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

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INTRODUCTION

This work represents a joint effort between my research group and that of Professor Donald S. McClure to correlate the nature of chemical reactions of aromatic carbonyl compounds and their excited states. The chemical experiments were carried out briefly in the beginning of this investigation by Dr Margaret J. Jorgenson and in major part by Dr Manesse Nussim; the physical measurements were made by Mr Steven Murov.

In a series of elegant investigations, Hammond demonstrated that the triplet state is the reactive state in the photoreduction 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 behaviour of benzophenone and acetonaphthone. The former has an $n \rightarrow \pi^*$ low-lying triplet state and is photoreduced by alcohols and alkylbenzenes; and the latter has a $\pi \rightarrow \pi^*$ low-lying triplet state and is only photoreduced in the presence of strong reducing agents[5, 6].

The photochemical formation of oxetanes from various aromatic carbonyl compounds and 2-methyl-2-butene and the phosphorescence emission of these compounds were investigated. The reaction 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 the Paterno-Büchi Reaction. Recently, the reaction had been examined by Arnold, Hinman and Glick[9]. The phosphorescence emissions of aromatic carbonyl compounds have been examined extensively by McClure[6] and by Ermolaev and Terenin[10].

THE REACTIONS OF BENZALDEHYDE, ACETOPHENONE AND BENZOPHENONE

Benzaldehyde reacts with 2-methyl-2-butene under the influence of ultraviolet light to give oxetanes (64 per cent), phenyl methylbutenyl carbionols (15 per cent) and dihydrobenzoins (11 per cent). The n.m.r. analysis of the oxetane fractions shows that all four possible oxetanes are present. 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 the two groups of isomers is approximately 1·6:1. The n.m.r. analysis of the unsaturated alcohol fractions shows the presence of two vinylic methyl groups and an olefinic hydrogen per molecule. These alcohols may be derived from the initial attack 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 trisdipivaloylmethide, 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.
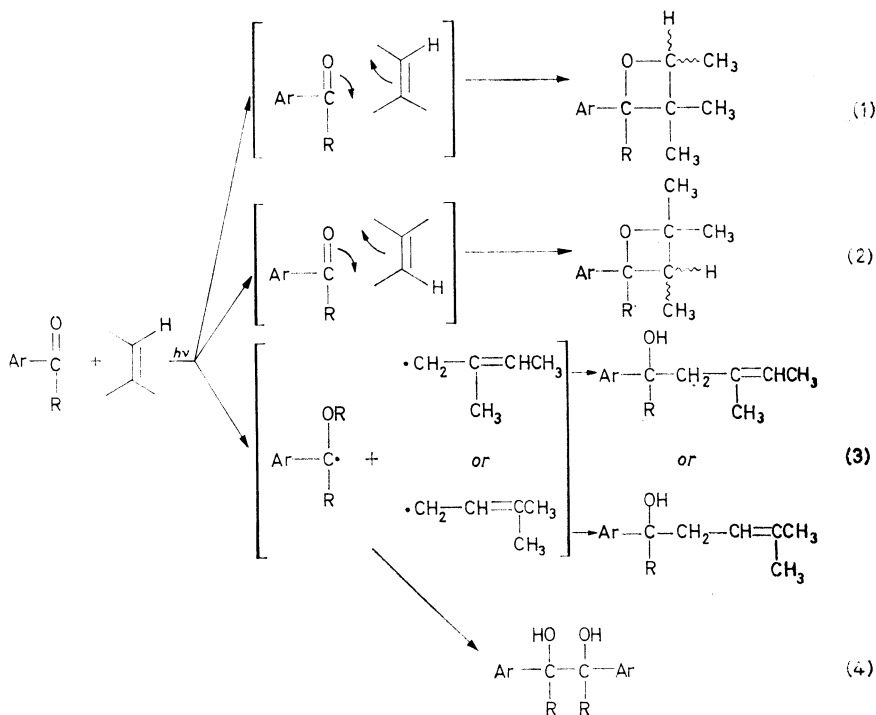
Acetophenone and benzophenone also react with 2-methyl-2-butene to form oxetanes. The oxetanes formed are stereoselective, and contained more than 90 per cent of the major isomer(s). A small amount (6 per cent) of benzpinacol was also formed from benzophenone. The quantum yield of oxetane formation from benzophenone is comparable with that of benzaldehyde but that of acetophenone is about 0·1.

The phosphorescence spectra 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. All

three compounds exhibit the characteristic quintet with the second member being the most prominent. The maxima positions were blue shifted as the medium was shifted from an aprotic one to a protic one. The vibrational splittings were about 1700 cm^{-1}, and the mean life-times were of the order of milli-seconds and the quantum yields of emission are from 0·4–0·7[6, 10]. The observations indicated that the nature of low-lying triplet states of these compounds is $n{\to}\pi^*$ in nature. 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 two 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 O–O band of benzaldehyde is not appreciably shifted from MCIP to EPA (not observable on our instrument) as compared with the shifts of acetophenone and benzophenone (about 300 cm^{-1}). This 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.

1-NAPHTHALDEHYDE, 1-ACETONAPHTHONE, 2-NAPHTHALDE-HYDE, 2-ACETONAPHTHONE AND 2-NAPHTHYL PHENYL KETONE

Both 1- and 2-naphthaldehyde react with 2-methyl-2-butene to give oxetanes in yields comparable to that of benzaldehyde but in lower quantum yields. The direction of addition of the major isomers of oxetanes is also similar to that of benzaldehyde. The major isomers are those with the CH$_3$CH— end of the olefin next to the oxygen atom of the oxetanes (II) and the proportion of the major isomers (II) to that of minor isomers (III) is about 3:2. The quantum yield is about 0·05.

In contrast to a current report that 2-naphthyl phenyl ketone does not react with isobutylene photochemically[9], we found that 2-naphthyl phenyl ketone reacts smoothly with 2-methyl-2-butene to give a good chemical yield of oxetanes. One particularly significant observation is that the direction of addition of the oxetane formation is as stereoselective as that of benzophenone. The major isomer(s) is again (II) with little or no minor isomer(s) (III) detected. The quantum yield of this reaction is very low and estimated at 0·005.

1-Acetonaphthone and 2-acetonaphthone were found to be unreactive under identical conditions.

McClure[6] pointed out that the phosphorescence spectra of carbonyl derivatives of naphthalene are distinctly different from those of benzene series. They are more similar to the emission of naphthalene both in their contours and life-times. These observations suggested that the energy of the excited state is mainly localized in the naphthalene moiety of the molecule but not in the carbonyl group. The low-lying triplet is $\pi{\to}\pi^*$ instead of $n{\to}\pi^*$ in nature as in the benzene series. We verified these fidings and observed that the first number of the emission multiplets is always the most prominent. The regular vibrational splitting by the carbonyl stretching

frequencies is not observed. The quantum yields of emission are low[10]. There is a slight medium dependence on the position of emission in the 1-naphthyl compounds, but the spectra are virtually identical in contour, lifetime as well as in position of the maxima in both MCIP and EPA. The positions of the O–O bands of 2-naphthaldehyde, 2-acetonaphthone and 2-naphthyl phenyl ketone are the same within experimental error (20,800 cm^{-1}), while those of 1-naphthyl series are at a longer wavelength (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 is a difference among their chemical behaviour. 1-Naphthaldehyde, 2-naphthaldehyde and 2-napthhyl 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 may be $n \rightarrow \pi^*$ in nature. Since 1-acetonaphthone 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 behaviours of these compounds.

FLOURENONE

Flourenone reacts with 2-methyl-2-butene photochemically to give 6,6-dimethyldibenzfulvene (equation 5). The hydrocarbon is a primary chemical product not formed during the work-up as indicated by the fact that the spectra of the crude reaction mixture are similar to those of the product. Acetaldehyde is also isolated from this reaction.

Flourenone emits strongly from its excited singlet state but weakly from its triplet in contrast to benzophenone. The phosphorescence may be detected by means of a phosphorescope. The maximum of emission is at 565 mμ (17,700 cm^{-1}) its lifetime is 2 milliseconds indicating the low-lying triplet may be $n \rightarrow \pi^*$ in nature. We wish to suggest the triplet reacts with


(5)
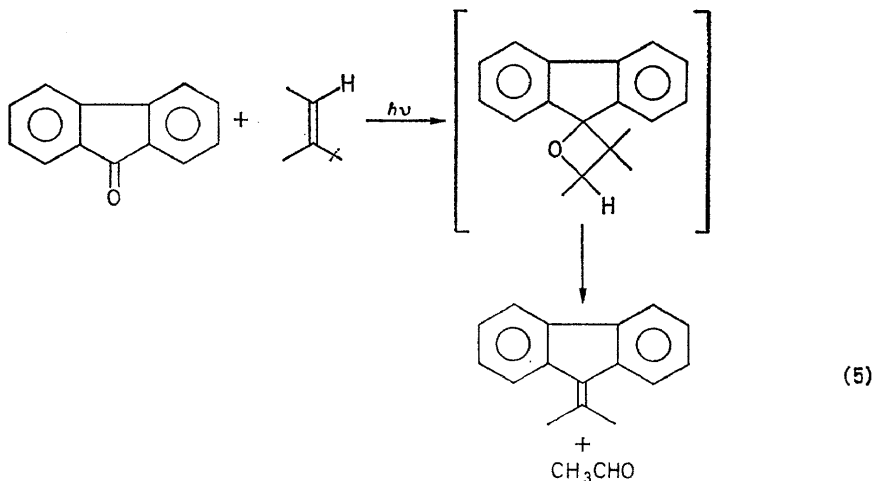
2-methyl-2-butene stereoselectively to form a metastable oxetane which decomposes to give the hydrocarbon and acetaldehyde.

CINNAMALDEHYDE AND CROTONALDEHYDE

Cinnamaldehyde and crotonaldehyde react with 2-methyl-2-butene to give oxetanes and cyclobutane aldehydes, but no dihydropyrans are detected (equation 6). These reactions indicate that "free" radical intermediate is unlikely in the Paterno-Büchi reactions.


$$\text{RCH=CHCHO} + \quad \xrightarrow{h\nu} \qquad\qquad\qquad\qquad\qquad (6)$$
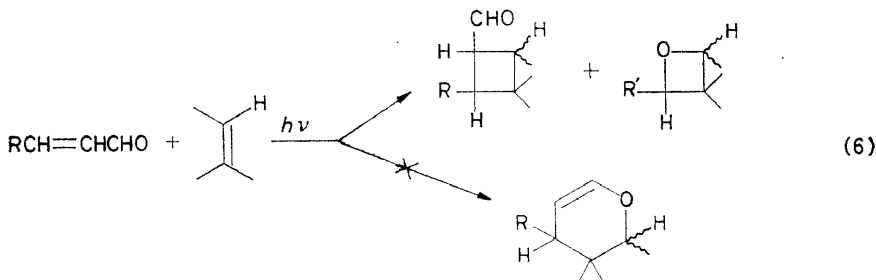
9-ANTHRALDEHYDE, AND 9-ACETYLANTHRACENE

The reactions of 9-anthraldehyde and 9-acetylanthracene were then investigated. The energy level[6] of the low-lying triplet of anthracene is at 14,800 cm^{-1}. We estimated by analogy that the low-lying triplet of 9-anthraldehyde will also be at about 14,800 cm^{-1} and $\pi \rightarrow \pi^*$ in nature. Assuming the energy level of $n \rightarrow \pi^*$ 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 $n \rightarrow \pi^*$ triplet of anthraldehyde will be considerable larger than the corresponding difference in naphthalene carbonyl compounds. The internal conversion between the triplet state of 9-anthraldehyde thus becomes a less likely event[11, 12]. If the $n \rightarrow \pi^*$ triplet 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 co-workers[13]. The principle reaction is the dimerization through the 9,10-positions of the anthracene nucleus. This is in agreement 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. 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 was reacted. This is in agreement with our prediction that the reaction may proceed through the $n \rightarrow \pi^*$ 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 the proper sharp-cut off filter, the oxetane formation from 9-anthraldehyde in 2-methyl-2-butene was completely suppressed with light longer than 410 mμ. Only 9-anthraldehyde dimer (60 per cent), anthrol, antraquinone together with some unidentified products were isolated as the products[14]. Since 9-anthraldehyde still absorbs strongly above 410 mμ, 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 analysed. 9-Acetylanthracene undergoes photodimerization in the presence or in the absence of 2-methyl-2-butene.

$$(7)$$
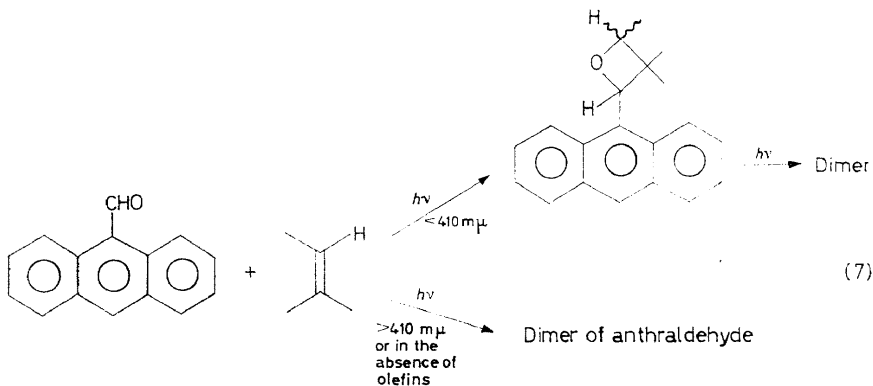
We have not as yet detected the phosphorescence from 9-anthraldehyde. Our earlier observation on the emission was due to the presence of a trace (less than 0·01 per cent) of anthraquinone in our samples of anthraldehyde.

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 state is a non-reactive one ($\pi \rightarrow \pi^*$) while the upper triplet is a reactive one ($n \rightarrow \pi^*$), the internal conversion between these two states may be sufficiently slow to allow a bimolecular chemical reaction to occur in solution in some instances.

References

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