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Behavior of Some 2(3*H*)-Furanones Bearing A Chromone Moiety as Alkylating Agents

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4-OXO-4*H*-chromen-3-carboxaldehyde (2) condensed with 3-aroylpropionic acids(1a-c) in the presence of thionyl chloride/ *N*,*N*- dimethylformamide mixture as a cyclodehydrating agent to yield5-aryl-3-chromonyllmethylene-2(3*H*)-furanones3a-c as mixtures of (*E*) and (*Z*) stereoisomers.These furanones treated with the Lewis acid $AlCl_3$ in benzene, toluene and chlorobenzene to furnish4,4-diaryl-1-(3-chromonyl)buta-1,3-diene-2-carboxylic acids 4a-fas mixtures of geometrical (*E*,*E*- and *E*,*Z*-) stereoisomers via an intermolecular alkylation mode. The unfavored intramolecular alkylation is explained on the basis of the decreased electron density at C_2 of the chromone moiety causing the attack of the intermediate carbocation on this position becomes difficult.

Keywords: 2(3*H*)-Furanones, Chromone-3-carboxaldehyde, Intermolecular alkylation, Intramolecular alkylation and Butadienecarboxylic acids.

2(3*H*)-Furanones represent a group of heterocyclesof special interest. This is due tothe facile opening of the lactone ring by both nucleophilic and electrophilic reagents. During the last decades, our research group were interested in the conversion of these furanones into a variety of heterocyclic systems of synthetic and biological importance, *e.g.* pyrrolones, pyrazoles, pyridazinones, triazoles, oxadiazoles, thiazoles and isothiazoles[1-28]. Also, the behavior of these compounds as alkylating agents has been extensively studied by us. It was found that 2(3*H*)-furanones having an aryl or heteryl group attached to an exocyclic double bond at position-3, when treated with $AlCl_3$ as the Lewis acid in benzene, toluene and anisole, undergo an alkyl-oxygen bond cleavage to give resonance-stabilized carbocations. The carbocation formed in each case either attacks the *o*-position of the aryl or heteryl group situated at position-3 intramolecularly, oris attacked by the solvent in an intermolecular fashion to produce the corresponding butadienecarboxylic acid. It was possible, via the intramolecular alkylation mode, to obtain fluoranthene[24], benzofuran[25], benzothiophene[27], carbazole[29] and quinoline[30] derivatives.

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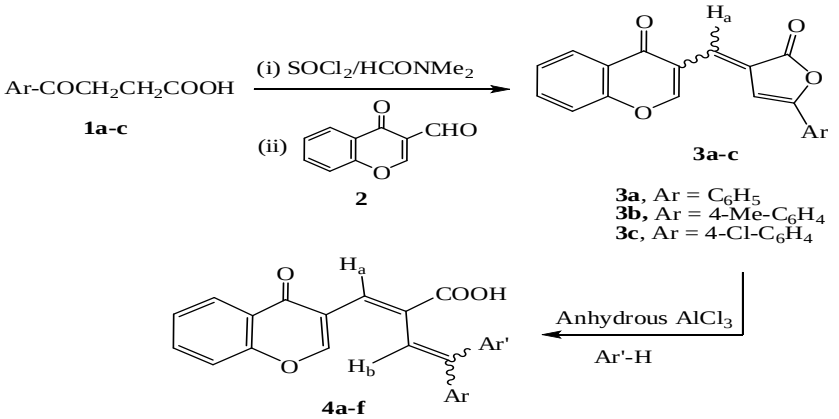
From our previous studies, it could be concluded that the fate of the carbocation intermediate, *i.e.* its intra- or inter-molecular alkylation depends mainly on three factors, (i) The nature of the substituents situated at position-3, In other words, the availability of electron density at the *o*-position of this substituent. Definitely higher electron density favors the intramolecular mode. (ii) the nucleophilicity of the solvent, for instance it was found that changing the solvent from benzene to the more nucleophilic solvents toluene and anisole changed the reaction pathway fromintramolecular to intermolecular mode[26]. (iii) the stability of the carbocation intermediate, it was found that a more stable carbocation, being more selective favors the formation of cyclic products via intramolecular alkylation[29].

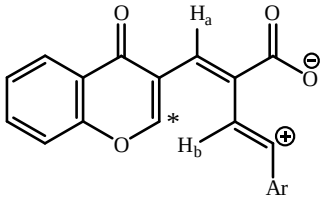
As continuation of our previous studies on the chemistry of furanones, we wish to report herein on the study of behavior of 2(3*H*)-furanones bearing a chromonyl group as alkylating agents. Thus, condensation of 4-oxo-4*H*-chromen-3-carboxaldehyde(2)[31] with 3-aroylpropionic acids (1a-c) using thionyl chloride in *N*,*N*-dimethylformamide as a cyclodehydrating agent[32]was found to afford the corresponding furanones, 5-aryl-3-chromonylmethylene-2(3*H*)-furanones (3a-c). The structures of these products were inferred from their analytical and spectral data. The IR spectra of compounds(3a-c) revealed the characteristic absorption bands for the lactone C=O at 1763-1756 cm^{-1} as well as the chromone C=O at 1652-1648 cm^{-1}(*Cf.* the Experimental part).

When the furanones3a-c were treated with$AlCl_3$a Lewis acid in the presence of benzene, toluene, chlorobenzene, ring opening occurred with the formation of the corresponding butadienecarboxylic acids (4a-f)(Scheme 1).



Scheme 1.

The structures of (4a-f) were determined on the basis of their analytical and spectroscopic data. The IR spectra of compounds (4a-f) were devoid from the absorption of the lactone C=O group and displayed the characteristic broad absorption band of O-H at 3430-3400 cm^{-1} as well as C=O group for the carboxylic group at 1700-1681 cm^{-1} and chromone C=O at 1667-1630 cm^{-1}. The ^{1}H-NMR spectra ofcompounds (4b,c,f) showed duplicate signals of different integrations for H_b proton and protons of CH_3 group for compounds (4b,f) which represent a good evidence for their existence as mixtures of two geometrical *E*,*E*- and *E*,*Z*-stereoisomers. The higher δ value for proton H_a as compared with H_b, in ^{1}H-NMR spectra, was attributed to that H_a is located in *β*–position of *α*,*β*–unsaturated system which make it downfield. The mass spectraexhibited the correct molecular ion peak beside some of abundant peaks (*Cf.* the Experimental part). Evidently,the butadienecarboxylic acids (4a-f) are formed via the intermediacy of the resonance-stabilized carbocation [A] formed by alkyl-oxygen cleavage of the furanone nucleus. The reaction is then completed by attack of the solvent: benzene, toluene or chlorobenzene in an intermolecular fashion to furnish the acids (4a-f).



[A]

It is to be mentioned that when the reaction was carried out in tetrachloroethane or nitrobenzene as solvents, no products of intramolecular alkylation were isolated. We believe that this unfavored intramolecular mode of reaction is not unexpected since C_2* in the chromone moiety is a part of *α*,*β*-unsaturated system. This results in a decrease of the electron density at this position to an extent that attack of the carbocationic center on this position becomes difficult.

Assignment of the configuration *cis*- (H_b/Ar) for the acids **4** is based on that the most stable configuration of the intermediate carbocation **[A]** is in *E*-configuration. In such configuration, the extended conjugation increases the stability of this carbocation. The attacking group: phenyl,*p*-tolyl or *p*-chlorophenyl should therefore be *trans*- to the H_b-atom.

Experimental

Melting points were measured on a Gallen Kamp electric melting point apparatus. The IR spectra were recorded using potassium bromide disks on a

Fourier transform infrared Thermo Electron Nicolet 7600 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) at the Central Laboratory of Faculty of Science, Ain Shams University. The ^{1}H-NMR spectra were run at 400 MHz on a GEMINI 400 BB NMR spectrometer (GEMINI, Manufacturing & Engineering Inc., Anaheim, CA, USA) using tetramethylsilane (TMS) as internal standard in deuterated dimethylsulphoxide (DMSO-d_6) at the Main Defense Chemical Laboratory, Cairo. The mass spectra were recorded on a Shimadzu GC-MS-QP-1000EX mass spectrometer (Shimadzu Scientific Instruments, Inc., USA) operating at 70 eV at the Micro analytical Center of Cairo University. The reactions were monitored by the thin layer chromatography using Merck Kiesel gel 60F_{254} analytical sheets obtained from Fluka.

General procedure for the synthesis of 5-aryl-3-(4-oxo-4H-chromen-3-yl) methylenefuran-2(3H)-ones 3a-c

(i) *(Chlorosulfinyloxy)-N,N-dimethylmethaniminium chloride (the cyclodehydrating agent)*

Into a 25-ml dropping funnel containing benzene (5 ml) and *N,N*-dimethylformamide (1 ml, 10.2 mmol), thionyl chloride (0.8 ml, 11 mmol) was added. After 5 min, the two phases were separated, and the reagent (lowerlayer) was used in the next step.

(ii) To a stirred solution of 3-aroylpropionic acid (1a-c) (10 mmol) in dichloromethane (25 ml) at 0^{o}C, the cyclodehydrating agent (10 mmol) prepared in step (i) was added. Stirring was continued for 15 min. 4-oxo-4*H*-chromen-3-carboxaldehyde 2(10 mmol) was added followed by triethylamine (30 mmol) in dichloromethane (15 ml). The resulting mixture was stirred at room temperature for 5 hr. The organic layer was washed with water (2 ×50 ml) and dried over anhydrous sodium sulfate and then evaporated to give2(3*H*)-furanones(3a-c).

3-((4-Oxo-4H-chromen-3-yl)methylene)-5-phenylfuran-2(3H)-ones 3a

Yellow crystals;mp.233-235^{o}C (benzene).Yield 70%.Anal.Calcd.for $C_{20}H_{12}O_4$ (316.07): C, 75.94; H, 3.82. Found: C, 75.82; H, 3.71. IR (KBr) (ν, cm^{-1}): 3115, 3070 (aryl-H), 1763 (C=O$_{Furanone}$), 1652 (C=O$_{Chromone}$), 1610 (C=C). ^{1}H-NMR (DMSO-d_6): δ(ppm) (*E*-form, 75%) 9.09 (s, 1H,C-H$_{Chromone}$), 8.18 (s, 1H,H$_a$), 7.88 -7.77 (m, 4H, Ar-H$_{Chromone}$), 7.74-7.39 (m, 6H, 5H$_{Phenyl}$ + 1H$_{Furanone}$); (*Z*-form, 25%)δ 8.16 (s, 1H, H$_a$). MS, *m/z* (%): 316 (M$^{\cdot+}$, 6), 288 (7), 183 (3), 155 (4), 111 (12), 105 (81), 92 (24), 77 (100).

3-((4-Oxo-4H-chromen-3-yl)methylene)-5-(4-tolyl)furan-2(3H)-ones 3b

Yellow crystals;mp.264-266^{o}C (benzene).Yield 79%.Anal.Calcd.for $C_{21}H_{14}O_4$ (330.09): C, 76.35; H, 4.27. Found: C, 76.24; H, 4.11. IR (KBr) (ν, cm^{-1}): 3126, 3028 (aryl-H), 2914 (alkyl-H), 1761 (C=O$_{Furanone}$), 1650 (C=O$_{Chromone}$), 1611 (C=C). ^{1}H-NMR (DMSO-d_6): (*E*-form, 70%)δ(ppm) 9.07

(s, 1H, C-$H_{Chromone}$), 8.18 (s, 1H,H_a), 7.91-7.72 (m, 4H, Ar-$H_{Chromone}$), 7.59-7.33 (m, 5H, $4H_{Tolyl}$ + $1H_{Furanone}$), 2.38 (s, 3H, CH_3);(*Z*-form, 30%)δ 8.16 (s, 1H, H_a). MS, *m/z* (%): 330 ($M^{\cdot+}$, 2), 292 (13), 276 (10), 237 (8), 194 (9), 177 (26), 149 (14), 120 (20), 119 (100), 105 (37), 91 (21), 77 (64).

5-(4-Chlorophenyl)-3-((4-oxo-4H-chromen-3-yl)methylene)furan-2(3H)-ones 3c

Yellow crystals; mp.308-310^{o}C (benzene).Yield 74%.Anal.Calcd.for $C_{20}H_{11}O_4Cl$ (350.03): C, 68.49; H, 3.16, Cl, 10.11. Found: C, 68.35; H, 3.04, Cl, 10.01. IR (KBr) (ν, cm^{-1}): 3127, 3084 (aryl-H), 1756 (C=$O_{Furanone}$), 1648 (C=$O_{Chromone}$), 1613 (C=C). ^{1}H-NMR (DMSO-d_6): (*E*-form, 75%)δ(ppm) 9.05 (s, 1H, C-$H_{Cromone}$), 8.16 (s, 1H,H_a), 7.89-7.72 (m, 4H, Ar-$H_{Chromone}$), 7.59-7.39 (m, 5H, $4H_{Chlorophenyl}$ + $1H_{Furanone}$);(*Z*-form, 25%)δ 8.16 (s, 1H, H_a). MS, *m/z* (%): 352 (M+2, 8), 350 ($M^{\cdot+}$, 25), 324 (6), 322 (17), 296 (2), 294 (5), 211 (7), 173 (8), 141 (30), 139 (100), 111 (58), 92 (25), 75 (27).

General procedure for the preparation of 2-((4-oxo-4H-chromen-3-yl) methylene)-4,4-diarylbut-3-enoic acid 4a-f

To a stirred solution of anhydrous aluminum chloride (0.03 mol) in dry benzene, toluene or chlorobenzene (100 ml), a solution of furanones (3a-c) (0.01 mol) in dry benzene, toluene or chlorobenzene was added dropwise at 10-20^{o}C. After complete addition, the whole mixture was stirred at room temperature for further 6 hr, heated on water bath for 2 hr, then left to stand overnight.The complex formed was decomposed with ice cold hydrochloric acid (50 ml) and hence steam-distilled to remove the excess of organic solvent. The residue was triturated with ether, filtered off,and recrystallized from the suitable solvent.

2-((4-Oxo-4H-chromen-3-yl)methylene)-4,4-diphenylylbut-3-enoic acid 4a

White crystals; mp.258-260^{o}C(Petroleum ether, 60-80^{o}C/benzene, 1:1).Yield 31%.Anal.Calcd.for $C_{26}H_{18}O_4$ (394.12):C, 79.17; H, 4.60. Found: C, 79.09; H, 4.51. IR (KBr) (ν, cm^{-1}): 3420 (OH), 3068 (aryl-H), 1700 (C=O_{acid}), 1630 (C=$O_{Chromone}$), 1610 (C=C). ^{1}H-NMR (DMSO-d_6): δ(ppm) 12.63 (s, 1H, COOH, *D_2O-exchangeable*), 8.04 (s, 1H, C-$H_{Chromone}$), 7.86-7.47 (m, 4H, Ar-$H_{Chromone}$), 7.36 (s, 1H,H_a), 7.28-7.04 (m, 10H, 2 Ar-H_{Phenyl}),7.02 (s, 1H, H_b). MS, *m/z* (%): 394 ($M^{\cdot+}$, 3), 350 (12), 322 (5), 293 (4), 237 (9), 197 (13), 151 (12), 139 (38), 111 (100), 92 (53), 76 (46), 63 (58).

2-((4-Oxo-4H-chromen-3-yl)methylene)-4-phenyl-4-p-tolylbut-3-enoic acid 4b

Faint brown crystals; mp.128-130^{o}C(benzene).Yield 35%.Anal.Calcd.for $C_{27}H_{20}O_4$ (408.14): C, 79.40; H, 4.94. Found: C, 79.31; H, 4.85. IR (KBr) (ν, cm^{-1}): 3426 (OH), 3078 (aryl-H), 1682 (C=O_{acid}), 1635 (C=$O_{Chromone}$),1615 (C=C). ^{1}H-NMR (DMSO-d_6):(*E,Z*-form, 60%)δ(ppm)12.70 (s, 1H, COOH, *D_2O-exchangeable*), 8.14 (s, 1H,C-$H_{Chromone}$), 8.08-7.50 (m, 4H, Ar-$H_{Chromone}$), 7.37 (s, 1H,H_a), 7.17-7.06 (m, 5H, Ar-H_{Phenyl}), 7.00-6.91 (m, 4H, Ar-H_{Tolyl}),6.89 (s, 1H, H_b),2.21 (s, 3H, CH_3);(*E,E*-form, 40%) δ6.87 (s, 1H, H_b),2.17 (s, 3H,

CH_3).MS, *m/z* (%): 408 ($M^{\cdot+}$, 1), 393 (2), 334 (46), 289 (31), 229 (70), 183 (34), 159 (28), 105 (100), 92 (22), 65 (21).

4-(4-Chlorophenyl)-2-((4-oxo-4H-chromen-3-yl)methylene)-4-phenylbut-3-enoic acid 4c

Yellow crystals; mp.208-209°C(Petroleum ether, 60-80°C/benzene, 1:1).Yield 28%.Anal.Calcd.for $C_{26}H_{17}ClO_4$ (428.08): C, 72.82; H, 4.00; Cl, 8.27. Found: C, 72.73; H, 3.89; Cl, 8.19. IR (KBr) (ν, cm^{-1}): 3430 (OH), 3078 (aryl-H), 1701 ($C=O_{acid}$), 1652 ($C=O_{Chromone}$),1619 (C=C). ^{1}H-NMR (DMSO-d_6):(*E,Z*-form, 65%)δ(ppm) 12.63 (s, 1H, COOH, D_2O-exchangeable), 8.52 (s, 1H,C-$H_{Chromone}$), 8.24-7.75 (m, 4H, Ar-$H_{Chromone}$), 7.64-7.39 (m, 4H, Ar-$H_{Chlorophenyl}$), 7.35 (s, 1H,H_a), 7.17-6.85 (m, 5H, Ar-H_{Phenyl}),6.83 (s, 1H, H_b);(*E,E*-form, 35%) δ6.65 (s, 1H, H_b).MS, *m/z* (%): 430 (M+2, 4), 428 ($M^{\cdot+}$, 11), 411 (13), 409 (12), 383(44), 381 (43), 347 (10), 289 (11), 262 (25), 237 (61), 235 (91), 202 (25), 199 (130), 165 (100), 146 (54), 121 (71), 92 (34), 77 (39).

2-((4-Oxo-4H-chromen-3-yl)methylene)-4,4-dip-tolylbut-3-enoic acid 4d

Faint brown crystals; mp.136-138°C (Petroleum ether, 60-80°C/benzene, 1:1).Yield 38%.Anal.Calcd.for $C_{28}H_{22}O_4$ (422.15): C, 79.60; H, 5.25. Found: C, 79.57; H, 5.22. IR (KBr) (ν, cm^{-1}): 3425 (OH), 3077 (aryl-H), 1682 ($C=O_{acid}$), 1636 ($C=O_{Chromone}$), 1615 (C=C). ^{1}H-NMR (DMSO-d_6):δ(ppm) 12.69 (s, 1H, COOH, D_2O-exchangeable), 8.13 (s, 1H,C-$H_{Chromone}$), 8.08-7.48 (m, 4H, Ar-$H_{Chromone}$), 7.38 (s, 1H,H_a), 7.22-6.89 (m, 8H, 2 Ar-H_{Tolyl}), 6.86 (s, 1H, H_b), 2.20 (s, 6H, 2 CH_3).MS, *m/z* (%): 422 ($M^{\cdot+}$, 2), 367 (3), 334 (44), 288 (13), 228 (38), 184 (19), 160 (12), 105 (100), 91 (28), 65 (20).

4,4-Bis(4-chlorophenyl)-2-((4-oxo-4H-chromen-3-yl)methylene)but-3-enoic acid 4e

Yellow crystals; mp.235-237°C(benzene).Yield 25%.Anal.Calcd.for $C_{26}H_{16}Cl_2O_4$ (462.04): C, 67.40; H, 3.48; Cl, 15.30. Found: C, 67.31; H, 3.38; Cl, 15.22. IR (KBr) (ν, cm^{-1}): 3400-3200 (OH), 3063 (aryl-H), 1695 ($C=O_{acid}$), 1667 ($C=O_{Chromone}$), 1625 (C=C). ^{1}H-NMR (DMSO-d_6): δ(ppm) 10.33 (s, 1H, COOH, D_2O-exchangeable), 8.02 (s, 1H,C-$H_{Chromone}$), 7.62-7.35 (m, 4H, Ar-$H_{Chromone}$), 7.50 (s, 1H,H_a),7.23-6.76 (m, 8H,2 Ar-$H_{Chlorophenyl}$),6.73 (s, 1H, H_b). MS, *m/z* (%): 462 ($M^{\cdot+}$, 1), 323 (2), 288 (5), 238 (12), 173 (17), 146 (18), 123 (56), 105 (100), 92 (36), 77 (29).

4-(4-Chlorophenyl)-2-((4-oxo-4H-chromen-3-yl)methylene)-4-p-tolylbut-3-enoic acid 4f

Faint brown crystals; mp.140-142°C(Petroleum ether, 60-80°C/benzene, 1:1).Yield 34%.Anal.Calcd.for $C_{27}H_{19}ClO_4$ (442.10): C, 73.22; H, 4.32; Cl, 8.00. Found: C, 73.11; H, 4.22; Cl, 7.87. IR (KBr) (ν, cm^{-1}): 3410 (OH), 3078 (aryl-H), 1681 ($C=O_{acid}$), 1636 ($C=O_{Chromone}$), 1615 (C=C). ^{1}H-NMR (DMSO-d_6): (*E,Z*-form, 75%) δ(ppm) 12.68 (s, 1H, COOH, D_2O-exchangeable), 8.15 (s, 1H,C-$H_{Chromone}$), 8.13-7.79 (m, 4H, Ar-$H_{Chromone}$), 7.68-7.48 (m, 4H, Ar-

$H_{Chlorophenyl}$), 7.37 (s, 1H,H_a), 7.16-6.98 (m, 4H, Ar-H_{Tolyl}),6.93 (s, 1H, H_b),2.20 (s, 3H, CH_3);(*E*,*E*-form, 25%) δ6.90 (s, 1H, H_b), 2.15 (s, 3H, CH_3). MS, *m/z* (%): 442 ($M^{\cdot+}$, missed), 407 (M-$Cl^{\cdot}$, 1), 393 (3), 334 (54), 316 (15), 289 (32), 183 (35), 121 (51), 105 (100), 77 (37), 65 (23).

Referneces

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سلوك بعض مركبات 2(*H*-3)فيورانونات والحاملة لمجموعة كرومون ككواشف ألكلة

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تتفاعل أحماض 3-ارويل بروبيونيك مع 4-اكسوكرومون-3-كربوكسالديهيد باستخدام مخلوط كلوريد ثيونيل وثنائى ميثيل فورماميد ككاشف لنزع الماء لتعطى 5-أريل-3-كرومونايل ميثيلين -2(*H*3)-فيورانونات كمخلوط من نظائر -*E*و-*Z*. وقد تفاعلت هذه الفيورانونات مع حامض لويس (كلوريد الالومنيوم اللا مائى) فى وجود البنزين ، الطولوين والكلوروبنزين لتعطى أحماض 4،4-ثنائى أريل-1-(3-كرومونايل)بيوتا-1و3-دايين-2-كربوكسيليك كمخلوط من نظائر -*E,E*و-*E,Z* عن طريق نظام الألكلة الخارجية. يمكن تفسير نظام الألكلة الداخلية الغير مناسب عن طريق نقص الكثافة الالكترونية عند موضع 2 فى مجموعة الكرومون مما يجعل هجوم الكربوكاتيون صعب عند هذا الموضع.