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Translated by I. Capek

Preparation of 2,4-Dichlorobenzoyl-Substituted Isoxazolines and Isoxazoles

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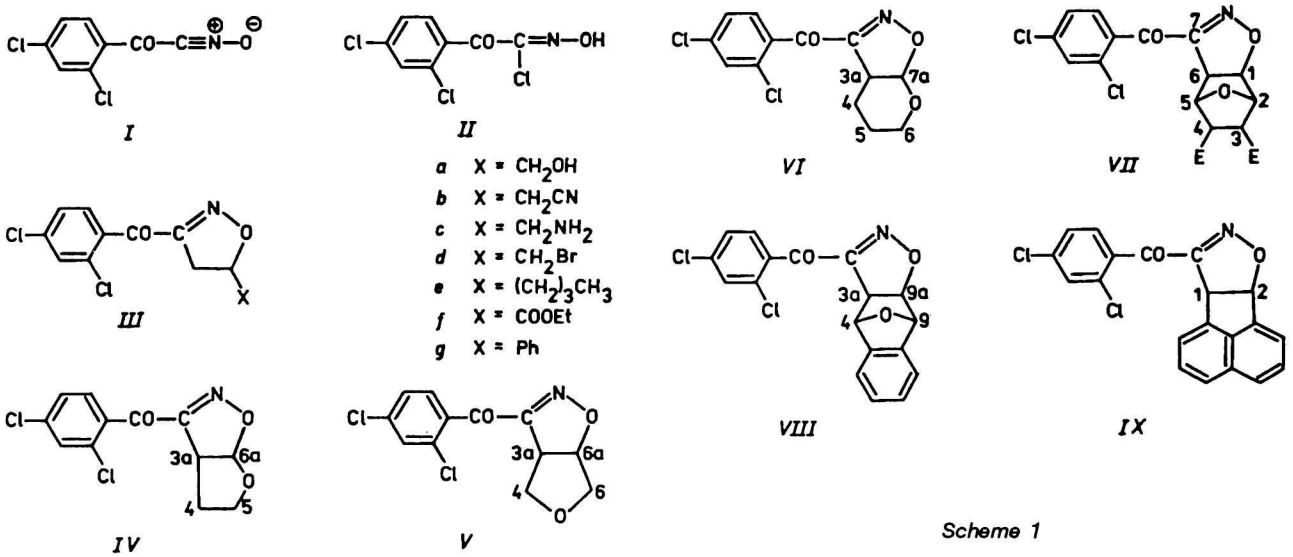
Received 4 June 1991

The synthesis of 2,4-dichlorobenzoyl-substituted isoxazolines and isoxazoles through the 1,3-dipolar cycloaddition of 2,4-dichlorobenzoylnitrile oxide is described. The regio- and stereoselectivity of the nitrile oxide cycloaddition with alkenes, alkynes, and oxygen-containing heterocycles is discussed. 2,4-Dichlorobenzoylnitrile oxide reacts with allylamine and yields the unexpected open-chain *N*-substituted amide oxime *XIV* and amide *XV*.

2,4-Dichloroacetophenone is a versatile and important intermediate for the preparation of biologically effective compounds. The 2,4-dichlorobenzoyl building block [1—3] is a characteristic feature of some commercial agrochemicals and drugs, and therefore as a part of research into applications of the 1,3-dipolar cycloadditions to the synthesis of antifungal compounds, we have made use of products originating from 1,3-dipolar cycloadditions leading to isoxazolines and isoxazoles substituted by the afore-mentioned building block. So far, only one example of the 1,3-dipolar cycloaddition of 2,4-dichlorobenzoylnitrile oxide on 3-butyn-1-ol has been reported [4]; this paper describes the reactivity and regio- and stereoselectivity of nitrile oxide *I* in 1,3-dipolar cycloaddition to some alkenes, alkynes, and oxygen-containing heterocycles.

2,4-Dichlorobenzoylnitrile oxide (*I*) was generated *in situ* from 2,4-dichlorophenylglyoxylohydroximoyl chloride (*II*, see Ref. [5]) and triethylamine in the presence of dipolarophiles. Cycloaddition of the nitrile oxide *I* to various alkenes such as allyl alcohol, allyl bromide, allyl cyanide, hexene, ethyl 2-propenoate, and styrene was regioselective and gave 5-substituted 3-(2,4-dichlorobenzoyl)isoxazolines *IIIa—IIIg* (Scheme 1) in modest yields (Table 1). The structure of *IIIa—IIIg* was determined by comparing the chemical shift data for H-5 methine and H-4 methylene protons with those published for the analogous 3-phenyl-substituted derivatives *III* [6] and by analyses of the ^{13}C NMR spectra. The individual signals were ascribed by means of *J*-resolved and heterocorrelated NMR spectroscopy.

Dipolar cycloadditions to monosubstituted alkenes led mainly to 5-substituted isoxazolines [7]. The FMO theory predicts [8] that 4-substituted regioisomers should be obtained where there is greater frontier interaction HOMO(dipole)—LUMO(dipolarophile). Substitution at the 1,3-dipole



Scheme 1

enhances its nucleophilic or electrophilic character, depending on the nature of substituents. The substitution with electron-withdrawing 2,4-dichlorobenzoyl group causes [9] a drop in LUMO energy of the dipole in comparison with the phenyl group; the frontier interaction LUMO(dipole)—HOMO(dipolarophile) is dominant [10] and therefore no formation of a 4-substituted isoxazoline could be expected with the cycloaddition of nitrile oxide *I* to the used monosubstituted alkenes.

Cycloaddition of nitrile oxide *I* with suitable oxygen-containing heterocycles, such as 2,3- and 2,5-dihydrofuran, 2,3-dihydropyran, 5,6-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene, 1,4-

Table 1. Physicochemical Data of Compounds *III*—*XII*

Compound	Formula M_r	w_i(calc.)/% w_i(found)/% C	H	N	Yield %	M.p. °C	λ_{max}/nm log {ε}	$\tilde{\nu}$(ν(C=O)) cm^{-1}
IIIa	$C_{11}H_9Cl_2NO_3$	48.19	3.31	5.10	47	97—98	371	1675
	274.1	47.93	3.31	5.01			2.36	
IIIb	$C_{12}H_8Cl_2N_2O_2$	50.99	2.83	9.91	18	94—96	265[a]	1674
	282.6	50.81	2.79	9.68			2.29	
IV	$C_{12}H_9Cl_2NO_3$	50.37	3.17	4.89	64	85—86	256	1672
	286.1	50.65	3.14	4.90			2.28	
V	$C_{12}H_9Cl_2NO_3$	50.37	3.17	4.89	10	121—122	266	1670
	286.1	50.48	3.23	5.07			2.34	
VI	$C_{13}H_{11}Cl_2NO_3$	52.02	3.69	4.67	33	82—85	261	1676
	300.1	51.79	3.75	4.72			2.23	
VII	$C_{18}H_{15}Cl_2NO_7$	50.48	3.50	3.27	80	204—206	268	1672
	428.2	50.23	3.51	3.27			2.32	
VIII	$C_{18}H_{11}Cl_2NO_3$	60.02	3.07	3.89	67	195—196	367	1670
	360.2	59.77	3.30	3.96			2.50	
IX	$C_{20}H_{11}Cl_2NO_2$	65.23	3.01	3.80	47	127—129	276	1668
	368.2	65.18	3.04	3.81			2.4	
XI	$C_{14}H_9Cl_2NO_6$	46.95	2.53	3.91	22	125—127	267[a]	1690
	358.1	47.06	2.50	4.00			2.10	
XIIa	$C_{10}H_5Cl_2NO_2$	49.61	2.08	5.78	45	96—99	263[a]	1686
	242.0	50.02	2.08	5.80			2.30	
XIIb	$C_{11}H_7Cl_2NO_3$	48.55	2.59	5.15	19	145—146	264[a]	1684
	272.08	48.60	2.61	5.21			2.26	
XIIc	$C_{11}H_6BrCl_2NO_2$	39.44	1.80	4.18	19	77—78	263[a]	1686
	334.98	39.84	1.76	4.18			2.23	
XIId	$C_{16}H_9Cl_2NO_2$	60.21	2.84	4.39	21	120—121	263[a]	1684
	319.2	60.20	2.90	4.53			2.70	
XIIe	$C_{13}H_{11}Cl_2NO_2$	54.95	3.90	4.93	18	148—150	260[a]	1705
	284.1	54.79	3.81	4.97			2.20	

a) EtOH, others in MeOH.

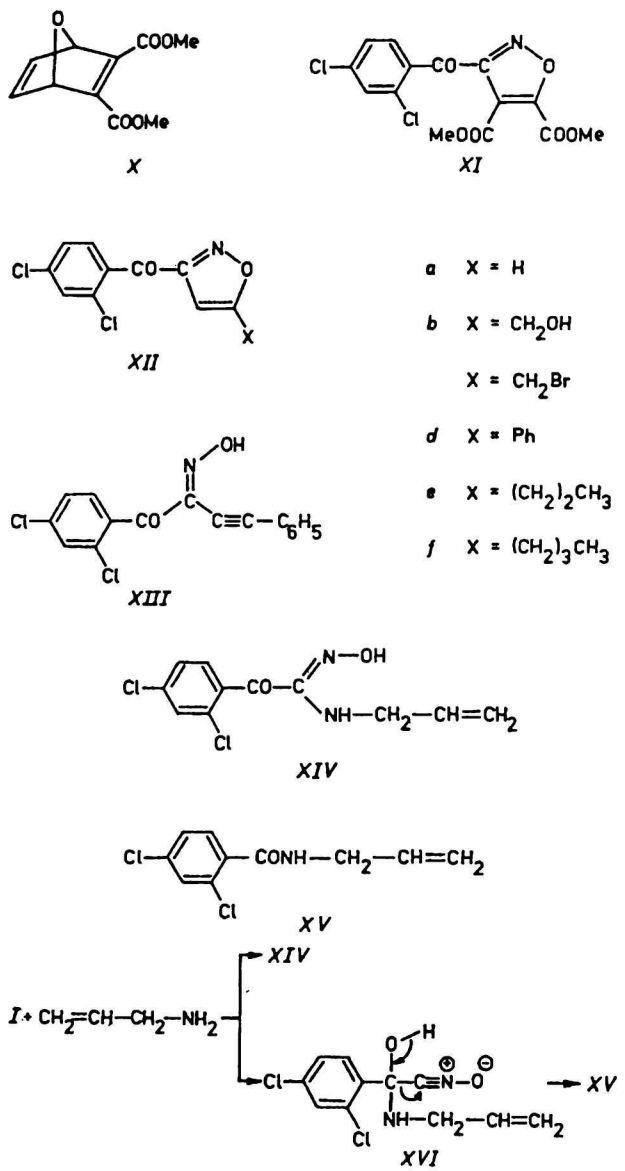
epoxy-1,4-dihydronaphthalene, and acenaphthalene furnished compounds *IV*—*IX*. Cycloadditions of *I* proceeded with yields comparable to those of benzonitrile oxide [11—13] and benzoylnitrile oxide [13]. In contrast to benzonitrile oxide, which needed high temperature for the reaction with 2,3-dihydropyran [13], nitrile oxide *I* reacted at temperature as low as 0—5 °C, but gave small yields.

Structure of the fused dihydroisoxazoles *IV*—*IX* has been determined mainly by correlation of the corresponding chemical shifts in ^{1}H and ^{13}C NMR spectra with those found for analogous derivatives [11—14]. Thus based on zero coupling constants $J_{1,2}$ and $J_{5,6}$ *exo* structure has been assigned to *VII* and *VIII* with respect to the oxygen bridge. Cycloaddition of *I* with 2,3-dihydrofuran and 2,3-dihydropyran gave exclusively the head-to-head regioisomer *IV* and *VI*, respectively, in accord with our previous results [13, 14].

A site selectivity was observed in cycloaddition of nitrile oxide *I* to 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (*X*) (Scheme 2). The intermediate cycloadducts undergo the Diels—Alder cycloreversion [15, 16] to form the furan, 3,4-dimethoxycarbonylfuran, and arylisoxazoles; the 3-(2,4-dichlorobenzoyl)isoxazole (*XIIa*) to 3-(2,4-dichlorobenzoyl)-4,5-dimethoxycarbonylisoxazole (*XI*) ratio was found to be 67 : 33 in favour of the cycloaddition to unsubstituted double bond. The opposite ratio 45 : 55 was found for benzoylnitrile oxide [16], since the 1,3-dipolar cycloaddition, controlled by the HOMO(1,3-dipole)—LUMO(dipolarophile) frontier interaction, should take place at the deactivated tetrasubstituted double bond, whereas addition to the disubstituted double bond of *X* should be controlled by the LUMO(1,3-dipole)—HOMO(dipolarophile) interaction. The two electron-accepting chloro atoms lower the LUMO energy of *I* and consequently, the formation of *XIIa* in comparison to *XI* is favoured.

Similarly, nitrile oxide *I* reacted regioselectively with monosubstituted alkynes (propargyl alcohol, propargyl bromide, pentyne or hexyne) to afford 5-substituted isoxazoles *XII* in fair yields. Cycloaddition of *I* to phenylacetylene furnished exclusively 5-phenyl-3-(2,4-dichlorobenzoyl)isoxazole (*XIId*) in 21 % yield; on the other hand, the alternative 1,3-addition product *XIII* described by the reaction with benzonitrile oxide [17, 18] was not found even in the crude reaction mixture.

Some allylamine derivatives have been reported to possess significant antifungal properties [19]. Therefore, allylamine was chosen as the dipolarophile. Benzonitrile oxide reacted with allylamine and gave not only a cycloadduct, but also an open-chain *N*-substituted amide oxime [19]. In contrast to other monosubstituted alkenes, in the reaction of nitrile oxide *I* with allylamine the formation of the isoxazoline *IIIc* was not observed. Two products *XIV* and *XV* in 26 % and 11 % yield, respectively, were isolated. The typical pattern of ABX system in ^{1}H NMR spectrum for both products is missing, therefore the structure of the isoxazoline can be excluded. ^{1}H and ^{13}C NMR spectra show the conservation of the allyl moiety in both isolated compounds. The presence of the molecular ion at m/z = 273 in mass spectrum as well as the presence of strong absorption bands of C=O and OH group indicated that the compound *XIV* was an open-chain *N*-substituted amide oxime. In the presence of two competitive functional groups in the allylamine molecule (namely, the free amino group and the allylic unsaturated bond), in addition to usual 1,3-cycloaddition product the 1,3-addition



Scheme 2

product *XIV* can be formed. In the case of using of benzonitrile oxide a 2.1 : 1 amide oxime to isoxazoline ratio was determined [19]. In our case the benzoyl group in nitrile oxide *I* increases its electrophilicity, hence only the product derived from 1,3-addition is formed.

Surprisingly, in contrast to all up-to-now investigated reactions of nitrile oxides with amines [19—21] we have isolated the anomalous product *XV* the spectral data of which are not in conformity with the spectra of either 1,3-cycloaddition or 1,3-addition product. The absence of the singlet at $\delta \approx 150$ in ^{13}C NMR spectra for the C=N group excluded the possible structures of *IIIc* and *XIV*. The presence of signals of allylic and C=O grouping proves the conservation of benzoyl and allylic skeleton. From this finding and further data such as $M^{+\cdot}$ at $m/z = 230$ in mass spectra the structure of *N*-allyl-2,4-dichlorobenzamide (*XV*) has been assigned. To the best of our knowledge the observed reaction is a novel preparation of an amide. We can suppose an attack of allylamine at the benzoyl group and the formed adduct *XVI* is then stabilized by elimination of fulminic acid. This has been proved by an experiment in which the nitrile oxide *I* was prepared by the reaction of *II* with triethylamine at − 40 °C and then allylamine was added and both *XIV* and *XV* were formed in the same ratio. In an independent experiment we have found that the derivative *XIV* is not the precursor for amide *XV*.

Compounds *IIIa*, *IIIb*, *IIId—IIIg*, *IV—IX*, *XI*, *XIIa—XIIf* displayed activity in antifungal screening albeit not as the reference compounds.

EXPERIMENTAL

Melting points are uncorrected, the ^1H and ^{13}C NMR spectra of deuterochloroform solutions were measured with Varian VXR 300 instrument, tetramethylsilane being the internal reference. Ultraviolet spectra were obtained on a spectrophotometer M-40 (Zeiss, Jena) in methanol or ethanol. Values of ε are given in $m^2\ mol^{-1}$. The IR spectra were taken with analytical PU 9800 FTIR spectrometer (Philips).

2,4-Dichlorophenylglyoxylohydroximoyl chloride (*II*) was prepared according to Ref. [5] and 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene (*X*) according to Ref. [16].

Isoxazolines *III* and Isoxazoles *IV—IX*, *XI*, *XII*

Triethylamine (13 mmol) in ether (30 cm^3) was added to a stirred solution of *I* (10 mmol) and the dipolarophile (10 mmol) in ether at 0—5 °C within 1 h. The mixture was stirred overnight at room temperature, the separated triethylammonium chloride was filtered off, removed by dissolving in water and the organic material was evaporated under diminished pressure, dried, triturated with a suitable solvent or separated by chromatography on a silica gel column and purified by crystallization.

3-(2,4-Dichlorobenzoyl)-5-(hydroxymethyl)isoxazoline (IIIa); ^1H NMR spectrum, δ: 3.66 (dd, 1H, H_A-4), $J_{4,5}$ = 4.5 Hz, 3.88 (dd, 1H, H_B-4), J_{AB} = 12.6 Hz, $J_{4,5}$ = 3 Hz, 4.96 (m, 1H, H-5), 3.28 (m, 2H, CH_2), 7.29—7.47 (m, H_{arom}). ^{13}C NMR spectrum, δ: 158.64 (C-3), 63.35 (C-4), 84.78 (C-5), 33.62 (CH_2), 186.88 (C=O), 126.96, 130.28, 130.93, 132.90, 135.19, 137.80 (C_{arom}).

3-(2,4-Dichlorobenzoyl)-5-(cyanomethyl)isoxazoline (IIIb); ^1H NMR spectrum, δ: 3.57 (dd, 1H, H_A-4), J_{AB} = 18 Hz, $J_{4,5}$ = 11.1 Hz, 3.23 (dd, 1H, H_B-4), $J_{4,5}$ = 6.6 Hz, 5.11 (m, 1H, H-5), 2.79 (m, 2H, CH_2), 7.31—7.52 (m, H_{arom}). ^{13}C NMR spectrum, δ: 157.59 (C-3), 37.29 (C-4), 78.27 (C-5), 23.63 (CH_2), 185.99 (C=O), 126.93, 130.29, 131.04, 132.86, 134.47, 138.02 (C_{arom}).

3-(2,4-Dichlorobenzoyl)-5-(bromomethyl)isoxazoline (IIId), yield = 60 %, obtained by column chromatography (silica, eluant hexane—ethyl acetate, φ_r = 7 : 2) as a yellow unstable oil. ^1H NMR spectrum (deuterochloroform), δ: 7.15—7.55 (m, 3H, H_{arom}), 5.01 (m, 1H, H-5), 3.20—3.47 (m, 4H, H_2-4, CH_2). ^{13}C NMR spectrum, δ: 186.47 (s, C=O), 157.63 (s, C=N), 137.87, 134.90, 132.92, 131.04, 130.29, 126.93 (C_{arom}), 82.48 (d, C-5), 36.91 (t, CH_2), 32.88 (t, C-4).

3-(2,4-Dichlorobenzoyl)-5-butylisoxazoline (IIIe), yield = 57 %. IR spectrum, $\tilde{\nu}$(ν(C=O)) = 1670 cm^{-1}. ^1H NMR spectrum, δ: 7.29—7.49 (m, 3H, H_{arom}), 4.86 (m, 1H, H-5), 3.34 (dd, 1H, H_B-4), J_{AB} = 17.7 Hz, $J_{4,5}$ = 6.6 Hz, 2.94 (dd, 1H, H_A-4), $J_{4,5}$ = 8.4 Hz, 1.79 (m, 1H, H_A-1′), 1.64 (m, 1H, H_B-1′), 1.32—1.44 (m, 4H, H_2-2′, H_2-3′), 0.92 (t, 3H, CH_3). ^{13}C NMR spectrum, δ: 187.29 (s, C=O), 158.16 (s, C=N), 137.51, 135.40, 132.83, 130.91, 130.18, 126.85 (C_{arom}), 85.31 (d, C-5), 37.03 (t, C-4), 34.87 (t, C-1′), 27.21 (t, C-2′), 22.40 (t, C-3′), 13.92 (q, C-4′).

3-(2,4-Dichlorobenzoyl)-5-(ethoxycarbonyl)isoxazoline (IIIf), yield = 33 %, obtained by column chromatography on a silica gel (eluant chloroform—hexane, φ_r = 3 : 1) as a yellow oil. IR spectrum, $\tilde{\nu}$(ν(C=O)) = 1674 cm^{-1}. ^1H NMR spectrum, δ: 7.32—7.55 (m, 3H, H_{arom}), 5.25 (t, 1H, H-5), 4.28 (q, 2H, OCH_2), 3.60 (d, 2H, H_2-4), J = 9.6 Hz, 1.33

(t, 3H, CH_3). ^{13}C NMR spectrum, δ: 185.98 (s, C=O), 168.69 (s, O–C=O), 157.35 (s, C=N), 138.11, 134.77, 133.14, 131.25, 130.41, 126.96 (C_{arom}), 80.48 (d, C-5), 62.36 (t, OCH_2), 36.69 (t, C-4), 14.08 (q, CH_3).

3-(2,4-Dichlorobenzoyl)-5-phenylisoxazoline (IIIg), yield = 70 %, obtained by column chromatography on a silica gel (eluant chloroform–cyclohexane, φ_r = 3 : 1) as a yellow oil. IR spectrum, $\tilde{\nu}$(ν(C=O)) = 1670 cm^{-1}. ^1H NMR spectrum, δ: 7.42–7.78 (m, 8H, H_{arom}), 5.96 (dd, 1H, H-5), $J_{5,4A}$ = 11.5 Hz, $J_{5,4B}$ = 9.1 Hz, 3.88 (dd, 1H, H_A-4), J_{AB} = 18 Hz, 3.29 (dd, 1H, H_B-4). ^{13}C NMR spectrum, δ: 186.90 (s, C=O), 157.77 (s, C=N), 139.20, 137.73, 135.27, 132.90, 130.95, 130.26, 129.05, 128.93, 128.79, 126.94, 125.90 (C_{arom}), 85.93 (d, C-5), 40.02 (t, C-4).

3-(2,4-Dichlorobenzoyl)-3a,4,5,6a-tetrahydrofuro-[2,3-d]isoxazole (IV) was obtained by chromatography on a silica gel column (eluant hexane–chloroform, φ_r = 2 : 1). ^1H NMR spectrum (deuterochloroform), δ: 7.34–7.41 (m, 3H, H_{arom}), 6.37 (d, 1H, H-6a), J = 6.3 Hz, 4.09–4.20 (m, 2H, H_2-5), 3.58–3.66 (m, 1H, H-3a), 2.21–2.40 (m, 2H, H_2-4). ^{13}C NMR spectrum, δ: 187.14 (s, C=O), 158.55 (s, C=N), 137.81, 135.26, 132.57, 130.59, 130.20, 127.09 (C_{arom}), 111.77 (d, C-6a), 67.17 (t, C-5), 49.45 (d, C-3a), 29.88 (t, C-4).

3-(2,4-Dichlorobenzoyl)-3a,4,6,6a-tetrahydrofuro-[3,4-d]isoxazole (V) was obtained by chromatography on a silica gel column, eluant chloroform. ^1H NMR spectrum (deuterochloroform), δ: 7.30–7.49 (m, 3H, H_{arom}), 5.46 (dd, 1H, H-6a), 4.22–4.35 (m, 3H, H_A-6, H_A-4, H-3a), 3.68–3.81 (m, 2H, H_B-6, H_B-4). ^{13}C NMR spectrum, δ: 186.91 (s, C=O), 158.09 (s, C=N), 137.76, 135.16, 132.84, 130.86, 130.27, 126.91 (C_{arom}), 89.48 (d, C-6a), 75.71 (t, C-6), 71.74 (t, C-4), 51.62 (d, C-3a).

3-(2,4-Dichlorobenzoyl)-3a,4,5,7a-tetrahydro-6H-pyrano[3,2-d]isoxazole (VI) was obtained by chromatography on a silica gel column (eluant chloroform–cyclohexane, φ_r = 4 : 1). ^1H NMR spectrum (deuterochloroform), δ: 7.32–7.48 (m, 3H, H_{arom}), 6.07 (d, 1H, H-7a), J = 8.2 Hz, 3.77 (m, 2H, H_2-6), 3.52 (qv, 1H, H-3a), 2.25 (m, 1H, H_B-4), 1.99 (m, 1H, H_A-4), 1.83 (m, 1H, H_B-5), 1.61 (m, 1H, H_A-5). ^{13}C NMR spectrum, δ: 187.49 (s, C=O), 160.13 (s, C=N), 137.76, 135.37, 132.63, 130.77, 130.24, 124.04 (C_{arom}), 104.92 (d, C-7a), 59.36 (t, C-6), 41.32 (d, C-3a), 19.35 (t, C-5), 17.22 (t, C-4).

3,4-Bis(methoxycarbonyl)-7-(2,4-dichlorobenzoyl)-8-aza-9,10-dioxatricyclo[4.3.0.$1^{2,5}$]decane (VII). ^1H NMR spectrum (deuterochloroform), δ: 7.31–7.46 (m, 3H, H_{arom}), 5.18 (s, 1H, H-7), 5.14 (s, 1H, H-4), 5.03 (d, H-7a), J = 8.1 Hz, 3.92 (d, 1H, H-3a), 3.71 (s, 6H, 2 x CH_3), 3.17 (d, 1H, H-6), J = 9 Hz, 3.01 (d, 1H, H-5). ^{13}C NMR spectrum, δ: 186.74 (s, C=O), 169.99 (s, O–C=O), 169.87 (s, O–C=O), 155.94 (s, C=N), 136.61, 134.82, 132.99, 131.02, 130.35, 126.94 (C_{arom}), 88.63 (d, C-1), 83.88 (d, C-2), 79.83 (d, C-5), 56.04 (d, C-6), 52.55, 52.59 (q, 2 x CH_3), 50.04 (d, C-3), 46.45 (d, C-4).

3-(2,4-Dichlorobenzoyl)-3a,4,9,9a-tetrahydro-4,9-epoxynaphthaleno[3,2-d]isoxazole (VIII). ^1H NMR spectrum (deuterochloroform), δ: 7.13–7.53 (m, 7H, H_{arom}), 5.63 (s, 1H, H-9), 5.58 (s, 1H, H-4), 5.08 (d, 1H, H-9a), J = 8.0 Hz, 3.89 (d, 1H, H-3a). ^{13}C NMR spectrum, δ: 187.07 (s, C=O), 155.83 (s, C=N), 144.69, 140.59, 137.82, 134.97, 132.95, 131.14, 130.32, 128.29, 127.78, 126.86, 121.09, 120.40 (C_{arom}), 90.66 (d, C-9a), 85.38 (d, C-9), 80.99 (d, C-4), 56.68 (d, C-3a).

3-(2,4-Dichlorobenzoyl)acenaphtheno[1,2-d]isoxazole (IX). ^1H NMR spectrum (deuterochloroform), δ: 7.0–7.8 (m, 9H, H_{arom}), 6.64 (d, 1H, H-2), J = 9.0 Hz, 5.59 (d, 1H, H-1). ^{13}C NMR spectrum, δ: 186.89 (s, C=O), 157.69 (s, C=N), 139.74, 138.77, 137.66, 136.71, 135.14, 132.95, 131.66, 131.04, 130.28, 128.59, 128.35, 126.73, 126.51, 124.57, 122.55, 122.25 (C_{arom}), 91.78 (d, C-2), 55.94 (d, C-1).

3-(2,4-Dichlorobenzoyl)-4,5-bis(methoxycarbonyl)-isoxazole (XI) was obtained by column chromatography on a silica gel (eluant chloroform–heptane, φ_r = 5 : 1). ^1H NMR spectrum (deuterochloroform), δ: 7.46–7.63 (m, 3H, H_{arom}), 4.03 (s, 3H, CH_3), 3.94 (s, 3H, CH_3). ^{13}C NMR spectrum, δ: 183.26 (s, C=O), 159.96 (s, O–C=O), 159.82 (s, O–C=O), 155.66 (s, C-5), 139.68, 134.38, 133.39, 132.43, 130.99, 127.37 (C_{arom}), 116.88 (s, C-4), 53.73, 53.46 (q, OCH_3).

Table 2. ^1H NMR Spectral Data of *XII*

Compound	δ (J/Hz)			
	H-4	CH_2	H_{arom}	Others
XIIa	6.92 (1.85)		7.37, 7.51, 7.64 (1.8, 8.2)	8.56 (H-5)
XIIb	6.90	4.70	7.72, 7.75, 7.84 (1.8, 8.4)	
XIIc	6.87	4.53	7.38, 7.52, 7.64 (1.8, 8.4)	
XIId	7.39		7.54–8.06	
XIIe	6.65	2.87	7.60–7.94	1.28–1.95 (CH_2), 1.05 (CH_3)
XIIf	6.82	2.87	7.47, 7.91	1.25–1.78 (CH_2)$_2$, 0.92 (CH_3)

Table 3. ^{13}C NMR Chemical Shifts of *XII*

Compound	δ					
	C-3	C-4	C-5	CH_2	C=O	C_{arom}
XIIa	160.93	104.47	160.05		185.44	127.04, 130.62, 131.55, 133.49, 134.83, 138.37
XIIb[a]	175.46	101.03	161.06	54.53	185.25	127.41, 129.69, 131.66, 133.46, 133.74, 135.24
XIIc	169.46	103.54	162.00	33.99	185.15	127.04, 130.67, 131.59, 133.55, 134.44, 138.51
XIId[a]	171.30	99.75	162.20		185.65	125.87, 127.41, 129.29, 129.78, 131.05, 131.90, 135.12, 136.99
XIIf[a, b]	176.03	100.54	161.14	61.54	185.92	127.35, 129.72, 131.75, 133.17, 135.33, 136.85

a) DMSO-d_6; *b*) 13.95 (q), 25.56 (t), 28.90 (t, $CH_2CH_2CH_3$).

N-Allyl-2,4-dichlorophenylglyoxylamide oxime (XIV) obtained in 26 % yield from the reaction of *I* with allylamine, experimental conditions are the same as for the preparation of *III*, eluant hexane–ethyl acetate (φ_r = 2 : 1), m.p. = 86–88 °C. For $C_{11}H_{10}Cl_2N_2O_2$ (M_r = 273.1) w_i(calc.): 48.55 % C, 3.71 % H, 10.29 % N; w_i(found): 48.87 % C, 3.82 % H, 10.34 % N. UV spectrum, λ_{max}/nm (log {ε}): 333 (1.7). IR spectrum, $\tilde{\nu}$/cm^{-1}: 3574 ν(OH), 3402 ν(NH), 1688 ν(C=O). ^1H NMR spectrum, δ: 8.33 (s, 1H, OH), 7.27–7.41 (m, 3H, H_{arom}), 5.93 (m, 1H, H-2), 5.14–5.25 (m, 3H, H_2-3, NH), 4.13 (t, 2H, H_2-1). ^{13}C NMR spectrum, δ: 187.97 (s, C=O), 149.99 (s, C=N), 137.34, 135.62, 132.91, 130.55, 129.94, 126.93 (C_{arom}), 135.78 (d, C-2), 116.24 (t, C-3), 45.91 (t, C-1). Mass spectrum, *m/z*: 272 ($M^{+\cdot}$), 255 ($M^{+\cdot}$ – OH$^{\cdot}$), 173 (base peak $C_6H_3Cl_2\dot{C}$=O).

N-Allyl-2,4-dichlorobenzamide (XV) was obtained from the second fraction, yield = 11 %, m.p. = 96–98 °C. For $C_{10}H_9Cl_2NO$ (M_r = 230.1) w_i(calc.): 52.20 % C, 3.96 % H, 6.09 % N; w_i(found): 52.39 % C, 4.06 % H, 6.17 % N. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3443 ν(NH), 1667 ν(C=O). ^1H NMR spectrum, δ: 7.27–7.59 (m, 3H, H_{arom}), 6.49 (s, 1H, NH), 5.93 (m, 1H, H-2), 5.25 (dd, 2H, H_2-3), 4.06 (t, 2H, H_2-1). ^{13}C NMR spectrum, δ: 165.44 (s, C=O), 136.80, 133.41, 131.56, 131.31, 130.08, 127.54 (C_{arom}), 133.55 (d, C-2), 117.01 (t, C-3), 42.54 (t, C-1). Mass spectrum, *m/z*: 229 ($M^{+\cdot}$), 214 ($M^{+\cdot}$ – $CH_3^{\cdot}$), 173 (base peak $C_6H_3Cl_2\dot{C}$=O).

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Translated by Ľ. Fišera