

THE PHOTOCHEMISTRY OF 1,2,2-TRIMESITYLETHANONE

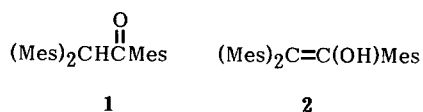
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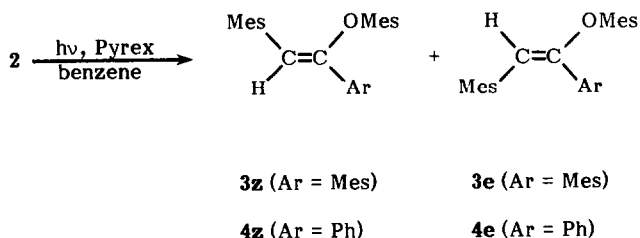
Abstract: Irradiation of 1,2,2-trimesitylethanone **1** gives the enol ethers **3** via a 1,3-mesityl shift in a highly efficient process; the postulated intermediacy of **1** in the photoisomerization of enol **2** is confirmed.

1,2,2-Trimesitylethanone **1**, the keto form of the stable, crystalline enol 1,2,2-trimesitylethenol **2**, has resisted synthesis,¹ and was until very recently unknown. We previously postulated that **1** was an intermediate in the photoisomerization of **2**.² We now provide direct evidence that this postulate was



correct and that the photochemistry of **1** is novel for an aryl ketone. We also respond to some recently published speculations³ regarding the photochemistry of **1**.

Previously we had found² that irradiation of benzene solutions of **2** through Pyrex gave the enol ethers **3z** and **3e**. The reaction proceeded very slowly (3-5 days) but with a high chemical yield. The postulated



mechanism for forming these products involved rearrangement of **2** to **1** (1,3-H shift) followed by rearrangement of **1** to **3** (1,3-mesityl shift). This mechanism was supported by the observation that

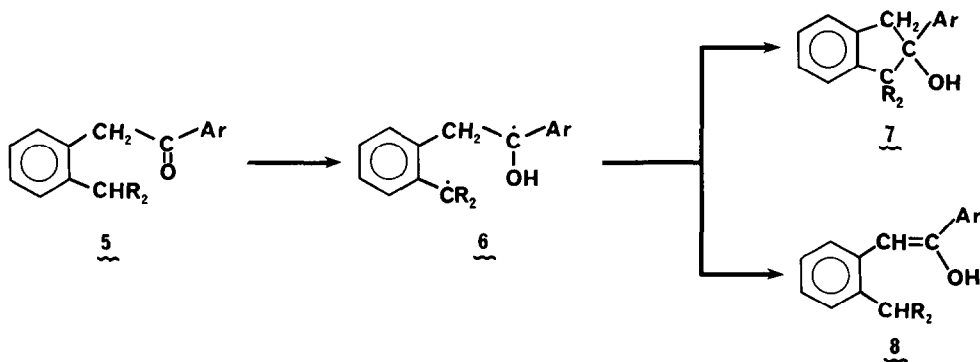
both $(\text{Mes})_2\text{C}=\text{C}(\text{OH})\text{Ph}$ and its known⁴ keto form $(\text{Mes})_2\text{CHC}(=\text{O})\text{Ph}$ gave analogous products **4**. However **1** could not be detected by physical methods (NMR, IR, UV) during irradiations of **2**.

Biali and Rappoport⁵ recently succeeded in synthesizing **1** for the first time, and kindly supplied us with a sample for photochemical study. Irradiation of **1** ($1.8 \times 10^{-2}\text{M}$ in C_6D_6 , Pyrex)⁶ gave **3**. Under conditions which required 5 days for complete conversion of **2** to **3**, the conversion of **1** to **3** was complete in about 30 minutes. It is thus clear why we could not previously detect the presence of **1** by spectroscopic methods in photolyses of **2**.

The yield of **3** from **1** was quantitative. However the **3z/3e** ratio was 1:1, whereas we had previously found² that this product ratio from **2** was about 24:1. This discrepancy in **z/e** ratios was resolved when we found that separate irradiation of **3e** ($3.6 \times 10^{-3}\text{M}$ in C_6D_6 , Pyrex) gave **3z/3e** mixtures, the ratio being 4:1 after two hours and 8:1 after 10 hours, to a limit of 24:1.⁷ Consistent with this result, we now find that irradiation of **2** to very low conversions also gives an initial 1:1 ratio of **3z/3e**.

These experiments confirm **1** as the intermediate in the photoisomerization of **2** to **3**. The formation of **3** from **1** is highly efficient, the quantum yield⁸ being 0.4. In contrast, the formation of **3** from **2** has a quantum yield of only about 3×10^{-3} . The isomerization of **1** to **3** was not quenched by *E*,*E*-2,4-hexadiene.⁹

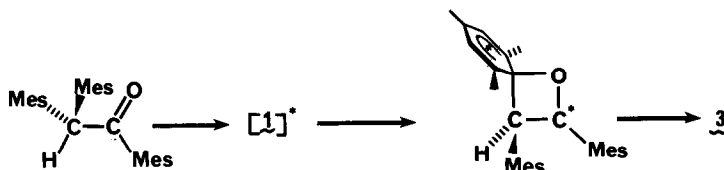
The efficient photoisomerization of **1** to **3** contrasts markedly with the results observed by Wagner and Meador^{3,10} for a series of related but somewhat less hindered ketones. They found that ketones of the type **5** photoisomerize via the triplet state to 1,5-biradicals **6** which either cyclize to indanols



7^{10} or rearrange to enols **8**.³ In comments³ on our original paper¹ they imply that the same type of biradical is involved in the photoisomerization of **2** (and **1**) to **3**, but they propose that with two α -mesityl groups the biradical is too hindered to cyclize to an indanol. They speculate that with **1** and **2** "a steady state favoring enol is probably established rapidly, with enol ether then forming slowly, probably from ketone...." This speculation is inconsistent with our present results. First, though it could easily have been detected, no **2** was formed during the irradiation of **1**. Second, conversion of **1** to **3** was rapid and efficient. Hence in the slow formation of **3** from **2**, the bottleneck must be the slow isomerization of **2** to **1**.¹¹

In an attempt to detect the possible presence of a biradical such as **6**, we irradiated **1** in a solvent that was predominantly CH_3OD .¹² No deuterium could be detected in the products **3** nor, in the case of incomplete conversions, in recovered **1**.

None of the expected photoreactions (i.e., γ - or δ -hydrogen abstraction or α -cleavage) for a benzylic aryl ketone such as **1** was observed. Only 1,3-aryl migration occurred. All our observations support the idea that the photoisomerization of **1** to **3** proceeds via an excited state in which intramolecular ipso attack by oxygen at an α -mesityl substituent is favored over other anticipated processes. This result may be a consequence of ground state conformations of **1** that are especially favorable to this process.¹³



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References and Notes

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2. Hart, H.; Giguere, R. J. *J. Am. Chem. Soc.* 1983, **105**, 7775.
3. Wagner, P. J.; Meador, M. A. *J. Am. Chem. Soc.* 1984, **106**, 3684.
4. Fuson, R. C.; Armstrong, L. J.; Chadwick, D. H.; Kneisley, J. W.; Rowland, S. P.; Shenk, W. J., Jr.; Soper, Q. F. *J. Am. Chem. Soc.* 1945, **67**, 386.
5. Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.*, manuscript submitted.
6. λ_{\max} 250nm (ϵ 11,000) in hexane.
7. We had previously approached this equilibrium from **3z** and did not detect an increase in amount of **3e**; we had not expected such a lop-sided ratio for this photostationary state (see ref. 2, footnote 9), since it is not that way with **4**.²
8. Benzene solutions of **1** (1.05×10^{-2} M) were irradiated at 313 nm using 0.1M valerophenone as the actinometer; Wagner, P. J.; Kempainen, A. E. *J. Am. Chem. Soc.*, 1968, **90**, 5896.
9. [Q], M X 10^{-2} 0.00 0.27 0.54 1.09
 ϕ app. **3** 0.40 0.41 0.45 0.41
10. Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* 1983, **105**, 4484.
11. There is still some uncertainty as to whether the isomerization of enol **2** to ketone **1** is photochemical or thermal. Biali and Rappoport⁵ found that the thermal isomerization of **1** at 80°C in hexane to a 98.8:1.2 equilibrium mixture of **2**:**1** proceeded extremely slowly (incomplete in 48 h and required catalysis by CF₃CO₂H to come to completion in a reasonable time); presumably ketonization of the enol would also be slow,³ particularly at the lower temperature at which the photolyses were conducted. However, the quantum yield for appearance of **3** from **2** (3×10^{-3}) is not far from the product of the quantum yield for the appearance of **3** from **1** times the fraction of **1** present at equilibrium ($0.4 \times 0.01 = 4 \times 10^{-3}$). This result may, however, be coincidental and it may well be that the slow step in photoconversion of **2** to **3** is the slow photoisomerization of **2** to **1**. This difficult question requires further study.
12. The solvent contained 15-20% C₆D₆ to increase the solubility of **1**.
13. The excited state may be a singlet, or it may be a triplet which rearranges to **3** faster than it abstracts a hydrogen from an ortho methyl of either the C₁- or C₂-mesityl group. The ground state conformations of **1** are exceptional.⁵ For example, conjugation between the Mes and C=O group of **1** appears to be substantially greater than in MesCOCH₃.