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PHOTOCHEMICAL REACTIONS OF CARBONYL COMPOUNDS IN SOLUTION
THE PATERNO-BÜCHI REACTION

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In a series of elegant investigations Hammond demonstrated that the triplet state is the reactive state in the photoreductions of aromatic carbonyl compounds and the photosensitized reactions by these compounds.[1] Independent contributions by Porter,[2] Pitts[3] and Backstrom[4] are in agreement with this finding. The importance of the nature of the low-lying triplet state is illustrated by the difference in the behavior of benzophenone and acetonaphthone. The former has an $n \rightarrow \pi^*$ low-lying triplet state and is photoreduced by alcohols and alkylbenzenes; the latter has a $\pi \rightarrow \pi^*$ low-lying triplet state and is only photoreduced in the presence of strong reducing agents.[5,6] In this investigation, the photochemical formation of oxetanes

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(1) G. S. Hammond, et al., J. Am. Chem. Soc., 83, 2789 (1961) and related papers.

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

(3) J. N. Pitts, H. W. Johnson, Jr. and T. Kawana, J. Phys. Chem., 66, 2456 (1962).

(4) H. L. Backstrom and K. Sandros, Acta Chim. Scand., 14, 48 (1960).

(5) G. S. Hammond and P. A. Leermaker, J. Am. Chem. Soc., 84, 207 (1962).

(6) D. S. McClure, J. Chem. Phys., 17, 905 (1949).

from aromatic carbonyl compounds and 2-methyl-2-butene, determination of the nature of low-lying triplet states of these carbonyl compounds by spectrophosphorimetry and the possible correlation between the course of this photochemical reaction of these carbonyl compounds with the nature of their low-lying triplet states are reported.

The photochemical formation of oxetanes was discovered by Paterno and Chieffi[7] and the mechanism and the structures of products were established by Büchi, Inman and Lipinsky.[8] For their contributions, the reaction is named as the Paterno-Büchi Reaction. Recently the reaction had been examined by Arnold, Hinman and Glick.[9]

Benzaldehyde reacts with 2-methyl-2-butene under the influence of ultraviolet light to give oxetanes (64%), phenylmethylbutenyl carbinols (15%) and dihydrobenzoins (11%).[10] The n.m.r. analysis of the oxetane fraction shows that all four possible oxetanes are present.[11] The direction of addition of the major isomer(s) may be rationalized through the initial addition of an electron deficient oxygen to form a more stable intermediate (equations 1 and 2, Ar=ϕ, R=H) as suggested by Büchi.[8] The ratio of two groups of isomers is approximately 1.6:1. The n.m.r. analysis of the unsaturated alcohol fraction shows the presence of two vinylic methyl groups and an olefinic hydrogen per molecule. These alcohols may be derived from the initial attack

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(7) E. Paterno and G. Chieffi, Gazz. chim. ital., 39, 341 (1909).

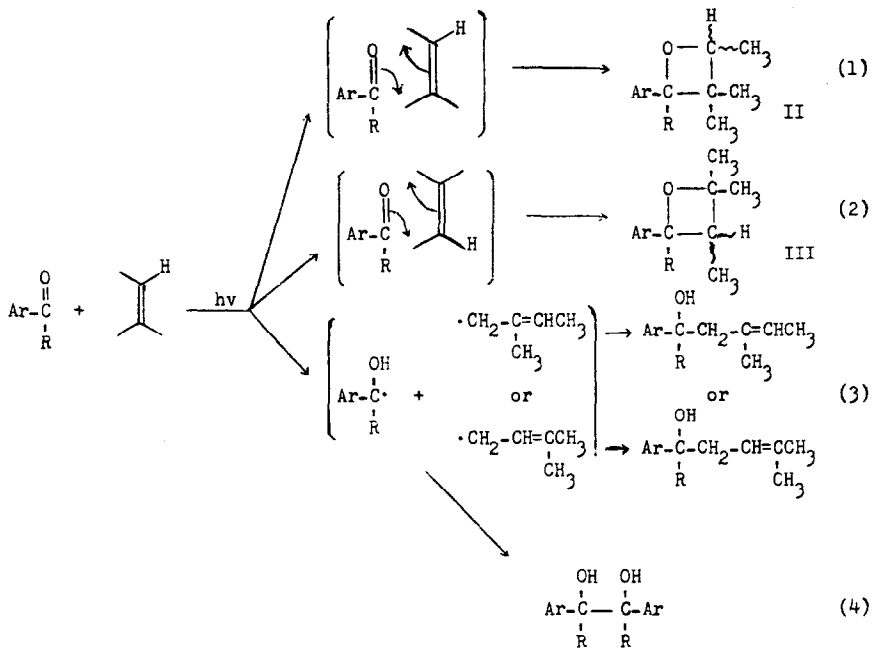
(8) G. Büchi, C. G. Inman and E. S. Lipinsky, J. Am. Chem. Soc., 76, 4327 (1954).

(9) D. R. Arnold, R. L. Hinman and A. H. Glick, Tetrahedron Letters, 1425 (1964).

(10) The reactions reported were carried out with a 450-watt Hanovia medium-pressure mercury arc and a Vycor immersion well unless otherwise stated. The solution of aromatic carbonyl compounds in 2-methyl-2-butene was flushed with high-purity nitrogen for 15 minutes before the irradiation

(11) The n.m.r. analysis was carried out by comparing the area of CH_3-$\underline{CH}$ (quartet, 5.6τ) in isomer II and in isomer III (multiplet, 7.5τ).

of an excited benzaldehyde molecule on a molecule of 2-methyl-2-butene to form an α-hydroxybenzyl radical and an allylic radical from 2-methyl-2-butene followed by the combination of these two radicals (equation 3). The mixture of meso- and d,l-dihydrobenzoin may be derived from the dimerization of α-hydroxybenzyl radicals (equation 4). The reaction may be retarded by the addition of a paramagnetic salt, ferric tris-dipivaloylmethide, indicating that a triplet state is a reactive intermediate. The quantum yield of formation of oxetane is 0.45±0.05 at 2537 Å. p-Methoxybenzaldehyde behaves similarly under these reaction conditions.



Acetophenone and benzophenone also react with 2-methyl-2-butene to form oxetanes.[7,3] The oxetanes formed are more stereoselective, and contained more than 90% of the major isomer(s) (II). A small amount (6%) of benzpinacol was also formed from benzophenone. The quantum yield of oxetane formation from benzophenone is comparable with that of benzaldehyde but that of acetophenone is about 0.1.

The phosphorescence emissions of benzaldehyde, acetophenone and benzophenone at 77°K in MCIP or EPA glass were also examined. Our observations closely correspond to those reported in the literature.[12,6] The observations indicated that the nature of low-lying triplet state of these compounds is $n \rightarrow \pi^*$ in nature.[13,6] The chemical reactions of these compounds indicated that the excited molecules react through an electron deficient oxygen and are quenchable by a paramagnetic salt. These observations indicated that the low-lying triplet states of these compounds may well be the reactive species in these reactions.

An interesting observation is that the 0-0 band of benzaldehyde is not appreciably shifted from MCIP to EPA (not observed in our instrument)[14] as compared with those of acetophenone and benzophenone (about 300 cm^{-1}). The observation suggests that the carbonyl oxygen in the excited benzaldehyde is less electron deficient than those of acetophenone and benzophenone which corresponds to the higher selectivity in the formation of isomeric oxetanes in the case of acetophenone and benzophenone.

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(12) V. Ermolaev, Usp. Fiz. Nauk., 80, 3 (1963).

(13) For a discussion on the characteristics of phosphorescence emissions from $n \rightarrow \pi^*$ triplet states of carbonyl compounds, see M. Kasha, Radiation Res. Suppl., 2, 265 (1960) and ref. 6.

(14) Y. Kanda, private communication, gave the shift at 165 cm^{-1}.

Both 1- and 2-naphthaldehyde react with 2-methyl-2-butene to give oxetanes in yields (70%) comparable to that of benzaldehyde but in lower quantum yields. The oxetanes were separated from the alcohol fractions by chromatography over alumina and purified by molecular distillation (bath temperature 60° at 10^{-5} mm.). They were characterized by their elemental analyses, infrared spectra and n.m.r. spectra. The direction of additions of the major isomers of oxetanes is also similar to that of benzaldehyde. The major isomers are II and the proportion of the II to III is about 3:2. The quantum yields are about 0.05. 2-Naphthyl phenyl ketone also reacts smoothly with 2-methyl-2-butene to give a good chemical yield (62%) of an oxetane (m. p. 135-6°). One particular significant observation is that the direction of addition in oxetane formation is as stereoselective as that of benzophenone. The major isomer is again II with little or no III detected. Quantum yield of this reaction is very low and estimated at 0.005. Both 1- and 2-acetonaphthone were found to be unreactive under similar conditions.

The phosphorescence emissions of 2-naphthaldehyde and 2-acetonaphthone have been reported by McClure[6] and by Ermolaev and Terenin.[15] McClure pointed out that the low-lying triplet state of naphthalene carbonyl compounds is $\pi \rightarrow \pi^*$ instead of $\underline{n} \rightarrow \pi^*$ in nature as in the benzene series.[6] We verified these findings and found that the position of the 0-0 bands of 2-naphthaldehyde, 2-acetonaphthone and 2-naphthyl phenyl ketone are at 480mμ (20,800 cm^{-1}) within experimental error, while those of 1-naphthyl series are at a longer wavelength (505mμ, 19,800 cm^{-1}).

Although there is a marked similarity among the phosphorescence spectra of 2-naphthaldehyde, 2-acetonaphthone and 2-naphthyl phenyl ketone indicating the low-lying triplet states of these compounds are $\pi \rightarrow \pi^*$ in nature, there

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(15) V. Ermolaev and A. Terenin, J. Chim. Phys., 55, 698 (1958).

is a difference among their chemical behaviors. 1-Naphthaldehyde, 2-naphthaldehyde and 2-naphthyl phenyl ketone react similarly to the corresponding phenyl derivatives but with diminished quantum yields. The direction of additions suggests that the reactions proceed through an electron deficient oxygen which implies the reactive species to be $\underline{n} \rightarrow \pi^*$ in nature. Since 1- and 2-acetonaphthone are unreactive, these observations indicate that there are factors additional to the nature of low-lying triplet states responsible for the chemical behaviors of these compounds.

The photochemical addition of 2-methyl-2-butene to 9-anthraldehyde was then investigated. The energy level of the low-lying triplet of anthracene is at 14,800 cm^{-1}.[6] We estimated by analogy that the low-lying triplet of 9-anthraldehyde will be also at about 14,800 cm^{-1} and $\pi \rightarrow \pi^*$ in nature. Assuming the energy level of the $\underline{n} \rightarrow \pi^*$ triplet state of a carbonyl compound is not appreciably changed by conjugation, the difference in energy levels between the low-lying $\pi \rightarrow \pi^*$ triplet and the $\underline{n} \rightarrow \pi^*$ triplet of anthraldehyde will be considerably larger than the corresponding difference in naphthalene carbonyl compounds. The internal conversion between the triplet states of anthraldehyde will thus become a less likely event.[16,17] If the $\underline{n} \rightarrow \pi^*$ triplet state is the reactive state in the Paterno-Büchi Reaction, 9-anthraldehyde will be more chemically reactive than the naphthaldehydes and may emit from the upper triplet state.

The photochemistry of 9-anthraldehyde has been recently investigated by Greene and his coworkers.[18] The principle reaction is the dimerization through the 9,10-positions of the anthracene nucleus. This is in agreement

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(16) G. W. Robinson and R. P. Frosch, J. Chem. Phys., 38, 1187 (1963).

(17) M. Beer and H. C. Longuet-Higgins, ibid., 23, 1390 (1955).

(18) F. D. Greene, S. L. Misrock and J. R. Wolff, Jr., J. Am. Chem. Soc., 77, 3852(1955); F. D. Greene, S. R. Ocamp and R. A. Kaminski, ibid., 79, 5957 (1957).

with the supposition that the low-lying triplet is $\pi \rightarrow \pi^*$ in nature and the excitation energy is mainly localized in the aromatic system. But we observed an entirely different reaction when 9-anthraldehyde was irradiated in 2-methyl-2-butene. We found that the main product is an oxetane fraction (m.p. 160-163°). The direction of addition is stereoselective in that only isomer(s) II is detected by n.m.r. spectrometry. The quantum yield of this reaction is higher than those for naphthaldehydes and the reaction is so rapid that no dimer was detected in the mixture when all the aldehyde had reacted. This is in agreement with our prediction that the reaction may proceed through the $\underline{n} \rightarrow \pi^*$ excited state. With prolonged irradiation, the oxetane(s) slowly dimerizes to give a highly insoluble dimeric fraction. Another interesting observation on the photochemical reactions of 9-anthraldehyde is that the reaction is wavelength dependent. By using a solution of 2,2'-dihydroxybenzophenone as a cut-off filter, the oxetane formation from 9-anthraldehyde in 2-methyl-2-butene was completely suppressed with light longer than 410mμ. Only 9-anthraldehyde dimer (60%), anthrol, anthraquinone together with some unidentified products were isolated as the products.[19] Since 9-anthraldehyde still absorbs strongly above 410mμ,[20] this experiment suggests that the lowest singlet excited state is an unlikely intermediate in the oxetane formation. The full significance of this experiment cannot be realized until the absorption spectrum of anthraldehyde is completely analyzed.

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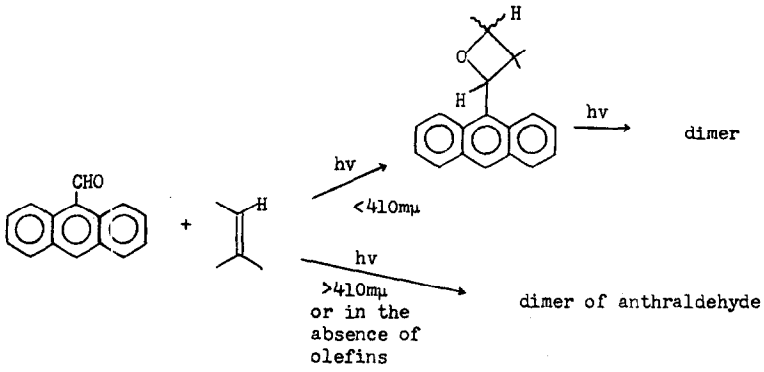
(19) F. D. Greene, Bull. soc. chim. France, 1356 (1960); our observation parallels this report by Greene that the photochemical reactions of 9-nitroanthracene is also wave length dependent and that the dimer is formed with light of wavelength longer than 410mμ while bianthrone is formed with shorter wavelength light.

(20) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds", John Wiley & Sons, New York, 1951, 394.



We have not as yet detected the phosphorescence emission from 9-anthraldehyde. Our earlier observation on the emission was due to the presence of a trace (less than 0.01%) of anthraquinone in our samples of anthraldehyde.

In conclusion, we wish to suggest that the photochemical reactions of aromatic carbonyl compounds depend on factors in addition to the nature of the low-lying triplet states. If the low-lying triplet is a non-reactive one ($\pi \rightarrow \pi^*$) while the upper triplet is a reactive one ($\underline{n} \rightarrow \pi^*$), the internal conversion between these two states may be sufficiently slow to allow a bimolecular chemical reaction to occur in solution in some instances.

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