Ring expansion in 5-aryl-3-arylmethylidenefuran-2(3*H*)-ones by the reaction with ethyl diazoacetate

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Reaction of arylmethylidene derivatives of furan-2(3*H*)-one with ethyl diazoacetate is accompanied by elimination of nitrogen and leads to the substituted pyran-3(2*H*)-ones.

Key words: 3-arylmethylidenefuran-2(3*H*)-one, ethyl diazoacetate, 4-arylmethylidenepyran-3-one, ring expansion.

An interest to 3-arylmethylidenefuran-2(3*H*)-ones is caused by the presence of different reaction centers in their structures, which makes them valuable substrates for organic synthesis. At the same time, there is only limited number of papers dealing with the transformations of 3-arylmethylidenefuran-2(3*H*)-ones upon treatment with diazo compounds.

There is information about reactions of diazo compounds with 5-aryl-2,3-dihydrofuran-2,3-diones, as well as with their hetero and benzo analogs.[1,2] These papers describe in detail the reactions of furan- and pyrrolediones with diazoalkanes, which proceed, as a rule, at the keto group to form diazo aldols and epoxy derivatives.

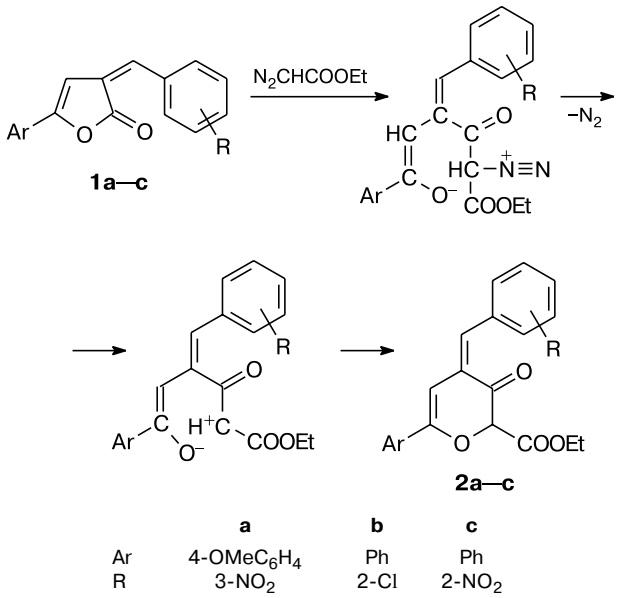
3-Arylmethylidenefuran-2(3*H*)-ones are known to react with diazomethane and diazoethane[3—6] to form products of the 1,3-dipolar addition at the *exo*-cyclic ethylene bond. No ring expansion was observed during this reaction.

In contrast to 3-arylmethylidenefuran-2(3*H*)-ones, the reaction of diazomethane with 5-arylmethylidenefuran-2(5*H*)-ones[7,8] proceeds as the insertion of methylene into C—H bond of the heterocycle.

Results and Discussion

Earlier,[9] we have shown that dichlorocarbene reacts with the double bond of the substituted in position 5 furan- or thiophen-2(3*H*)-ones to form, after cyclopropyl-allyl rearrangement, the corresponding pyran-2-one. In the present work, we studied a reaction of ethyl diazoacetate with 3-arylmethylidenefuran-2(3*H*)-ones **1a—c**, containing few reaction centers in the molecule: *endo*- and *exo*-cyclic double bonds, carbonyl group, and active C—H-bonds.

It turned out that arylmethylidene derivatives of furan-2-ones **1a—c** do not react with ethyl diazoacetate at 20 °C. However, evolution of nitrogen and formation of 6-aryl-4-(R-phenylmethylidene)-2-ethoxycarbonylpyran-3-ones (**2a—c**) in 52—69% yield are observed at 60 °C. It should be noted that the reaction takes place only when electron-withdrawing substituent (NO_2, Cl) is presented in arylmethylidene fragment of compounds **1a—c**.



	a	b	c
Ar	4-$OMeC_6H_4$	Ph	Ph
R	3-NO_2	2-Cl	2-NO_2

In the ^{1}H NMR spectra of compounds **2a—c**, a singlet of the methyne proton at ~5.1 ppm and signals of the protons in ethoxy group at ~1.5 and 4.2—4.3 ppm are always presented.

In the ^{13}C NMR spectrum of compound **2b**, signals of two carbon atoms of the ester and adjacent carbonyl groups at 157.5 and 168.2 ppm, signals of sp^2-hybridized carbon atoms of the pyran ring at 78.5 and 135.3 ppm, and signals

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of the *exo*-cyclic carbon atom at 133.2 ppm are observed. Carbon atoms of the aromatic fragments resonate in the region 125.1—130.4 ppm. Signals of the sp^3-hybridized carbon atoms are observed at 14.8 (Me), 62.5 (CH_2), and 99.1 ppm (for tertiary C(2) carbon atom).

Apparently, pyranones **2a—c** are formed as a result of the attack of the nucleophilic center of ethyl diazoacetate at the carbon atom of the carbonyl group, which leads to the furan ring cleavage and to the formation of zwitterionic intermediate, the subsequent heterocyclization of which gives the six-membered heterocycle.

Thus, the reaction of arylmethylidene derivatives of furan-2(3*H*)-one with ethyl diazoacetate is accompanied by elimination of nitrogen and leads to the substituted pyran-3-ones.

Experimental

IR spectra were recorded on a FSM 1201 IR Fourier spectrometer in Nujol and hexachlorobutadiene. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 (400 MHz) spectrometer in dimethylsulfoxide-d_6 with $SiMe_4$ as the internal standard. 3-Arylmethylidenefuran-2(3*H*)-ones **1a—c** (see Ref. 9) and ethyl diazoacetate[10] were obtained according to the known procedures.

6-Aryl-2-ethoxycarbonyl-4-(R-phenylmethylidene)pyran-3-ones (general procedure). 3-Arylmethylidenefuran-2(3*H*)-one (**1a—c**) (1.5 mmol) and ethyl diazoacetate (1.5 mmol) in chloroform (30 mL) were heated for 6—8 h. The crystals formed after evaporation of the solvent were recrystallized from ethanol.

2-Ethoxycarbonyl-6-(4-methoxyphenyl)-4-(3-nitrophenylmethylidene)pyran-3-one (2a). The yield was 0.33 g (54%), m.p. 196—198 °C. Found (%): C, 64.99; H, 4.46; N, 3.87. $C_{22}H_{19}NO_7$. Calculated (%): C, 64.54; H, 4.68; N, 3.42. IR, ν/cm^{-1}: 1777 (C=O), 1765 (COOEt), 1175 (C—O—C), 1624 (=CHAr). ^{1}H NMR, δ: 1.49—1.52 (t, 3 H, $CH_2\underline{CH_3}$, J = 6.9 Hz); 3.81 (s, 3 H, OMe); 4.21—4.30 (q, 2 H, $\underline{CH_2}$Me, J = 7.1 Hz); 5.09 (s, 1 H, CH); 6.29 (s, 1 H, =CH); 6.74 (s, 1 H, =CH); 7.24—7.71 (m, 9 H, Ar). ^{13}C NMR, δ: 14.7 (Me), 55.8 (OMe), 62.5 (CH_2), 79.9 (C(5)), 99.1 (C(2)), 115.3, 125.8, 127.2, 127.7, 128.6, 129.5, 130.0, 130.4, 130.6, 130.9, 135.3, 142.5, 157.5 (COOEt), 168.2 (CO).

4-(2-Chlorophenylmethylidene)-2-ethoxycarbonyl-6-phenylpyran-3-one (2b). The yield was 0.46 g (83%), m.p. 134—136 °C. Found (%): C, 68.40; H, 4.62; Cl, 9.71. $C_{21}H_{17}ClO_4$. Calculated (%): C, 68.39; H, 4.64; Cl, 9.61. IR, ν/cm^{-1}: 1776 (C=O), 1765 (COOEt), 1176 (C—O—C), 1620 (=CHAr). ^{1}H NMR, δ: 1.49—1.54 (t, 3 H, $CH_2\underline{Me}$, J = 6.9 Hz); 4.21—4.30 (q, 2 H, $\underline{CH_2}$Me, J = 7.1 Hz); 5.10 (s, 1 H, CH); 6.76 (s, 1 H, =CH); 7.21 (s, 1 H, =CH); 7.33—8.11 (m, 9 H, Ar). ^{13}C NMR, δ: 14.8 (Me), 62.5 (CH_2), 78.5 (C(5)), 99.1 (C(2)), 125.1, 126.8, 127.2, 127.5, 128.6, 129.5, 130.0, 130.4, 130.6, 130.9, 133.2, 135.3, 157.5 (COOEt), 168.2 (CO).

2-Ethoxycarbonyl-4-(2-nitrophenylmethylidene)-6-phenylpyran-3-one (2c). The yield was 0.38 g (67%), m.p. 146—148 °C. Found (%): C, 66.40; H, 4.38; N, 4.09. $C_{21}H_{17}NO_6$. Calculated (%): C, 66.49; H, 4.52; N, 3.69. IR, ν/cm^{-1}: 1776 (C=O), 1765 (COOEt), 1174 (C—O—C), 1620 (=CHAr). ^{1}H NMR, δ: 1.49—1.54 (t, 3 H, $CH_2\underline{Me}$, J = 6.9 Hz); 4.21—4.30 (q, 2 H, $\underline{CH_2}$Me, J = 7.1 Hz); 5.10 (s, 1 H, CH); 6.77 (s, 1 H, =CH); 7.19 (s, 1 H, =CH); 7.45—8.21 (m, 9 H, Ar). ^{13}C NMR, δ: 14.7 (Me), 62.3 (CH_2), 78.3 (C(5)), 99.1 (C(2)), 125.1, 126.7, 127.2, 127.7, 128.4, 129.3, 129.9, 131.4, 131.8, 132.9, 133.7, 135.3, 157.5 (COOEt), 168.4 (CO).

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