Photo-oxidation of Crystalline α-Benzoylbenzyl Ethers by Atmospheric Oxygen

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Summary Solid α-benzoylbenzyl ethers reacted efficiently with atmospheric oxygen upon irradiation, yielding benzoic acid and alkyl benzoates in high yield, presumably *via* a benzoyl–benzyl radical pair.

α-BENZOYLBENZYL ETHERS[1] undergo photochemical α-cleavage to form a benzoyl–benzyl radical pair which subsequently undergoes free-radical reaction in solution to give benzaldehyde, benzil, and pinacol ethers. In oxygen-saturated solution, however, the radical pair is trapped by oxygen to give perbenzoic acid and the alkyl benzoate *via* peroxyl radicals.[2] We report here that α-benzoylbenzyl ethers are photo-oxidised rapidly even in the crystalline phase and that this photo-oxidation is quite different from that in solution. Although thermal and/or photochemical oxidation of crystalline 11-hydroxy-steroids to the corresponding ketones by atmospheric oxygen has been reported,[3] the reaction is not well understood.

In a typical reaction, 100 mg of α-benzoylbenzyl methyl ether (**1a**) was crystallised on the surface of a cylindrical Pyrex tube of 10 cm diameter and 25 cm length by evaporation of a benzene solution, and was photolysed with a 300 W

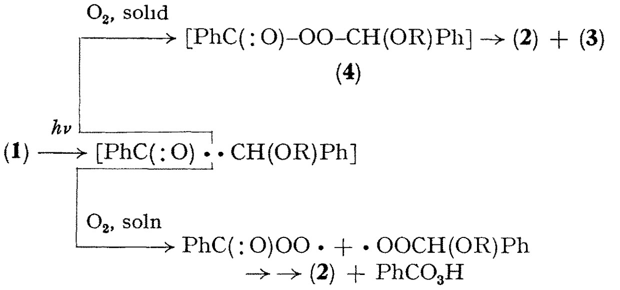
Hg lamp filtered through Pyrex under air at room temperature The reaction mixture gradually liquefied as *ca* 1 mol equiv of oxygen was gradually taken up, and turned to a semisolid at the end of the irradiation process The reaction mixture was washed out with acetone and g l c analyses showed that no trace of benzaldehyde, benzil, or pinacol ethers was formed Silica gel chromatography yielded methyl benzoate (**2a**) (76%) and benzoic acid (**3**) (72%)

$$\underset{\substack{\textbf{(1)}\ \textbf{a},\ R = \mathrm{Me} \\ \textbf{b},\ R = \mathrm{Et} \\ \textbf{c},\ R = \mathrm{Pr^i}}}{\mathrm{PhCOCH(OR)Ph}} \xrightarrow[\text{crystal}]{h\nu/\mathrm{O_2}} \underset{\textbf{(2)}}{\mathrm{PhCO_2R}} + \underset{\textbf{(3)}}{\mathrm{PhCO_2H}}$$

Similar products were obtained from the solid phase irradiation of the ethers (**1b**) and (**1c**) When the irradiation was carried out in the absence of O_2 the starting material was recovered unchanged even after prolonged irradiation

Striking differences between the solution and solid phase photo-oxidation of (**1**) were observed both in the reaction products and in the structure–reactivity relationships Thus, in the solid phase photo-oxidation, the yield of peracid determined iodometrically was less than 10%, although perbenzoic acid was stable under these conditions In the solution phase, however, perbenzoic acid was produced almost quantitatively and benzoic acid was not detected [2] (It should be noted that >3 mol equiv of oxygen is consumed in the solution phase oxidation) [2] Secondly, benzoin acetate, PhCOCHPhOAc, as well as benzoin itself was almost completely inert to the photo-oxidation in the crystalline phase, whereas they were photo-oxidised equally efficiently in the solution phase

There are several *a priori* mechanisms to explain these data The possibility that direct attack of oxygen on the carbonyl group might be involved was eliminated since benzil, which has been shown[4] to be oxidised *via* such a mechanism in the solution phase, was inert to the solid-phase photo-oxidation Photoenolisation of (**1**),[5] followed by addition of oxygen to the double bond to give dioxetan, was also eliminated since neither olefins (*e g* , stilbenes) nor enolizable β-diketones (*e g* , dibenzoylmethane) was photo-oxidised in the solid phase Thus, the most likely explanation at present must involve initial photochemical α-cleavage of (**1**), followed by trapping of the resulting radical pair by oxygen to form a peroxide (**4**), which subsequently collapses to produce (**2**) and (**3**) either thermally or photochemically (Scheme) Presumably the radical pair generated in crystalline phase cannot diffuse apart owing to the limited diffusivity[6] and hence is allowed to undergo incorporation of atmospheric oxygen This is in sharp contrast with the mechanism suggested[2] for the radical pair in solution where the members of the pair can diffuse apart before they are attacked by oxygen Although attempts to detect (**4**) have so far been unsuccessful, such a scheme could account for the strikingly low yields of perbenzoic acid and for the nearly stoicheiometric uptake of oxygen in the solid phase reaction Furthermore, the high sensitivity of the structure to this photo-oxidation process might be related to the fact[1] that α-oxygen substituents have a marked effect on α-cleavage rate constants For example, alkyl α-benzoylbenzyl ethers are 20 and 400 times more reactive than the parent benzoin itself and its acetate, respectively Moreover, benzil apparently does not fragment upon irradiation [5]†



$$\textbf{(1)} \xrightarrow{h\nu} [\mathrm{PhC(:O)}\cdot\ \cdot\mathrm{CH(OR)Ph}]$$

$$\xrightarrow{\mathrm{O_2,\ solid}} \underset{\textbf{(4)}}{[\mathrm{PhC(:O)\text{–}OO\text{–}CH(OR)Ph}]} \rightarrow \textbf{(2)} + \textbf{(3)}$$

$$\xrightarrow{\mathrm{O_2,\ soln}} \mathrm{PhC(:O)OO}\cdot + \cdot\mathrm{OOCH(OR)Ph} \rightarrow\rightarrow \textbf{(2)} + \mathrm{PhCO_3H}$$

SCHEME

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† We found that (**2c**) was formed even during the irradiation of a mixed crystal of (**1c**) and 1,4-diazabicyclo[2 2 2]octane (1 : 0 5), suggesting that a mechanism involving $^1O_2$ can be eliminated

[1] See for example, F D Lewis, R T Lauterbach, H -G Heine W Hartman and H Rundolph, *J Am Chem Soc* , 1975, **97**, 1519

[2] S Adam, H Gusten and D Schulte-Frohlinde *Tetrahedron*, 1974 **30** 4249

[3] M L Lewbart, *Nature*, 1969, **222**, 623, G Brennet F E Roberts, A Hainows, A Hainowski, J Budavori, B Powell, D Hinkley, and E Schoenewaldt, *Angew Chem* , *Int Ed Engl* , 1969, **8** 957

[4] N Shimizu and P D Bartlett, *J Am Chem Soc* , 1976, **98**, 4193

[5] A Ledwith, P J Russell, and L H Sutcliffe, *J Chem Soc* , *Perkin Trans* 2, 1972, 1925

[6] M D Cohen, *Angew Chem* , *Int Ed Engl* , 1975, **14**, 387