November, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***56****, 3497—3498 (1983)* 3497

The Wavelength Dependence of the Photochemical Reaction of 9-Anthracenecarbaldehyde with 2-Methyl-2-butene

Fujio Tanaka and Shigeru Yamashita*

College of Integrated Arts and Sciences, University of Osaka Prefecture, Mozu-umemachi, Sakai, Osaka 591

(Received February 28, 1983)

Synopsis. Photochemical reaction of 9-anthracenecarbaldehyde with 2-methyl-2-butene was studied under irradiation of >410 and 366 nm. Oxetane formation is predominant in both the wavelength cases, as revealed through isolation of reaction products and examination of their NMR, mass, and UV spectra.

In recent years, photocycloaddition reaction of carbonyl compounds to olefins yielding oxetanes has been an interesting subject for many workers.1) A wide variety of reaction mechanisms have been proposed with many kinds of excited species as photoreactive states depending on the combination of carbonyl compounds and olefins.

Generally speaking, mechanisms for the oxetane formation by photocycloaddition of excited carbonyl compounds with acyclic olefins have been elucidated for many cases, and several reviews have been published.1l,1m)

The photochemical reaction of 9-anthracenecarbaldehyde (9-CHO-A) having the $T_1(\pi,\pi^*)$ state with olefins has been studied by many workers with diverse results. Yang1d) observed an oxetane formation in an irradiation at <410 nm on a mixture of 9-CHO-A and 2-methyl-2-butene, while under an irradiation at longer than 410 nm no oxetane formation was observed and the main product was the dimer of 9-CHO-A. Though Warwick and Wells8) ascertained a similar wavelength effect on the carbonyl photoreaction using 2,3-dimethyl-2-butene as olefin, the main product was found to be pinacol and not oxetane as reported by Yang. Porter and Suppan9,10) found spectroscopically the photoreduction of the carbonyl group to occur regardless of irradiation wavelength and suggested that the lowest excited singlet state (S_1) is the reactive state. Hirayama11) supported the reaction mechanism *via* the upper triplet state on the basis of a spectroscopic ground. It was pointed out1n) that the irradiation at a longer wavelength (440 nm) was effective for the formation of oxetane in the case of 9-CHO-A with 2,3-dimethyl-2-butene, suggesting the necessity of reexamination of the previous result for the case of 9-CHO-A with 2-methyl-2-butene. However, no detailed description has been reported. At any rate, the effect of wavelength on the formation of oxetanes in the photochemical reaction of 9-CHO-A and simple olefins remains unclarified without any further reports concerning this point.

The diversity of the results obtained by the previous workers about the wavelength dependence of the reaction seems to be closely associated with the fact that oxetane, which is thought the most probable product, has not been isolated for identification under the irradiation of longer wavelengths. The isolation of oxetane was reported in only one case of shorter wavelength irradiation.1d)

In the present work, we have reinvestigated the photochemical reaction of 9-CHO-A with 2-methyl-2-butene in order to isolate and identify the reaction products and to ascertain the wavelength dependence of the reaction. A solution containing 206 mg of 9-CHO-A in 50 ml of 2-methyl-2-butene was irradiated under the condition of λ>410 nm. All runs were carried out without deaeration since the absence of influence by oxygen was already confirmed.1b,10,11)

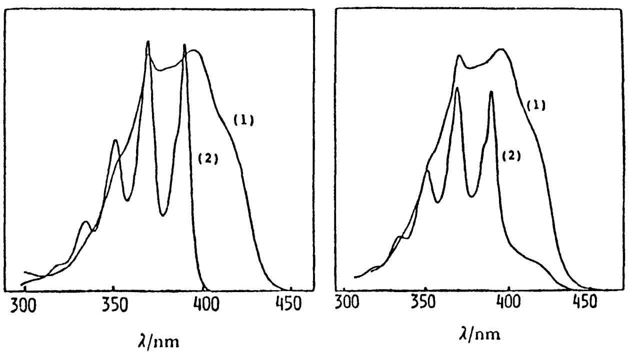


Fig. 1. The change of absorption spectrum by the irradiation of >410 nm(left) and 366 nm(right). (1): Before and (2): after the irradiation. The concentration for reaction is 2×10^{-2} M. The spectra were measured by diluting to 1/250 with hexane.

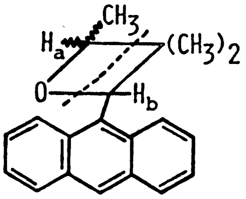
The absorption spectra obtained before and after the irradiation are shown in Fig. 1(left). The appearance of the band structure typical of the anthracene ring indicates that the carbonyl group is photoreduced keeping the anthracene ring unchanged.

In the process of trying to isolate reaction products, we found that the main product was unstable in neat or concentrated conditions while it was stable in dilute solution. The absorption band in the near UV region disappeared gradually as the degradation of the main product proceeded. With the lability of the main product taken into account, the separation of products from the reaction mixture was carefully performed by column chromatography (silica gel–benzene).

The main product (*ca.* 100 mg) thus obtained was an oily substance with a peak for the 0-0 band (λ_{0-0}) at 390 nm in hexane. The ^{1}H NMR spectrum of this compound shows a distinct signal of quartet at 4.70 ppm, assigned to H_a of the oxetane isomer **1** formed by the photoreaction of carbonyl compounds with 2-methyl-2-butene.1b) The mass spectrum showing peaks at m/e=276 (the molecular ion of formula **1**) and 232 (the fragment ion shown by the broken line) also supports the molecular structure predicted on ^{1}H NMR.

As a minor product, an unidentified compound showing the absorption of λ_{0-0} at 386 nm and mass spectral peaks at m/e=276 and 259 was separated.

A similar experiment was carried out under irradiation of 366 nm. The change in absorption spectrum with the irradiation for 8 h is shown in Fig. 1 (right). Since the reaction product suffered a further photochemical change at this wavelength, the isolation



Formula **1**. H$_a$ displays a ^{1}H NMR signal of quartet at 4.7 ppm. A broken line shows the fragmentation causing a peak of $m/e=232$ in the mass spectrum.

of products was performed before reaction of the entire 9-CHO-A had been completed.

The main product obtained by the 366 nm irradiation was found to be oxetane **1** again the same as the product obtained under the irradiation of $\lambda>410$ nm, as inferred from the absorption spectra and ^{1}H NMR spectra.

Thus the results obtained indicate that oxetane is formed in both the 366 nm and >410 nm excitations, no significant wavelength dependence being able to be observed.

Since the photodimer of 9-CHO-A posseses no absorption band in the wavelength region longer than 300 nm, the ratio of photoreaction of carbonyl to photodimerization is obtained from the absorption spectra before and after the photoreaction. The ratios for the irradiation of $\lambda>410$ nm were found 73/27 at 2×10^{-2} M (1 M=1 mol dm^{-3}) of 9-CHO-A and 86/14 at 2×10^{-3} M of 9-CHO-A. The photodimerization was negligible at concentrations lower than 2×10^{-4} M. The quantum yield of the photoreaction of carbonyl by the excitation with 436 nm was 3.4×10^{-2} at the concentration 2×10^{-3} M of 9-CHO-A. Potassium ferrioxalate was used as a chemical actinometer.

Under the experimental conditions of this work, the primary process is the photoexcitation of 9-CHO-A to its S_1 state followed by the intersystem crossing to the $T_n(n\pi^*)$ state located about 60 kcal/mol higher than the ground state.[11,8)] The primary process from S_1 to T_n by intersystem crossing has also been found in the photochemical reaction of β,γ-unsaturated ketone.[12)] When the triplet level of carbonyl compound is lower than that of olefin compound, oxetane formation has been found predominant since the energy transfer to olefin molecule causing dimerization of olefin is improbable. This reaction energetics has been seen in reactions of carbonyl compounds and norbonene. The same situation seems to be applicable in the present study on the 9-CHO-A and 2-methyl-2-butene system. The T_1 energy of 2-methyl-2-butene is supposed to be about 80 kcal/mol in view of T_1 levels of other olefins being higher than the above-mentioned $T_n(n\pi^*)$ state of 9-CHO-A.

Therefore, any energy transfer to olefins from 9-CHO-A is improbable and oxetane formation is predominant regardless of the exciting wavelengths as has been found in the present work.

Experimental

The preparation of 9-CHO-A was carried out according to the literature.[13)] An ultra high pressure mercury lamp (Ushio USH 500) was used as the light source. The wavelengths of >410, 366, and 436 nm were isolated with Toshiba filters V-Y43, (UV35+UV-D1b), and (V-Y43+V40), respectively.

*Isolation of Oxetane **1** and Spectroscopic Measurements.* 2-Methyl-2-butene was evaporated from the irradiated solution, and the hexane-soluble part of the residue was chromatographed on silica gel using benzene as eluent. The main fractions following the degradation products were collected, and a check was made on the UV spectra of effluents. After the removal of benzene the hexane-soluble part was submitted to spectroscopic measurements. To reduce the degradation of oxetane, the chromatographic separations were performed on a smaller scale in UV and MS measurements where only a little sample was needed. The recorded ^{1}H NMR spectrum showed a fairly clear pattern, though the contamination due to degradation could not entirely be avoided: ^{1}H NMR (C_6D_6) $\delta=0.50$ (CH_3 with a slight split by isomers), 1.20—1.28 (m, $2\times CH_3$), 4.70 (q, $J=3.8$ Hz, H$_a$), 6.98 and 7.08 (s, H$_b$ isomers), and 7.18—8.25 (aromatic); MS (70 eV) m/e (%) 276 (2.5), 232 (72), 217 (100), and 206 (50), and (20 eV) 276 (16), 232 (57), 217 (60), and 206 (100); UV$_{max}$(hexane) 390, 369.5, 351 and 257 nm.

We wish to thank Drs. Setsuo Taniguchi, Shun-ichi Kawamura, and Mitsuo Chubachi of Radiation Center of Osaka Prefecture for the measurements of NMR and mass spectra.

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