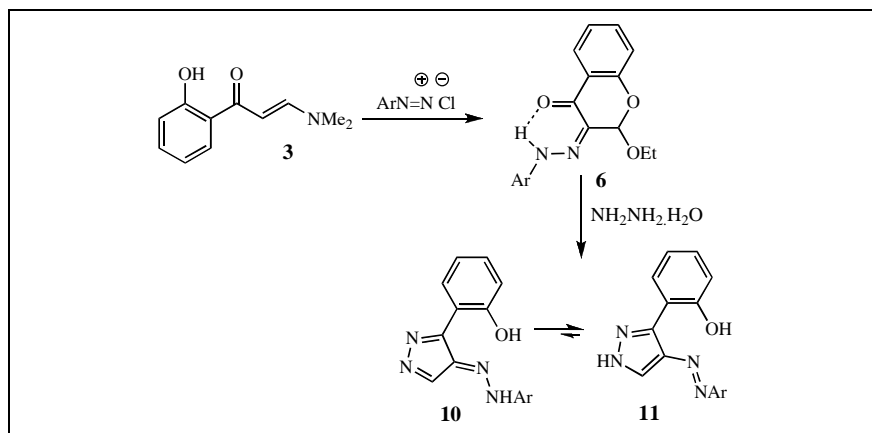


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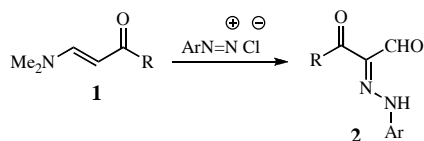


Coupling the title compound **3** with arenediazonium salts affords the aryldiazonochromones **6**. The latter compounds react with hydrazine hydrate to yield novel pyrazoles **11**.

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INTRODUCTION

Enaminones are versatile reagents and their chemistry is receiving now considerable attention [1-5]. Some time ago, we reported that enaminones **1** couple with aromatic diazonium salts to yield 2-aryldiazonopropanals [6]. This reaction has been extensively utilized for synthesis of polyfunctionally substituted heteroaromatics by us [7-12] and also other groups [13].

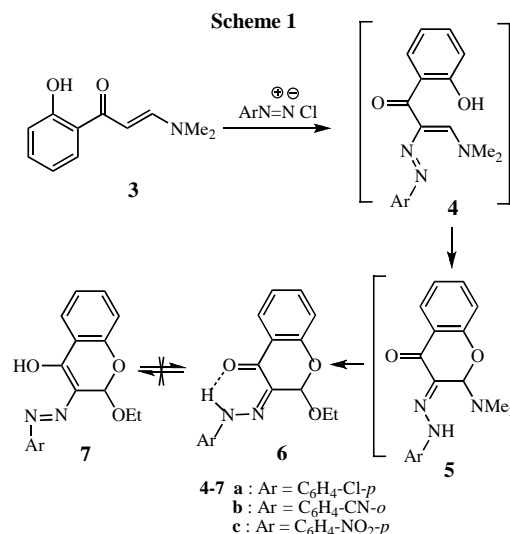


RESULTS AND DISCUSSION

In conjunction of this work, we have investigated the coupling reaction of **3** with aromatic diazonium salts with the aim of obtaining **4**. The target molecules were not obtained instead cyclic N,O-acetals **6** were formed in good yields. We believe that the formed enazo compound **4** was initially cyclized into **5** that reacted with ethanol to yield the final isolable products **6** (Scheme 1).

Both ¹³C and ¹H NMR spectra of the reaction products fit completely with the proposed structure. Thus ¹³C NMR reveals two carbon signals at $\delta = 15.4$ and 64.4 ppm for the ether moiety. The sp^3 (C-2) appears at $\delta = 98.2$ ppm. The ¹H

NMR spectrum shows the ether triplet and quartet at $\delta = 1.0$ and 3.8 ppm and a singlet at $\delta = 5.9$ ppm for (H-2) in the chromone ring. The D₂O-exchangable signal at $\delta = 14.1$ ppm is attributed to a NH proton which is hydrogen-bonded to a carbonyl group. We considered it possible, however, that **7** can exist in the enol azo form. To confirm with certainty the exact structure of **6a-c**, an X-ray crystal structure determination of **6a** was carried out [14]. It confirmed the existence of the hydrazono-chromone form (Figure 1). Some bond lengths and angles are given in Table 1.



It can thus be stated that typical for an sp^3 (C-5) bond lengths with (O-2) and (CH) are 1.43 and 1.49 Å respectively. The distance C16-O4 (1.23 Å) is typical for a C=O bond. However, the arylhydrazone bond lengths (C11-N6) and N6-N9 are little shorter than N-N bond lengths. This may be a result of the presence of an intramolecular hydrogen bond N9-H-O4

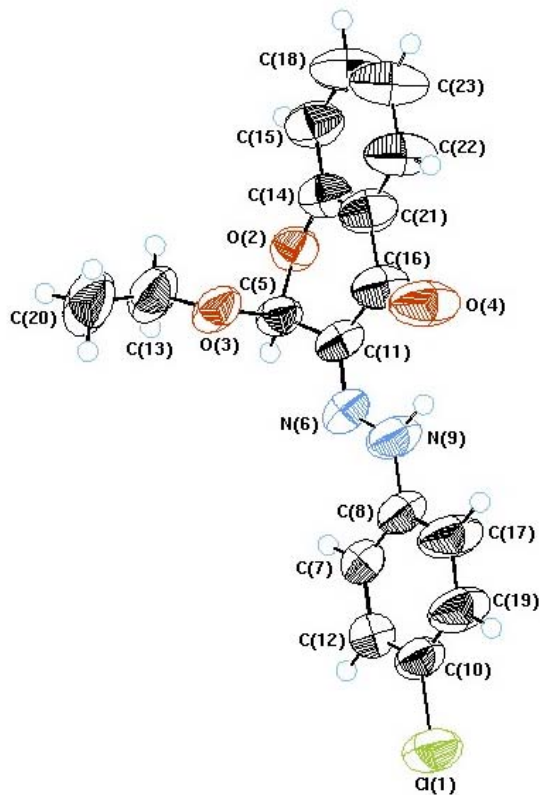


Figure 1. Solid state structure of compound **6a** (ellipsoid of thermal represent a 90% probability).

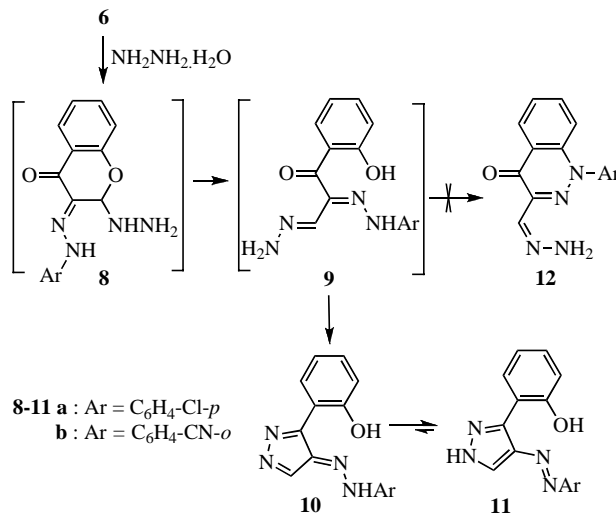
The reaction of **6** with hydrazine hydrate afforded products that may be formulated as pyrazoles **10**, **11** or cinnolines **12** (Scheme 2).

Table 1

Selected bond lengths and bond angles of **6a**.

Bond	Bond length (Å)	Bond	Bond angle (°)
O2-C5	1.43	C5-O2C14	116.1
O2-C14	1.37	C5-O3-C14	113.4
O3-C5	1.39	O2-C5-O3	109.7
O3-C13	1.43	O2-C5-C11	112.7
O4-C16	1.23	N9-N6-C11	118.0
C5-C11	1.49	N6-N9-C8	120.0
N6-N9	1.32	C7-C8-N9	122.5
N6-C11	1.31		
C11-C16	1.44		
N9-H0	0.96		

Scheme 2



The cinnoline structure was easily excluded because of the absence of an NH_2 signal in the IR spectrum and of azomethine carbon and hydrogen in the NMR spectra.

The 1H NMR spectrum indicated the pyrazole proton 5-H as a doublet at $\delta = 7.04$ ppm, in support of structure **11**. Although azo compounds usually prefer the hydrazone form, the aromaticity of the pyrazole ring tends to favor **11** over tautomer **10**.

EXPERIMENTAL

All melting points were measured on a Gallenkamp Electrothermal melting point apparatus and are uncorrected. The IR absorption spectra were measured on a Nicolet Magna 520 FT IR Spectrophotometer. 1H and ^{13}C NMR spectra were recorded in deuterated dimethylsulfoxide [D_6]-DMSO at 400 MHz on a Bruker DPX spectrometer using tetramethylsilane (TMS) as an internal reference; chemical shift are expressed as δ values. Mass spectra were performed on a Shimadzu GCMS-QP 1000 Ex mass spectrometer at 70 eV. Microwave irradiation was carried out using a commercial microwave oven (SGO 390 W). Elemental analyses were carried out at the Microanalytical Center at Cairo University.

Crystallographic analysis. The crystals were mounted on a glass fiber. All measurements were performed on an ENRAF NONIUS FR 590. The data were collected at a temperature of $20 \pm 1^\circ C$ using the ω scanning technique to a maximum of 27.12° . The structure was solved by direct method using SIR 92 and refined by full-matrix least squares [14]. Non hydrogen bond atoms were refined anisotropically. Hydrogen atoms were located geometrically and were refined isotropically. Full data can be obtained on request from the CCDC [14].

General Procedure for the Preparation of 6a-c [5]. A cold solution of aryl diazonium salt (0.1 mol) was prepared by adding a solution of sodium nitrite (1.5 g in 10 ml H_2O) to a cold solution of aryl amine (0.1 mol) in concentrated HCl (5 ml) with stirring as described earlier. The resulting solution of the aryl diazonium salt was then added to a cold solution of enaminones **3** in EtOH (50 mL) containing sodium acetate (0.1 mol). The mixture was stirred at room temperature for 1 h and

the solid product so formed was collected by filtration and crystallized from ethanol.

3-[4-Chlorophenyl]hydrazono]-2-ethoxychroman-4-one (6a). M.p. 120°C; orange crystals from ethanol; yield 90%; IR ν = 3220(NH), 3080 (CH Aromatic), 2946 (CH aliphatic), 1660 (C=O) and 1607 (C=N) cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, $[\text{D}_6]$ -DMSO): δ = 1.07 (t, 3H, CH_3CH_2), 4.03 (q, 2H, CH_2CH_3), 5.95 (s, 1H, CH), 7.18-7.52 (m, 8H, Ar-H) and 13.75 (s, 1H, NH) ppm; $^{13}\text{C-NMR}$ (100 MHz, $[\text{D}_6]$ -DMSO): δ = 15.44 ($\text{CH}_3\text{CH}_2\text{O}$), 64.19 ($\text{CH}_3\text{CH}_2\text{O}$), 100.88 (CH), 117.44, 119.21, 122.46, 123.30, 127.14, 128.38, 129.1639, 129.88, 137.18, 141.69 (aromatic carbons), 156.48 (C=N-N), and 177.46 (C=O) ppm; MS (EI, 70eV): m/z (%) = 330 $[\text{M}^+]$ - $\text{C}_{17}\text{H}_{15}\text{ClN}_2\text{O}_3$ (330.77): calcd. C 61.73; H 4.57, N 8.47; found: C 61.32; H 4.12, N 8.07.

3-[2-Cyanophenyl]hydrazono]-2-ethoxy-chroman-one (6b). M.p. 154°C; Dark orange crystals from ethanol; yield 90 %; IR ν = 3200 (NH), 3081 (CH Aromatic), 2944 (CH aliphatic), 2221 (CN), 1651 (C=O) and 1605 (C=N) cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, $[\text{D}_6]$ -DMSO): δ = 1.10 (t, 3H, CH_3CH_2), 3.82 (q, 2H, CH_2CH_3), 5.98 (s, 1H, CH), 7.20-8.75 (m, 8H, Ar-H) and 14.10 (s, 1H, NH) ppm; $^{13}\text{C-NMR}$ (100 MHz, $[\text{D}_6]$ -DMSO): δ = 15.40 ($\text{CH}_3\text{CH}_2\text{O}$), 64.41 ($\text{CH}_3\text{CH}_2\text{O}$), 98.23 (CH), 116.18 (CN), 100.42, 119.37, 122.20, 123.54, 124.47, 127.52, 131.68, 133.68, 135.43, 137.919, 145.05, 163.20 (aromatic carbons), 156.77 (C=N-N), and 178.62 (C=O) ppm; MS (EI, 70eV): m/z (%) = 321 () $[\text{M}^+]$ - $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_3$ (321.33): calcd. C 67.28; H 4.71, N 13.08; found: C 67.68; H 4.31, N 13.44.

2-Ethoxy-3-[4-nitro-phenyl]-hydrazono]-chroman-one (6c). M.p. 90°C; orange crystals from ethanol; yield 92%; IR ν = 3200(NH), 3100 (CH Aromatic), 2950 (CH aliphatic), 1665 (C=O) and 1607 (C=N) cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, $[\text{D}_6]$ -DMSO): δ = 1.12 (t, 3H, CH_3CH_2), 4.34 (q, 2H, CH_2CH_3), 5.99 (s, 1H, CH), 7.21-8.27 (m, 8H, Ar-H) and 13.59 (brs, 1H, NH) ppm; $^{13}\text{C-NMR}$ (100 MHz, $[\text{D}_6]$ -DMSO): δ = 15.43 ($\text{CH}_3\text{CH}_2\text{O}$), 64.40 ($\text{CH}_3\text{CH}_2\text{O}$), 100.81(CH), 119.39, 122.33, 123.50, 126.14, 127.37, 131.79, 137.81, 143.15, 148.29, 164.33 (aromatic carbons), 156.78 (C=N-N), and 178.0031 (C=O) ppm; MS (EI, 70eV): m/z (%) = 341 $[\text{M}^+]$ - $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_5$ (341.32) :calcd. C 59.82; H 4.43, N 12.31; found: C, 59.42; H 4.01, N 12.72.

General Procedure for the Preparation of 11a,b: Method A: A mixture of compound **3a,b** (0.10 mol) and hydrazine monohydrate (0.12 mol) were refluxed in ethanol (30 ml) for 2 h, then left to cool to room temperature and the solid was collected and crystallized from ethanol.

Method B: Compound **3a,b** (0.10 mol) and hydrazine monohydrate (0.12 mol), were placed in the microwave oven and irradiated at 390 W for 2 min., then left to cool to room temperature and the solid was collected and crystallized from ethanol.

2-[4-(4-Chlorophenylazo)-1H-pyrazol-3-yl]-phenol (11a). M.p. 118°C; dark yellow crystals from ethanol; yield 78% (Method A), 96%(Method B); IR ν = 3400 (OH), 3220(NH), 3080 (CH Aromatic) and 1657 (C=N) cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, $[\text{D}_6]$ -DMSO): δ = 5.21 (s, 1H, OH), 7.70(d, 1H, H-5 pyrazole), 6.97-8.07 (m, 8H, Ar-H) and 12.01(s, 1H, NH) ppm; $^{13}\text{C-NMR}$ (100 MHz, $[\text{D}_6]$ -DMSO): δ = 104.22(C-N=N), 134.10(C-5 pyrazole), 152.00 (C-3 pyrazole), 116.41, 122.46, 123.36, 127.14, 128.39, 129.16, 129.88, 137.18, 141.69, 155.88 (aromatic carbons) and 155.88 (C-OH) ppm; MS (EI, 70eV): m/z (%) = 298 $[\text{M}^+]$ - $\text{C}_{15}\text{H}_{11}\text{ClN}_4\text{O}$ (298.73): calcd C 60.31; H 3.71, N 18.76; found: C 60.71; H 3.30, N 18.32.

2-[3-(2-Hydroxyphenyl)-1H-pyrazol-4-ylazo]benzointrile (11b). M.p. 142° C; light orange crystals from ethanol; yield 75% (Method A), 98%(Method B) ; IR ν = 3400 (OH), 3200(NH), 3080 (CH Aromatic), 2218(CN), and 1651 (C=N) cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, $[\text{D}_6]$ -DMSO): δ = 5.22 (s, 1H, OH), 7.95(d, 1H, H-5 pyrazole), 6.99-8.04 (m, 8H, Ar-H) and 12.11(s, 1H, NH) ppm; $^{13}\text{C-NMR}$ (100 MHz, $[\text{D}_6]$ -DMSO): δ = 108.2 (C-N=N), 134.16(C-5 pyrazole), 152.20(C-3 pyrazole), 116.12 (CN), 100.40, 119.38, 122.20, 123.55, 124.48, 127.44, 131.66, 133.70, 135.43, 137.919, 145.05, 156.22 (aromatic carbons) and 156.22 (C-OH) ppm; MS (EI, 70eV): m/z (%) = 289 $[\text{M}^+]$ - $\text{C}_{16}\text{H}_{11}\text{N}_4\text{O}$ (289.29): calcd. C 66.43; H 3.83, N 24.21; found: C 66.02; H 3.42, N 24.61.

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- [14] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 282473. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).