CHEMISTRY OF OXALYL DERIVATIVES OF METHYL KETONES.
40.* REACTION OF 5-ARYL-2,3-DIHYDRO-2,3-FURANDIONES WITH ARYL AND AROYL CYANAMIDES

Yu. S. Andreichikov and D. D. Nekrasov

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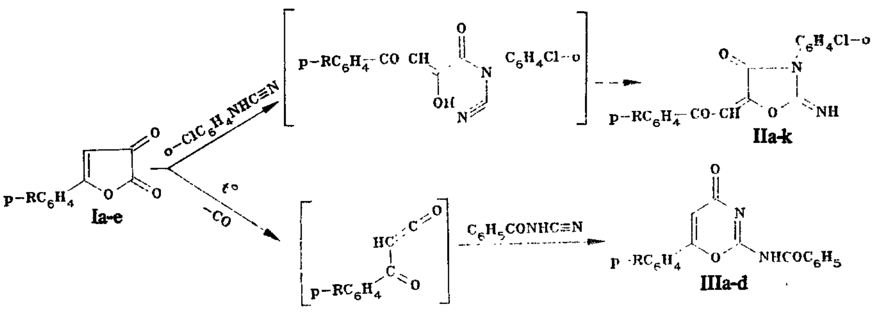
Starting from 5-aryl-2,3-dihydro-2,3-furandiones and benzoyl cyanamide, 2-benzoylamino-6-aryl-1,3-oxazin-4-ones were obtained. It was shown that on reaction of o-chlorophenyl cyanamide with furandiones, 2-imino-3-(o-chlorophenyl)-5-phenacyliden-4-oxazolidones are formed which in acid medium rearrange to 3-(o-chlorophenyl)-5-phenacylideneimidazolidin-2,4-diones and on thermolysis in acid medium they form 2-(o-chloroanilino)-6-aryl-1,3-oxazin-4-ones.

We have previously shown that aroyl ketones formed by thermal decarbonylation of 5-aryl-2,3-dihydro-2,3-furandiones (I) enter into a [4π + 2π]-cycloaddition reaction at the $C \equiv N$ bond of disubstituted cyanamides, the products of which are 2-substituted 6-aryl-1,3-oxazin-4-ones [1]. At the same time, it is known that BH nucleophiles under mild conditions open up the furan ring of compound (I), forming the corresponding derivatives of aroylpyruvic acids [2]. For that reason investigation of the reaction of compound (I) with monosubstituted cyanamides, combining the properties of dienophiles and BH nucleophiles, is of interest.

As we have established, compound (I) reacts with o-chlorophenyl cyanamides at 20-40°C, i.e., under conditions preventing the formation of aroyl ketones. The reaction products are 2-imino-3-(o-chlorophenyl)-5-phenacyliden-4-oxazolidones (IIa-e), evidently formed as a result of breaking the furandione ring of compound (I) by the amino group of the substituted cyanamide. The intermediately formed o-chlorophenyl cyanamides of aroylpyruvic acids, like other amides of these acids [2], are entirely in the α-enol form. The reaction is accompanied by addition of the enol hydroxyl to the $C \equiv N$ bond.



I, II, III a R=H; b R=CH_3; c R=Cl; d R=Br; e R=OCH_3

Benzoyl cyanamide reacts with compound (I) may under conditions of decarbonylation of the latter (80-110°C). In this instance, just as in the case of disubstituted cyanamides products are formed from [4π + 2π]-cycloadditions of aroyl ketenes to the $C \equiv N$ bond of the benzoyl cyanamide, i.e., 2-benzolyamino-6-aryl-1,3-oxazin-4-ones (IIIa-d), which is caused by the lowered nucleophilicity of the nitrogen atom associated with the $C \equiv N$ group on the introduction of the benzoyl substituent into the cyanamide. The benzoyl cyanamide as a result loses its capability for breaking the furandione ring as a result of which the possibility of decarbonylation of compound (I) exists as well as the subsequent reaction of cycloaddition.

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*For Communication 39, see [1].

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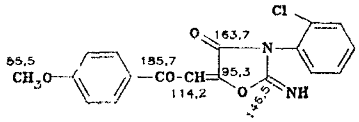
In the IR spectra of compounds (IIa-e) are noted absorption bands caused by N—H stretching in the >N—H (3250-3300 cm^{-1}), the carbonyl group in position 4 of the oxazolidone ring (1725-1732 cm^{-1}), the C≡B bond (1678-1681 cm^{-1}), the carbonyl groups in the phenacylidene substituent (1621-1635 cm^{-1}), which is in agreement with the data of [4]. In the PMR spectra of these compounds taken in $CDCl_3$ are observed the singlet of the methine proton at 6.71-7.05 ppm, and the multiplet of the aromatic protons with a center at 7.63-7.71 ppm on which is superimposed the signal of the proton of the imino group. In the ^{13}C NMR spectrum of compound (IIe) are contained the signals

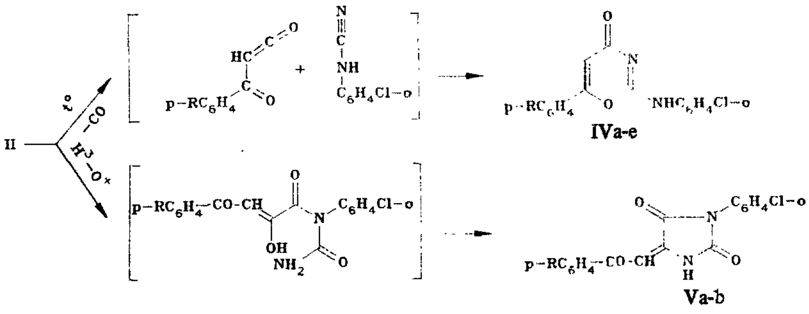


Moreover, in the spectra are present the superimposed signals of the two benzene rings at 131.6, 130.9, 129.9, 129.7, 129.6, 129.2 and 128.3 ppm, the assignments of which are difficult.

In the IR spectra of compounds (IIIa-d) are noted intensive absorption bands at 1712-1725 (C=O in $NHCOC_6H_5$), 1648-1661 (C=O in the oxazine ring), and also broad weak bands around 3190 cm^{-1} (NH). In the PMR spectra of these compounds are observed the singlet of the methine proton at 6.38-6.51 ppm, the multiplet of the aromatic protons with a center at 7.68-7.76 ppm, and also the broad signal of the NH group at 11.50 ppm.

In the mass spectrum of compound (IIId) the molecular ion peak at m/z 370/372 and also the peaks of ion fragments $[M-C_6H_5]^+$ (293/295), $[M-C_6H_4CO]^+$ (267/269), $[BrC_6H_4COCH{=}C{=}O]^{+\cdot}$ (224/226), $[BrC_6H_4CO]^+$ (183/185), $[BrC_6H_4]^+$ (155/157), $[C_6H_5CONH]^+$ (121), $[C_6H_5CO]^+$ (105), $[C_6H_5]^+$ (77), and $[COCHCO]^+$ (69) are present. The IR, PMR, and mass spectra data obtained agree well with the corresponding data for 2-benzoylamino-6-methyl-1,3-oxazin-4-ones [5].

On heating in xylene, compounds (IIa-e) are subjected to decarbonylation with the formation of 2-(o-chloroanilino)-6-aryl-1,3-oxazin-4-ones. As in the instance of the thermolysis of compound (I) the reaction in this case evidently proceeds with the formation of aroyl ketenes and of cyanamides then goes over to the [4π + 2π]-cycloaddition reaction [6].



IV, Va R=H· b R=CH_3; c R=Cl; d R=Br; e R=OCH_3

The IR and PMR spectra of compounds (IVa-e) are analogous to the spectra of compounds (IIIa-e). However, in the IR spectra of compounds (Ia-e) the N—H stretching band is shifted to 3248-3352 cm^{-1} and the band for the amide carbonyl group in position 2 is absent, which agrees with the data of [7]. The mass spectrum of compound (IVd) contains a peak for the molecular ion at m/z 328/330 and also peaks for ion fragments $[M-Cl]^+$(293), $[CH_3OC_6H_4COCH{=}C{=}O]^{+\cdot}$ (176), $[ClC_6H_4NHC{\equiv}N]^{+\cdot}$ (152/154), $[CH_3OC_6H_4CO]^+$ (135), and $[ClC_6H_4NH]^+$ (125/127) .

On heating compounds (IIa,b) in dioxane in the presence of conc. HCl there was obtained 3-(o-chlorophenyl)-5-phenacylideneimidazolidin-2,4-diones (Va, b). Evidently, the rearrangement of compounds (II) into compounds (V) proceeds through the intermediate formation of ureides of aroylpyruvic acids.

In the IR spectra of compounds (Va, b) were recorded bands at 3328-3338 cm^{-1} (NH), 1780-1790 cm^{-1} (C=O in position 4), 1740-1752 (C=O in position 2), and 1668-1681 (C=O in the side chain). In the UV spectra λ_{max} is found at about 330 nm. Spectral characteristics of compounds (Va, b) are similar to the spectral characteristics of the previously described 5-

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Mp, deg C	Found, %				Molecular formula	Calculated, %				Yield, %
		C	H	Hal	N		C	H	Hal	N	
II a	152—154	62,50	3,35	10,75	8,52	$C_{17}H_{11}ClN_2O_3$	62,49	3,36	10,85	8,57	92
II b	145—146	63,39	3,71	10,35	8,12	$C_{18}H_{13}ClN_2O_3$	63,45	3,82	10,41	8,22	88
II c	155—157	56,45	2,73	19,62	7,71	$C_{17}H_{10}Cl_2N_2O_3$	56,53	2,77	19,65	7,76	89
II d	148—150	50,25	2,44		6,85	$C_{17}H_{10}BrClN_2O_3$	50,33	2,47		6,90	90
II e	169—171	60,46	3,62	9,87	7,79	$C_{18}H_{13}ClN_2O_4$	60,59	3,64	9,94	7,85	89
III a	169—170	70,12	4,18		9,54	$C_{17}H_{12}N_2O_3$	69,86	4,11		9,58	67
III b	211—212	70,44	4,40		9,18	$C_{18}H_{14}N_2O_3$	70,58	4,57		9,15	70
III c	214—215	62,61	3,28	10,88	8,65	$C_{17}H_{11}ClN_2O_3$	62,49	3,37	10,85	8,57	65
III d	194—195	55,11	3,04	21,44	7,52	$C_{17}H_{11}BrN_2O_3$	54,98	2,96	21,56	7,54	66
IV a	196—198	64,21	3,74	11,72	9,12	$C_{16}H_{11}ClN_2O_2$	64,33	3,68	11,87	9,38	74
IV b	222—224	65,30	4,15	11,29	8,92	$C_{17}H_{13}ClN_2O_2$	65,29	4,16	11,35	8,96	89
IV c	244—245	57,61	3,11	21,08	8,33	$C_{16}H_{10}Cl_2N_2O_2$	57,67	3,00	21,29	8,41	76
IV d	239—240	50,81	2,57		7,22	$C_{16}H_{10}BrClN_2O_2$	50,86	2,65		7,42	72
IV e	219—220	61,87	3,93	10,41	8,46	$C_{17}H_{13}ClN_2O_3$	62,11	3,95	10,79	8,52	92
V a	212—214	62,50	3,35	10,82	8,54	$C_{17}H_{11}ClN_2O_3$	62,49	3,36	10,85	8,57	85
V b	223—224	63,25	3,71	10,50	8,11	$C_{18}H_{13}ClN_2O_3$	63,44	3,81	10,41	8,22	81

phenylacylideneimidazolidin-2,4-diones not having substituents in position 3 [8].

EXPERIMENTAL

The IR spectra were recorded on a UR-20 apparatus in mineral oil mulls; the UV spectra, on a Specord UV-Vis spectrograph in alcohol. The PMR spectra were recorded on the PC-60. The ^{13}C NMR spectra were taken on a Bruker HX-90 in DMSO-D_6. Mass spectra were obtained on an AEJM-50 instrument.

Characteristics of the compounds synthesized are shown in Table 1.

2-Imino-3-(o-chlorophenyl)-5-p-R-phenacylidene-4-oxazolidones (IIa-e). To a suspension of 0.01 mole of compound (I) in 20 ml of dry benzene was added 0.01 mole of o-chlorophenyl cyanamide at 20-40°C. The reaction mixture was stirred 2-4 h at room temperature. The precipitate was recrystallized from ethyl acetate.

2-Benzoylamino-6-aryl-1,3-oxazin-4-ones (IIIa-d). A suspension of 0.01 mole of furandione (I) and 0.01 mole of benzoyl cyanamide in 25 ml anhydrous toluene was refluxed 1 h. The residue after removal of the solvent was recrystallized from ethyl acetate.

2-(o-Chloroanilino)-6-aryl-1,3-oxazin-4-ones (IVa-e). A suspension of 0.01 mole of oxazolidone (II) in 15 ml xylene was refluxed 1 h. The residue after solvent removal was recrystallized from ethanol.

3-(o-Chlorphenyl)-5-p-R-phenacylideneimidazolidin-2,4-diones (Va, b). To a suspension of 0.01 mole of oxazolidone (II) in 5 ml dioxane was added 5 ml of conc. HCl and the mixture heated 2 h at 100-102°C. After cooling the solution the precipitate was filtered off, washed with water, dried, and recrystallized from acetonitrile.

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