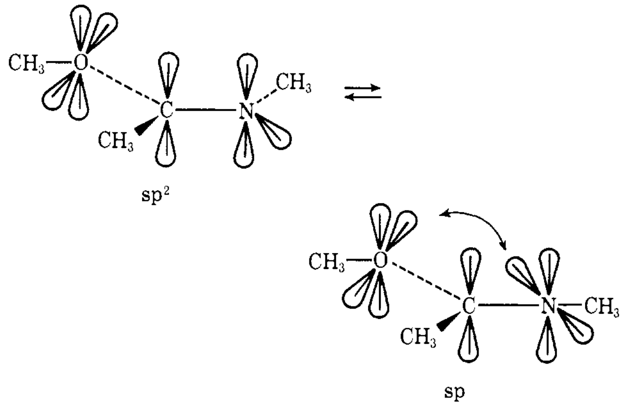
90 hr. This, of course, agrees with a syn form for both the imidate and conjugate acid. Neither form can accommodate an anti imino group. However, the 11-, 13-, and 16-membered systems did undergo equilibration. The ratios found were: 11, anti:syn, 1:1; 13, 1:2; 16, 1:1.5. These results indicate an anti configuration for the free imidate for the 13 and 16 rings which upon protonation goes to a mixture of the predominant syn conjugate acids. The 11-membered ring is of syn configuration in the unprotonated form; the protonated forms in this system are of about equal energy.

We interpret the high barrier to inversion at nitrogen in the *O*-methyl imidates as resulting from interorbital electron repulsion between the nonbonding electrons on oxygen and the electrons localized in a p orbital on nitrogen in the transition state for the $sp^2 \rightleftarrows sp \rightleftarrows sp^2$ inversion process.



The same destabilizing interaction, likewise, may account for the configurational instability of the syn isomer. Protonation relieves this interaction and rotational equilibration of the conjugate acid yields isomers in which relative stabilities are chiefly dependent upon steric interactions.

Studies are underway to support this interpretation with appropriate model compounds, as well as to examine chemical consequences of the higher energy of the syn isomers in small and medium rings.

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* Address correspondence to this author.

Robert M. Moriarty,* Chin-Lung Yeh
Department of Chemistry, University of Illinois
Chicago Circle, Illinois 60680

Kermit C. Ramey, Philip W. Whitehurst
Research and Development Department
Arco Chemical Company
A Division of Atlantic Richfield Company
Glenolden, Pennsylvania 19036

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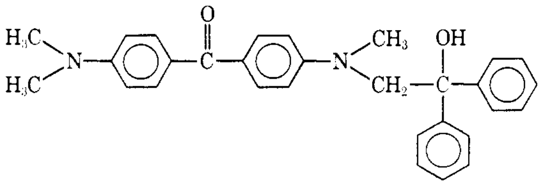
Photoreaction of Michler's Ketone with Benzophenone. A Triplet Exciplex

Sir:

We have discovered that Michler's ketone (4,4′-bis-(dimethylamino)benzophenone) (MK) undergoes a photoreaction with benzophenone, yielding the coupling product I. Because this photoreaction proceeds from the triplet state of MK, yet has its closest analogies in the reactions of triplet benzophenone, we visualize that the photoreaction proceeds through a triplet "exciplex."

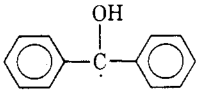
Irradiation of 1.0×10^{-3} *M* MK plus 1.0×10^{-3} *M* benzophenone in 2-propanol in a 366-nm merry-go-round apparatus[1] leads to formation of photoproduct I with a quantum efficiency of 0.079 ± 0.010.



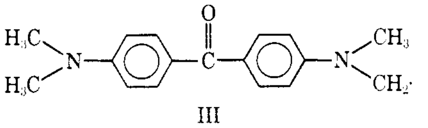
I

The following properties were observed for I: mp 173–175°; mass spectrum[2] *m/e* 450 (M^+); ir (Nujol) 1600 (strong), 3400 cm^{-1} (broad); uv (CH_2Cl_2) 245 (ϵ 1.9×10^4), 356 nm (ϵ 3.5×10^4).

By flash photolysis studies,[3] the presence of two photointermediates was demonstrated. One photointermediate was benzophenone ketyl radical (II), identified by its characteristic absorption spectrum (λ_{max} 546 nm)[4] and second-order decay kinetics ($k = 3.1 \times 10^7$ M^{-1} sec^{-1} in 2-propanol).[5] The second photointermediate shows a broad absorption with λ_{max} 500 nm, and we believe this to be either the radical cation of MK or the corresponding deprotonated species (III). At present, we cannot differentiate between radical or radical-ion intermediates.



II



III

The disappearance of III was monitored at 600 nm, where II does not absorb, and found to follow second-order decay kinetics ($k/\epsilon = 5.3 \times 10^5$ cm sec^{-1}). These kinetics were unaffected by variation in the concentration of benzophenone and by the addition of the triplet quencher 1,3-cyclohexadiene (CHD). These kinetics were taken to represent the coupling of the free radicals II and III to give the final photoproduct I. The kinetics will be second order if II and III are formed in equal amounts and maintain themselves in approximately equal concentrations. This was shown to be essentially true, although there must be some concentration imbalance since the decay of residual II can be observed (*vide supra*) after III is undetectable.

The addition of CHD did diminish the initial concentration of II and III and correspondingly quenched the quantum yield of photoproduct formation. This was the expected consequence of the triplet state of MK.

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(1) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).

(2) Taken by Dr. Alan Duffield with the Stanford University MS-9 low-resolution mass spectrometer.

(3) Using the apparatus and techniques described by W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

(4) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).

(5) Using ϵ_{II} (546 nm) 5100 M^{-1} cm^{-1}: A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

The triplet lieftime of MK was shown to be quenched by CHD at a rate of $1.8 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, near the maximum rate expected in 2-propanol.[6] Since the addition of CHD establishes a competition between CHD and benzophenone for MK triplets, the quenching of the photoreaction by added CHD allows an estimate of the rate at which benzophenone reacts with the triplet state of MK. This rate is about $8 \times 10^6\ M^{-1}\ \text{sec}^{-1}$. These considerations have led us to postulate Scheme I as the mechanism for the photoreaction of MK with benzophenone.

Scheme I

$$\text{MK} \xrightarrow{h\nu} \text{MK}^1 \longrightarrow \text{MK}^3$$

$$\text{MK}^3 \xrightarrow{k_1} \text{MK}$$

$$\text{MK}^3 + \text{Ph}_2\text{CO} \xrightarrow{k_2} [\text{MK}\cdots\text{Ph}_2\text{CO}]^3$$

$$\text{MK}^3 + \text{CHD} \xrightarrow{k_3} \text{MK} + \text{CHD}^3$$

$$[\text{MK}\cdots\text{Ph}_2\text{CO}]^3 \xrightarrow{k_4} \text{II} + \text{III}$$

$$[\text{MK}\cdots\text{Ph}_2\text{CO}]^3 \xrightarrow{k_5} \text{MK} + \text{Ph}_2\text{CO}$$

$$\text{II} + \text{III} \xrightarrow{k_6} \text{I}$$

$$\text{II} + \text{III} \xrightarrow{k_7} \text{MK} + \text{Ph}_2\text{CO}$$

$$\Phi = \frac{abk_2[\text{Ph}_2\text{CO}]}{k_1 + k_2[\text{Ph}_2\text{CO}] + k_3[\text{CHD}]}$$

$$a = k_4/(k_4 + k_5) \qquad b = k_6/(k_6 + k_7)$$

$$k_1 = 1.4 \times 10^4\ \text{sec}^{-1}$$

$$k_2 = 8.0 \times 10^6\ M^{-1}\ \text{sec}^{-1}$$

$$k_3 = 1.8 \times 10^9\ M^{-1}\ \text{sec}^{-1}$$

$$k_6 + k_7 = 5.3 \times 10^5 \epsilon_{\text{III}}\ (600\ \text{nm})$$

$$\Phi_{\max} = ab = 0.22$$

There are a number of apparent analogies for this photoreaction, but all are derived from reactions of photoexcited benzophenone. That is, benzophenone in its triplet state interacts with amines to give charge transfer,[7,8] or, in the case of amines with α hydrogens, ultimate hydrogen abstraction.[9,10] Diphenylamine has been found to undergo photochemical electron transfer to the ground state of benzophenone, but this process requires a two-quantum excitation of the amine.[11]

The intermediacy of triplet benzophenone in this photoreaction can be rather rigorously excluded. MK absorbs over 99% of the incident light at 366 nm, and undergoes intersystem crossing with unit efficiency.[12] Thus the energy for the photoreaction initially resides in the triplet state of MK. This energy cannot be transferred to benzophenone in a triplet energy-transfer process, since this process would be more than 7 kcal/mol endothermic,[13] and on these grounds would be expected to occur at a rate about two orders of magnitude less than the observed rate of interaction, $8 \times 10^6\ M^{-1}\ \text{sec}^{-1}$.[3,14] Furthermore, the triplet state of MK is not expected to undergo any photoreactions at all in 2-propanol solution.[15]

Interactions in excimers and exciplexes have been shown to depend upon both excitation resonance and charge-transfer contributions.[16–18]

$$\text{A*B} \longleftrightarrow \text{AB*} \longleftrightarrow \text{A}^+\text{B}^- \longleftrightarrow \text{A}^-\text{B}^+$$

In this case we might expect both excitation resonance and charge transfer from MK to benzophenone to be of importance.

$$\text{MK}^3\cdots\text{Ph}_2\text{CO} \longleftrightarrow \text{MK}\cdots\text{Ph}_2\text{CO}^3 \longleftrightarrow \text{MK}^{+}\cdots\text{Ph}_2\text{CO}^-$$

Even small contributions of the type indicated to the structure of the exciplex could play an important role in directing the internal conversion process so as to give rise to the observed photointermediate.

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(19) National Science Foundation Graduate Fellow, 1966–1969.

* Address correspondence to this author.

Carl C. Wamser,[19] George S. Hammond*
Contribution No. 4014
Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California 91109

Catherine T. Chang, Charles Baylor, Jr.
E. I. du Pont de Nemours & Company, Incorporated
Experimental Station, Photoproducts Department
Wilmington, Delaware 19898

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Cyclization *via* Solid Phase Synthesis. Unidirectional Dieckmann Products from Solid Phase and Benzyl Triethylcarbinyl Pimelates

Sir:

The Dieckmann cyclization of mixed esters has not been previously reported. In a study of the application of solid phase synthesis[1] to cyclization, we have isolated the products from the essentially unidirectional closure of unsubstituted and 3-ethyl-substituted 1-triethylcarbinyl-7-aralkyl pimelates-*7*-^{14}C (**1**) to triethylcarbinyl 2-oxocyclohexanecarboxylates-*2*-^{14}C (**2**). The preparation of **2b** is particularly significant since the closure of dialkyl 3-alkyladipates, pimelates, and suberates in the opposite direction is well documented.[2–4] We also have observed that replacement of the triethylcarbinyl by ethyl in **1a** and **1b** yields β-keto ester with the label extensively scrambled. This scrambling results from intervention of kinetically competitive transesterification of the original diester prior to cyclization. Use of the triethylcarbinyl moiety as one of the ester groups and as the base minimizes this transesterification, and the extent of transesterification can be mea-

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