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## A NEW APPROACH TO THE SYNTHESIS OF CHROMENE DERIVATIVES

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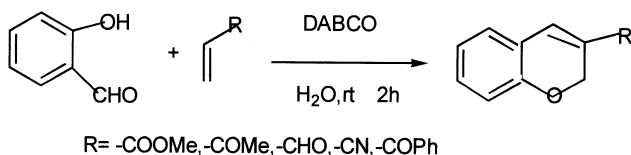
### ABSTRACT

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<sup>1–4</sup> might prove useful synthetic intermediates for the synthesis of certain naturally occurring substances, such as Miroestrol.<sup>5</sup> 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<sup>6</sup> 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<sup>7</sup> 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<sup>8</sup> 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<sup>9–13</sup>. Accidentally, 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<sup>a,b</sup>

Compound	R	Yield <sup>c</sup> (%)	M.p.(°C)
<b>1a</b>	COOMe	74	171
<b>1b</b>	COCH <sub>3</sub>	73	51–54
<b>1c</b>	COC <sub>6</sub> H <sub>5</sub>	71	63
<b>1d</b>	CN	79	<b>52</b>
<b>1e</b>	CHO	73	69–71
<b>1f<sup>d</sup></b>	COOH	77	187

<sup>a</sup>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.

<sup>b</sup>Satisfactory spectral data IR, <sup>1</sup>H (200 MHz), and <sup>13</sup>C NMR (50 MHz) and elemental analysis<sup>14</sup> were obtained.

<sup>c</sup>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.<sup>7</sup>

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### REFERENCES AND NOTES

1. Pierre, M. J. *Heterocyclic Chem.* **1985**, 22, 45.
2. Heathcock, C.H.; Pirrung, M.C. *J. Org. Chem.* **1974**, 39, 2426.
3. Mannich, C.; Heilner, C. *Chem. Ber.* **1992**, 55, 356.
4. Bachman, L. J. *Am. Chem. Soc.* **1948**, 70, 599.
5. Corey, E.J.; Lawrence, I. J. *Am. Chem. Soc.* **1993**, 115, 9327.
6. Taylor, H.V.; Tomlinson, M.L. *J. Chem. Soc. Chem. Commun.* **1950**, 50, 272.
7. DeBoer, J. *Org. Chem.* **1974**, 39, 2426.
8. Kaye, P.T.; Robinson, R.S. *Synth. Commun.* **1996**, 26, 2085–2097.
9. Basavaiah, D.; Bharathi, T.K.; Gowriswari, V.V.L. *Synth. Commun.* **1987**, 17, 1893.
10. Hoffmann, H.M.R.; Rabe, J. *Helv. Chem. Acta.* **1984**, 67, 413.
11. Hoffmann, H.M.R.; Rabe, J. *Angew. Chem.* **1983**, 22, 795.
12. Issacs, N.S.; Hill, J. European Patent, 200442, **1986**.
13. Fikentcher, R.; Hahn, E.; Kud, A.; Oftring, A. *Chem. Abstr.* **1986**, 105, 115538k.
14. Elemental analysis calculated for (**1d**) C<sub>10</sub>H<sub>7</sub>ON: 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<sub>10</sub>H<sub>8</sub>O<sub>3</sub>: C, 68.2; H, 4.5% and found C, 68.4; H, 4.6.

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