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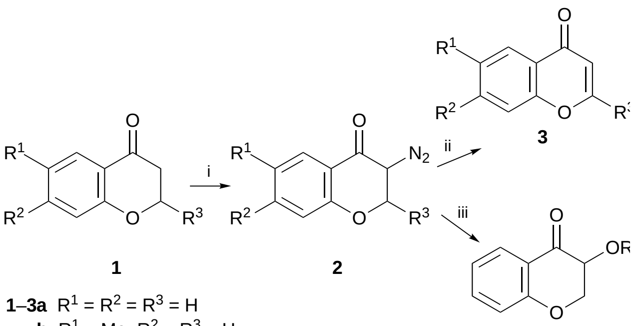
Lewis Acid-catalysed Facile Elimination of the Diazo Group in 3-Diazochromanones. Novel Conversion of Chromanones into Chromones†

Pranab Mandal and Ramanathapuram V. Venkateswaran*

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India

3-Diazochromanones undergo rapid elimination of the diazo group in presence of $BF_3{\cdot}Et_2O$ to furnish chromones.

The ready accessibility of α-diazocarbonyl compounds and the versatility of their transformations have made them one of the most useful functional groups in organic synthesis;[1] the wide variety of α-diazocarbonyl compounds which have been brought within the scope of such transformations attest to the immense potential of this functional group. However, extension of such varied transformations to carbocyclic diazoketones has been rather limited and there has been no report of any transformation involving the 3-diazo-4-chromanone system. As an extension of our continuing synthetic studies involving chromone precursors,[2] we have also started investigations into the possible utilisation of 3-diazochromanones and herein report the facile elimination of the diazo group in the presence of $BF_3{\cdot}Et_2O$ to furnish chromones (Scheme 1). The 3-diazochromanones were prepared from the corresponding chromanones *via* a formylation and deformylative diazo transfer reaction and were obtained in overall yields of 55–60%. Treatment of these diazochromanones (**2a–e**) with a catalytic amount of $BF_3{\cdot}Et_2O$ in methylene chloride at ambient temperature for 1–1.5 h furnished the chromones **3a–e**, respectively, in excellent yields, providing a new procedure for the conversion of chromanones into chromones (Table 1).[3] The structures of the products were established through detailed spectral analysis and comparison with authentic samples. When methanol was added to the reaction medium, **2a** afforded a mixture of chromone **3a** and 3-methoxychromanone (**4a**, Scheme 1), in varying proportions, and when methanol alone was used as the solvent, it gave **4a** exclusively in more than 85% yield. Similarly, in presence of allyl alcohol, the allyl derivative **4b** was obtained in very good yield. This suggests a route to various 3-alkoxy substituted chromanones.



1–3a $R^1 = R^2 = R^3 = H$
b $R^1 = Me, R^2 = R^3 = H$
c $R^1 = R^3 = H, R^2 = Me$
d $R^1 = H, R^2 = R^3 = Me$
e $R^1 = R^3 = H. R^2 = OMe$

4a R = Me
b $R = CH_2{-}CH{=}CH_2$

Scheme 1 *Reagents*: i, (a) $NaH/HCO_2Et/Et_2O$ (b) Et_3N/TsN_3; ii, $BF_3.Et_2O/CH_2Cl_2$; iii, (a) $BF_3.Et_2O/MeOH$ (b) $BF_3.Et_2O/CH_2{=}CH{-}CH_2{-}OH$

When this diazo elimination reaction was extended to the alicyclic situation, as in 2-diazotetralin-1-one, it furnished α-naphthol in over 70% yield as a result of elimination and consequent aromatisation.

The metal-catalysed decomposition of a diazoketone containing an α-hydrogen has been reported to lead to an alkene, depending on the nature of the ligand on the metal.[1] In keeping with this, decomposition of 3-diazochromanone **2a** with a catalytic amount of dirhodium tetraacetate in benzene furnished chromone **3a** in more than 70% yield.

In summary, we describe an interesting Lewis acid-catalysed elimination of the diazo group in 3-diazochromanones as a novel route to chromones. This should serve as a useful complementary procedure to other existing methods for the transformation of chromanones into chromones.[3]

Experimental

General Procedure as Illustrated for **3a**.—To a stirred slurry of sodium hydride (1.44 g) in diethyl ether (40 ml) under nitrogen was added a drop of ethanol followed by a solution of chromanone (**1a**) (2.96 g) in diethyl ether (5 ml). The reaction mixture was cooled in an ice-bath and ethyl formate (4.44 g) was added dropwise, and the mixture stirred overnight. The reaction mixture was then poured into ice-cold water, the diethyl ether layer separated and the aqueous layer acidified with cold dil. HCl and extracted with diethyl ether. The ethereal extracts were combined, washed with brine, dried (Na_2SO_4) and concentrated to afforded the 3-formylchromanone (2.95 g, 83%) which was used directly in the next step.

The above formylchromanone was dissolved in methylene chloride (20 ml) and triethylamine (3.75 g) was added. The reaction mixture was cooled in an ice-bath and a solution of toluene-*p*-sulfonyl azide (7.3 g) in methylene chloride (5 ml) was added dropwise. The cold reaction mixture was stirred for 3 h and subsequently overnight at room temp. Aqueous potassium hydroxide (10%, 20 ml) was then added and the solution stirred for 30 min. The layers produced were separated and the aqueous layer extracted with diethyl ether. The combined organic extracts were washed with aqueous potassium hydroxide (5%) and water, and then dried (Na_2SO_4). Removal of the solvent followed by chromatography of the oily residue over neutral alumina (benzene–light petroleum, bp 40–60 °C, 2:3) furnished the 3-diazochromanone **2a** (2.1 g, 72%) as a yellow solid, mp 52–55 °C; ν_{max}/cm^{-1} 2100, 1670; δ_H (ppm) ($CDCl_3$, 60 MHz) 5.22 (s, 2 H), 7.0–7.52 (m, 3 H), 7.96 (d, 1 H, *J* 8 Hz).

Compound **2a** (1 g) was taken in methylene chloride (5 ml) and a drop of boron trifluoride etherate was added by syringe. The reaction mixture was stirred for 1.5 h at room temp. and decomposed with aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer extracted with diethyl ether. The combined organic extracts were washed with water, dried and the solvent distilled off, to furnish chromone **3a** (0.79 g, 95%) in satisfactorily pure form, identical with an authentic sample.

Table 1 lists the physical data and yields of the diazochromanones **2a–e** and the products **3a–e**.

Formation of 3-Methoxychromanone (**4a**) *from 3-Diazochromanone* (**2a**).—The above reaction was carried out using methanol as solvent in place of methylene chloride. After 1.5 h the reaction mixture was decomposed with aqueous $NaHCO_3$ and extracted with

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*To receive any correspondence..

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Table 1 Yields and mps of diazochromanones **2a–e** and product chromones **3a–e**

Diazochromanone	Mp (°C)	Yield (%)[a]	Product	Yield (%)	Mp (lit.) (°C)
2a	52–55	(60)	**3a**	95	59 (59[4])
2b	85–88	(58)	**3b**	95	87–88 (88–89[5])
2c	118–120	(60)	**3c**	95	84–86 (72[5])[b]
2d	109–110	(55)	**3d**	90	98–99 (98[4])
2e	114–116	(60)	**3e**	90	110 (110[6])

[a] Overall yield for the two steps of formylation and diazotransfer. [b] The Mp differed from that reported, possibly due to better purity of present sample. Spectral data corroborated the structure.

diethyl ether. The ethereal extracts were washed with water, dried (Na_2SO_4) and the residual oil, after removal of diethyl ether, was distilled to furnish 3-methoxychromanone (**4a**, 880 mg, 86%), bp (bath temperature) 115–18 °C (5 mmHg); δ_H (CCl_4, 60 MHz) 3.50 (s, 3 H), 3.73 (t, 1 H, *J* 5 Hz), 4.4 (d, 2 H, *J* 5 Hz), 6.8–7.5 (m, 3 H), 7.76 (d, 1 H, *J* 8 Hz) (Found: C, 67.23; H, 5.65. $C_{10}H_{10}O_3$ requires C, 67.40; H, 5.66%).

Using allyl alcohol in the above experiment afforded the 3-allyloxychromanone **4b** in 80% yield; bp (bath temperature) 125–126 °C (5 mmHg); δ_H ($CDCl_3$, 300 MHz) 4.11–4.21 (m, 2 H), 4.34–4.48 (m, 3 H), 5.21–5.36 (m, 2 H), 5.91–6.14 (m, 1 H), 6.95–7.06 (m, 2 H), 7.45–7.51 (m, 1 H), 7.88 (d, 1 H, *J* 9 Hz); δ_C 69.67, 71.82, 74.47, 117.67, 118.37, 119.76, 121.63, 127.42, 133.65, 136.06, 161.08, 190.95 (Found: C, 70.24; H, 6.28. $C_{12}H_{12}O_3$ requires C, 70.57; H, 5.92%).

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