

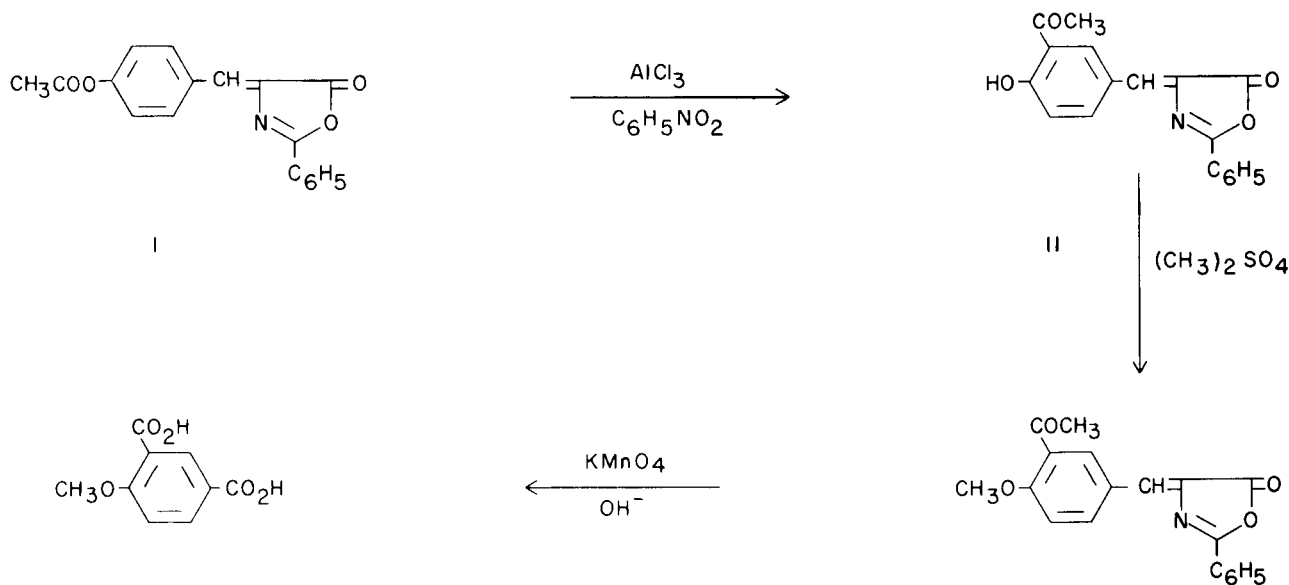
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Fries Rearrangement of an Acetoxy Azlactone

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In the course of our studies on the behavior of azlactones under Friedel-Crafts conditions (1), it was noted that 2-phenyl-4-(4'-acetoxybenzylidene)-5(4H)-oxazolone (I) gave a product whose infrared spectrum indicated the presence of two different types of carbonyl groups. When the reaction was conducted in nitrobenzene, a medium in which solvent participation does not occur and the hetero ring is not opened, a new azlactone, 2-phenyl-4-(4'-hydroxy-3'-acetylbenzylidene)-5(4H)-oxazolone (II) was obtained. Compound II formed a 2,4-dinitrophenylhydrazone and the infrared spectrum of II revealed strong carbonyl bands near 1790 cm^{-1} (lactone) and 1685 cm^{-1} (conjugated ketone). II could be methylated with dimethyl sulfate and oxidation of the resulting compound yielded 4-methoxyisophthalic acid (2), thus establishing structure II as the product of Fries rearrangement.

The reactions are summarized below.



EXPERIMENTAL (3)

2-Phenyl-4-(4'-acetoxybenzylidene)-5(4H)-oxazolone (I).

This compound was prepared from *p*-hydroxybenzaldehyde, hippuric acid, and acetic anhydride, according to a procedure described previously (4).

Fries Rearrangement of I.

Compound I (10 g.) was heated on a steam bath ($95\text{--}100^\circ$) for 2 hrs. with 50 ml. of nitrobenzene containing 10 g. of anhydrous aluminum chloride. The reaction mixture was decomposed with 100 ml. of dilute hydrochloric acid and the solvent removed by steam distillation. The residue was filtered and crystallized from 95% ethanol to give

5.1 g. (51%) of II, m.p. 201° .

Anal. Calcd. for $\text{C}_{18}\text{H}_{13}\text{NO}_4$: C, 70.35; H, 4.26. Found: C, 70.12; H, 4.41.

Infrared spectrum (KBr disc): 3450 cm^{-1} (phenolic OH), $1790\text{--}1785\text{ cm}^{-1}$ (lactone C=O), $1685\text{--}1680\text{ cm}^{-1}$ (ketone C=O).

This compound formed a 2,4-dinitrophenylhydrazone, m.p. 232° .

Anal. Calcd. for $\text{C}_{24}\text{H}_{17}\text{N}_5\text{O}_7$: N, 14.36. Found: N, 14.12.

Methylation of Compound II.

Compound II (1 g.) was heated in 20 ml. of dry acetone containing 2 g. of anhydrous potassium carbonate and 2 ml. of dimethyl sulfate. The inorganic material was filtered and the acetone removed by heating on a water bath to give an oily material which did not crystallize.

Oxidation of Methylated Product.

The oil was treated with alkaline potassium permanganate solution and heated for 10 minutes. Manganese dioxide was removed by filtration. On acidification, the filtrate gave 4-methoxyisophthalic acid, m.p. 274° (2).

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