Norrish Type I Photoreaction in the Presence of Phenols; an Intermolecular Photo-Fries Rearrangement

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Pinacolone photolysis in the presence of phenols leads to phenyl acetates and hydroxy acetophenones; Norrish type I cleavage and subsequent hydrogen abstraction from the phenol by the *tert*-butyl radical gives rise to acyl–aryloxy radical pairs which recombined constituting an intermolecular photo-Fries rearrangement.

After much attention the ketone carbonyl group has gained undeniable prominence as the most appealing chromophore for photochemical studies.[1] A large number of publications have been published concerning both α-cleavage and hydrogen abstraction by excited carbonyl groups.[2,3]

Very little is known about the course of such photochemical processes in the presence of phenols, in spite of the considerable interest attracted by the photochemistry of the latter compounds, not only from the fundamental but also from the applied point of view.[4] A noticeable exception is the abstraction of phenolic hydrogens by excited ketones, which has been used as a probe for the study of decay processes in micellar medium.[5,6] By contrast, no reports have been made relating to the parallel Norrish type I photoreaction of ketones in phenol-containing media. Here we show that the primary intermediates resulting from α-cleavage react under these conditions to afford acyl–aryloxy radical pairs. Recombination gave rise to aryl acetates plus acylphenols. The overall process was thus an intermolecular counterpart of the photo-Fries rearrangement (PFR).[7]

A mixture of pinacolone and *p*-*tert*-butylphenol **1a** was irradiated. This ketone was chosen in order to achieve a high photofragmentation quantum yield,[2,8] while the substituted phenol was selected in principle to hinder *p*-acylation. Excitation through a pyrex filter ($\lambda > 280$ nm) was used to make sure that pinacolone was the light absorbing species. The results (Table 1, entry 1) show that *p*-*tert*-butylphenyl acetate **3a** and 2-acetyl-4-*tert*-butylphenol **4a** were the major products. A significant amount of *tert*-butyl ether **2a** was also obtained. A simple rationalisation for these observations is given in Scheme 1.

A control experiment showed that the acetate **3a** remained unreacted upon photolysis under the same conditions. Conversely, direct irradiation of **3a** through quartz afforded **4a** as the major product. This was in agreement with expectations since the PFR is known to occur from an excited singlet state.[7] Hence, photosensitisation of **3a** by pinacolone should not result in its rearranged product.

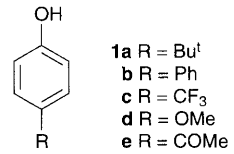


Table 1 Photolysis of ketone–phenol mixtures[a]

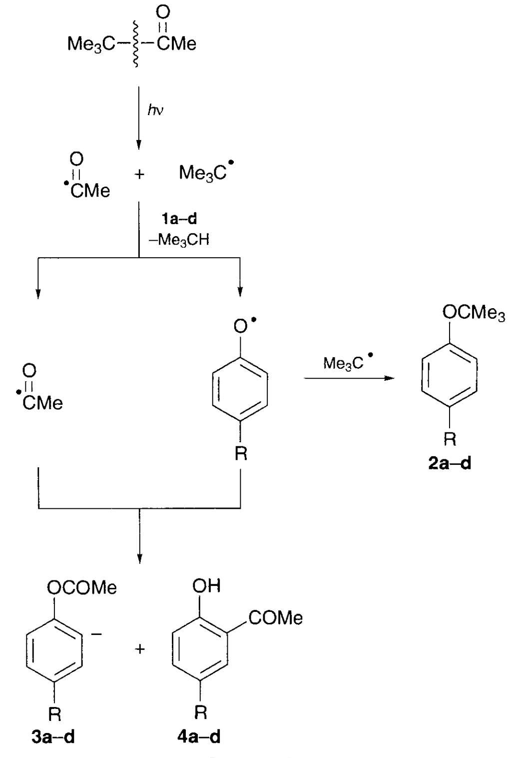
Entry	Phenol **1**	Phenol conversion (%)	Mass balance (%)[b]	Product distribution (%)[c] **2**	**3**	**4**	Others
1	**a**	49	92	22	36	42	—
2	**b**	50	89	27	31	42	—
3	**c**	25	83	—	37	63	—
4	**d**	100	81	11	15	30	44[d]

[a] Benzene solutions (20 ml) of **1a–d** (10^{-2} mol dm^{-3}) and pinacolone (3×10^{-2} mol dm^{-3}) were placed in pyrex test tubes around a central quartz cooling jacket containing a 125 W medium pressure Hg lamp and irradiated for 5 h. [b] Includes recovered **1**. [c] Determined by product isolation by preparative layer chromatography. The values are essentially coincident with those determined by GC. [d] Includes two products; **1a** (36%) and *p*-acetylphenol (**1e**, 8%).

It is generally accepted that the PFR is an intramolecular process,[7,9] In fact, attempted crossover by irradiation of **3a** and *p*-methoxyphenyl butyrate led to no detectable acyl exchange in the resulting *o*-acylphenols. In contrast, when mixtures of **1a** and pinacolone are photolysed the observed phenol acetylation must be intermolecular.

There is some indication in the literature supporting that, in the PFR, recombination within the solvent cage occurs to a certain extent, resulting in the starting compounds.[7,10] However, direct evidence supporting this proposal has been difficult to obtain because of the impossibility of distinguishing between the 'reacted' and 'unreacted' fractions of the recovered aryl esters. In this context, the formation of *p*-*tert*-butylphenyl acetate in the pinacolone-sensitised photolysis of *p*-*tert*-butylphenol constitutes unambiguous proof for the reverse of the carbonyl–oxygen bond cleavage taking place.

In the case of *p*-phenylphenol **1b** and *p*-trifluoromethylphenol **1c** the corresponding O- and C-acetyl derivatives **3b,c** and **4b,c** were again obtained as the major products (Table 1, entries 2 and 3). However, when a mixture of *p*-methoxyphenol **1d** and pinacolone was irradiated, a more complex reaction pattern was observed (Table 1, entry 4). The usual processes leading to **2d–4d**, ring substitution of the *p*-methoxy group by



Scheme 1

tert-butyl or acetyl to afford **1a** or **1e** took place. This is in good agreement with the fact that compound **1e** is also formed as a byproduct during the PFR of **3d**.[11]

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