A Simple Synthesis of Chromones

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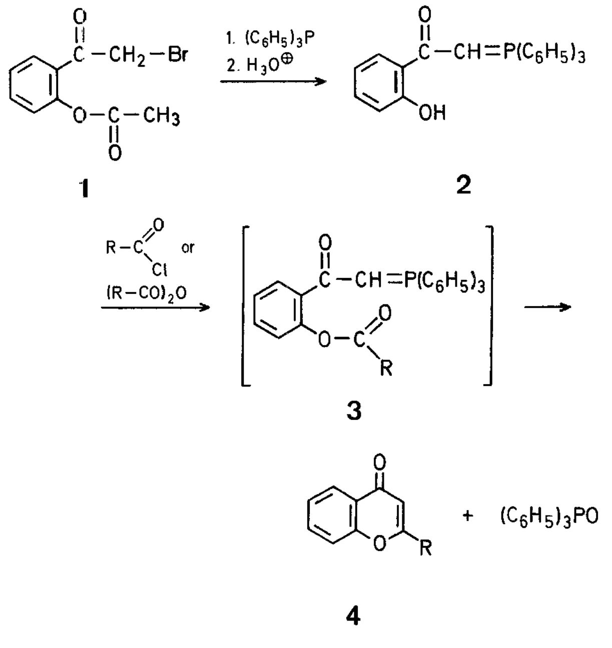
We have previously reported a simple preparation of 1-benzofurans from *o*-hydroxybenzylidenetriphenylphosphorane[1] by intramolecular olefination of the ester carbonyl group. Recently, two 3-methoxycarbonylchromones were obtained from the reaction of 2-acyloxybenzoyl chlorides with methoxycarbonylmethylenetriphenylphosphorane[2]. We now describe a convenient synthesis of chromones (**4**) from *o*-hydroxyphenacylidenetriphenylphosphorane (**2**) under mild conditions.

Phosphorane **2** is readily obtained from the reaction of triphenylphosphine with *o*-acetoxyphenacyl bromide (**1**), followed by acid hydrolysis and treatment of the reaction mixture with sodium carbonate. Reaction of phosphorane **2** with carboxylic acid chlorides or anhydrides in boiling toluene in the presence of pyridine gives the unstable phosphorane **3** which undergoes spontaneous intramolecular olefination of its ester carbonyl group to afford the chromone **4**.



This method is of general applicability and may be used for the synthesis of flavones (e.g., **4d, e**) in high yields.

***o*-Acetoxyphenacyl Bromide (1, 2-Acetoxy-ω-bromoacetophenone):** Bromine (5.5 ml, 0.1 mol) is added within 5 min to a stirred solution of 2-acetoxyacetophenone (17.8 g, 0.1 mol) in boiling carbon tetrachloride (200 ml). The solvent is then removed under vacuum, a mixture (1/1; 100 ml) of ether and petroleum ether is added, and the solution cooled. The precipitated product **1** is isolated by suction; yield: 21 g (81%); m.p. 72–73 °C (Ref.[8], m.p. 67 °C).

***o*-Hydroxyphenacylidenetriphenylphosphorane (2):**
To a stirred solution of *o*-acetoxyphenacyl bromide (**1**; 13 g, 0.05 mol) in toluene (100 ml), a solution of triphenylphosphine (13 g, 0.05 mol) in toluene (100 ml) is added, the mixture is heated under reflux for 1 h, and then cooled. The precipitated phosphonium salt (26 g, 100%) is

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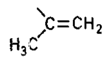
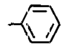
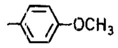
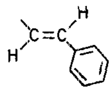
isolated by suction and suspended in 40% hydrobromic acid (100 ml). The mixture is heated under reflux for 1 h, then cooled, made alkaline with sodium carbonate, and the phosphorane **2** is extracted with chloroform (2 x 100 ml). The organic solution is dried with magnesium sulfate and the solvent removed under vacuum; yield: 17.1 g (90%). This material is sufficiently pure for the following step, but pure **2** can be obtained by recrystallisation from chloroform; m.p. 210 °C.

$C_{26}H_{21}O_2P$	calc.	C 78.77	H 5.34	P 7.81
(396.4)	found	78.52	5.20	7.68

Flavone (4d); Typical Procedure:

o-Hydroxyphenacylidenetriphenylphosphorane (**2**; 7.92 g, 0.02 mol) is dissolved in boiling dry toluene (80 ml) and benzoyl chloride (3.1 g, 0.022 mol) or benzoic anhydride (9 g, 0.04 mol) and pyridine (3.6 g, 0.04 mol) are added. The mixture is refluxed for 5 h and then allowed to cool. The pyridinium salt is separated by filtration, the filtrate is washed with aqueous 15% sodium carbonate (50 ml), and the toluene distilled off. The solid residue is column-chromatographed on silica gel (0.063-0.2 mm) using ether/toluene (2/3) as eluent. Pure **4d** is eluted whereas triphenylphosphine oxide is retained on the column; yield: 4.26 g (96%); m.p. 97 °C (Ref.[5], m.p. 97 °C).

Table. Chromones (4) prepared

4	R	Yield[a] [%]	m.p.[b] [°C]	Molecular formula or m.p. [°C] reported	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm] of 3-H
a	H_3C	76	71-72°	70-71°[3]	6.16
b		55	77-78°	$C_{12}H_{10}O_2$ (186.2)[c]	6.38
c		76	139-140°	138°[4]	6.76
d		96	97°	97°[5]	6.68
e		97	157-158°	158°[6]	6.80
f		65	141-142°	131°[7]	6.36

[a] Obtained with acid anhydride (**4a**) or acid chloride (**4b–e**).

[b] Recrystallized from ethanol.

[c]
calc.	C 77.40	H 5.41
found	77.12	5.37

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