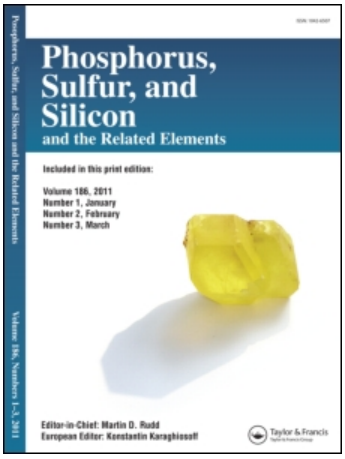

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Communication

THE REACTIVITY OF NAPHTHOPYRAN-2-ONE DERIVATIVES TOWARD NUCLEOPHILIC AND ELECTROPHILIC REAGENTS

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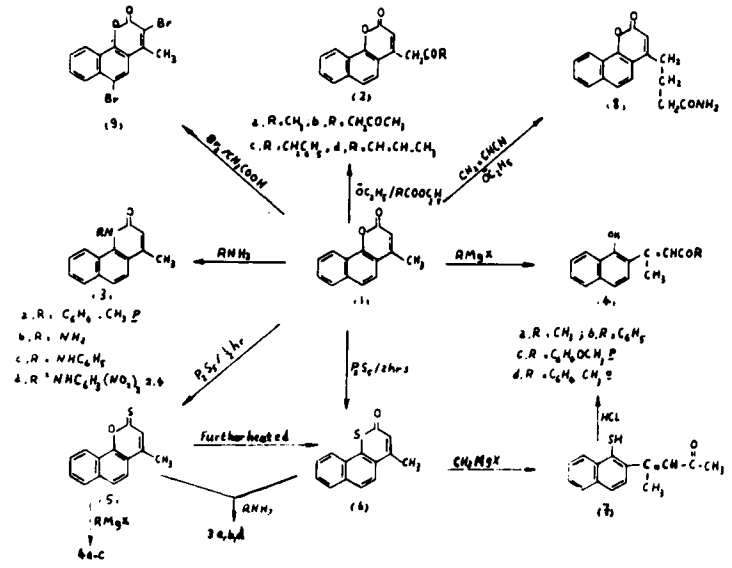
Claisen condensation of 4-methyl(2H)naphtho[1,2-*b*]pyran-2-one (**1**) with esters, gave 4-acetonyl (2H) naphtho[1,2-*b*]pyran-2-one derivatives (**2a–d**), while compound (**1**) condensed with hydrazines and primary amines and gave N-(substituted)-4-methyl benzo [*h*] quinoline-2 (1H) one derivatives (**3a–d**). Compound (**1**) reacted with Grignard reagents and gave alkyl (or aryl) 2-methylethyl 1-hydroxy-naphthyl ketones (**4a–d**), while (**1**) reacted with P_2S_5 and gave 4-methyl (2H) naphtho[1,2-*b*]pyran-2-thione (**5**) and 4-methyl(2H)naphtho[1,2-*b*]thiopyran-2-one (**6**). Compound (**5**) reacted with Grignard reagents and gave (**4a–c**) too. Compound (**6**) reacted with Grignard reagents and gave (**7**). Both compounds (**5** and **6**) reacted with primary amines and gave compound (**3**). The addition of (**1**) to acrylonitrile gave 2-Oxo(2H)naphtho[1,2-*b*]pryan-4-butyramide (**8**), while bromination of (**1**) gave 3,6-dibromo-4-methyl(2H)naphtho[1,2-*b*]pyran-2-one (**9**).

Recently,[1] the Claisen condensation of 6-acetyl (or 8-acetyl) 7-hydroxy-4-methyl coumarin with ethylacetate has been studied, which gave 6,7-(2-methyl-4-pyronyl) 4-acetonyl coumarin or 7,8-(2-methyl-4-pyronyl) 4-acetonylcoumarin. As a point of interest in the present work, the authors investigated the claisen condensation of 4-methyl-2H-naphtho[1,2-*b*]-pyran-2-one (**1**) with esters; namely, ethylacetate, ethylacetoacetate, ethylphenylacetate and/or ethyl crotonate by fusion in the presence of sodium ethoxide to give the corresponding 4-acetonyl-2*H*-naphtho[1,2-*b*]pyran-2-one derivatives (**2**a–d). The structure was supported by IR spectra which showed bands broadened at 1660–1720 cm^{-1} (νCO, δ-lactone and ketonic carbonyl). According to the effect of nitrogen nucleophiles on α-pyrone,[2–4] the condensation reaction of (**1**) with nitrogen nucleophiles such as hydrazines and primary amines; namely, *p*-toluidine, hydrazinehydrate, phenylhydrazine and 2,4 dinitrophenylhydrazine by fusion at 140–160° gave the N-substituted-4-methylbenzo[h]quinolin-2(1H)one (**3a–d**) respectively.

The structure of (**3a–d**) was supported as follows:

i-3a–d Resist cyclisation by Ac_2O and also insoluble in aqueous sodium hydroxide solution.

ii-IR spectra of (**3a,b**) showed bands at 1705–1690 (νCO,δ-lactam), while (**3a–d**) showed bands at 3540–3500 cm^{-1} (νNH).



Extending our studies[5–10] on the behaviour of α-pyrones toward Grignard reagents, compound (**1**) was reacted with Grignard reagents; namely, methylmagnesiumiodide, phenylmagnesiumbromide, *p*-anisylmagnesiumbromide and/or *O*-tolylmagnesiumbromide and gave alkyl (or aryl)-2-(methylethyl)-1-hydroxynaphthylketones (**4a–d**). The IR spectra of (**4a–d**) showed bands at 1705–1680 cm^{-1} (νCo, ketonic), 1605–1638 (νC=C, olefinic) and a broad band centred at 3400 cm^{-1} (νOH). The NMR spectra (**4b**) ($CDCl_3$) showed signals at δ2.45 (*s*, 3H, CH_3), δ5.4 (*s*, 1H, OH), δ6.4 (*s*, 1H, olefinic proton) and δ7.6 (*m*, 11H, aromatic protons).

By refluxing compound (**1**) with P_2S_5 in dry xylene for half an hour, 4-methyl (2H) naphtho[1,2-*b*]pyran-2-thione (**5**) was obtained. On the other hand, compound (**1**) and/or compound (**5**) yielded 4-methyl(2H)naphtho[1,2-*b*] thiopyran-2-one (**6**) by refluxing with P_2S_5 for 2 hrs. The IR spectrum of (**5**) showed a band of thione at 1640 cm^{-1} while that of compound (**6**) showed a band at 1705 cm^{-1} (νCO). The NMR spectrum of (**6**) in ($CDCl_3$) showed signals at δ2.45 (*s*, 3H, CH_3) and δ 7.2–7.8 (*m*, 7H, aromatic and olefinic protons). Moreover, the structures of compounds (5 and 6) were supported chemically. Thus, compound (**5**) was reacted with Grignard reagents and yielded alkyl (or aryl)-2-(methylethenyl-1-hydroxy)-naphthyl ketones (**4a–c**) which were identified by their m.p. and m.m.p. determinations. On the other hand, compound (**6**) was reacted with Grignard reagent and gave 4-(1-mercapto-2-naphthyl) pent-3-ene 2-one (**7**).

The IR spectrum of (**7**) showed bands at 1620 cm^{-1} (νC=C olefinic) and at 1670–1660 (νC—S). Moreover, by boiling (**7**) with HCl (10%) gave (**4a**) which was identified by its m.p. and m.m.p. determinations. The reaction of compounds (5 and 6) with *p*-toluidine and/or hydrazines; namely, hydrazine hydrate, and 2,4-dinitrophenylhydrazine gave the corresponding quinolin-2 (1H) ones (**3a,c**

and **d**) respectively. The latter compounds were identified by their m.p. and m.m.p. determinations.

By fusing compound (**1**) with acrylonitrile[7,9] at 150–170°; in the presence of sodium ethoxide, we have obtained 2-oxo(2H)naphtho[1,2-*b*]pyran-4-butyramide (**8**) which was identified by its IR spectrum. The spectrum showed bands at 3300, 1705–1720, and 1620 cm^{-1} attributable to νNH, (νCO, α, B-unsaturated lactone) and (νC=C, olefinic).

Finally, the bromination of compound (**1**) by bromine in acetic acid yielded the 3,6-dibromo-4-methyl(2H)naphtho [1,2-*b*]pyran-2-one (**9**). Compound (**9**) was characterized by its IR spectrum, which revealed the presence of νC=C, olefinic, at 1590–1615 cm^{-1} and showed a band at 1735 cm^{-1} (νCO, α, B-unsaturated δ-lactone).

TABLE I

Yield and physical data of prepared compounds

Compd	M.p. °C (colour)	Solvent† (yield%)	Formula (M.wt)	Analysis % Calc./Found C	H	N(S or Br)
2a	168 (pale brown)	A(70)	$C_{16}H_{12}O_3$ (252)	76.19 76.20	4.76 4.80	
2b	165 (grey)	A(65)	$C_{18}H_{14}O_4$ (294)	72.97 72.40	4.72 5.10	
2c	162 (brown)	A(60)	$C_{22}H_{16}O_3$ (328)	80.48 80.50	4.87 4.95	
2d	160 (pale brown)	A(65)	$C_{18}H_{14}O_3$ (273)	79.12 79.10	5.12 5.15	
3a	168 (brown)	A(55)	$C_{20}H_{17}ON$ (287)	83.62 84.00	5.92 5.70	4.88 4.90
3b	170 (pale yellow)	B(60)	$C_{14}H_{12}N_2O$ (224)	75.00 75.50	5.36 5.11	12.50 12.40
3c	140 (brown)	A(58)	$C_{20}H_{16}N_2O$ (300)	80.00 80.10	5.33 5.40	9.33 9.50
3d	180 (red)	B(75)	$C_{20}H_{15}N_4O_5$ (391)	61.38 61.50	3.84 3.60	14.32 14.10
4a	168 (brown)	L.P(60)	$C_{15}H_{14}O_2$ (226)	79.64 79.80	6.19 6.20	
4b	143 (brown)	B(50)	$C_{20}H_{16}O_2$ (288)	83.33 83.20	5.55 5.60	
4c	172 (orange)	L.P(55)	$C_{21}H_{18}O_3$ (318)	79.20 79.10	5.66 5.74	
4d	170 (brown)	B(65)	$C_{21}H_{18}O_2$ (302)	83.44 83.20	5.96 5.74	
5	202 (yellow)	B(75)	$C_{14}H_{10}OS$ (226)	74.30 74.20	4.42 4.25	14.15 14.20
6	150 (yellow)	B(70)	$C_{14}H_{10}OS$ (226)	74.30 74.15	4.42 4.21	14.15 14.30
7	170 (brown)	B(75)	$C_{15}H_{14}OS$ (242)	74.38 74.20	5.78 5.55	13.22 13.40
8	168 (yellow)	B(65)	$C_{17}H_{15}O_3N$ (281)	72.60 72.51	5.20 5.10	5.10 4.88
9	210 (yellow)	B(85)	$C_{14}H_8O_2Br_2$ (368)	45.70 45.52	2.30 2.10	43.50 43.35

† A = Acetic acid, B = Benzene, L.P = Light petroleum (60–80).

EXPERIMENTAL

All the melting points are uncorrected and the IR spectra were determined by a Unicam Sp 1200 spectrophotometer. The NMR spectra were determined by BM 360 A varian (60 MHZ). The yield and physical data are shown in Table I.

(*i*) *Claisen condensation of* (**1**) *with esters.* Formation of (**2a–d**). A mixture of (I) (0.01 mole), sodium ethoxide (0.02 mole) and esters; namely, ethylacetate, ethylacetoacetate, ethylphenylacetate and/or ethylcrotonate (3 ml) was heated at 170°C for 3 hours. The reaction mixture was cooled, washed with HCl (50 ml 10%). The solid that obtained was crystallized from the proper solvent to give 4-acetonyl(2H)naphtho [1,2-*b*]pyran-2-one derivatives (**2a–d**) respectively.

(*ii*) *Action of primary amines on* (**1**). Formation of N-substituted-4-methyl-benzo[h]quinolin-2 (1H)-one (**3a–d**). A mixture of (**1**) (0.01 mole) and amines; namely, *p*-toluidine, hydrazine hydrate, phenylhydrazine and/or 2,4-dinitrophenylhydrazine (0.01 mole) was heated on oil bath for 3 hrs at 140–160°C. The reaction mixture was cooled, washed with HCl (50 ml 10%). The solid that obtained was crystallized from proper solvent to give (**3a–d**) respectively.

(*iii*) *Reaction of* (**1**) *with* P_2S_5. Formation of 4-methyl-2*H*-naphtho[1,2-*b*]pyran-2-thione (**5**) and 4-methyl-2*H*-naphtho[1,2-*b*]thiopyran-2-one (**6**). A mixture of (**1**) (0.01 mole) and P_2S_5 (0.01 mole) in dry xylene (30 ml) was refluxed for half an hour. The reaction mixture was filtered off while hot, the xylene layer was concentrated, cooled. The solid product was filtered off and crystallized from the proper solvent to give (**5**). When (**1** or **5**) (0.01 mole) was refluxed in dry xylene (30 ml) for 2 hrs, the reaction mixture was filtered off while hot, the xylene layer was concentrated, cooled, the solid product that separated was crystallized from the proper solvent to give (**6**).

(*iv*) *Action of amines and hydrazines on* (**5**) *and/or* (**6**). Formation of (**3a,b** and **d**). A solution of (**5**) or (**6**) (0.01 mole), p-toluidine, hydrazine hydrate and/or 2,4 dinitrophenylhydrazine (0.01 mole) in ethanol (50 ml) was heated for 6 hrs. The product that separated after concentration and cooling was crystallized from a suitable solvent to give (**3a,b** and **d**) respectively.

(*v*) *Addition of* (**1**) *to acrylonitrile.* Formation of 2-Oxo 2H)naphtho[1,2-*b*]pyran-4-butyramide (**8**). A mixture of (**1**) (0.01 mole), acrylonitrile (3 ml) and sodium ethoxide (0.02 mole) was heated at 150–170°C for 3 hrs. The reaction mixture was cooled, washed with dil. HCl (50 ml, 2%). The solid that obtained was filtered off and crystallized from a suitable solvent to yield (**8**).

(*vi*) *Bromination of* (**1**). Formation of 3,6 dibromo-4-methyl(2H)naphtho[1,2-*b*]pyran-2-one (**9**). A solution of (**1**) (0.01 mole) and bromine (2 gm in 30 ml acetic acid) was refluxed for 4 hrs, cooled, and poured into 50 ml water. The product that obtained was crystallized from a suitable solvent to give (**9**).

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