trans-1-Aryl-2-aroyloxyethylenes. Persulfate Oxidation of Chalcones and Chalcone Analogues

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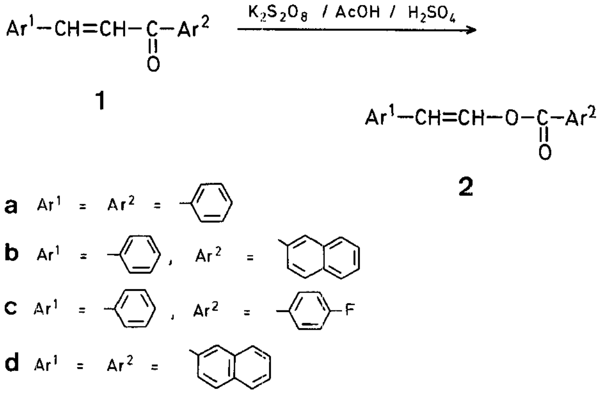
Earlier investigations[1,2] on the oxidation of chalcone (**1**, $Ar^1 = Ar^2 = C_6H_5$) under Baeyer-Villiger and similar conditions resulted in the formation of anomalous products. Thus, Weitz and Scheffer[1] reported the isolation of the epoxyketone (89%), by the reaction of chalcone with hydrogen peroxide. Subsequently, Tokoyama and Nohara[2] carried out the oxidation of chalcone with peroxybenzoic acid. Without isolation of the products, these authors proposed the formation of epoxyesters in this reaction. It was, therefore, interesting to find out a suitable peroxy derivative which would yield the normal Baeyer-Villiger oxidation product of chalcone. Herein we wish to report the successful application of peroxydisulfuric acid (in glacial acetic acid) for this purpose. Thus, the oxidation of various chalcones and chalcone analogues (**1**) yielded the corresponding aromatic unsaturated esters, identified as *trans*-1-aryl-2-aroyloxyethylenes (**2**) by spectroscopic evidences.



Oxidation of Chalcone (1a) to *trans*-1-Phenyl-2-benzoyloxy-ethylene:

A mixture of chalcone **1a** (2.08 g, 10 mmol), potassium peroxydisulfate (5.4 g, 20 mmol), conc. sulfuric acid (5 ml), and glacial acetic acid (70 ml) were kept at room temperature (~17°), with intermittent shaking, for 170 hr. The mixture was neutralized with potassium hydroxide solution (10 g in 60 ml of water) with ice cooling so as not to allow the temperature to exceed 20°. The precipitated salts were removed by filtration and the filtrate was extracted with ether. The ethereal layer was dried ($MgSO_4$), solvent distilled off, and the residue was chromatographed on a column of silica gel. Elution with petroleum ether afforded compound **2a** as colorless needles; yield: 450 mg (20%); m.p. 62°.

$C_{15}H_{12}O_2$			
	calc.	C 80.34	H 5.39
	found	80.35	5.21

I.R. (KBr): $\nu_{max} = 1724$, 1258, 1114 (ester); 1656, 935 (*trans* double bond); 1605, 752, 709 cm^{-1} (aromatic).

U.V. (Ethanol): $\lambda_{max} = 272$ nm (log $\varepsilon = 4.45$) indicating the absence of the enone system as it lacks the n-π^* band at 310–330 nm.

Mass Spectrum: $m/e = 224$ (M^+), other peaks at $m/e = 105$ $(M-O—CH=CH—C_6H_5)^{\oplus}$, 91 (tropylium ion), 77 $(M-CO—O—CH=CH—C_6H_5)^{\oplus}$ and 65 $(C_5H_5)^{\oplus}$.

^1H-N.M.R. ($CDCl_3$, 60 MHz): $\delta = 6.55$ (d, 1H, olefinic, $J_{HH} = 12$ Hz), 7.42 (m, 8H, aromatic), 8.10 (m, 3H, aromatic two ortho protons and one olefinic proton, coupled (*trans*) to the proton at 6.55). The chemical shift of the aromatic protons (ortho) is in excellent agreement with the calculated value[3], 8.07.

Further elution of the column, with a series of solvents of increasing polarity afforded the unreacted chalcone (20%), benzoic acid (39%), and a resin.

Oxidation of 3-(2-Naphthyl)-3-oxo-1-phenylpropene (1b) to *trans*-1-phenyl-2-(2-naphthoyloxy)-ethylene (2b):

A mixture of compound **1b** (1.3 g, 5 mmol), potassium peroxydisulfate (2.75 g, 10 mmol), conc. sulfuric acid (4 ml), and glacial acetic acid (50 ml) was kept at room temperature, with occasional shaking, for 170 hr. The mixture was worked up as before, and was chromatographed over silica gel. Elution with petroleum ether/benzene (4:1) gave ester **2b** as light yellow needles; yield: 330 mg (25%); m.p. 112°.

$C_{19}H_{14}O_2$			
	calc.	C 83.19	H 5.14
	found	82.98	5.43

I.R. (KBr): $\nu_{max} = 1724, 1253, 1109$ (ester); 1653, 932 (*trans* double bond); 1600, 752, 691 cm^{-1} (aromatic).

Further elution of the column gave unreacted compound **1b** (25%), 2-naphthoic acid (33%), and a resin.

Oxidation of 4'-Fluorochalcone (1c) to *trans*-1-Phenyl-2-(4-fluorobenzoyloxy)-ethylene (2c):

4'-Fluorochalcone (1.3 g, 5 mmol), potassium peroxydisulfate (2.75 g, 10 mmol), conc. sulfuric acid (4 ml), and glacial acetic acid (40 ml) were mixed and kept at room temperature with intermittent shaking for 50 hr. The preliminary work-up of the reaction mixture was carried out as described earlier. The mixture was then chromatographed over silica gel. Elution with petroleum ether afforded compound **2c** as colorless needles; yield: 440 mg (37%); m.p. 80°.

$C_{15}H_{11}O_2F$	calc.	C 74.38	H 4.58
	found	74.28	4.67

I.R. (KBr): $\nu_{max} = 1730, 1258, 1105$ (ester); 1652, 931 (*trans* double bond); 1602, 848, 759 cm^{-1} (aromatic).

In addition, unreacted 4'-fluorochalcone (15%), 4-fluorobenzoic acid (30%), and a resin were isolated.

Oxidation of 1,3-Bis-[2-naphthyl]-propeneone to *trans*-1-(2-Naphthyl)-2-(2-naphthoyloxy)-ethylene (2d):

A mixture of compound **1d** (1.54 g, 5 mmol), potassium peroxydisulfate (2.75 g, 10 mmol), conc. sulfuric acid (4 ml), and glacial acetic acid (40 ml) was shaken mechanically at room temperature for 24 hr. The reaction mixture was worked up as before and chromatographed over silica gel. Elution with petroleum ether gave ester **2d** as colorless solid; yield: 300 mg (19%); m.p. 179-80°.

$C_{23}H_{16}O_2$	calc.	C 85.16	H 4.97
	found	85.41	5.37

I.R. (KBr): $\nu_{max} = 1724, 1255, 1107$ (ester); 1650, 933 (*trans* double bond); 1595, 776, 754 cm^{-1} (aromatic).

Unreacted compound **1d** (30%), 2-naphthoic acid (40%), and a resin were obtained from the flowing chromatogram.

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