra-

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(1) Harding, L. B.; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1980**, *84*, 3394.

(2) See, for example (a) Beynon, J. H.; Fontaine, A. E.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Phys.* **1968**, *1*, 1. (b) Bertrand, M.; Beynon, J. H.; Cooks, R. G. *Ibid.* **1972**, *9*, 346. (c) Bertrand, M.; Beynon, J. H.; Cooks, R. G. *Org. Mass Spectrom.* **1973**, *7*, 193. (d) Cooks, R. G.; Hendricks, L.; Beynon, J. H. *Ibid.* **1975**, *10*, 625.

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(4) Farnell, L.; Nobes, R. H., unpublished material.