Thermal Rearrangement of Chloroarylidenetetrahydrofuran-2,4,5-triones to Aroylchloromaleic Anhydrides

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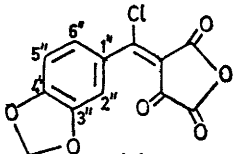
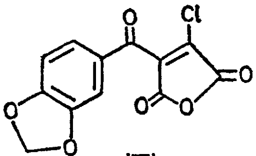
Summary The chloroarylidenetetrahydrofuran-2,4,5-trione (I) rearranges on heating to the aroylchloromaleic anhydride (II); a mechanism involving an oxet is suggested.

On heating above its m.p., (I)[1] undergoes rearrangement to give a product (75%), m.p. 143—145°, retaining the aromatic proton resonances and having ν_{max} ($CHCl_3$) 1873, 1797, 1660, 1620 cm^{-1} and an m.s. base peak of 149. The product is formulated as the chloroanhydride (II) on the following grounds. Hydrolysis (water) gave (III) which on hydrogenation over palladium catalyst in 0·5 N-NaOH yielded (IV): this could be lactonised (trifluoroacetic acid) to (V), identical with an authentic specimen. Thermal lactonisation of (IV) gave the *cis*-isomer of (V), converted into *trans*-(V) by acid. Direct hydrogenation of (II) in ethyl acetate produced the aroylanhydride (VI), which after hydrolysis and decarboxylation gave (VII). On heating, (VI) formed the β-unsaturated γ-lactone (VIII).

This unusual rearrangement does not involve migration to C-6″ of the aromatic ring, which might pass unnoticed in (I), as the 3,4,5-trimethoxy-analogue of (I) gave the corresponding 3,4,5-trimethoxy-analogue of (II). ^{14}C-Labelling was undertaken. 3,4-Methylenedioxyphenylmagnesium bromide, with $^{14}CO_2$, gave 3,4-methylenedioxy[1-^{14}C]benzoic acid (1·68 μCi/mmol). Conversion into the acid chloride and treatment with $Ph_3P{=}CHCO_2Me$ gave (IX) which on pyrolysis[2] and hydrolysis yielded 3,4-methylenedioxyphenyl-[3-^{14}C]propiolic acid. Treatment with oxalyl chloride gave (I) (1·66 μCi/mmol), pyrolysed to (II) (1·68 μCi/mmol). Oxidation of the latter ($KMnO_4$) produced 3,4-methylenedioxybenzoic acid (1·68 μCi/mmol), decarboxylated (copper chromite–quinoline) to $^{14}CO_2$ (1·69 μCi/mmol). It follows that the integrity of the carbon attached to the aromatic ring is maintained in the rearrangement.



(I)



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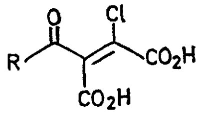

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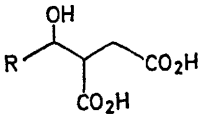

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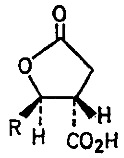
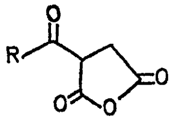
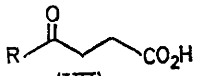


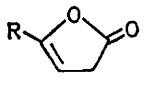
(V)



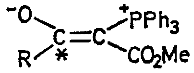
(VI)



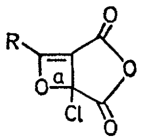
(VII)



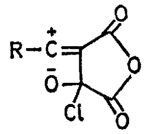
(VIII)



(IX)



(X)



(XI)

R = 3,4-Methylenedioxyphenyl.

In the light of these findings, a suitable mechanism for the rearrangement (I) → (II) involves intermediate formation of an oxet[3] (X), possibly *via* initial migration of chlorine to give (XI) [*cf.* the formation of (I)[1]]. Electrocyclic opening of the oxet at bond "a" leads to the thermodynamically more stable (II).

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