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THE MECHANISM OF PHOTOENOLIZATION: o-METHYLVALEROPHENONE

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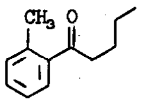
Aryl ketones with ortho alkyl substituents are noteworthy for their photochemical stability, found to be due to a very efficient and reversible hydrogen abstraction reaction.[1] Although apparently mechanistically similar to the Type II photoelimination, a number of authors[1,2,3] have recently suggested that a direct conjugative link between reaction centers may provide a unique and energetically favorable mechanism for photoenolization. Evidence has been presented[2] for the direct formation of an excited triplet enol (in contrast to the 1,4 biradical formed in the Type II reaction).

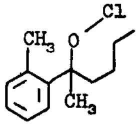
Photoexcited o-methylvalerophenone, 1, has available two chemical options: abstraction by oxygen of an ortho methyl hydrogen (photoenolization) or a γ-hydrogen from the alkyl chain (photoelimination). First investigation of 1 noted that no photoelimination occurred.[3] The use of bimolecular hydrogen abstraction reactions by alkoxy radicals as a model for aryl ketone reactivity[4] would not have placed any strong preference for a primary benzylic hydrogen over a secondary aliphatic.[5] It is tempting, then, to account for the strong preference in terms of an energetic favorability for abstraction at the ortho methyl site.

With these considerations in mind we offer three categories of explanations for this behavior: 1) Geometrical and statistical factors which may contribute significantly in this intramolecular process, 2) Fundamental differences in the two processes as suggested above and 3) Unsuitability of alkoxy radicals as models for these reactions. (Because an n,π* is believed to be the reactive state in photoreactions of aryl ketones, perhaps a model somewhat more electron deficient on oxygen than a free radical is required.)

Decomposition of hypochlorite 2 in CCl_4 solution with weak UV initiation afforded a mixture of chloroalcohols (*inter alia*) which after treatment with sodium hydride in ether[6] generated a high yield of cyclic ethers[7] identified as 3 and *cis* and *trans* 4 by synthesis[8] and their spectral and analytical properties.[9] The ratio of **3** to combined **4** remained invariant at 30 ± 3:1 through a variety of reaction conditions.[10] It is well established that this reaction involves a free radical chain process.[14]



1



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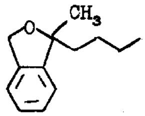

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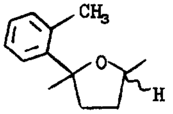

4
(*cis* and *trans*)

Photolysis of *o*-methylvalerophenone results in *o*-methylacetophenone formation, the quantum yield for the process in hexane or benzene, Φ = 0.010 ± 0.001. This value is small relative to the value Φ = 0.41 for valerophenone itself.[15] A *m*- or *p*-methyl substituent does not change the valerophenone value to any large degree,[16] so one can assume that the major lowering effect in the *o*-methyl case is photoenolization. A potential complicating feature in determining relative reactivities of ortho hydrogens *vs.* γ-hydrogens in the photochemical system is the much discussed reversal[17] of initially-formed biradical to the original ketone. Following Wagner's assumption that addition of alcohol to the solvent system retards this reversal,[18] and further that with sufficient alcohol it does not occur,[15a] it can be noted in the accompanying plot (Figure I) that a value Φ = 0.038 ± 0.002 was obtained. Since valerophenone achieves unity quantum efficiency, and since significant reactionless decay would not be anticipated for *o*-methylvalerophenone one obtains a selectivity factor of 26:1 for total abstraction of *o*-methyl *vs.* γ-methylene hydrogens. This value is quite close to the value 30:1 for total *o*-methyl *vs.* γ-methylene in the free-radical system. The closeness of these values affirms the usefulness of the free-radical model in aryl ketone photochemistry and also demonstrates that no kinetic difference can be detected between photoenolization and the photoelimination reaction.

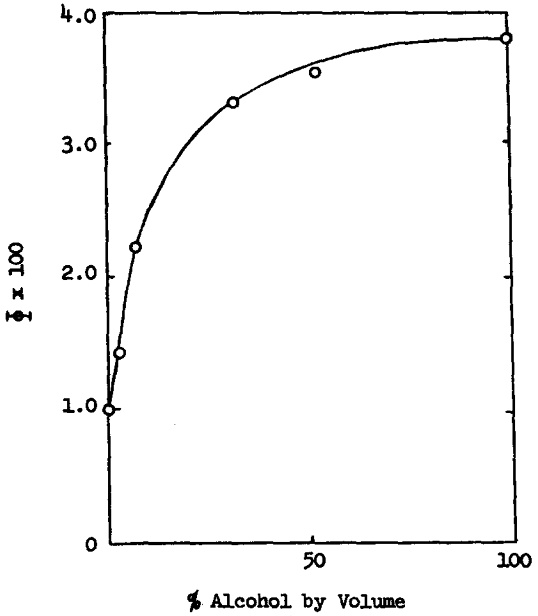

Figure 1: Effect of added *t*-butyl alcohol on quantum yield of photoelimination for *o*-methylvalerophenone.

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7. Other products included 2-(o-tolyl)-1-hexene and 2-(o-tolyl)-2-hexene and traces of o-methylacetophenone and o-methylvalerophenone. Overall yield of ethers 3 and 4 ranged up to 80%. Mass balance was good.
8. The two isomeric ethers 4 were prepared by treatment of 2,5-hexanedione with one equivalent of 2-methylphenyl magnesium bromide followed by reduction with lithium aluminum hydride followed by reduction with lithium aluminum hydride followed by ring closure of the 2,5-diol in acidic ether.
9. Compound 3 had m/e 190 (M^+), 133 (base); nmr (CCl_4) δ 1.5 (12H, m), 5.1 (2H, s), 7.3 (4H, m). Compounds 4 had m/e 190 (M^+), 175, 119; nmr (CCl_4) δ 1.23, 1.27 (3H, d, J = 6 Hz), 1.47 (3H, s); 2.43, 2.78 (3H, s); 2.13 (4H, m); 3.93, 4.17 (1H, m, J = 6 Hz), 7.21 (4H, m). All new compounds gave satisfactory combustion analyses and infrared spectral properties.
10. Interestingly a reaction thought to involve a cationic oxygen, treatment of 2-(o-tolyl)2-hexanol with bromine and silver oxide in the dark[11] generated the same ratio of ethers. The intermediacy of an oxygen cation in this system has been seriously challenged, however.[12,13]
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