Studies in Thio-Claisen Rearrangement; A Facile Synthesis of Thiochroman-3-carboxylic Acids

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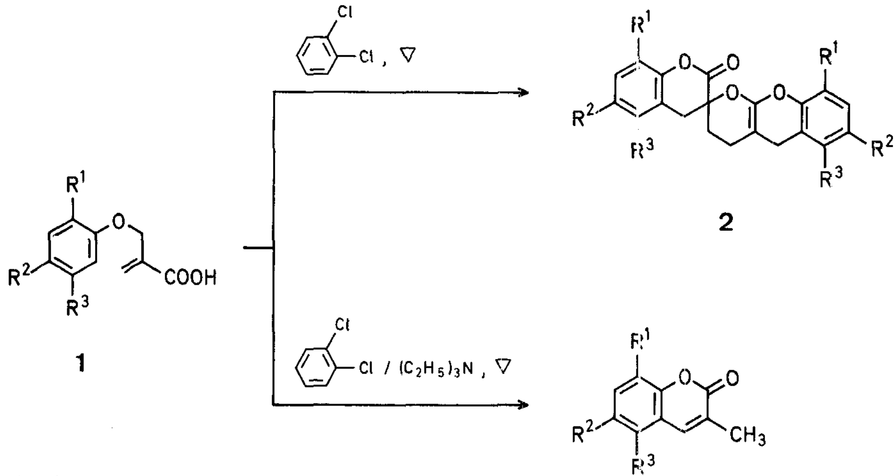
In earlier publications we have reported the formation of spirodimers of the type **2** and 3-methylcoumarins (**3**) by the thermal rearrangement of α-aryloxymethylacrylic acids (**1**)[1,2].

In this communication we report a facile catalysed Thio-Claisen rearrangement of α-arylthiomethylacrylic acids (**6**) when heated with triethylamine in *o*-dichlorobenzene to afford the unknown thiochroman-3-carboxylic acids (**7**). In



the absence of triethylamine, there is no rearrangement under the same conditions and the starting material is recovered quantitatively. The conversion probably involves an initial Thio-Claisen rearrangement assisted by an intramolecular participation of the carboxylate group as pictured, followed by a Michael addition to yield the product. The α-arylthiomethylacrylic acids (6) were prepared from thiophenols (4) and α-iodomethylacrylic acid[3] (5) in the presence of alkali.

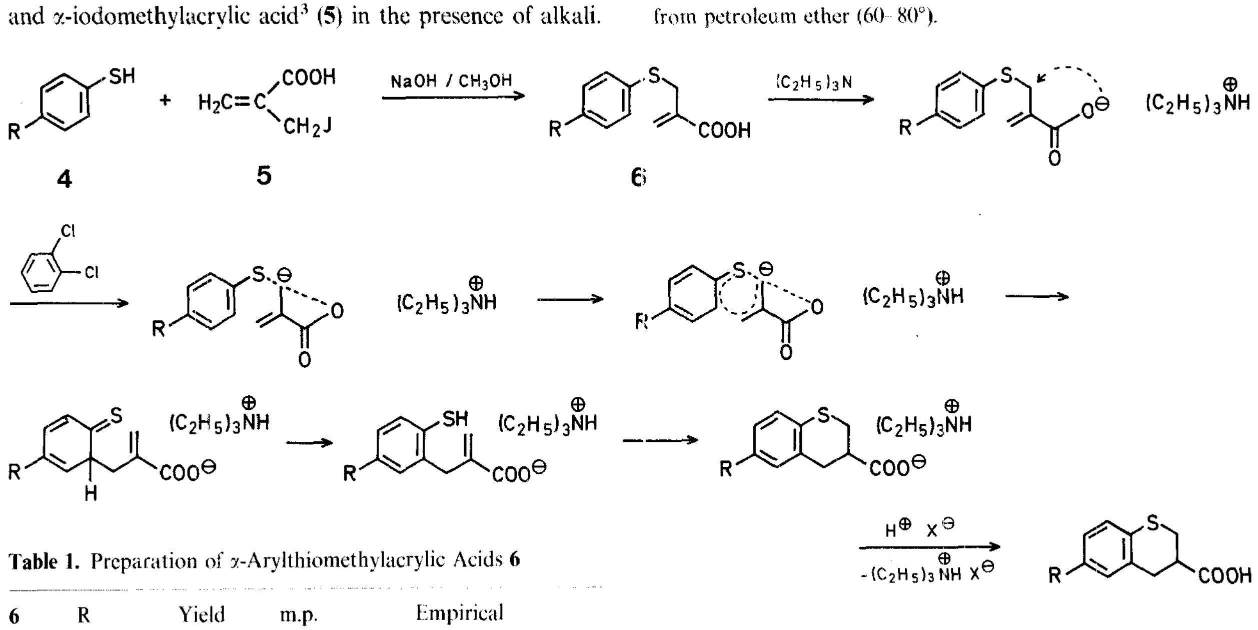


Table 1. Preparation of α-Arylthiomethylacrylic Acids **6**

6	R	Yield (%)	m.p.	Empirical formula[a]
a	H	66	65–66°	$C_{10}H_{10}O_2S$ (194.3)
b	CH_3	55	90–92°	$C_{11}H_{12}O_2S_2$ (208.3)
c	t-C_4H_9	15–16	66–68°	$C_{14}H_{18}O_2S_2$ (250.4)

[a] All compounds gave satisfactory elemental analyses (C ±0.22%, H ±0.45%) and spectral data.

Preparation of α-Arylthiomethylacrylic Acids (6); General Procedure:

A solution of the thiophenol **4** (0.1 mol) in methanol (50 ml) is heated with powdered sodium hydroxide (0.2 mol) on a water bath until all the solid dissolves. α-Iodomethylacrylic acid (**5**; 0.1 mol) in methanol (50 ml) containing dimethylformamide (5 ml) is then added during 15 minutes and heating is continued for 4 h. Most of the solvent is removed under reduced pressure and the residue is poured on to crushed ice and acidified with concentrated hydrochloric acid. The resulting sticky material is taken up in ether (2 × 100 ml) and the acidic material is extracted with saturated sodium hydrogen carbonate solution. Acidification with ice-cold concentrated hydrochloric acid precipitated the acid **6**, which is collected, washed with water, dried and recrystallised from petroleum ether (60–80°).

Improved Preparation of α-(4-*t*-Butylphenyl)-thiomethyl Acrylic Acid (6c):

A mixture of 4-*t*-butyl-thiophenol (4.1 g, 0.024 mol) and α-iodomethylacrylic acid (5.2 g, 0.024 mol) in dry acetone (75 ml) containing anhydrous potassium carbonate (6.6 g, 0.048 mol) is refluxed on a water bath for 12 h. The reaction mixture is cooled, filtered, and acetone distilled. The residue left after removal of acetone and the filtered solid are combined, dissolved in water (50 ml), acidified with cold concentrated hydrochloric acid, and extracted with ether (2 × 50 ml). The ether extract is worked up for acidic material as before to give a colourless solid; yield: 3.6 g (60%); m.p. and mixture m.p. 66–68°.

Preparation of Thiochroman-3-carboxylic Acids 7; General Procedure:

A solution of the α-arylthiomethylacrylic acid (**6**) and triethylamine (0.25 mol/mol of the acid) in *o*-dichlorobenzene (10 ml/g of the acid) is heated at reflux for 6 h in an atmosphere of carbon dioxide. *o*-Dichlorobenzene is distilled under reduced pressure and the residue taken up in ether. The ether solution is washed with saturated sodium hydrogen carbonate solution till all the

Table 2. Preparation of Thiochroman-3-carboxylic Acids **7**

7	R	Yield (%)	m.p.	Empirical formula[a]	Mass spectrum *m/e*
a	H	86	125–126°	$C_{10}H_{10}O_2S$ (194.3)	194 ($M^{\oplus}$, 78.2%), 149 (34.7%), 148 (100%), 147 (89.8%), 121 (40.5%), 116 (42%)
b	CH_3	50	131–132°	$C_{11}H_{12}O_2S$ (208.3)	208 ($M^{\oplus}$. 98.8%), 162 (100%), 161 (97.2%), 147 (55.3%), 136 (36.8%), 135 (43%), 130 (49.7%), 115 (40.7%), 91 (44.6%)
c	*t*-C_4H_9	24	92–93°	$C_{14}H_{18}O_2S$ (250.4)	250 ($M^{\oplus}$, 97.1%), 237 (73%), 236 (88.1%), 235 (88.7%), 207 (41.5%), 189 (57%), 161 (71.3%), 156 (78%), 147 (100%), 141 (41%), 128 (57.3%), 115 (98.3%), 91 (54%), 57 (87.6%), 55 (71.9%), 43 (96.6%), 41 (82%), 39 (59.5%)

[a] All compounds gave satisfactory elemental analysis (C ±0.24%, H ±0.33%) and the expected I.R. and N.M.R. spectra.

acidic material is extracted. The hydrogen carbonate extract is acidified with cold concentrated hydrochloric acid and the precipitated acid **7** is filtered, washed with water, dried, and recrystallised from ethyl acetate/petroleum ether (60–80°).

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