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AN ANALOGUE OF THE PHOTO-FRIES REARRANGEMENT; THE PHOTOLYSIS OF VINYL BENZOATE.

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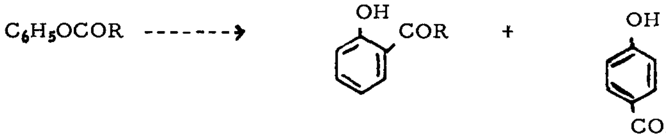
The classical Fries rearrangement,[2] a well known acid-catalyzed process illustrated in equation 1, can be effected in the absence of acid catalysts by means of ultraviolet light.[3-6]

(1)



Esters successfully rearranged by the photo-Fries reaction include phenyl acetate[3] (equation 1, R = CH_3) and catechol acetate,[3] the para-tert-butylphenyl esters of a number of aromatic acids,[6] phenyl benzoate,[5] a number of variously substituted phenyl benzoate derivatives[4,5] and phenyl ferrocene carboxylate.[5] The structures of the products[3-6] indicate predominate, if not ex-

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[1] Undergraduate research assistant supported by a grant from the Petroleum Research Fund (#710-A) administered by the American Chemical Society.

[2] A. H. Blatt, Org. Reactions I, 342 (1942).

[3] J. C. Anderson and C. B. Reese, Proc. Chem. Soc. 217 (1960).

[4] C. H. Kuo, R. D. Hoffsommer, H. L. Slates, D. Taub, and N. L. Wendler, Chem. and Ind. 1627 (1960).

[5] R. A. Finnegan and J. J. Mattice, experiments to be published.

[6] H. Kobsa, J. Org. Chem. 27, 2293 (1962).

clusive, migration of the acyl group to *ortho* and/or *para* positions[7,8] as in the acid-catalyzed process.[2] The results of mixed irradiation experiments[3,5] support the suggestion[3] that the reaction is intramolecular and it has been proposed[6] that the initial step is the photo-dissociation of the ester to a radical pair which undergoes subsequent reaction within a solvent cage.

Formal structural considerations suggest that the reaction need not be limited to the case of phenyl esters. For example, the bond undergoing cleavage might involve atoms other than carbon and oxygen, and furthermore, a phenyl ring may not be uniquely required to furnish the site of the migration terminus. A simple analogue of the photo-rearrangement of phenyl benzoate to *ortho*- and *para*-hydroxybenzophenones[5] (Equation 1, $R = C_6H_5$) would be the rearrangement of vinyl esters I to β-dicarbonyl compounds II (Equation 2).

$$(2) \quad \underset{\text{I}}{RCO_2CR'{=}CR_2''} \dashrightarrow \underset{\text{II}}{RCOCR_2''COR'}$$

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[7] Migration of the acyl group to *both* the *ortho* and *para* positions of the phenol moiety seems to be the rule when these positions are unsubstituted. An interesting exception to this behavior is the rearrangement of phenyl ferrocene carboxylate to *para*-hydroxybenzoylferrocene.[5] None of the *ortho* isomer was detected, and furthermore, since the *ortho* isomer was stable under the reaction conditions it could not have been an intermediate. A specific role for the iron atom in this rearrangement would seem to be indicated.

[8] The reluctance of aryl esters to rearrange to *meta*-hydroxyketones is emphasized by the failure of 3,4-benzocoumarin to provide 4-hydroxyfluorenone in any detectable amount under similar conditions of irradiation.[9] Such a rearrangement in this case would require the phenol ring to be substituted in the *meta* position by the benzoyl moiety.

[9] R. A. Finnegan, A. W. Hagen, and A. M. Bachmann, unpublished experiments.

This analogy derives close support from the results of thermal rearrangement of vinyl esters;[10] for example, the conversion of vinyl benzoate (I, R =C_6H_5, R' = R'' =H) to benzoylacetaldehyde (II, R = C_6H_5, R' =R'' =H) accompanied by the formation of acetophenone (by decarbonylation of II) as well as benzoic acid and other products.[10,11]

We wish to make a preliminary report of observations which indicate that the irradiation of vinyl benzoate provides products in parallel with the thermal reaction, and indeed, that the reaction constitutes an analogy to the photo-Fries rearrangement as suggested above. Thus, when ~1% solutions of vinyl benzoate[12] in dioxane or Skelly-solve B were irradiated for 50-150 hours at room temperature with a 100 watt medium pressure mercury arc lamp, acetophenone and benzoic acid were readily identified as reaction products. Acetophenone (2 - 4% conversion) was identified by infrared spectroscopy and by gas chromatography while the benzoic acid (10 - 15% conversion, crude) was identified by mixed melting point and infrared comparisons with an authentic speciman. When a similar irradiation was carried out using benzene as the solvent only traces of acetophenone were detected, however, an oil was obtained (6% conversion, crude) whose infrared spectrum showed it to be benzoylacetaldehyde by comparison with that of an independently prepared sample.[10] The identity of the product with benzoylacetaldehyde, the presumed

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[10] R. J. P. Allan, R. L. Forman, and P. D. Ritchie, J. Chem. Soc. 2717 (1955), and references contained therein.

[11] R. B. Rashbrook and G. W. Taylor, Chem. and Ind. 215 (1962).

[12] Acetophenone free. Compare ref. 10.

precursor of acetophenone,[13] was also supported by infrared comparisons of their respective copper salts. In addition, other as yet unidentified products as well as polymers were obtained.

The apparent solvent effect would seem to require some comment. The photolytic decarbonylation of aldehydes in the gas phase is well established[14] and it is considered to be a primary process in the liquid phase as well, although less extensively studied.[15] Since one of the processes for aldehyde decarbonylation requires light of shorter wavelength[14-16] it is possible that in benzene solution decarbonylation is suppressed by the filtering or absorption of the requisite light by the solvent. Thus, in benzene benzoylacetaldehyde is preserved as a primary rearrangement product in contrast to the results in the transparent solvents, dioxane and Skelly-solve B, where its decarbonylation product acetophenone is found.

Finally we suggest that the formation of benzoylacetaldehyde from vinyl benzoate and the photo-Fries reaction are examples of a general class of photochemical rearrangements which may be represented by the expression $X\text{-}ABC \longrightarrow ABC\text{-}X$ where X contains a chromophore capable of excitation and ABC is a triad capable of stabilizing a radical by resonance delocalization:

$$\cdot A\text{-}B{=}C \longleftrightarrow A{=}B\text{-}C\cdot$$

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[13] *Vide infra.*

[14] J. N. Pitts, *J. Chem. Ed.* **34**, 112 (1957).

[15] a J. C. Chen and D. H. Volman, *J. Am. Chem. Soc.* **83**, 1047 (1961). b J. R. McNesby and T. W. Davis, *ibid.* **76**, 2148 (1954).

[16] The decarbonylation of formate esters is analogous. P. Ausloos, *ibid.* **80**, 1310 (1958), *Can. J. Chem.* **36**, 383 (1958).