An Acetylenic Cyclisation Leading to Chloroarylidenetetrahydrofuran-2,4,5-triones

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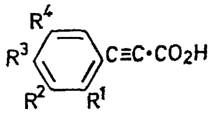
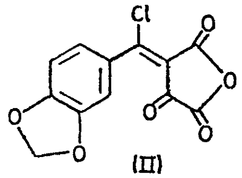
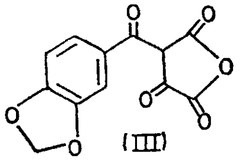
Summary Phenylpropiolic acids, containing suitable electron releasing groups, react with oxalyl chloride, to give the chloroarylidenetetrahydrofuran-2,4,5-triones (II).

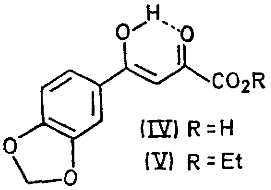
3,4-Methylenedioxyphenylpropiolic acid (Ia), with oxalyl chloride, gives neither the simple acid chloride, nor a 1-arylnaphthalene (*cf.* VI), but a bright red compound (75%), m.p. 155° (decomp.). The new compound [λ_{max} ($CHCl_3$) 274sh (ϵ 7020), 288 (8200), 364 (5300), 425sh (8700), and 473 nm (13000), ν_{max} ($CHCl_3$) 1869, 1838, 1788, 1723 cm^{-1}] is readily hydrolysed by water in ethyl acetate, one mole giving an enol of (III) and excess giving (IV), thermally degraded to 3,4-methylenedioxyacetophenone. Treatment of the red compound with ethanol gave (V) identical with a synthetic specimen. The new trione is formulated as (II).†

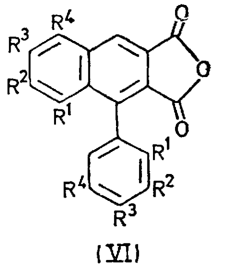

(I)

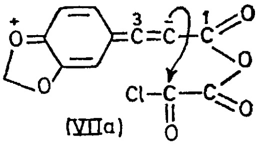
	R^1	R^2	R^3	R^4
a;	H	-O·CH$_2$·O-		H
b;	H	OMe	OMe	OMe
c;	H	OMe	OMe	H
d;	H	H	OMe	H
e;	H	H	Me	H
f;	H	H	H	H
g;	OMe	H	H	H
h;	H	H	Cl	H

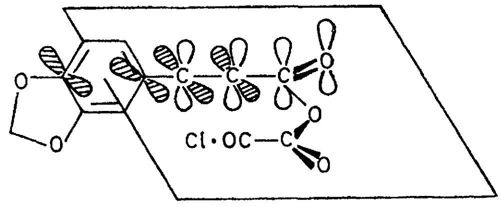

(II)


(III)


(IV) R = H
(V) R = Et


(VI)


(VIIa)


(VIIb)

Formation of the red compounds (II) occurs only when the aromatic ring contains substituents giving sufficient electron release (Ia—d). Acetylenes (Ie—h) gave no triones, yielding mixtures of the acetylenic acid chlorides and the arylnaphthalene anhydride (VI), formed *via* acetylenic acid anhydrides.[1]

The trione-forming reaction involves a nucleophilic displacement by C-2 of the acetylene in the mixed anhydride (VIIa). In the transition state for cyclisation the aromatic ring is envisaged as being orthogonal to the forming trione ring. Overlap of the aromatic orbitals with the shaded orbitals of the rehybridising acetylene (*cf.* VIIb) implies that the electronic effect of substituents in the aromatic ring is of cardinal importance in stabilising the developing positive charge at C-3, whilst the carbonyl overlap with the unshaded orbitals has little influence.

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† A recent *X*-ray study in our laboratory (Dr. M. J. Begley) shows the crystals examined to be mainly of the (*Z*) geometry shown with about 15% of the *E* stereoisomer included in the lattice.

[1] J. Cley and J. F. Arens, *Rec. Trav. chim.*, 1959, **78**, 929; F. G. Baddar, G. E. M. Moussa, and M. T. Omar, *J. Chem. Soc.* (*C*), 1968, 110.