Reactivity of some structural analogs of dehydroacetic acid with *o*-phenylenediamine

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Abstract

4-Hydroxy-6-methyl-3-(3-arylpropanoyl)-2*H*-pyran-2-ones **14a-c** and 4-hydroxy-6-methyl-3-(5-phenylpentanoyl)-2*H*-pyran-2-one **15**, which are structural analogs of dehydroacetic acid (DHA) **1**, react with *o*-phenylenediamine **2** according to the solvents and reaction conditions. New heterocyclic compounds have been obtained and characterized.

Keywords: DHA analogs, pyrone, triacetic acid lactone, *o*-phenylenediamine, benzimidazole, MW irradiation

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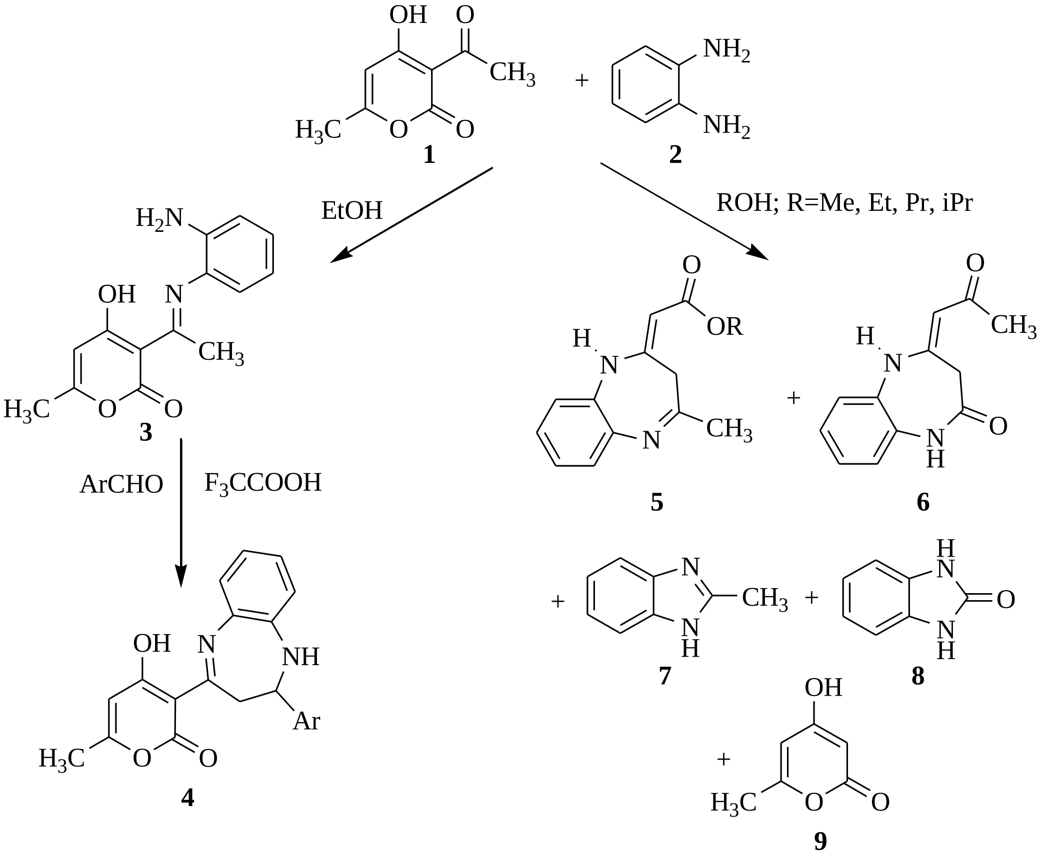
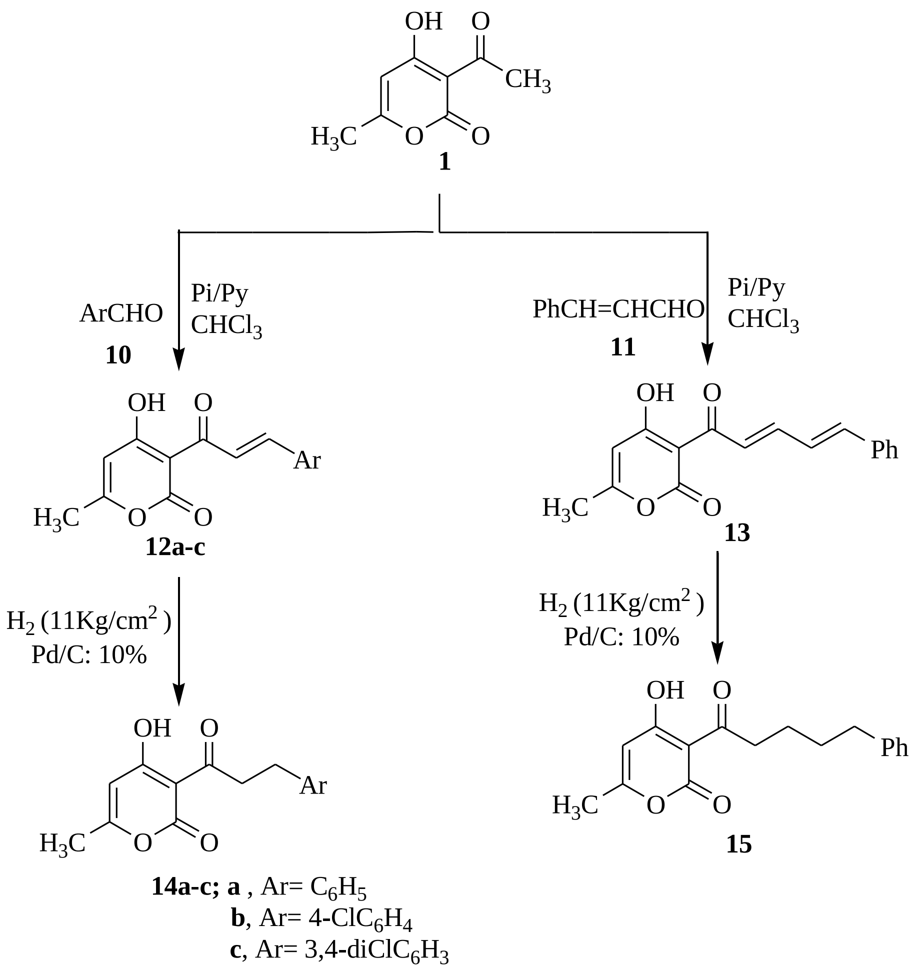
Introduction

3-Acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one (dehydroacetic acid: DHA) **1** displays a rich and varied chemistry. It can be readily converted into the other heterocyclic systems, e.g., pyrazoles,[1,2] benzothiazepines,[3] benzodiazepines,[4-6] and pyrimidines,[7] through its condensation with a variety of bis-nucleophiles. The literature[4,5] indicates that refluxing DHA **1** with *o*-phenylenediamine (*o*-PDA) **2** in ethanol gives the drivative 3-[(1*E*)-*N*-(2-aminophenyl) ethanimidoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one **3**, which can used as first stage in the formation of 3,4-dihydro-1,5-benzodiazipines **4** by the addition of aromatic aldehydes in the presence of trifluoroacetic acid as catalyst.[4] However, El Abassi and coworkers[6] indicated that the reaction of DHA **1** with *o*-PDA **2** in different alcohols leads to 2-alkoxycarbonylmethyl 4-methyl-1,5-benzodiazepines **5**, 4-acetyl methylene 1,5-benzodiazepin-2-one **6**, benzimidazole **7** and benzimidazolone **8** and 4-hydroxy-6-methyl-2-pyrone (triacetic acid lactone: TAL) **9** which is not isolated (Scheme 1). The TAL **9** is a natural product of polyketide origin[8] but it can also be obtained by deacetylation of DHA **1** in sulfuric acid.[9]



Scheme 1

In this work, we were interested in exploring some chemistry of the structural analogs 4-hydroxy-6-methyl-3-(3-arylpropanoyl)-2*H*-pyran-2-ones **14a-c** and 4-hydroxy-6-methyl-3-(5-phenylpentanoyl)-2*H*-pyran-2-one **15** of DHA **1** with *o*-PDA **2** (Scheme 2). It appeared to us that this study is interesting because it lets suppose the formation of the analogs of the compound **3**, which can give access to the formation of the 2-alkylbenzimidazole with the separation of TAL **9** or to the formation of the benzodiazepines by an intramolecular attack of the free -NH_2 group at position 2 or position 4 of the pyrone ring.



Scheme 2

Results and Discussion

4-Hydroxy-6-methyl-3-(3-arylpropanoyl)-2*H*-pyran-2-ones **14a-c** and 4-hydroxy-6-methyl-3-(5-phenylpentanoyl)-2*H*-pyran-2-one **15** were obtained via a selective hydrogenation reaction of 4-hydroxy-6-methyl-3-[(2*E*)-3-arylprop-2-enoyl]-2*H*-pyran-2-ones **12a-c** and 4-hydroxy-6-methyl-3-[(2*E*,4*E*)-5-phenylpenta-2,4-dienoyl]-2*H*-pyran-2-one **13**. This method uses palladium on carbon (Pd/C: 10%) as catalyst under a pressure of 11Kg/cm^2 of hydrogen in ethyl acetate [10] (Scheme 2).

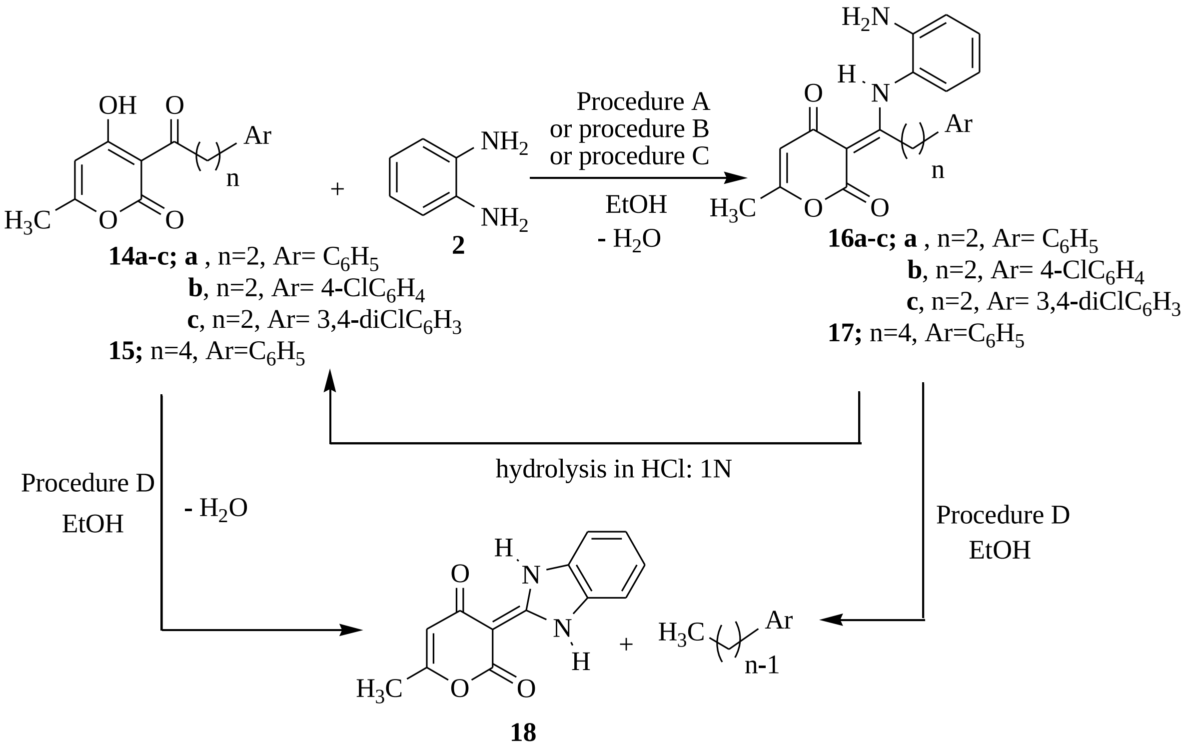
The compounds **12a-c** and **13** were obtaineded by Knœvenagel condensation of DHA **1** with the corresponding aldehydes **10a-c** and **11,** using pyridine and piperidine as catalysts under thermal refluxing or under microwave MW irradiation in chloroform as solvent.[2,10,11] As far as we are aware, the spectroscopic analysis of compounds **14c** and **15** have not been reported in the literature. We give in this work their detailed spectroscopic data.

The electron impact mass spectra (EI MS) showed the addition of one molecule of hydrogen to the compound **12c** and two molecules of hydrogen to the compound **13**. The ^{1}H NMR spectra showed the existence of two methylenes –CH$_2$- in the structure of **14c** and four methylenes –CH$_2$- in the structure of **15**. The ^{1}H NMR spectra of the compounds **14c** and **15** also presented the signals at 16.56 ppm and at 16.10 ppm, respectively. These signals assigned to proton H-O at the site 4 of the pyrone ring. The position of H-O in the structures of **12c** and **13** has been confirmed by HMBC spectrum which showed their connectivities with C-3, C-4 and C-5 of the pyrone ring (Figure 1).

The study of the reactivity of the compounds **13a-c** and **14** with *o*-PDA **2** was achieved in ethanol and in toluene as solvents under several reaction conditions.

We reacted compounds **14a-c** and **15** with *o*-PDA **2** in ethanol at room temperature for 6 hours (procedure A), under thermal refluxing for 30 minutes (procedure B) and under MW irradiation at 100 °C during 1 minutes (procedure C) and 4 minutes (procedure D).

For the first three procedures (A, B and C), the same products **16a-c** and **17** were separated for the four chosen cases. The best yields were obtained at room temperature (procedure A) (Scheme 3).



Scheme 3. Procedure A: at rt for 6 h; Procedure B: thermal refluxing for 1 h; Procedure C: MW irradiation at 100 W for 1 min; Procedure D: MW irradiation at 100 W for 4 min.

For the procedure using MW irradiation for 4 minutes (procedure D) the behaviour of **14a-c** and **15** with *o*- PDA **2** was very different. The four compounds give the same product **18** (Scheme 3) with departure of one molecule of water and a molecule of alkylbenzene. We notes that the temperature of the mixture at the end of the reaction for the procedure C was 77 - 78 °C, whereas the temperature of the mixture at the end of the reaction for the procedure D was 89-92 °C.

We have prolonged the agitation at room temperature for one week and the refluxing thermal for 24 hours, but we did not succeed in obtaining the compound **18**; it was always the derivatives **16a-c** and **17** which were formed.

Compound **18** was also obtained from **16a-c** and **17** in ethanol, under MW irradiation at 100 W for 4 min.

The EI MS of **16a-c** and **17** confirmed the condensation of only one molecule of *o*-PDA with loss of one molecule of water during the reaction. The ^{1}H NMR spectra showed a signal at 3.70-3.82 ppm attributed to two equivalent protons where HSQC experiment confirmed that these two protons are carried by an heteroatom, which can be only a nitrogen atom. ^{1}H NMR spectra showed the signals at 5.72 ppm and at 2.22 ppm, assigned to the protons H-C5 of the pyrone ring and H-C7 of the methyl, respectively. The ^{1}H NMR spectra also showed a signal at 15.30 ppm. Originally, we considered a structure analogous to the compound **3**, but the HMBC experiment showed some connectivities between this signal at 15.30 ppm and the three signals of the carbons C-3, C-3' and the C-4', which confirmed that this proton is not carried by the oxygen atom at the site 4, but it is carried by the nitrogen atom at the site 3' (Figure 1), where the derivatives **15a-c** and **16** were obtained.

The hydrolysis reaction of **15a-c** and **16** in HCl: 1N under thermal refluxing for 1 hour or under MW irradiation at 100 W for 3 minutes permitted the recuperation of **13a-c** and **14** with *o*-PDA **2** (Scheme 3).

The EI MS of the compound **18** showed the condensation of only one molecule of o- PDA **2** with loss of one molecule of water and a molecule of alkylbenzene by the observation of the molecular peak at 242(80%), where the molecular formula $C_{13}H_{10}N_2O_3$ was confirmed.

The ^{1}H NMR spectra confirmed the structure of the compound **18** by the observation of two signals at 2.15 ppm and at 5.83 ppm assigned to the protons H-C7 of the methyl and H- C5 of the pyrone ring, respectively. The ^{1}H NMR spectra showed also two doublets of doublets in the domain of the aromatic protons at 7.32 ppm and at 7.75 ppm, each one of them assigned to two protons of the aromatic ring in symmetry, which is in perfect accord with the ^{13}C NMR spectra data, where the presence of two intense signals, each one of them represented two carbons (C5’, C8’) and (C6’, C7’) of the aromatic ring in symmetry. These data were confirmed by HSQC experiment. The ^{1}H NMR spectra showed a signal centered on 13.15 ppm represented the sum of two protons, which is assigned to the two protons H-N in symmetry. The position of these protons was confirmed by an HMBC experiment (Figure 1).

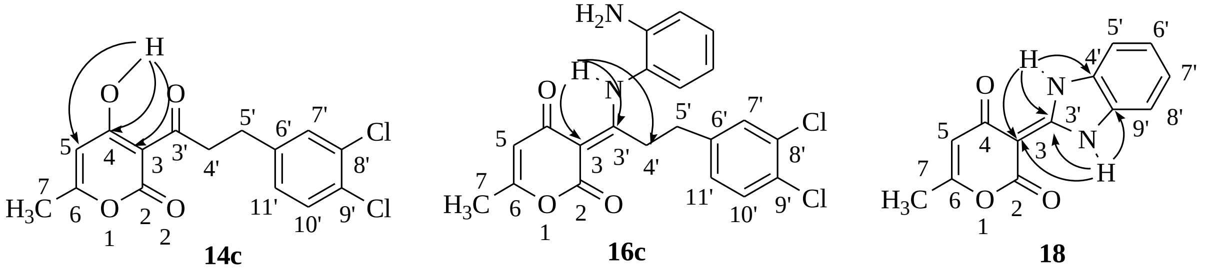
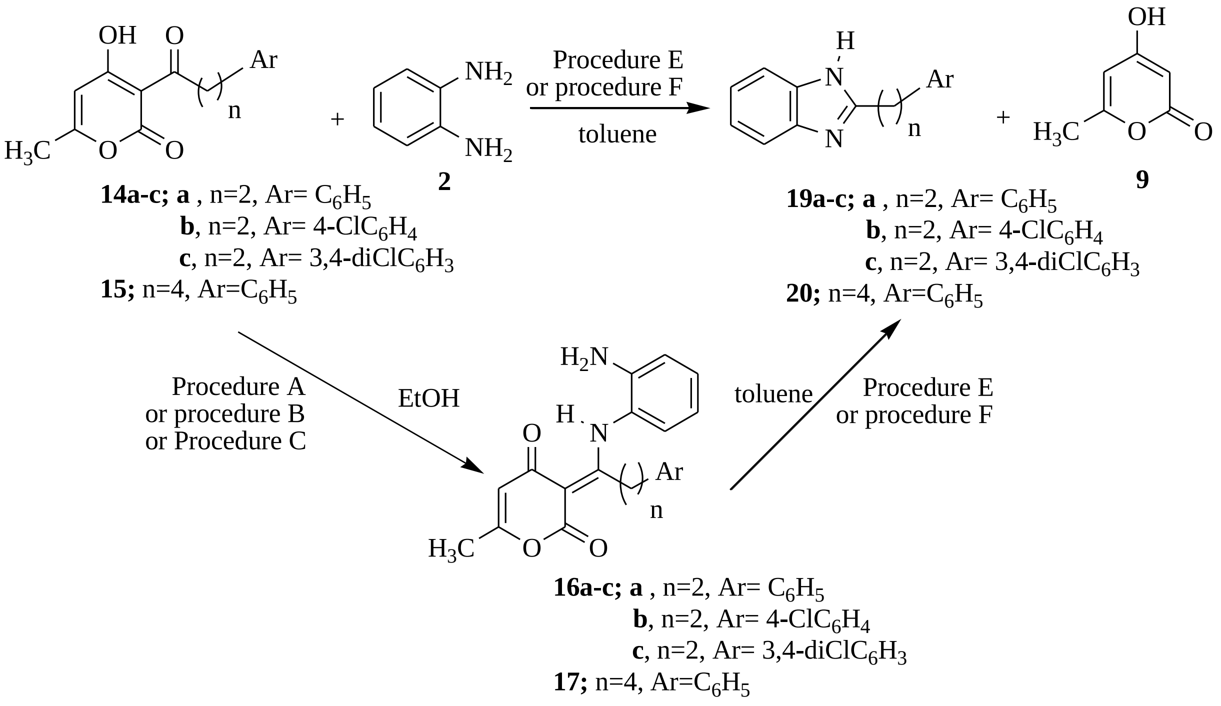


Figure 1. Important connectivities found in the HMBC spectra of compounds **14c**, **16c** and **18**.

In toluene, under thermal refluxing for 3 hours or under MW irradiation at 200 W for 4 minutes, we could separate two products from every compound **13a-c** and **14** with *o*-PDA **2**. The first product is the same for the four reactions. It was separated by filtration at ebullition (111 °C). Its spectroscopic data revealed that it was the TAL **9**.

After the cooling of every filtrate and filtration, the second products **19a-c** or **20** were separated (Scheme 4).



14a-c; a , n=2, Ar= C_6H_5
b, n=2, Ar= 4-ClC_6H_4
c, n=2, Ar= 3,4-diClC_6H_3
15; n=4, Ar=C_6H_5

19a-c; a , n=2, Ar= C_6H_5
b, n=2, Ar= 4-ClC_6H_4
c, n=2, Ar= 3,4-diClC_6H_3
20; n=4, Ar=C_6H_5

16a-c; a , n=2, Ar= C_6H_5
b, n=2, Ar= 4-ClC_6H_4
c, n=2, Ar= 3,4-diClC_6H_3
17; n=4, Ar=C_6H_5

Scheme 4. Procedure A: at rt for 6 h; Procedure B: thermal refluxing for 1 h; Procedure C: MW irradiation at 100 W for 1 min; Procedure D: MW irradiation at 100 W for 4 min; Procedure E: thermal refluxing for 3 h; Procedure F: MW irradiation at 200 W for 4 min.

The formation of the derivatives 2-alkylbenzimidazoles **18a-c** and **19** was confirmed initially by EI MS where the fixing of only one molecule of o-PDA **2** with the departure of TAL **9** molecule. These compounds were also confirmed by ^{1}H and ^{13}C NMR spectra. The derivatives **18a-c** and **19** with TAL **9** were also obtained from **16a-c** and **17** under the same reaction conditions **(** Procedures E or F).

Table 1. Procedures and physical data of the products **16a-c**, **17**, **18**, **19a-c**, **20** and **9**

Product	Procedure	Yield (%)	Mp (°C)
16a	A	72	220
	B	65	
	C	70	
16b	A	86	164
	B	81	
	C	82	
16c	A	93	179
	B	82	
	C	89	
17	A	96	165
	B	90	
	C	92	
18	D	87 (from **14a**) 81 (from **14b**) 90 (from**14c**) 93 (from**15**)	45
19a	E	75	132
	F	84	
19b	E	78	165
	F	86	
19c	E	79	160
	F	84	
20	E	71	130
	F	92	
9	E	72 (from**14a**)	187
	F	78 (from**14a**)	
	E	70 (from**14b**)	
	F	81 (from**14b**)	
	E	75 (from**14c**)	
	F	80 (from**14c**)	

Table 1. Continued

Product	Procedure	Yield (%)	Mp (°C)
	E	79 (from**15**)	
	F	87 (from**15**)	

Procedure A: reaction mixture steered at rt for 6h, solvent: ethanol.
Procedure B: reaction mixture submitted to the thermal reflux for 1h, solvent: ethanol.
Procedure C: reaction mixture submitted to the MW irradiation for 1min, solvent: ethanol.
Procedure D: reaction mixture submitted to the MW irradiation at 100 W for 4min, solvent: ethanol.
Procedure E: reaction mixture submitted to the thermal reflux for 3h, solvent: toluene.
Procedure F: reaction mixture submitted to the MW irradiation at 200 W for 4min, solvent: toluene.

Conclusions

The study of the reactivity of the compounds **14a-c** and **15**, analogs of the DHA **1**, with *o*-PDA **2** permitted the synthesis some new heterocyclic compounds. The compounds **14a-c** and **15** with *o*-PDA **2** react according to the reaction conditions. In ethanol, under thermal refluxing, under agitation at room temperature or under MW irradiation at 100 W for 1 minute we obtained **16a-c** and **17**. However, under MW irradiation at 100 W for 4 minutes, we obtained the product **18**. In toluene, under thermal refluxing or under MW irradiation at 200 W, we have achieved an important reaction of deacylation, where we have separated the TAL **9** and 2-arylalkylbenzimidazoles compounds **19a-c** and **20** with good yields.

Experimental Section

General. The catalytic reductions of **12a-c** and **13** were carried out in a quick closure autoclave (Prolabo). The reactions were carried out in a microwave oven dedicated to organic synthesis (Milestone, Lab Terminal 800 controller) at P=1 bar.

Melting points were determined on a Stuart scientific SPM3 apparatus fitted with a microscope and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 spectrometer, operating at 300.13 and 75.47 MHz, respectively; the chemical shifts are expressed in δ (ppm) and coupling constants (J) in (Hz). ^{1}H and ^{13}C NMR assignments were made using HSQC and HMBC experiments. Electron impact mass spectra (EI MS) were obtained at 70 eV electron impact ionisation using Nermag R 10-10C Quadruple mass spectrometer. Infrared spectra were recorded on Magna-IR 550 series II Nicolet apparatus, using potassium bromide pellets. UV spectra were recorded on Cary 50 Scan UV-Visible spectrometer in acetonitrile and elemental analyses CHN performed with a Perkin-Elmer 2400 series II CHNO/S at the Scientific

and Technical Research Center in Physical and Chemical Analyses (C.R.A.P.C), Algiers, Algeria.
The compounds **12a-c** and **13** were prepared by following the literature.[11] The compounds **14a-b** were obtained according to the method described in literature,[10] which is the same synthesis method used for **14c** and **15**. The yields of all compounds are reported in Table 1.

General method for preparation 3-[3-(3,4-dichlorophenyl)propanoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (14c) and 4-hydroxy-6-methyl-3-(5-phenylpentanoyl)-2-*H*-pyran-2-one (15)

A mixture of **12c** (6.52, 20 mmol) or **13** (5.64, 20 mmol) with 10% of its weight of Pd/C:10% in ethyl acetate (50 ml) was introduced in autoclave under pressure 11Kg/cm^2 of hydrogen H_2 for 24 h at rt. After filtration and evaporation of solvent, the resultant was crystallized from ethanol.
3-[3-(3,4-Dichlorophenyl)propanoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-one (14c). Yield (6.10 g, 93%) as Pale yellow powder; mp 118 °C; ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3H,7-CH3), 3.01(t, *J* 6.12 Hz, 2H, H-C4'), 3.32(t, *J* 6.12 Hz, 2H, H-C5'), 5.91 (s, 1H, H-5), 7.12-7.20 (m, 3H, Ar), 16.18 (s, 1H, OH); ^{13}C NMR ($CDCl_3$) δ 20.69(C-7), 29.30 (C-5'), 43.13 (C-4'), 99.49 (C-3), 101.50 (C-5), 132.18(C-8'), 129.74(C-10'), 132.43(C-9'), 130,67(C-7'), 135.40(C-11'), 140.54 (C-6'), 160.98 (C-2), 168.85 (C-6), 181.19 (C-4), 207.70 (C-3'); EI MS *m/z* % 326 (27 , $M^{+.}$); IR (ν, cm^{-1}) 3450, 1735, 1720, 1632, 1618 ; UV (λ_{max} (ε 10^{-1}) nm) 228 (860), 260 (700); Anal. Calcd. for $C_{15}H_{12}Cl_2O_4$: C, 55.07; H, 3.70. Found: C, 55.10; H, 3.62.
4-Hydroxy-6-methyl-3-(5-phenylpentanoyl)-2*H*-pyran-2-one (15). Yield (5.50 g, 96%) as Pale yellow microcrystals; mp 96 °C; ^{1}H NMR ($CDCl_3$) δ 1.73(m, *J* 6.20 Hz, *J* 7.34 Hz, *J* 7.47 Hz, 4H, H-C5',H-C6'), 2.27 (s, 3H,7-CH3), 3.11(t, *J* 6.20 Hz, 2H, H-C4'), 3.12(t, *J* 7.34 Hz, 2H, H-C7'), 5.94 (s, 1H, H-5), 7.19-7.31(m, 5H, Ar), 16.10 (s, 1H, OH); ^{13}C NMR ($CDCl_3$) δ 20.64(C-7), 23.60 (C-5'), 30.88 (C-6'), 35.75 (C-7'), 41.43 (C-4'), 99.50 (C-3), 101.52 (C-5), 125.70 (C-11'), 128.28 (C-10', C-12'), 128,41 (C-9', C-13'), 142.26 (C-8'), 160.96 (C-2), 168.87 (C-6), 181.25 (C-4), 207.68 (C-3'); EI MS *m/z* % 286 (10 , $M^{+.}$); IR (ν, cm^{-1}) 3482, 1736, 1722, 1638, 1616 ; UV (λ_{max} (ε 10^{-1}) nm) 230 (940),280 (760); Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.28; H, 6.39.

General method for preparation (3*E*)-3-{1-[(2-aminophenyl)amino]-3-arylpropylidene}-6-methyl-2*H*-pyran-2,4(3*H*)-diones (16a-c) and (3*E*)-3-{1-[(2-aminophenyl)amino]-5-phenylpentylidene}-6-methyl-2*H*-pyran-2,4(3*H*)-dione (17)

A solution of **14a-c** or **15** (1 mmol) with o-PDA (0.108 g, 1 mmol) in ethanol (10 ml) was steered at rt for 6 h or refluxed under thermal heating for 30 min or under MW irradiation at 100 W for 1 min . After cooling and filtration, the resultants were crystallized from ethanol to afforded the corresponding compounds **16a-c** or **17**.
(3*E*)-3-{1-[(2-Aminophenyl)amino]-3-phenylpropylidene}-6-methyl-2*H*-pyran-2,4(3*H*)-dione (16a). Beige powder; M.p. 220 °C; ^{1}H NMR(CDCl3) δ 2.22(s, 3H,7-CH3), 3.21(t, *J* 6.98 Hz, 2H, H-C4'), 2.85(t, *J* 6.98 Hz, 2H, H-C5'),3.70(s, 2H, NH_2), 5.79 (s, 1H, H-C5), 6.78-7.26(m, 9H, Ar, Ar'-N), 15.29 (s, 1H, NH); ^{13}C NMR(CDCl3) δ 19.93(C-7), 33.62(C-4'), 33.86

(C-5’), 96.69 (C-3), 107.21 (C-5), 116.32 (C-5″), 118.55 (C-8″), 121.80 (C-4"), 126.26 (C-11"), 127.31(C-6"), 128.42 (C-9’, C-13’), 128.50 (C-10’, C-12’), 129.68(C-7"),140.39(C-9"), 162.67(C-6), 163.64(C-4), 180.60 (C-3’), 185.79 (C-2) ; EI MS *m/z* (%) 348(59, M$^{+\cdot}$) ; IR (ν, cm^{-1}) 3022, 1684(C=O), 1600, 1332; UV (λ_{max} (ε 10^{-1}) nm) 228 (818), 315(620). Anal. Calcd. for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 72.32; H, 5.83; N, 8.11.

(3*E*)-3-{1-[(2-Aminophenyl)amino]-3-(4-chlorophenyl)propylidene}-6-methyl-2*H*-pyran-2,4(3*H*)-dione (16b). Beige powder; M.p. 164 °C; ^{1}H NMR(CDCl3) δ 2.19 (s, 3H,7-CH3), 3.15(t, *J* 6.97 Hz, 2H, H-C4’), 2.81(t, *J* 6.97 Hz, 2H, H-C5’),3.75(s, 2H, NH$_2$), 5.79 (s, 1H, H-C5), 6.78-7.26(m, 8H, Ar, Ar’-N), 15.28 (s, 1H, NH); ^{13}C NMR(CDCl3) δ 19.93(C-7), 32.90(C-4’), 33.78 (C-5’), 96.67 (C-3), 107.21 (C-5), 116.36 (C-5″), 118.55 (C-8″), 121.67 (C-4"), 132.03 (C-11"), 127.22(C-6"), 129.78 (C-9’, C-13’), 128.50 (C-10’, C-12’), 129.82(C-7"),138.84(C-9"), 162.69(C-6), 163.71(C-4), 180.20 (C-3’), 185.77 (C-2) ; EI MS *m/z* (%) 382(40, M$^{+\cdot}$); IR (ν, cm^{-1}) 3051, 1685(C=O), 1600, 1333; UV (λ_{max} (ε 10^{-1}) nm) 228 (896), 316(698). Anal. Calcd. for $C_{21}H_{19}ClN_2O_3$: C, 65.88; H, 5.00;N, 7.32. Found: C, 65.83; H, 5.09;N, 7.29.

(3*E*)-3-{1-[(2-Aminophenyl)amino]-3-(3,4-dichlorophenyl)propylidene}-6-methyl-2*H*-pyran-2,4(3*H*)-dione (16c). Beige powder; m.p. 179 °C; ^{1}H NMR(CDCl$_3$) δ 2.19 (s, 3H,7-CH3), 3.15(t, *J* 6.98 Hz, 2H, H-C4’), 2.78(t, *J* 6.98 Hz, 2H, H-C5’),3.84(s, 2H, NH$_2$), 5.78 (s, 1H, H-C5), 6.78-7.26(m, 7H, Ar, Ar’-N), 15.28 (s, 1H, NH); ^{13}C NMR(CDCl3) δ 19.91(C-7), 32.54(C-4’), 33.49 (C-5’), 96.62 (C-3), 107.18 (C-5), 116.44 (C-5″), 118.54 (C-8″), 121.48 (C-4"), 132.18 (C-11"), 127.12(C-6"), 130.36(C-9’), 130.26(C-13’), 130.23(C-10’), 127.91(C-12’), 129.89(C-7"),140.57(C-9"), 162.69(C-6), 163.76(C-4), 179.82 (C-3’), 185.71(C-2) ; EI MS *m/z* (%) 416(40, M$^{+\cdot}$); IR (ν, cm^{-1}) 3053, 1684(C=O), 1601, 1332; UV (λ_{max} (ε 10^{-1}) nm) 229 (983), 317(709). Anal. Calcd. for $C_{21}H_{18}Cl_2N_2O_3$: C, 60.44; H, 4.35; N, 6.71. Found: C, 60.49; H, 4.31; N, 6.73.

(3*E*)-3-{1-[(2-Aminophenyl)amino]-3-phenylpentylidene}-6-methyl-2*H*-pyran-2,4(3*H*)-dione (17). Pale-brown powder; mp.165 °C; ^{1}H NMR(CDCl$_3$) δ 2.18(s, 3H,7-CH3), 3.14(t, *J* 6.98 Hz, 2H, H-C4’), 2.60(t, *J* 6.74 Hz, 2H, H-C7’), 1.44-1.48(m, *J* 6.98 Hz, *J* 6.74 Hz, *J* 6.23 Hz, 4H, H-C5’, H-C6’),3.73(s, 2H, NH$_2$), 5.78 (s, 1H, H-C5), 6.70-7.26(m, 9H, Ar, Ar’-N), 15.27 (s, 1H, NH); ^{13}C NMR(CDCl3) δ 19.91(C-7), 33.92(C-4’), 29.52(C-5’),28.45(C-6’),35.41(C-7’),96.65 (C-3), 107.18 (C-5), 116.24 (C-5″), 118.49 (C-8″), 121.72 (C-4"), 127.27(C-6"), 127.73 (C-11"), 129.39 (C-9’, C-13’), 129.61 (C-10’, C-12’), 129.67(C-7"),140.10(C-9"), 163.58(C-6), 163.78(C-4), 178.35 (C-3’), 185.60 (C-2) ; EI MS *m/z* (%) 376(25, M$^{+\cdot}$); IR (ν, cm^{-1}) 3051, 1682(C=O), 1596, 1334; UV (λ_{max} (ε 10^{-1}) nm) 228 (1060), 319(764). Anal. Calcd. for $C_{23}H_{24}N_2O_3$: C, 73.38; H, 6.43;N, 7.44. Found: C, 73.42; H, 6.38;N, 7.50.

Method for preparation 3-(1,3-dihydro-2*H*-benzimidazol-2-ylidene)-6-methyl-2*H*-pyran-2,4(3*H*)-dione (18). A solution of **14a-c** or **15** (1mmol) with o-PDA (0.108 g, 10 mmol) in ethanol (10 ml) was refluxed under MW irradiation at 100 W for 4 min. After cooling and filtration, the resultant was crystallized from ethanol to give the compound **18** as light-brown powder; mp. 45 °C; ^{1}H NMR(DMSO) δ 2.15(s, 3H,7-CH3), 5.83 (s, 1H, H-C5), 7.32(d.d, *J* 8.59

Hz, *J* 1.32 Hz, *J* 7.10 Hz, 2H, H-C6’, H-C9’), 7.75(d.d, *J* 7.10 Hz, *J* 1.32 Hz, *J* 8.59 Hz, 2H, H-C7’, H-C8’), 13.15 (s, 2H, H-N4’, H-N11’); ^{13}C NMR(DMSO) δ 19.33(C-7), 84.91(C-3), 107.63 (C-5), 113.11(C-5’, C-8’), 123.77 (C-6’, C-7’), 129.76(C-4’, C-9’), 149.15(C-3’), 161.35(C-6), 163.56(C-2), 179.42 (C-4) ; EI MS *m/z* (%) 242(18, M$^{+\cdot}$); IR (ν, cm^{-1}) 1698(C=O), 1602, 1422; UV (λ_{max} (ε 10^{-1}) nm) 238 (1256), 330(7854). Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16;N, 11.56. Found: C, 64.52; H, 4.1;N, 11.60.

General method for preparation 2-(2-arylethyl)-1*H*-benzimidazoles 19a-c and 2-(4-phenylbutyl)-1*H*-benzimidazole (20)

A solution of **14a-c** (1 mmol) or **15** (1 mmol) with o-PDA (0.108 g, 1 mmol) in toluene (10 ml) was refluxed under thermal heating or under MW irradiation at 200 W for 4 min. After filtration at ebullition, TAL **9** was isolated and crystallized. After the cooling of the filtrate and filtration, the resultants were i crystallized from ethanol to yield the corresponding compounds **19a-c** or **20**.

2-[2-(4-Dichlorophenyl)ethyl]-1*H*-benzimidazole (19a). Brown powder; mp. 220 °C; ^{1}H NMR(DMSO) δ 2.90 (t, *J* 7.41 Hz, 2H, H-C5’), 3.10(t, *J* 7.41 Hz, 2H, H-C4’), 7.02-7.43(m, 9H, Ar, Ar'), 9.85 (1H, H-N3); ^{13}C NMR (DMSO): 32.10(C-4’), 33.14 (C-5’),113.60(C-6), 113.98(C-9), 122. 39(C-7), 124.40(C-8), 127.51(C-9’), 128.34(C-8’, C-10’), 128.04(C-7’,C-11’), 140.07(C-5), 140.31 (C-4), 140.96(C-6’), 160.11(C-2); EI MS *m/z* (%) 222(55, M$^{+\cdot}$); IR (ν, cm^{-1}) 3180, 3087, 1622, 1554, 1440; UV (λ_{max} (ε 10^{-1}) nm) 228 (1015), 315(964); Anal. Calcd. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35. Found: C, 81.10; H, 6.32.

2-[2-(4-Dichlorophenyl)ethyl]-1*H*-benzimidazole (19b). Brown powder; mp. 165 °C; ^{1}H NMR(DMSO) δ 2.87(t, *J* 7.52 Hz, 2H, H-C5’), 3.05(t, *J* 7.52 Hz, 2H, H-C4’), 7.08-7.44(m, 8H, Ar, Ar'), 9.86 (1H, H-N3); ^{13}C NMR (DMSO) 32.04(C-4’), 33.27 (C-5’),113.58(C-6), 113.94(C-9), 122. 42(C-7), 124.38(C-8), 126.51(C-9’), 128.90(C-8’, C-10’), 129.33(C-7’,C-11’), 140.10(C-5), 140.29 (C-4), 140.97(C-6’), 160.10(C-2); EI MS *m/z* (%) 256(50, M$^{+\cdot}$); IR (ν, cm^{-1}) 3178, 3050, 1624, 1556, 1446; UV (λ_{max} (ε 10^{-1}) nm) 228 (1015), 315(964). Anal. Calcd. for $C_{15}H_{13}ClN_2$: C, 70.18; H, 5.10. Found: C, 70.24; H, 5.07.

2-[2-(3,4-Dichlorophenyl)ethyl]-1*H*-benzimidazole (19c). Brown powder; mp. 160 °C; ^{1}H NMR(DMSO) δ 2.89 (t, *J* 7.47 Hz, 2H, H-C5’), 3.07(t, *J* 7.47 Hz, 2H, H-C4’), 7.12-7.43(m, 7H, Ar, Ar'), 9.83 (1H, H-N3); ^{13}C NMR (DMSO):, 32.06(C-4’), 33.51 (C-5’),113.57(C-6), 113.92(C-9), 122. 44(C-7), 124.29(C-8), 126.57(C-9’), 133.89(C-8’), 131.22(C-10’), 129.91(C-7’),129.45(C-11’), 140.12(C-5), 140.27 (C-4), 140.25(C-6’), 160.08(C-2); EI MS *m/z* (%) 290(30, M$^{+\cdot}$); IR (ν, cm^{-1}) 3174, 3056, 1620, 1556, 1447; UV (λ_{max} (ε 10^{-1}) nm) 226 (1025), 311(812). Anal. Calcd. for $C_{15}H_{12}Cl_2N_2$: C, 61.87; H, 4.15. Found: C, 61.84; H, 4.20.

2-(4-Phenylbutyl)-1*H*-benzimidazole (20). Brown powder; mp. 130 °C; ^{1}H NMR(DMSO) δ 1.42-1.50(m, *J* 6.98 Hz, *J* 7.19 Hz, *J* 7.27 Hz, 4H, H-C5’, H-C6’), 2.80(t, *J* 7.27 Hz, 2H, H-C7’), 3.02(t, *J* 6.98 Hz, 2H, H-C4’) 7.10-7.49(m, 9H, H-Ar, Ar'), 9.87 (1H, H-N3); ^{13}C NMR(DMSO) δ 24.51(C-6’), 25.47 (C-5’), 30.41(C-4’), 35.63(C-7’), 113.21(C-6), 113.96(C-9), 122.57(C-7), 124.40(C-8), 126.42(C-11’), 129.30(C-10’, C-12’), 129.73(C-9’,C-13’), 140.12(C-5), 140.14 (C-4), 141.24(C-8’), 160.02(C-2); EI MS *m/z* (%) 250(45, M$^{+\cdot}$); IR (ν, cm^{-1})3180, 3097, 3048, 1628, 1552, 1441; UV (λ_{max} (ε 10^{-1}) nm) 225 (1148), 311(945). Anal. Calcd. for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25. Found: C, 81.61; H, 7.18.

4-Hydroxy-6-methyl-2-pyrone (triacetic acid lactone: TAL 9). White compound; mp. 187 °C; ^{1}H NMR(DMSO) δ 2.19 (s, 3H, H-C7), 5.24(d, *J* 2.23 Hz, 1H, H-C3) 5.98(m, *J* 2.23 Hz, *J* 1.13 Hz, 1H, H-C5), 11.5 (s, 1H, H-O); ^{13}C NMR(DMSO) δ 19.37(C-7), 88.15 (C-5), 100.12(C-3), 163.18(C-4), 163.87(C-6), 170.47(C-2), EI MS *m/z* (%) 126(81, $M^{+\cdot}$); IR (ν, cm^{-1})3100, 2967, 1763, 1726, 1590, 1512, 1368, 1347; UV (λ_{max} (ε 10^{-1}) nm) 286 (785). Anal. Calcd. for $C_6H_6O_3$: C, 57.14; H, 4.80. Found: C, 57.21; H, 4.76.

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