

A PHOTO-INDUCED REARRANGEMENT INVOLVING ARYL PARTICIPATION^{1,2}

J.C. Anderson and C.B. Reese

University Chemical Laboratory, Lensfield Road, Cambridge

(Received 29 December 1961)

OUR observation of a photo-induced Fries rearrangement³ prompted us to study the photochemistry of some of the expected primary products. For this reason we investigated the effect of ultra-violet light on alcoholic solutions of substituted phenacyl chlorides (I, Y = Cl).



Previous work³ led us to irradiate a 1% ethanolic solution of *p*-hydroxyphenacyl chloride (I, X = *p*-OH, Y = Cl). Within 2 hours, the carbonyl stretching frequencies of the starting material (1678, 1690 cm⁻¹) disappeared and two new strong bands at 1671 and 1725 cm⁻¹ were apparent. The former band was due to *p*-hydroxyacetophenone (I, X = *p*-OH, Y = H), isolated as its 2:4-dinitrophenylhydrazone, m.p. 257-259° and the latter band to ethyl-(*p*-hydroxyphenyl)-acetate (II, X = *p*-OH, R = Et) isolated as its *p*-nitrobenzoate, m.p. 100-102°. We propose that the rearranged ester resulted from an Ar₁-3 participation reaction^{1,2} through a neutral intermediate (III) or a radical intermediate (IV, X = OH *para* to spiro-carbon). This is reminiscent of the Favorskii rearrangement.⁴ The formation of *p*-hydroxyacetophenone could proceed initially by loss of a chlorine atom to

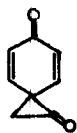
¹ S. Winstein, R. Heck, S. Lapporte and R. Baird, *Experientia* **12**, 138 (1956).

² S. Winstein and R. Baird, *J. Amer. Chem. Soc.* **79**, 756, 4238 (1957).

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

⁴ A.S. Kende, *Organic Reactions* Vol. 11, pp. 261-316. John Wiley, New York (1960).

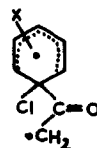
yield a ketonyl radical, which could then abstract a hydrogen atom from the solvent. It has been suggested that the conversion of chloroacetone to acetone and acetylacetone by irradiation in the vapour phase involves respectively hydrogen abstraction by and dimerization of an initially formed acetyl radical.⁵



III



IV



V

Attack by ethanol at the methylene rather than at the carbonyl carbon atom of the cyclopropanone ring of the spiro-intermediate (III) would yield *p*-hydroxyphenacyl ethyl ether (I, X = *p*-OH, Y = OEt) which was not detected. However, this compound was obtained in 85% yield, m.p. 136-138°, ν_{\max} , 1691 cm^{-1} . (Found: C, 66.8; H, 6.8. $\text{C}_{10}\text{H}_{12}\text{O}_3$ requires: C, 66.7; H, 6.7%), by the action of ethoxide ion on *p*-hydroxyphenacyl chloride. This reaction may also proceed through the intermediate (III), and contrasts with the Darzens-type dimerization of phenacyl bromide by alkoxide ion.⁶ However, no isomeric ester accompanied the ether.

We examined our aryl participation hypothesis by irradiating 1% alcoholic solutions of the phenacyl chlorides (I) with varying substituents X and found that electron-donating groups in *ortho*- or *para*-positions were necessary for ester (II) formation. Such substituents could help stabilize the radical intermediate (IV), or even more its cationoid counterpart, which would result from the further loss of an electron. The irradiation source

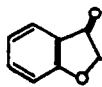
⁵ A.N. Strachan and F.E. Blacet, *J. Amer. Chem. Soc.* **77**, 5254 (1954).

⁶ J.A. Berson, *J. Amer. Chem. Soc.* **74**, 5175 (1952).

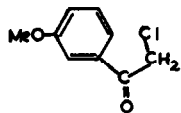
was a 500 W Hanovia mercury arc, and reactions were normally complete in 1-2 hours. The course of each reaction was followed by infra-red spectroscopy and vapour phase chromatography. Yields listed in Table 1 were estimated by vapour phase chromatography and by the isolation of the products or derivatives of them whenever possible.

TABLE 1

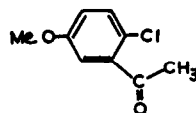
Starting material (I) Y = Cl X =	% Yield of rearranged ester (II)	% Yield of acetophenone (I, Y = H)	% Yield of other products
p-OH	32	26	p-chlorophenol 2
p-OMe	32	30	p-chloroanisole 16
o-OH	-	3	coumaran-3-one 40
o-OMe	32	16	o-chloroanisole 11
p-Me	4	58	
H	-	53	
p-CO ₂ Me	-	48	
p-Cl	-	55	
o-Cl	-	45	
m-OMe	-	15	2-chloro-5-methoxy acetophenone (VIII) 50



VI



VII



VIII

It is noteworthy that the phenacyl chlorides which provide the highest yields of rearranged ester are partly degraded to the corresponding chlorobenzene derivatives at the same time, by the extrusion of the elements of ketene. A possible intermediate (V) is suggested; it could also be the precursor of (IV). Ortho-hydroxyphenacyl chloride is clearly atypical as the ease of cyclization to coumaran-3-one (VI) prevents the normal reaction path. The small yield of ester from the irradiation of *p*-methylphenacyl chloride is interesting as the methyl group cannot stabilize an intermediate like (IV) by normal mesomerism.

Finally, it was important to discover whether an electron-donating group in the meta-position would promote ester formation. Irradiation of a 1% solution of *m*-methoxyphenacyl chloride (VII) in ethanol for 1 hour yielded besides the corresponding ketone (I, X = *m*-OMe, Y = H) (See Table 1), 50% of 2-chloro-5-methoxyacetophenone (VIII). This was isolated as its 2:4-dinitrophenylhydrazone, m.p. 223-226° (Found: C, 49.6; H, 4.0; N, 15.6; Cl, 10.1. $C_{15}H_{13}ClN_4O_5$ requires: C, 49.4; H, 3.6; N, 15.4; Cl, 9.7%) and its orientation established by hypochlorite oxidation and comparison with an authentic sample of 2-chloro-5-methoxybenzoic acid.⁷ Infra-red spectroscopy suggested the absence of rearranged ester in the products.

The previously undescribed phenacyl chlorides were prepared from the corresponding benzoic acids via the diazoketones.⁸ They were:

p-carbomethoxyphenacyl chloride (I, X = *p*-CO₂Me, Y = Cl) m.p. 148-150°

(Found: C, 56.6; H, 4.5 $C_{10}H_9ClO_3$ requires: C, 56.5; H, 4.2%).

m-methoxyphenacyl chloride (I, X = *m*-OMe, Y = Cl) m.p. 76-78°

(Found: C, 58.5; H, 4.7. $C_9H_9ClO_2$ requires: C, 58.5; H, 4.9%).

o-chlorophenacyl chloride (I, X = *o*-Cl, Y = Cl) b.p. 148-149°/19 mm

(Found: C, 50.9; H, 3.5. $C_8H_6Cl_2O$ requires: C, 50.8; H, 3.2%).

One of us (J.C.A.) thanks the D.S.I.R. for the award of a maintenance grant.

⁷ G.P. Gibson, J. Chem. Soc. 1424 (1926).

⁸ F. Arndt, B. Eistert and W. Partale, Chem. Ber. 60, 1364 (1927).