The Photoinduced Cleavage of Aryl Pinacols

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Summary Aryl pinacols are cleaved on photolysis to give α-hydroxyarylmethyl radicals, which have been characterised by e.s.r.

PHOTOLYSIS[1] of aryl pinacols in the presence of ketones and quinones produces an aryl carbonyl compound and a reduction product of the ketone or quinone. A knowledge of the mechanism of this reaction is necessary to ascertain the part played by this reaction in the well known photochemical reduction of aryl ketones.

$$Ar_2C{=}O \xrightarrow{h\nu} Ar_2C{=}O_{S_1} \xrightarrow[\text{crossing}]{\text{intersystem}} Ar_2C{=}O_{T_1}$$

$$Ar_2C{=}O_{T_1} + R_2CHOH \xrightarrow{1} Ar_2\dot{C}OH + R_2\dot{C}OH$$

$$2R_2\dot{C}OH \xrightarrow{2} R_2CHOH + R_2C{=}O$$

$$Ar_2\dot{C}OH + R_2\dot{C}OH \xrightarrow{3} Ar_2C{=}O + R_2CHOH$$

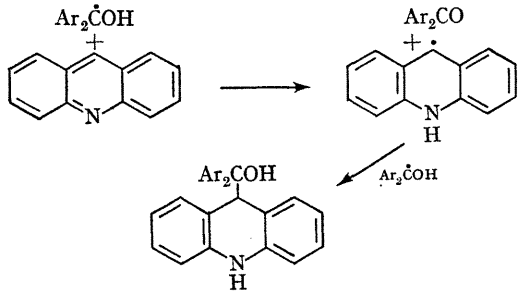
$$2Ar_2\dot{C}{-}OH \underset{5}{\overset{4}{\rightleftharpoons}} Ar_2COH \,|\, Ar_2COH$$

$$Ar_2\dot{C}OH + R_2C{=}O \xrightarrow{6} Ar_2C{=}O + R_2\dot{C}OH$$

Previous work[2,3] on the mechanism of the photoreduction of benzophenone by secondary alcohols ($\lambda > 300$ nm.), has established that reactions 2 and 3 do not occur. Schönberg[1] clearly showed that reactions 5 and 6 can take place and their occurrence may well explain the low quantum yields observed for the photoreduction of some ketones. Flash photolysis studies have also indicated[4] that aryl pinacols can be cleaved on photolysis.

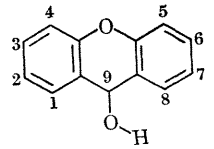
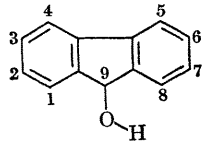
The formation of α-hydroxyarylmethyl radicals on photolysis of aryl pinacols was unequivocally established when it was found that photolysis of xanthopinacol and fluoropinacol, in a variety of solvents, gave the 9-hydroxyxanthyl and 9-hydroxyfluorenyl radicals, respectively. These radicals were positively identified by their e.s.r. spectra, data for which (Table) are comparable to data obtained previously on the same radicals in different systems.[5,6]

Chemical evidence for the formation of these radicals was obtained by photolysis of xanthopinacol in the presence of acridine when 9-(9′-acridaryl)-9-hydroxyxanthene was obtained. The work of Vander Donckt and Porter[7] on the photoreduction of acridine by benzophenone suggests that the reaction proceeds *via* transfer of a hydrogen atom from the 9-hydroxyxanthyl radical to acridine.



The photoreactions[1] of xanthopinacol and fluoropinacol with quinones have been successfully repeated using light of wavelength 310 nm. in place of sunlight. When light of wavelength 360 nm., which only the quinone absorbs, was used very little reaction occurred. Excitation by triplet sensitisers (*e.g.* triphenylamine and triphenylene) in acetone solution containing xanthopinacol also leads to very little reaction (<5%). These results, coupled with

Isotropic proton hyperfine coupling constants (G) *for the 9-hydroxyxanthyl and 9-hydroxyfluorenyl radicals*

Radical	Solvent	Temp.	$a_1 = a_8$	$a_2 = a_7$	$a_3 = a_6$	$a_4 = a_5$	a_{OH}
	Benzene	14°	3·98	0·91	3·70	0·57	2·83
		28°	3·99	0·94	3·71	0·58	3·02
		54°	3·99	0·93	3·70	0·59	3·21
	1,2-Dimethoxyethane	−73°	4·06	0·92	3·78	0·57	1·83
		−22°	4·06	0·95	3·78	0·58	2·50
		28°	4·05	0·95	3·75	0·61	3·07
	1,2-Dimethoxyethane	−73°	3·24	0·73	3·64	0·73	1·13
		−22°	3·28	0·76	3·68	0·76	0·77
		2°	3·29	0·75	3·68	0·75	0·63
	Toluene	2°	3·30	0·75	3·69	0·75	0·61

The formation of α-hydroxyarylmethyl radicals on photolysis of aryl pinacols was unequivocally established when it was found that photolysis of xanthopinacol and the fact that naphthalene does not quench the photoreduction of acetone by xanthopinacol, indicates that cleavage does not occur efficiently, if at all, from its triplet

state and therefore it must presumably take place in either its singlet or a vibrationally excited ground state. Both xanthopinacol and fluoropinacol show end-absorption above 300 nm. and it must therefore be the light absorbed in this region which is bringing about reaction. The photoreduction of ketones and quinones by benzopinacol can be effected by the use of light of wavelength 254 nm., whereas light of wavelength 310 nm. is ineffective. This result is not surprising since benzopinacol does not absorb above 280 nm. and this further substantiates the claim that the excitation of the pinacol is the primary photochemical process.

The cleavage of the aryl pinacols (reaction 5) followed by reaction 6 in photoreductions will not manifest itself unless the exciting light is of such wavelength as to excite the pinacol. The amount of cleavage produced by triplet–triplet energy transfer from excited carbonyl compounds will be extremely small, if not negligible.

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