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AN UNUSUAL EFFECT OF THE NITRO SUBSTITUENT IN THE TYPE II PHOTOELIMINATION REACTIONS OF ARYL KETONES

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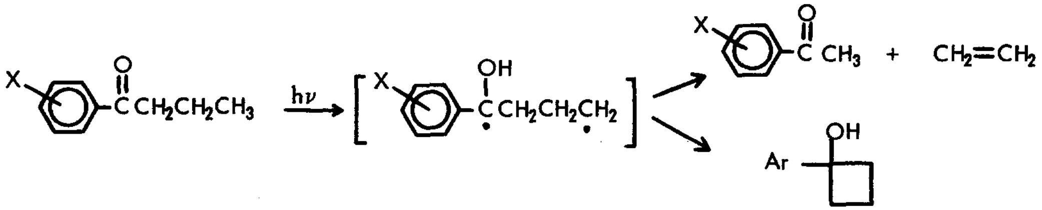
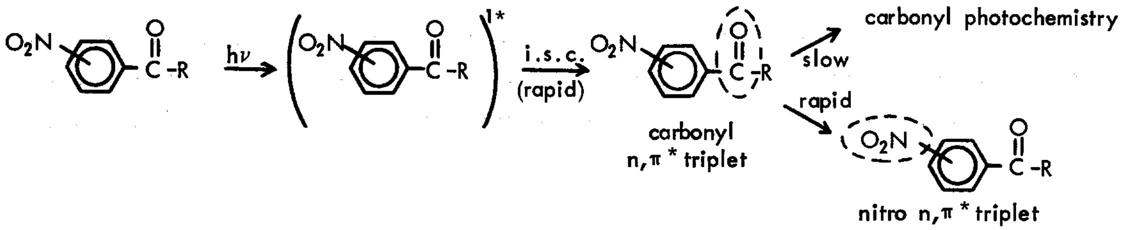
The influence of ring substituents on aromatic carbonyl photochemistry has received considerable attention.[1] The most thoroughly studied photoprocess in this regard is hydrogen abstraction. An intramolecular example is illustrated below. It is well known that electron-donating substituents decrease the rate constant for the initial abstraction and that electron-withdrawing substituents enhance this process.[2] However, unless the rate constant for hydrogen abstraction is quite low ($<10^7 \text{sec}^{-1}$), other processes available to deactivate the excited state are not competitive. Thus the 1,4-hydroxy biradical intermediate can be formed with high quantum efficiency even for unfavorable substituents. This intermediate is known to disproportionate back to the original ketone in solvents which do not hydrogen bond to the hydroxy biradical. Wagner has demonstrated that, with respect to this disproportionation, there is a small ring substituent effect whereby product formation is more favorable for biradicals with electron-donating substituents than for those with electron-withdrawing substituents.[3] Consequently the possibility exists that ketones which are less reactive photochemically can undergo photoelimination with higher quantum efficiency. Thus the different roles played by ring substituents are often not obvious from quantum yields for product formation. In spite of the many studies involving substituent effects on aromatic ketone photochemistry, there is a conspicuous absence



of "positive" results for nitro substituted aromatic ketones.[4] We report here the first examples of such and discuss yet another role played by the nitro group.

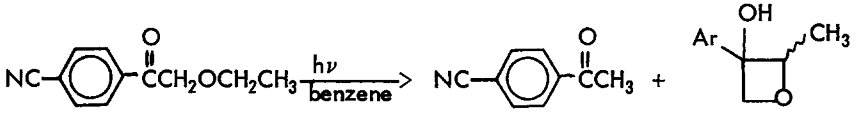
We have found that m-nitrobutyrophenone is photochemically inert under conditions for which high quantum yields for the Type II photoelimination reaction are expected. We can assign an upper limit of less than 2×10^{-5} to the quantum yield for formation of m-nitroacetophenone. An attractive explanation for this lack of photochemistry is that an excited state localized on the nitro substituent is lower in energy than the state known to be responsible for aromatic carbonyl photochemistry ($^3n,\pi^*$ localized on the carbonyl; $E_T = 73 \pm 2$ Kcal-mole^{-1}).[5] We hypothesize that, while the carbonyl localized state may be populated with high quantum efficiency,[6] rapid deactivation occurs to populate the lower lying nitro localized state. A proposed scheme is given below.



A prediction of this scheme is that carbonyl photochemistry will begin to compete with deactivation by altering the nature of the side chain to enhance the reactivity of the hydrogen toward abstraction. The extent to which this occurs should parallel the relative reactivity of the γ-hydrogen. These values are known for a large number of phenyl ketones. Accordingly we have synthesized a series of nitro substituted ketones with more reactive γ-hydrogens. In the table a comparison is made between the hydrogen abstraction rate constants and our observed Type II quantum yields for the corresponding p-nitro substituted derivatives. Minimally a qualitative correlation exists between these values. In fact the close correlation suggests that hydrogen abstraction does indeed compete with a constant process in the nitro ketone series as predicted by the scheme above. In spite of the dramatic increase in carbonyl photochemistry as the side chain is changed from n-propyl to ethoxymethyl, the quantum yields are moderately low even for the most favorable case. Thus it appears that deactivation of the carbonyl $^3n,\pi^*$ state to the nitro localized $^3n,\pi^*$ state is an extremely facile process. Other potential factors must be considered, however, before concluding that the deactivation process is totally responsible for the inefficiency in nitro substituted aromatic ketone photochemistry.

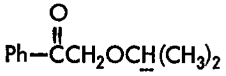
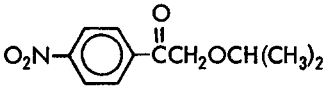
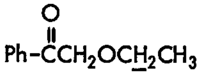
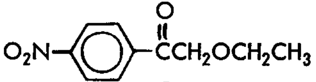
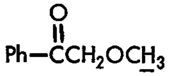
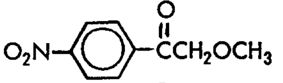
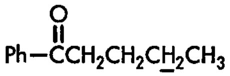
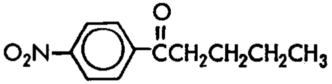
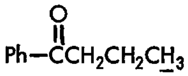
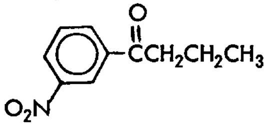
As indicated previously, for alkyl aryl ketones a portion of the inefficiency is due to disproportionation of the hydroxy biradical intermediate. The extent of this can be readily determined by using a hydrogen-bonding solvent which effectively eliminates the disproportionation pathway. We have found that the quantum yield in the case of p-nitrovalerophenone is enhanced by only a factor of two to three in various alcoholic solvents. For m-nitrobutyrophenone the solvent effect is insufficient to render the photochemistry detectable.

Disproportionation is not likely to be an important factor for the α-alkoxy aryl ketones, which are ordinarily extremely efficient in terms of cyclization and elimination.[7] However the effects of ring substituents have not been as thoroughly studied for the α-alkoxy ketones. A particularly pertinent case for comparison is the cyano substituent, which exhibits inductive and resonance behavior very similar to the nitro group[9], but does <u>not</u> have a localized excited state lower in energy than that of the carbonyl (E_T for benzonitrile = 77 Kcal-mole^{-1}).[10] We have studied the photochemistry of p-cyano-α-ethoxyacetophenone and found that it undergoes efficient carbonyl photochemistry as shown below. There is no precedent for enhancing efficiencies for product formation in the α-alkoxy ketone series by using hydrogen bonding solvents, but we have found that there is a small increase (approximately two-fold) for the nitro substituted derivatives.



ϕ = 0.35 ϕ = 0.55

Table. Comparison of the Hydrogen Abstraction Rate Constants for Phenyl Ketones with the Type II Quantum Efficiencies for the Analogous Nitro Substituted Phenyl Ketones

<u>Phenyl Ketone</u>	<u>k, sec^{-1}</u>	<u>(ref)</u>	<u>Nitro Ketone</u>	<u>$\phi^{(a)}$</u>
 $\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}CH_2OC\underline{H}(CH_3)_2}$	8.2 x 10^9	(7)		0.035
 $\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}CH_2OC\underline{H}_2CH_3}$	8.4 x 10^9	(7)		0.048
 $\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}CH_2OC\underline{H}_3}$	3.2 x 10^9	(7)		0.015
 $\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}CH_2CH_2C\underline{H}_2CH_3}$	1.2 x 10^8	(8)		0.00013
 $\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}CH_2CH_2C\underline{H}_3}$	7.5 x 10^6	(8)		<0.00002

(a) total quantum yield for elimination and cyclization; quantum yields were measured using 0.1 M solutions in benzene irradiated with 313 nm light in a conventional merry-go-round apparatus. The valerophenone to acetophenone conversion was used as an actinometer. Conversions were ~5%. The solutions were deoxygenated, but no dependence on the presence of oxygen was observed. No wavelength effect (254 and 366 nm) has been observed.

Finally, the arguments outlined above suggest that the nitro localized excited state is populated efficiently for each of the compounds studied. Thus photochemistry of the nitro group should be observable. Nitrobenzene is photochemically inert in benzene (which was used in the studies discussed above), but it undergoes photoreduction in 2-propanol.[11] We have studied the photochemistry of p-nitro-α-methoxyacetophenone in 2-propanol and found that it undergoes photoreduction of the nitro group with an efficiency comparable to that of other "carbonyl" substituted nitrobenzenes.[11] As required by our hypothesis, the carbonyl Type II photochemistry proceeds unimpaired ($\phi = 0.03$).

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9. For example, the Taft σ_R and σ_I parameters are 0.10 and 0.58 for -CN and 0.16 and 0.63 for $-NO_2$.
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