

Five-Membered 2,3-Dioxo Heterocycles: XLV.* Thermolysis of 5-Aryl-4-phenyl-2,3-dihydrofuran-2,3-diones in the Absence of Other Partners and in the Presence of Carbonyl Compounds

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Abstract—Aroyl(phenyl)ketenes generated by thermolysis of 5-aryl-4-phenyl-2,3-dihydrofuran-2,3-diones undergo [4+2]-cycloaddition to 3-aryloxy-6-aryl-3,5-diphenyl-3,4-dihydro-2*H*-pyran-2,4-diones. Heating of the latter leads to rearrangement with formation of 4-aryloxy-6-aryl-3,5-diphenyl-2*H*-pyran-2-ones. Thermolysis of 5-aryl-4-phenyl-2,3-dihydrofuran-2,3-diones in the presence of carbonyl compounds yields 6-aryl-5-phenyl-4*H*-1,3-dioxin-4-ones.

5-Aryl-2,3-dihydrofuran-2,3-diones containing no substituent in position 4 are thermally unstable. They undergo decomposition on heating to a temperature near the melting point (130–140°C). The temperature of their decomposition in solution is lower by 50–70°C. The process is accompanied by elimination of carbon(II) oxide to give reactive aroylketenes [2–5]. Stabilization pathways of the latter are determined by the nature of substituent in position 4 of their furandione precursor. The most probable pathway is intermolecular [4+2]-cycloaddition ([4+2]-cycloaddition), where one aroylketene molecule acts as diene (aroylketene fragment O=C–C=C), and the other, as dienophile (ketene C=C bond).

5-Aryl-4-methyl-2,3-dihydrofuran-2,3-diones under thermolysis conditions give rise to aroyl(methyl)ketenes which are stabilized according to the above [4+2]-cycloaddition pathway to afford 3-aryloxy-6-aryl-3,5-dimethyl-3,4-dihydro-2*H*-pyran-2,4-diones [2]. Aroylketenes generated from 4-unsubstituted 5-aryl-2,3-dihydrofuran-2,3-diones are converted into 3-aryloxy-6-aryl-4-hydroxy-2*H*-pyran-2-ones as a result of 1,3-H shift in the primary [4+2]-cycloadducts [3]. Thermolysis of 5-aryl-4-halo-2,3-dihydrofuran-2,3-diones gives aroyl(halo)ketenes which undergo cyclodimerization to 3-aryloxy-6-aryl-3,5-dihalo-3,4-dihydro-2*H*-pyran-2,4-diones. Hydrolysis of the latter on attempted recrystallization yields 3-aryloxy-6-aryl-5-halo-4-hydroxy-2*H*-pyran-2-ones. The dimeric prod-

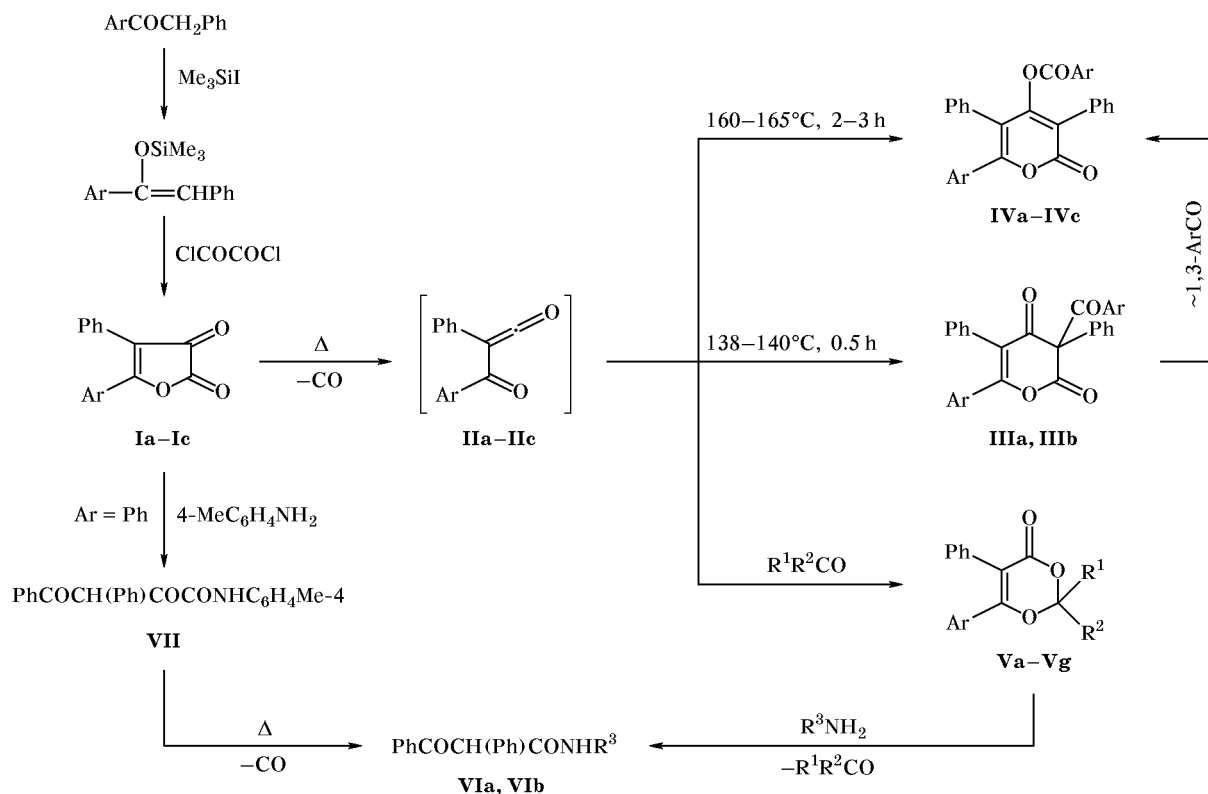
uct having two halogen atoms was isolated only from 4-chloro-5-*p*-tolyl-2,3-dihydrofuran-2,3-dione [4].

With the goal of estimating the effect of phenyl group in position 4 of 5-aryl-2,3-dihydrofuran-2,3-diones on their thermal decomposition, we synthesized 5-aryl-4-phenyl-2,3-dihydrofuran-2,3-diones **Ia–Ic** and studied their thermolysis both in the absence of other reaction partners and in the presence of carbonyl compounds. Substituted furandiones **Ia–Ic** were prepared by reaction of the corresponding aryl benzyl ketones with iodotrimethylsilane [5] and subsequent treatment of the resulting trimethylsilyl enol ethers with oxalyl chloride in boiling chloroform (reaction time 2–3 h; Scheme 1). Furandiones **Ia–c** (Table 1) are yellow–orange crystalline substances, readily soluble in polar aprotic organic solvents and poorly soluble in alkanes. They react with water and alcohols and lose their color on storage in air due to reaction with atmospheric moisture (addition of water leads to opening of the furan ring).

The IR spectra of **Ia–Ic** (Table 2) contain bands due to stretching vibrations of the lactone carbonyl group (C²=O; 1810–1825 cm⁻¹) and ketone carbonyl group (C³=O; 1705–1730 cm⁻¹), in keeping with published data for analogous compounds having no substituent in position 4 and 4-methyl and 4-halogen derivatives [6–8]. In the ¹³C NMR spectrum of compound **Ic**, signals from the furan ring carbon atoms appear at δ_C 154.16 (C²), 178.96 (C³), 118.31 (C⁴), and 176.31 ppm (C⁵). The downfield position of the C⁵ signal and the upfield position of the C² signal

* For communication XLIV, see [1].

Scheme 1.



Ia-IVa, Va, Vb, VIa, VIb, Ar = Ph; **Ib, IIb, IVb, Vc**, Ar = 4-MeC₆H₄; **Ic, IIc, IIIb, IVc, Vd-Vg**, Ar = 2,5-Me₂C₆H₃; **Va**, R¹ = Ph; **Vb-d**, R¹ = H; **Va**, R² = CH₂Ph; **Vb, d**, R² = 4-BrC₆H₄; **Vc**, R² = 4-MeOC₆H₄; **Ve**, R¹R² = (CH₂)₄; **Vf**, R¹R² = (CH₂)₆; **Vg**, R¹R²C=O = 2-adamantanone; **VIa**, R³ = 4-MeC₆H₄; **VIb**, R³ = 4-MeOC₆H₄.

are well consistent with the known data for 4-unsubstituted analogs [9].

Heating of furandiones **Ia-Ic** in *p*-xylene at 135–140°C for 30–40 min resulted in their decarbonylation to give aroyl(phenyl)ketenes **IIa-IIc** which underwent [4+2]-cycloaddition with formation of 3-aryloxy-6-aryl-3,5-diphenyl-3,4-dihydro-2H-pyran-2,4-diones **IIIa** and **IIIb** (Scheme 1). The products showed in the IR spectra (Table 2) absorption bands belonging to stretching vibrations of the lactone carbonyl group (C²=O, 1720–1745 cm⁻¹) and ketone carbonyl groups (C⁴=O, 1690–1695 cm⁻¹; ArC=O, 1652–1660 cm⁻¹). The ¹³C NMR spectrum of **IIIa** contained signals from aromatic carbon atoms (δ_C 126.10–135.00 ppm), and those belonging to the pyran ring and benzoyl carbonyl, δ_C, ppm: 154.51 (C²), 66.11 (C³), 194.35 (C⁴), 116.66 (C⁵), 170.03 (C⁶), 178.88 (PhCO). These data are consistent with the assumed structure.

When thermolysis of furandiones **Ia-Ic** was performed under more severe conditions, by heating in 1,2,4-trimethylbenzene or decane at 160–165°C for

2–3 h, we isolated 4-aryloxy-6-aryl-3,5-diphenyl-2H-pyran-2-ones **IVa-IVc** (Table 1). Compounds **IVa-IVc** are colorless or pale yellow crystalline substances which are readily soluble in common organic solvents (except for alkanes) and poorly soluble in water. Their IR spectra (Table 2) are characterized by the presence of lactone carbonyl (C²=O) absorption at 1735–1755 cm⁻¹ and ester carbonyl (4-OCOAr) absorption at 1720–1735 cm⁻¹. In the ¹³C NMR spectrum of **IVb** we observed signals from aromatic carbon atoms in the region δ_C 123.49–145.94 ppm, methyl groups at δ_C 20.64 and 20.94 ppm, and carbon atoms of the pyran ring and ester carbonyl group, δ_C, ppm: 161.92 (C²), 116.80 (C³), 158.59 (C⁴), 115.69 (C⁵), 168.54 (C⁶), 161.20 (4-OCO). The mass spectrum of **IVb** contained the following ion peaks, *m/z* (*I*_{rel}, %): 472 (6) [M]⁺, 119 (100) [4-MeC₆H₄CO]⁺, 91 (24) [MeC₆H₄]⁺.

Presumably, compounds **IVa-IVc** are formed as a result of [1,3]-acylotropic shift of the aroyl group in the primary [4+2]-cycloadducts like **III**. A similar

Table 1. Yields, melting points, and elemental analyses of compounds **I** and **III–VI**

Comp. no.	Yield, %	mp, °C (solvent)	Found, %		Formula	Calculated, %	
			C	H		C	H
Ib	48	154–155 (decomp., CHCl ₃ –hexane)	77.15	4.60	C ₁₇ H ₁₂ O ₃	77.26	4.58
Ic	47	131–132 (decomp., CHCl ₃ –hexane)	77.70	5.03	C ₁₈ H ₁₄ O ₃	77.68	5.07
IIIa	65	160–161 (cyclohexane)	81.02	4.55	C ₃₀ H ₂₀ O ₄	81.07	4.54
IIIb	55	160–162 (cyclohexane)	82.25	5.68	C ₃₄ H ₂₈ O ₄	82.24	5.68
IVa	95	195–196 (1,4-dioxane)	81.03	4.54	C ₃₀ H ₂₀ O ₄	81.07	4.54
IVb	87	241–243 (1,4-dioxane)	81.35	5.10	C ₃₂ H ₂₄ O ₄	81.34	5.12
IVc	85	214–216 (<i>i</i> -PrOH)	82.23	5.69	C ₃₄ H ₂₈ O ₄	82.24	5.68
Va	94	157–158 (CCl ₄)	83.20	5.31	C ₂₉ H ₂₂ O ₃	83.23	5.30
Vb^a	83	205–206 (1,2-dichloroethane)	64.89	3.70	C ₂₂ H ₁₅ BrO ₃	64.88	3.71
Vc	79	151–153 (CCl ₄)	77.38	5.44	C ₂₄ H ₂₀ O ₄	77.40	5.41
Vd^b	78	137–139 (CCl ₄ –hexane)	66.25	4.39	C ₂₄ H ₁₉ BrO ₃	66.22	4.40
Ve	75	132–133 (hexane)	79.04	6.60	C ₂₂ H ₂₂ O ₃	79.02	6.63
Vf	87	141–142 (cyclohexane)	79.53	7.24	C ₂₄ H ₂₆ O ₃	79.53	7.23
Vg	90	165–166 (cyclohexane)	80.98	7.04	C ₂₇ H ₂₈ O ₃	80.97	7.05
VIa^c	88/82	186–187 (<i>i</i> -PrOH)	80.22	5.80	C ₂₂ H ₁₉ NO ₂	80.22	5.81
VIb^d	93	189–190 (<i>i</i> -PrOH)	76.52	5.50	C ₂₂ H ₁₉ NO ₃	76.50	5.54

^a Found Br, %: 19.39. Calculated Br, %: 19.62.

^b Found Br, %: 18.07. Calculated Br, %: 18.35.

^c Found N, %: 4.20. Calculated N, %: 4.25.

^d Found N, %: 3.98. Calculated N, %: 4.06.

shift was observed previously in the thermolysis of 3,3,5-tribenzoyl-5-phenyl-3,4-dihydro-2*H*-pyran-2,4-dione [10] which is structurally related to **III**.

We also examined thermal decomposition of furandiones **Ia–Ic** in the presence of carbonyl compounds. A mixture of **Ia–Ic** and benzyl phenyl ketone, substituted benzaldehyde, cycloalkanone, or 2-adamantanone was heated in an inert aprotic solvent (dowtherm A [11], 1,2,4-trimethylbenzene, or *m*-xylene) at 140–170°C for 20–30 min. As in the preceding cases, aroyl(phenyl)ketenes **IIa–IIc** were generated as a result of thermal decarbonylation of furandiones **Ia–Ic**. The subsequent [4+2]-cycloaddition of aroylketene **II** (through the C=C–C=O fragment) at the C=O group of aldehyde or ketone afforded 6-aryl-5-phenyl-4*H*-1,3-dioxin-4-ones **Va–Vg** (Table 1). Compounds **Va–Vg** are colorless crystalline substances, readily soluble in common organic solvents, poorly soluble in alkanes, and insoluble in water.

The IR spectra of **Va–Vg** (Table 2) contain a strong lactone carbonyl band at 1720–1740 cm⁻¹ and a weak band at 1610–1615 cm⁻¹, the latter belonging to stretching vibrations of the C⁵=C⁶ band. The observed

IR patterns are in agreement with published data for analogs of **V** having no substituent on C⁵ [12]. The ¹H NMR spectra of **Va–Vg** (Table 2) contain signals from protons of the aromatic substituents and groups attached thereto, a doublet of doublets (*AB* system) from diastereotopic protons of the benzyl CH₂ group (δ 3.54 and 3.61 ppm, compound **Va**), a singlet from 2-H (δ 6.56–7.05 ppm, **Vb–Vd**), methylene proton signals (δ 1.62–2.41 ppm, **Ve** and **Vf**), and signals from protons of the adamantane moiety in **Vg** (δ 1.73–2.67 ppm). The following signals were present in the ¹³C NMR spectrum of **Vf**, δ_C, ppm: 126.88–134.43 (C_{arom}), 18.50–36.76 (CH₂, CH₃), 110.16 (C²), 160.32 (C⁴), 108.72 (C⁵), 163.52 (C⁶). The mass spectrum of **Vb** contains low-intense molecular ion peak, *m/z* 407 (*I*_{rel} 1%) and fragment ion peaks with *m/z* (*I*_{rel}, %) 222 (60) [Ph(PhCO)C=C=O]⁺, 105 (100) [PhCO]⁺, and 77 (34) [Ph]⁺.

Heating of dioxinone **Va** in dowtherm A at 140–142°C for 20–25 min in the presence of arylamines induced its retro-Diels–Alder decomposition with elimination of benzyl phenyl ketone and generation of benzoyl(phenyl)ketene. The latter reacted with aryl-

Table 2. IR and ^1H NMR spectra of compounds **I** and **III–VI**

Comp. no.	IR spectrum, ν , cm^{-1}	^1H NMR spectrum, δ , ppm
Ib	1825 ($\text{C}^2=\text{O}$), 1715 ($\text{C}^3=\text{O}$)	
Ic	1825 ($\text{C}^2=\text{O}$), 1730 ($\text{C}^3=\text{O}$)	2.11 s (3H, Me), 2.30 s (3H, Me), 7.16–7.30 m (8H, H_{arom})
IIIa	1745 ($\text{C}^2=\text{O}$), 1690 ($\text{C}^4=\text{O}$), 1652 (PhCO), 1610 w ($\text{C}^5=\text{C}^6$)	6.98–7.72 m (H_{arom})
IIIb	1720 ($\text{C}^2=\text{O}$), 1695 ($\text{C}^4=\text{O}$), 1660 (ArCO), 1613 w ($\text{C}^5=\text{C}^6$)	2.52 s (3H, Me), 2.54 s (3H, Me), 2.56 s (3H, Me), 2.58 s (3H, Me), 6.90–7.70 m (16H, H_{arom})
IVa	1755 ($\text{C}^2=\text{O}$), 1735 (PhOCO), 1608 w ($\text{C}^5=\text{C}^6$)	7.04 d (2H), 7.25–7.81 m (18H, H_{arom})
IVb	1735 ($\text{C}^2=\text{O}$), 1730 (4-OCO), 1610 w ($\text{C}^5=\text{C}^6$)	2.31 s (3H, Me), 2.34 s (3H, Me), 7.11–7.48 m (18H, H_{arom})
IVc	1747 ($\text{C}^2=\text{O}$), 1720 (4-OCO), 1610 w ($\text{C}^5=\text{C}^6$)	2.52 s (6H, Me), 2.54 s (6H, Me), 6.96–7.56 m (16H, H_{arom})
Va	1740 ($\text{C}^4=\text{O}$), 1610 w ($\text{C}^5=\text{C}^6$)	3.54 d and 3.61 d (AB), 6.75–7.50 m (20H, H_{arom})
Vb	1728 ($\text{C}^4=\text{O}$), 1612 w ($\text{C}^5=\text{C}^6$)	7.05 s (1H, 2-H), 7.20–7.70 m (14H, H_{arom})
Vc	1728 ($\text{C}^4=\text{O}$), 1615 w ($\text{C}^5=\text{C}^6$)	2.1 s (3H, Me), 3.5 s (3H, OMe), 7.0 s (1H, 2-H), 7.2–7.9 m (13H, H_{arom})
Vd	1740 ($\text{C}^4=\text{O}$), 1613 w ($\text{C}^5=\text{C}^6$)	2.17 s (3H, Me), 2.22 s (3H, Me), 6.94 s (1H, 2-H), 7.00–7.65 m (12H, H_{arom})
Ve	1730 ($\text{C}^4=\text{O}$), 1597 w ($\text{C}^5=\text{C}^6$)	2.07 s (3H, Me), 2.19 s (3H, Me), 1.80–1.95 m and 2.25–2.53 m (8H, CH_2), 6.98–7.25 m (8H, H_{arom})
Vf	1720 ($\text{C}^4=\text{O}$), 1615 w ($\text{C}^5=\text{C}^6$)	2.07 s (3H, Me), 2.15 s (3H, Me), 1.62 s and 2.35 q (12H, CH_2), 6.98–7.16 m (8H, H_{arom})
Vg	1735 ($\text{C}^4=\text{O}$), 1610 w ($\text{C}^5=\text{C}^6$)	1.98 s (3H, Me); 2.23 s (3H, Me); 1.78 t, 1.92 t, 2.05 s, and 2.67 s (14H, adamantane); 6.96–7.16 m (8H, H_{arom})
VIa	1689 ($\text{C}^3=\text{O}$), 1670 ($\text{C}^1=\text{O}$), 3300 (NH), 1560 (δNH)	2.28 s (3H, Me), 5.90 s (1H, CH), 7.00–8.05 m (14H, H_{arom}), 10.10 s (1H, NH)
VIb	1690 ($\text{C}^3=\text{O}$), 1670 ($\text{C}^1=\text{O}$), 3320 (NH), 1570 (δNH)	3.70 s (3H, OMe), 5.94 s (1H, CH), 6.85–8.03 m (14H, H_{arom}), 10.29 s (1H, NH)

amine, yielding *N*-aryl- α -phenylbenzoylacetyl amides **VIa** and **VIb**. Amides **VIa** and **VIb** (Table 1) are colorless crystalline substances, readily soluble in common organic solvents, poorly soluble in alkanes, and insoluble in water. The IR spectra of **VIa** and **VIb** (Table 2) contain a band at 3300–3340 cm^{-1} due to NH stretching vibrations, amide I band at 1670–1675 cm^{-1} , ketone carbonyl band at 1689–1690 cm^{-1} , and amide II band at 1560–1570 cm^{-1} . In the ^1H NMR spectra, the 2-H signal appears as a singlet at δ 5.90–5.94 ppm, and the NH proton gives a singlet at δ 10.10–10.29 ppm. Also, signals from aromatic protons and protons of methyl (**VIa**) or methoxy group (**VIb**) were present.

The structure of amide **VIa** was proved by independent synthesis, by thermolysis of *N*-*p*-tolyl-2,4-dioxo-3,4-diphenylbutanamide (**VII**) [13].

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The ^1H NMR spectra were measured on RYa-2310 (60 MHz) and Bruker DRX-400 (400 MHz) instruments using $\text{DMSO}-d_6$ as solvent and TMS as internal reference. The ^{13}C NMR spectra were obtained on a Bruker DRX-400 spectrometer at 100 MHz using $\text{DMSO}-d_6$ as solvent.** The mass spectra (70 eV) were run on an MKh-1320 mass spectrometer. The purity of the products was checked by TLC on Silufol plates using ethyl acetate, ethyl acetate–benzene (1:5),

** The NMR studies were performed at the *Ural–YaMR TsKP* (Russian Foundation for Basic Research, project no. 00-03-40139).

and benzene as eluent; the chromatograms were developed with iodine vapor.

5-Aryl-4-phenyl-2,3-dihydrofuran-2,3-diones Ia–Ic [12]. A solution of 0.1 mol of 1-aryl-1-trimethylsiloxy-2-phenylethene and 0.1 mol of oxalyl chloride in 60 ml of dry chloroform was heated for 2–4 h under reflux. The solvent was distilled off under reduced pressure (water-jet pump) on heating on a water bath, 100 ml of dry hexane was added, the mixture was heated to the boiling point and cooled, and the precipitate was filtered off.

3-Aroyl-6-aryl-3,5-diphenyl-3,4-dihydro-2H-pyran-2,4-diones IIIa and IIIb. A solution of 0.01 mol of furandione **Ia** or **Ic** in 20 ml of dry *p*-xylene was heated for 20–30 min under reflux. The solvent was removed.

4-Aroyloxy-6-aryl-3,5-diphenyl-2H-pyran-2-ones IVa–IVc. A solution of 0.01 mol of furandione **Ia–Ic** in 20 ml of dry 1,2,4-trimethylbenzene was heated for 2–3 h under reflux, and the solvent was removed.

6-Aryl-5-phenyl-4H-1,3-dioxin-4-ones Va–Vg. A solution of 0.01 mol of furandione **Ia–Ic** and 0.01 mol of the corresponding carbonyl compound in 20 ml of dry *p*-xylene was heated for 30–40 min under reflux, and the solvent was removed.

N-Aryl- α -benzoyl(phenyl)acetamides VIa and VIb. *a.* A solution of 0.01 mol of compound **Va** and 0.01 mol of *p*-toluidine or *p*-anisidine in 5 ml of dowtherm A was heated to the boiling point. It was then cooled, 50 ml of hexane was added, and the precipitate was filtered off.

b. A solution of 0.005 mol of *N-p*-tolyl-2,4-dioxo-3,4-diphenylbutanamide (**VII**) in 3 ml of dowtherm A was heated to the boiling point. The mixture was cooled, 25 ml of hexane was added, and the precipitate of amide **VIa** was filtered off.

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