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THE PHOTOREACTIVE STATES OF 9-ANTHRALDEHYDE

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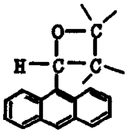
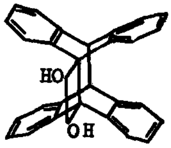
The recent publication by Yang and Loeschen (1) on the photochemical reaction of 9-anthraldehyde with 2,3-dimethyl-2-butene prompts us to report our findings on this and other systems involving 9-anthraldehyde. We have studied the photo-reaction of 9-anthraldehyde with 2,3-dimethyl-2-butene under experimental conditions ($\lambda = 3660^{\circ}$A, temp. = 30-35°) which differ from those of Yang et al. (2). Whereas Yang (3) has found that the oxetane I was the major product of the reaction when light of wavelength shorter than 400 mμ was used, we have found that under our conditions the pinacol II and polymeric material are the major products of the reaction and that oxetane I and also the dimer of 9-anthraldehyde are minor products. Pinacol II was also formed in the photo-reaction of 9-anthraldehyde with toluene under our experimental conditions along with the dimer of 9-anthraldehyde, polymeric material and dibenzyl.



I



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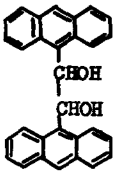
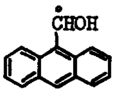
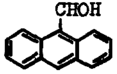


III

Pinacol II was characterised by elemental analysis, the infrared spectrum (-OH stretching band at 3460 cm^{-1}), the ultraviolet spectrum (lack of 'anthracene type' absorption in the region 300-400 mμ) and the mass spectrum (molecular ion peak m/e 414, base ion peak m/e 207). Pinacol II is most probably formed in the reaction sequence

(9-anthraldehyde) + hv → (9-anthraldehyde)* (1)

(9-anthraldehyde)* + RH →  + R• (2)

2  → Pinacol III (3)

Pinacol III + hv → Pinacol II (4)

Absorption of light energy by pinacol III will lead to pinacol II (step 4) by a process analagous to that by which 1,2-bis(9-anthryl)ethane is linked across the 9,10 positions of the anthracene systems (4).

The relative product yields in the reaction of 9-anthraldehyde with 2,3-dimethyl-2-butene depend upon the wavelength of the incident light, and under our conditions as under those of Yang et al. (3), the major product of the reaction when light of wavelength longer than 410 mμ is used is the dimer of 9-anthraldehyde.

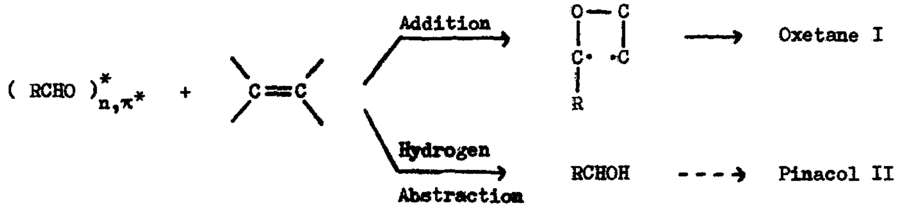
The ability of an aryl ketone to abstract hydrogen from a substrate is dependent upon the nature of the reactive triplet state of the ketone; compounds with reactive n,π^* states are photoreduced with ease (5) while those with reactive π,π^* triplet states are not readily photoreduced (6). Since the photoreactive state of 9-anthraldehyde abstracts hydrogen from substrates, such as 2,3-dimethyl-2-butene and toluene, which are not attacked by aryl ketones with reactive π,π^* triplet states, it would appear that the reactive state of 9-anthraldehyde is an n,π^* triplet state. Also, the fact that the photoreduction reactions are inhibited by triplet state quenchers (see Table I) is indicative that the reactive state is a triplet state and not a singlet state as has been previously suggested (7). The energy of the reactive triplet state of 9-anthraldehyde has been estimated by means of the quenching experiments reported in Table I. Benzene solutions containing 0.01M 9-anthraldehyde, 0.68M 2,3-dimethyl-2-butene and quencher were degassed and irradiated with monochromatic light of 366 mμ (8). The quantum yield for the disappearance of 9-anthraldehyde was determined by spectrophotometric measurement of the concentration of 9-anthraldehyde before and after reaction and by measuring the light energy absorbed by the reactant solutions using a benzophenone-benzhydrol actinometer (9). The quantum yield values given below are corrected for the small percentage of light absorbed by the quencher.

TABLE I

Quencher	Conc.	E_T (Kcal/mole)	ϕ
None	-	-	0.012
Naphthalene	0.80M	60.9	0.012
2-Acetonaphthone	0.02M	59.3	0.011
1-Naphthaldehyde	0.02M	56.3	0.010
Benzil	0.02M	53.7	0.009
Pyrene	0.02M	48.7	0.009
Azulene	0.02M	31-39	0.009

As can be seen from Table I there is a small but significant decrease in the quantum yield for the disappearance of 9-anthraldehyde in the presence of 2-acetonaphthone, 1-naphthaldehyde, benzil, pyrene and azulene. The reaction is not quenched by naphthalene, even when present in high concentration, indicating that the energy of the reactive triplet state is similar to or lower than that of naphthalene. If the energy of the reactive triplet state is close to that of naphthalene then the rate of reversible energy transfer from the triplet state of naphthalene to the reactive triplet state may be such that quenching would not be observed under the conditions of our experiments. Coupled transitions between the reactive triplet state of 9-anthraldehyde and the triplet state of naphthalene would be expected to occur with reasonable probability even if the difference between the energies of the lowest vibrational levels of the two states was of the order of 3 Kcal/mole. Yang and Loeschen have shown by means of photosensitisation experiments (1) that the energy of the reactive triplet state must be above 58 Kcal/mole and this result taken in conjunction with the present results places the energy limits for the reactive triplet state of 9-anthraldehyde between 58 to 64 Kcal/mole. These limits for the energy of the reactive triplet state provide additional evidence that this state is n,π^* in character since aromatic carbonyl compounds with reactive π,π^* triplet states of similar energy are unable to abstract hydrogen from substrates such as toluene and isopropanol (6).

Yang et al. (10) have suggested that in the photoreaction of 9-anthraldehyde with 2,3-dimethyl-2-butene there are two excited states of 9-anthraldehyde involved in the reaction leading to oxetane I; one state being responsible for 77% of the oxetane formed and the other for 23%. The nature of these states is not known conclusively but Yang and Loeschen's evidence from photosensitisation experiments (1) suggests that both states lie in the triplet manifold. The recent observation (11) that the energy of the lowest triplet state of 9-anthraldehyde is 43.5 Kcal/mole above the ground state excludes the possibility that this state is active in either the reaction forming oxetane I or that leading to pinacol II. In view of the present evidence which indicates that the reactive state in the reaction leading to pinacol II is an n,π^* triplet state, it is reasonable to assume that this state is responsible for the 77% of the oxetane formed under the conditions of Yang and Loeschen's experiments. This is supported by previous work of Yang et al. (3) which indicates that the formation of oxetanes from 1-naphthaldehyde and 2-naphthaldehyde, which possess lowest π,π^* triplet states, occurs via an n,π^* species. Thus it would appear that the n,π^* triplet state of 9-anthraldehyde, like that of other carbonyl compounds (12), can either add across the double bond of an olefin or else abstract a hydrogen atom (see scheme below). However the possibility that hydrogen abstraction occurs via an n,π^* triplet state while addition across the double bond occurs mainly via a π,π^* triplet state cannot be ruled out.



At elevated temperatures the biradical intermediate in the oxetane forming sequence may well readily dissociate before ring closure can occur to form starting materials in the ground state. Consequently the hydrogen abstraction process would become more predominant at elevated temperatures, especially since the activation energy for this process would be expected to be higher than that for the addition process.

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