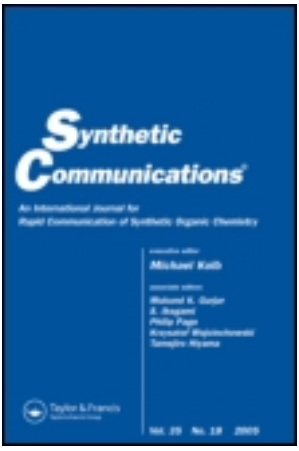

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A NEW APPROACH TO THE SYNTHESIS OF CHROMENE DERIVATIVES

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A NEW APPROACH TO THE SYNTHESIS OF CHROMENE DERIVATIVES

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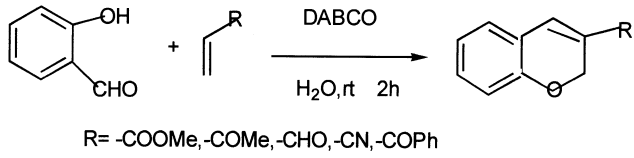
ABSTRACT

3-Acetyl-5,6-benzopyran and 3-benzoyl-5,6-benzopyran have been simply prepared by condensation of methylvinyl ketone and phenylvinyl ketone with salicylaldehyde in an aqueous DABCO medium at room temperature.

Some chromene derivatives[1–4] might prove useful synthetic intermediates for the synhesis of certain naturally occurring substances, such as Miroestrol.[5] Also, in a study of the photochemistry of some structurally related unsaturated ketones, the chromenes were needed. Many works describing chromene derivatives preparation have been reported. Attempts to prepare 3-acetyl-5,6-benzopyran, 3-benzoyl-5,6-benzopyran, and 1:2-benzopyran-3-carboxaldehyde by the method of Taylor and Tamlinson[6] gave only polymeric mixtures. Attempts to convert 1:2-benzopyran-3-carboxylic acid to 1:2-benzopyran-3-carboxaldehyde, 1:2-benzopyran-3-methylcarboxylate, or 3-benzoyl-5,6-benzopyran by conventional reactions (Friedal-Crafts, Grignard, reduction, etc.) also failed, or at best gave poor yields with many side-products. Later, DeBoer reported[7] vapor-

phase introduction of vinyl ketones in Michael addition, which apparently prevents polymerization and gives desired products in reasonable yields. In recent years, Kaye and Robinson[8] attempted to prepare chromene derivatives, but the isolated yields were very low.

Recently, it has been reported that polyfunctional vinylic compounds can be prepared by using 1,4-diazabicyclo[2.2.2]octane **(DABCO)** as a catalyst by coupling various aldehydes with monofunctional vinylic substrates[9–13] Accidently, I undertook an investigation to prepare chromene derivatives (**1a**–**1f**). It seems desirable to publish some of my results at this stage. During my study in this direction, I first carried out the reaction of salicylaldehyde(0.6106 g, 5 mM) in water (5 mL) and 20 mol% of 1,4-diazabicyclo[2.2.2]octane **(DABCO)**, followed by 10 mM (0.83 mL) of methyl vinyl ketone **(mvk)**, and the stirring continued at room temperature for 2 h. Then the reaction mixture was acidified with 2 mL of concentrated HCl and the lower layer was separated, washing the water layer with dichloromethane (DCM). The organic layer was dried and, after vacuum distillation, provided the desired 3-acetyl-5,6-benzopyran (**2a**) in 73% yield



Scheme 1.

Table 1. Synthesis of Chromene Derivatives[a,b]

Compound	R	Yield[c](%)	M.p.(°C)
1a	COOMe	74	171
1b	$COCH_3$	73	51–54
1c	COC_6H_5	71	63
1d	CN	79	**52**
1e	CHO	73	69–71
1f[d]	COOH	77	187

[a]All reactions were carried out in 5 mM scale of salicylaldehyde in water (5 mL) and 20 mol% DABCO, followed by 10 mM of the corresponding substrates at room temperature for 2 h.

[b]Satisfactory spectral data IR, ^1H (200 MHz), and ^{13}C NMR (50 MHz) and elemental analysis[14] were obtained.

[c]Isolated yields after column chromatography (silica gel, 1% ethyl acetate in hexane).

(1.273 g). This interesting result encourages me to continue my investigations with other substrates, like **1b**–**1e** under similar reaction conditions to provide a simple and convenient synthesis of chromene derivatives (**2a**–**2e**) in reasonable yields Table 1, Scheme 1.

In conclusion, this condensation method offers an alternative route for the simple synthesis of chromene and takes advantage over the vapor-phase introduction.[7]

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14. Elemental analysis calculated for (**1d**) $C_{10}H_7ON$: C, 76.4; H, 4.5; N 8.9% and found C, 76.3; H, 4.7; N, 8.7. Elemental analysis calculated for (**1f**) $C_{10}H_8O_3$: C, 68.2; H, 4.5% and found C, 68.4; H, 4.6.

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