Reactions of azlactones with amino compounds. VI.* Synthesis of some *p*-nitrophenylhydrazides of α,β-disubstituted acrylic acids and 1-arylamino-2-aryl-4-arylidene-2-imidazoline-5-ones

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Treatment of unsaturated azlactones with *p*-nitrophenylhydrazine in boiling xylene gives the corresponding α,β-disubstituted acrylic acid *p*-nitrophenylhydrazides. Boiling in acetic acid of some unsaturated azlactones with phenylhydrazine or *p*-nitrophenylhydrazine gave in one step *N*-anilino- or *N*-(*p*-nitroanilino)-2,4-disubstituted 2-imidazoline-5-ones.

Ненасыщенные азлактоны расщепляются с *п*-нитрофенилгидразином в среде кипящего ксилола с образованием *п*-нитрофенилгидразидов соответствующих α,β-двухзамещенных акриловых кислот. Кипячением некоторых ненасыщенных азлактонов с фенилгидразином или с *п*-нитрофенилгидразином в уксусной кислоте подготовлены в одной реакционной степени *N*-анилино- или *N*-(*п*-нитроанилино)-2,4-двухзамещенные 2-имидазолин-5-оны.

The cleavage of unsaturated azlactones (*I*) with hydrazine and some derivatives thereof, as well as cyclization of the formed products was dealt with in previous parts of this Series [1—5]. The cleavage of azlactones with *p*-nitrophenylhydrazine and the structure of the products (*II*) have also been reported [3]. The present work describes further *p*-nitrophenylhydrazides of α,β-disubstituted acrylic acids *IIa—d* (Table 1, Scheme 1) obtained in the same manner, *i.e.* by boiling unsaturated azlactones with an excess of *p*-nitrophenylhydrazine in xylene. The cyclizations of the obtained products and other substances of the same class, to give substituted imidazolinones (*III*), are described elsewhere [6]. The *N*-anilino-2,4-disubstituted 2-imidazoline-5-ones (*IIIa—k,* Table 2) can be obtained conveniently in one step by treatment of the respective azlactone with phenylhydrazine or *p*-nitrophenylhydrazine in boiling acetic acid (Scheme 1). The reaction of azlactone with phenylhydrazine and *p*-nitrophenylhydrazine is conducted with a large excess of the former and one molar proportion of the latter. There is only one imidazolinone

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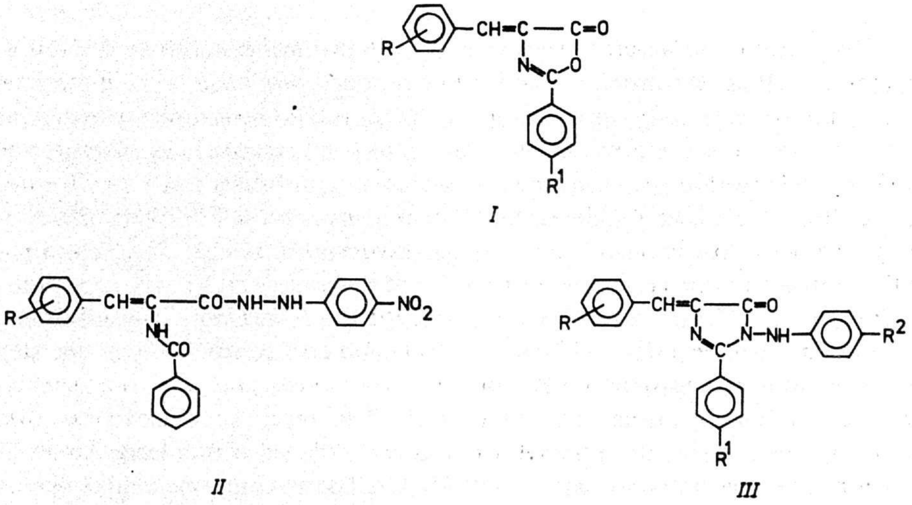
* For Part V see Ref. [5].

of this type described in the literature [7]. The identity of the prepared imidazolinones, which can be alternatively obtained by cyclization of the corresponding *p*-nitrophenylhydrazides [6], was determined by i.r. spectroscopy.

Table 1

p-Nitrophenylhydrazides of α,β-disubstituted acrylic acids (*II*)

Compound	R	Formula	*M*	Calculated/found			Yield %	M.p. °C
				% C	% H	% N		
IIa	*p*-Methoxy	$C_{23}H_{20}O_5N_4$	432.42	63.88	4.66	12.96	99.0	266—269
				63.60	4.62	12.85		
IIb	*p*-Chloro	$C_{22}H_{17}O_4N_4Cl$	436.85	60.48	3.92	12.82	97.1	264—267
				60.21	3.96	12.83		
IIc	3,4,5-Trimethoxy	$C_{25}H_{24}O_7N_4$	492.47	60.97	4.91	11.38	93.9	261—264
				61.17	4.78	11.19		
IId	3,4-Methylenedioxy	$C_{23}H_{18}O_6N_4$	446.41	61.88	4.06	12.55	90.8	256—259
				62.14	4.20	12.39		



I

II

III

Scheme 1

Table 2

1-Arylamino-2-aryl-4-arylidene-2-imidazoline-5-ones (*III*)

Compound	R	R^1	R^2	Formula	*M*	Calculated/found % C	% H	% N	Yield %	M.p. °C
IIIa	*o*-Methoxy	H	H	$C_{23}H_{19}O_2N_3$	369.41	74.78	5.18	11.38	94.1	211—213
						74.80	5.34	11.55		
IIIb	*p*-Methoxy	H	H	$C_{23}H_{19}O_2N_3$	369.41	74.78	5.18	11.38	82.3	222—224
						74.69	5.38	11.09		
IIIc	*p*-Chloro	H	H	$C_{22}H_{16}ON_3Cl$	373.85	70.68	4.31	11.24	81.4	242—244
						70.87	4.47	11.34		
IIId	*p*-Nitro	H	H	$C_{22}H_{16}O_3N_4$	384.38	68.74	4.20	14.58	90.3	259—261
						68.55	4.31	14.32		
IIIe	3,4-Methylenedioxy	H	H	$C_{23}H_{17}O_3N_3$	383.39	72.05	4.47	10.96	92.8	238—241
						72.24	4.64	10.72		
IIIf	3,4,5-Trimethoxy	H	H	$C_{25}H_{23}O_4N_3$	429.46	69.91	5.40	9.79	87.3	241—242
						70.10	5.23	10.09		
IIIg	H	—NO_2	H	$C_{22}H_{16}O_3N_4$	384.38	68.74	4.20	14.58	97.3	250—252
						68.51	4.31	14.31		
IIIh	H	H	—NO_2	$C_{22}H_{16}O_3N_4$	384.38	68.74	4.20	14.58	93.4	259—261
						68.57	4.39	14.34		
IIIi	*o*-Methoxy	H	—NO_2	$C_{23}H_{18}O_4N_4$	414.41	66.66	4.38	13.52	95.6	216—218
						66.70	4.62	13.77		
IIIj	*p*-Methoxy	H	—NO_2	$C_{23}H_{18}O_4N_4$	414.41	66.66	4.38	13.52	91.4	287—290
						66.80	4.34	13.48		
IIIk	*p*-Methoxy	—$NHCOCH_3$	—NO_2	$C_{25}H_{21}O_5N_5$	471.46	63.68	4.49	14.86	92.4	335—337
						63.60	4.56	14.56		

Experimental

Melting points were determined on a Kofler hot-stage. The microanalyses were performed with Perkin—Elmer Elemental Analyzer, Model 240. The i.r. spectra in Nujol mull were obtained with UR-20 (Zeiss, Jena) spectrometer. The substances were dried at 140°C for 4 h. The starting unsaturated azlactones *Ia—i* were prepared according to the literature (Table 3).

Table 3

Azlactones *Ia—i*

Ia	R = H	R^1 = H	Ref. [8]
Ib	R = 2-CH_3	R^1 = H	Ref. [9]
Ic	R = 4-CH_3	R^1 = H	Ref. [10]
Id	R = 4-NO_2	R^1 = H	Ref. [11]
Ie	R = 3,4-O_2CH_2	R^1 = H	Ref. [11]
If	R = 4-Cl	R^1 = H	Ref. [12]
Ig	R = 3,4,5-$(CH_3O)_3$	R^1 = H	Ref. [13]
Ih	R = H	R^1 = NO_2	Ref. [14]
Ii	R = 4-CH_3O	R^1 = $NHCOCH_3$	Ref. [15]

p-Nitrophenylhydrazides of substituted acrylic acids (IIa—d)

A mixture of the respective azlactone (1 equiv.) and *p*-nitrophenylhydrazine (2 equiv.) in tenfold (w/w) of dry xylene was heated under reflux for 15 min. The solid dissolved after 5 min and at the end of the reaction time crystalline material started to separate. The mixture was cooled, filtered, the solid sucked dry and washed with ethanol. Compounds *IIa—c* were purified by crystallization (twice) from ethanol—benzene (1 : 1) and compound *IId* by crystallization from ethanol (twice). The relevant data for the prepared substances are given in Table 1.

1-Arylamino-2-aryl-4-arylidene-2-imidazoline-5-ones (IIIa—k)

A mixture of the respective azlactone (1 equiv.) and phenylhydrazine (3 equiv.), or *p*-nitrophenylhydrazine (1 equiv.) in a twofold (w/w) of acetic acid was heated under reflux for 4 h (*IIIh* is formed after 10 min). The mixture was cooled to room temperature and when the product separated in a crystalline form (2 h for *IIIa, IIIc—g, IIIj,* and *IIIk* ; 48 h for *IIIb*) the mixture was filtered and the crystals washed with cold ethanol and dried. Compound *IIIi* was induced to crystallize by an addition of two volumes of cold water to the reaction mixture. The prepared substances were purified by recrystallization (twice) from

Table 4

Infrared spectral data for substituted 2-imidazoline-5-ones

Compound	cm^{-1}
IIIa	703, 750, 822, 865, 888, 915, 1022, 1042, 1160, 1182, 1230, 1252, 1280, 1296, 1392, 1482, 1528, 1595, 1695
IIIb	752, 835, 1030, 1162, 1175, 1258, 1290, 1308, 1495, 1512, 1595, 1640, 1705
IIIc	748, 760, 828, 928, 962, 1012, 1051, 1105, 1173, 1243, 1290, 1307, 1375, 1487, 1521, 1638, 1708
IIId	760, 775, 830, 851, 1182, 1240, 1285, 1348, 1450, 1512, 1595, 1632, 1728
IIIe	760, 808, 852, 900, 932, 1042, 1162, 1225, 1270, 1339, 1396, 1485, 1495, 1596, 1615, 1638, 1710
IIIf	760, 798, 808, 854, 883, 900, 934, 1042, 1108, 1166, 1227, 1290, 1340, 1456, 1496, 1598, 1616, 16,40, 1711
IIIg	758, 864, 1168, 1293, 1346, 1519, 1592, 1605, 1639, 1709
IIIh	752, 770, 778, 832, 845, 932, 972, 1025, 1048, 1112, 1128, 1160, 1256, 1318, 1449, 1522, 1600, 1718, 1735
IIIi	751, 762, 1043, 1161, 1182, 1250, 1338, 1488, 1595, 1631, 1710
IIIj	750, 788, 813, 843, 903, 1029, 1112, 1162, 1258, 1295, 1308, 1350, 1426, 1515, 1600, 1648, 1718, 1732
IIIk	752, 842, 1028, 1112, 1162, 1178, 1260, 1308, 1349, 1485, 1512, 1600, 1639, 1688

ethanol (*IIIa—d, IIIg, IIIh, IIIk*) or ethanol—benzene (1:1) (*IIIe, IIIf, IIIi, IIIj*). The characteristic data for yellow crystalline products are given in Table 2, and their spectral data in Table 4.

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