333. *The Photochemical Fries Reaction.*

By J. C. Anderson and C. B. Reese.

Aryl esters of aliphatic and aromatic carboxylic acids undergo light-catalysed Fries reactions in alcoholic solution. A predominantly intramolecular mechanism of rearrangement is favoured.

As part of a programme concerned with the effect of ultraviolet light on some aromatic systems, we have studied a photo-induced Fries reaction. Some of our preliminary results have been reported;[1] we now discuss this reaction in more detail. After we had completed our studies, Kobsa[2] reported that the ultraviolet irradiation of *p*-t-butylphenyl esters of aromatic carboxylic acids (I; R = aryl, R′ = Bu^t) in benzene or alcohol solution gave the corresponding *o*-hydroxy-ketones (II) in good yield. Before our communication[1] such a rearrangement had not been described in the literature. However, it was possibly implied in some observations made by Klinger, who found that exposure of 9,10-phenanthraquinone to sunlight[3] in the presence of an aldehyde (R·CHO) gave the corresponding 9-acyloxy-10-dihydroxyphenanthrene (III) whereas *p*-benzoquinone, treated in the same way,[4] did not give the *p*-hydroxyphenyl ester (I; R′ = OH) but the ketone (II; R′ = OH).

We found that ultraviolet irradiation of an ethanol solution of pyrocatechol monoacetate (IV) led to a 40% yield of mixed dihydroxyacetophenones (V) and (VI) with a slight preponderance of the former, together with 46% of pyrocatechol. The corresponding

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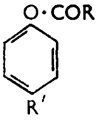
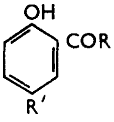
[1] Anderson and Reese, *Proc. Chem. Soc.*, 1960, 217.
[2] Kobsa, *J. Org. Chem.*, 1962, **27**, 2293.
[3] Klinger, *Annalen*, 1884, **249**, 137.
[4] Klinger and Standke, *Ber.*, 1891, **24**, 1340.

acid-catalysed Fries reaction was reported[5] to give a much greater yield of 3,4-dihydroxyacetophenone (VI) but much less of the isomer (V). Irradiation of an ethanol solution of phenyl acetate (I; R = Me, R′ = H) gave 2- (19%) and 4-hydroxyacetophenone (15%) and phenol (28%). A trace (not more than 0·3%) of 3-isomer was detected, as its methyl ether, by vapour-phase chromatography. In the same way, phenyl benzoate (I; R = Ph, R′ = H) gave 2- (20%), and 4-hydroxybenzophenone (28%) and phenol (14%). In all cases, the photochemical changes were followed by observing the disappearance of the ester-carbonyl bands and the appearance of the ketone-carbonyl bands in the infrared spectra of the crude products. The yields were estimated in several ways (see Experimental section). No 4-hydroxyindan-1-one was observed in the photolysis products of an alcoholic solution of 3,4-dihydrocoumarin (VII), but only ethyl β-*o*-hydroxyphenylpropionate (VIII). This confirms the relative resistance to the formation of *meta*-rearranged products.



(I)



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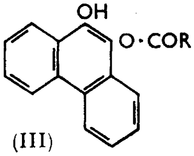

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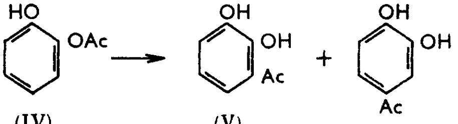
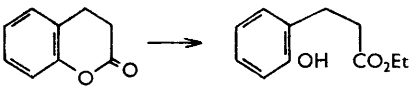
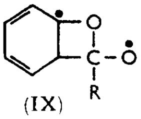


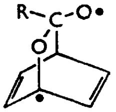
(IV) (V) (VI)



(VII) (VIII)



(IX)



(X)

Some experiments were conducted to help elucidate the mechanism of this reaction. The ketones (V) and (VI) were stable under the irradiative conditions, excluding the possibility that one isomer is an intermediate in the formation of the other. Similarly 2- and 4-hydroxyacetophenone were both stable. When a solution containing phenol and pyrocatechol monoacetate (IV) had been irradiated, no 2-hydroxyacetophenone was detected by vapour-phase chromatography, though the presence of a very small amount of 4-methoxyacetophenone was suggested by a similar analysis after the products had been methylated with diazomethane. Apart from this evidence, the photochemical reaction or reactions appear to be intramolecular. It seems likely that the large excess of ethanol present would be involved in an intermolecular reaction whether this were a photo-induced solvolysis, as observed in the irradiation of dihydrocoumarin (VII), or involved acyl free radicals. In all the reactions in which Fries rearrangement occurs, an appreciable yield of phenol, corresponding to de-acylated starting material, was obtained. This could have been formed by an independent intermolecular pathway, similar to the observed solvolysis of dihydrocoumarin. The other product of such a solvolysis would be an ethyl ester; this is not an intermediate in the Fries reaction as no hydroxyacetophenone is obtained when a solution of phenol in ethanol–ethyl acetate is irradiated. Kobsa[2] has suggested that the *ortho*-rearrangement could proceed by homolysis of the starting material into an aryloxy- and an acyl radical, held together in a solvent cage, with subsequent rearrangement. We prefer the possibility that the diradicals (IX) and (X) are the respective intermediates in the *ortho*- and *para*-rearrangements. The diradical intermediates could then collapse to dienones, which would enolise to the corresponding aromatic hydroxy-ketones.

EXPERIMENTAL

Solutions, contained in stoppered quartz tubes, were irradiated at a distance of *ca.* 6 cm. from a 500 w Hanovia mercury-arc lamp. Infrared spectra of chloroform solutions were

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[5] Miller, Hartung, Rock, and Crossley, *J. Amer. Chem. Soc.*, 1938, **60**, 7.

measured on a Perkin-Elmer model 21 spectrophotometer. Vapour-phase chromatography was conducted on a 6 ft. × 4 mm. column packed with silicone oil (10%) on 60—80 mesh Celite.

Irradiation of Pyrocatechol Monoacetate (IV).—A solution of pyrocatechol monoacetate[6] (1·0 g.) in absolute ethanol (11 c.c.) was irradiated at ~30° for 10 days, during which the ester-carbonyl band (1756 cm.$^{-1}$) disappeared. The ethanol was evaporated under reduced pressure and the residue, dissolved in methylene chloride, was absorbed on a silica-gel column (75 g.). The column was eluted first with methylene chloride, giving fractions (*a*) (0·227 g.) and (*b*) (0·336 g.), and then with chloroform giving fraction (*c*) (0·185 g.). Yellow crystals (0·16 g.), m. p. 98°, were obtained by recrystallising fraction (*a*) from cyclohexane. The material sublimed at 80°/0·7 mm. and its m. p. was undepressed on admixture with 2,3-dihydroxyacetophenone (Found: C, 63·3; H, 5·5. Calc. for $C_8H_8O_3$: C, 63·2; H, 5·3%). It had $\nu_{max.}$ 1645 cm.$^{-1}$.

Fraction (*b*) had m. p. 105° and was pyrocatechol. Fraction (*c*) recrystallised from benzene as colourless needles (0·065 g.), m. p. 122° (after sublimation) (Found: C, 63·0; H, 5·6. Calc. for $C_8H_8O_3$; C, 63·2; H, 5·3%). It was 3,4-dihydroxyacetophenone, $\nu_{max.}$ 1672 cm.$^{-1}$.

Irradiation of Phenyl Acetate.—(*a*) A solution of phenyl acetate (1·36 g.) in ethanol (45 c.c.) was irradiated for 3 days at ~30°. The ester-carbonyl band (1766 cm.$^{-1}$) gradually disappeared and was replaced by bands at 1642 and 1672 cm.$^{-1}$. The ethanol was evaporated under reduced pressure, and the residue steam-distilled. The non-volatile material was extracted with hot water. On cooling, crystalline 4-hydroxyacetophenone (0·20 g., 15%), m. p. and mixed m. p. 107—109°, was precipitated (Found: C, 70·9; H, 6·2. Calc. for $C_8H_8O_2$: C, 70·6; H, 5·9%). The steam-distillate was extracted with chloroform, and the dried ($MgSO_4$) extract evaporated to an oil (0·20 g.) which was dissolved in ethanol and added to a solution of 2,4-dinitrophenylhydrazine (0·30 g.) in boiling ethanol, acidified with hydrochloric acid. The crystalline precipitate obtained on cooling was recrystallised from ethanol–chloroform and had m. p. 208—210° (undepressed on addition of the 2,4-dinitrophenylhydrazone of 2-hydroxyacetophenone) (Found: C, 53·4; H, 3·5; N, 17·8. Calc. for $C_{14}H_{12}N_4O_5$: C, 53·2; H, 3·8; N, 17·7%). The yields of 2-hydroxyacetophenone and phenol were estimated, by vapour-phase chromatography of the steam-distillate, to be 19% and 28%, respectively.

(*b*) A solution of phenyl acetate (0·61 g.) in ethanol (27 c.c.) was irradiated for 3 days and then steam-distilled. The steam involatile fraction was extracted with chloroform. The dried extract was evaporated and the residue (0·173 g.) treated in methanol (5 c.c.) with ethereal diazomethane (10 mol.). The product was shown by vapour-phase chromatography at 125° to contain 4- and 3-methoxyacetophenone in the approximate ratio of 50 : 1. The yield of 3-hydroxyacetophenone from the irradiation of phenyl acetate was thus estimated to be *ca.* 0·3%.

Irradiation of Phenyl Benzoate.—A solution of phenyl benzoate (0·40 g.) in ethanol (50 c.c.) was irradiated at ~30° for 3 days during which the ester-carbonyl band (1725 cm.$^{-1}$) disappeared and was replaced by a weak band (1710 cm.$^{-1}$) and a strong band (1632 cm.$^{-1}$) with a shoulder (1650 cm.$^{-1}$). The products were steam-distilled and the yield of 2-hydroxybenzophenone [$\lambda_{max.}$ (in 95% ethanol), 335 mμ (ε 5370)] in the distillate was estimated to be 20%, spectrophotometrically. Phenol and ethyl benzoate were detected in the distillate by vapour-phase chromatography. The yield of the former was estimated to be 14%. The distillate was extracted with chloroform, and the dried extract was evaporated, redissolved in ethanol, and added to a solution of 2,4-dinitrophenylhydrazine in boiling ethanol acidified with hydrochloric acid. The crystalline precipitate of the 2,4-dinitrophenylhydrazone of 2-hydroxybenzophenone, obtained on cooling, recrystallised from ethanol–chloroform and had m. p. 249—251° (Found: C, 59·9; H, 3·8; N, 14·4. Calc. for $C_{19}H_{14}N_4O_5$: C, 60·3; H, 3·7; N, 14·8%).

The steam-involatile material was extracted with chloroform. The residue (0·213 g.), after evaporation of the chloroform, was chromatographed on silica gel. Evaporation of the chloroform eluate yielded a solid which was extracted with hot water. Pale yellow crystals of 4-hydroxybenzophenone, m. p. 130—132°, were precipitated from the cooled extract (Found: C, 78·6; H, 5·4. Calc. for $C_{13}H_{10}O_2$: C, 78·8; H, 5·1%). They had $\lambda_{max.}$ (in 95% EtOH) 295 mμ (ε 13,500). The yield of 4-hydroxybenzophenone was estimated to be 28%, spectrophotometrically.

Irradiation of 2,3-*Dihydrocoumarin* (VII).—A solution of 2,3-dihydrocoumarin (0·30 g.) in ethanol (10 c.c.) was irradiated for 3 days. The original carbonyl bands (1762, 1777 cm.$^{-1}$)

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[6] Green, *J.*, 1927, 500.

disappeared and were replaced by a carbonyl band (1715 cm.$^{-1}$) and an O–H stretching band (3400 cm.$^{-1}$). The residue, after evaporation of the ethanol, was chromatographed on silica gel. Elution with methylene chloride yielded a colourless, alkali-soluble material, m. p. 30—33° (m. p.[7] of ethyl β-*o*-hydroxyphenylpropionate 36—36·5°). The material had the same infrared spectrum and vapour-phase chromatographic retention time at 161° as material obtained by heating a solution of the dihydrocoumarin (VII) (0·12 g.) in ethanol (15 c.c.) containing sodium ethoxide (2 mol.) under reflux for 1 hr.

Mixed Irradiation of Pyrocatechol Monoacetate (IV) *and Phenol.*—A solution of pyrocatechol monoacetate (0·31 g.) and phenol (0·22 g., 1 mol.) in ethanol (13 c.c.) was irradiated for 3 days. Vapour-phase chromatography of the products at 125° indicated the presence of 2,3-dihydroxyacetophenone (V) but no 2-hydroxyacetophenone. The ethanol was evaporated under reduced pressure and the residue treated in methanol (10 c.c.) with ethereal diazomethane (5 mol.). The methylated products were analysed by vapour-phase chromatography and a very weak peak with the same retention time as 4-methoxyacetophenone was observed.

Irradiation of Phenol in the Presence of Ethyl Acetate.—A solution of phenol (0·30 g.) in ethyl acetate (5 c.c.) and ethanol (5 c.c.) was irradiated for 3 days. Vapour-phase chromatography indicated that the products contained no 2-hydroxyacetophenone. After the products had been methylated, as above, no 4-methoxyacetophenone was detected.

Irradiation of Primary Photo-products.—2% Solutions of (*a*) 2,3-dihydroxyacetophenone (V), (*b*) 3,4-dihydroxyacetophenone (VI), (*c*) 2-hydroxyacetophenone, and (*d*) 4-hydroxyacetophenone in ethanol remained unchanged, as indicated by infrared spectroscopy, after irradiation for 3 days.

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[7] Claisen, *Ber.*, 1921, **54**, 200.