AZOLES AND AZINES.

62.\* STRUCTURE OF 2-ARYL-1, 3-OXAZINE-4, 6-DIONES

 V. É. Zakhs, I. P. Yakovlev, N. A. Smorygo,
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 V. A. Gindin, and B. A. Ivin
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<sup>1</sup>H, <sup>13</sup>C NMR, IR, and UV spectra have been studied for solutions of a number of potentially tautomeric 2-aryl-1,3-oxazine-4,6-diones and their 5-methyl substituted analogs with variation of substituent at the para position of the benzene ring, as well as compounds with a fixed structure that simulates possible tautomeric forms. The data have been compared with the results of quantum chemical calculations carried out in SSO MO LCAO approximation by the CNO, CNDO/2, and MPNDO/3 methods. In DMSO and THF solution the test compounds exist predominantly as 2-aryl-4-hydroxy-6H-1,3-oxazin-6-ones. The para substituent in the benzene ring does not affect the composition of the tautomer mixture significantly.

2-Aryl-1,3-oxazine-4,6-diones (I, II) are potentially tautomeric compounds, and can exist in the following tautomeric forms: dicarbonyl (A), two enolic forms (B and C), and bipolar ion (D):



I, II a R=H, b  $R=NO_2$ , c R=CI, d  $R=CH_3$ , e  $R=CH_3O$ , f  $R=N(CH_3)_2$ ; I  $R^1=H$ ; II  $R^1=CH_3$ 

There are no unequivocal data on the structure of substances I and II in the literature. Thus 2-phenyl-1,3-oxazine-4,6-dione (Ia) and its 5-alkyl substituted analogs were at one time assigned structure C without sufficient reason [2, 3]. The authors of [4] believed that according to IR and PMR data 2,5-dibenzyl-1,3-oxazine-4,6-dione exists in the crystalline state and in dimethyl sulfoxide solution as a mixture of forms A and B. But when the spectral data for only the oxazinediones themselves are considered, it is impossible, strictly speaking, to decide on their structure. In an attempt to obtain additional information about the structure of the test compounds and their relative stability in the ground state, we carried out a quantum chemical calculation in an MO LCAO approximation by the CNO, CNDO/2, and MPNDO/3 methods for the tautomers A-C. The fundamental structural parameters of the tautomers being analyzed were taken from [5]. Calculation for the bipolar-ionic form (D) was not carried out due to the absence of sufficiently strict geometric parameters; furthermore in our view this form is least likely for compounds I and II in the ground state. It should also be noted that the CNO method was calculated for application to completely conjugated systems. Structure A, which contains an sp<sup>3</sup> hybridized carbon atom cannot be calculated directly by this method. Nevertheless there are a number of original publications (e.g., [6]) in which it is shown that the energy of an  $sp^3$  hybridized bond can be approximated by the sum of the energies of the component  $\sigma$ -bonds. The accuracy of such an estimate of the energy of dicarbonyl form A can be verified by calculating the relative stabilities of tautomers A-C by the MPNDO/3 method by the proposed scheme. The data thus obtained are evidence that form B is most favored energetically. The advantages in energy of formation of tautomer B over those of forms A and C, calculated by the MPNDO/3 method, are 212 and 11 kcal/mole respectively; these are in good agreement with the differences in

\*For Communication 61, see [1].

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Com-	R	mp, ℃•	R <sub>1</sub> **	Found, %		%	Empirica1	Calculated, %			Vield %
pound				с	н	N (Cl)	formula	с	н	N (Cl)	, ,,
Id	CH₃	142-144		64,9	4,6	7,0	C <sub>11</sub> H <sub>9</sub> NO <sub>3</sub>	65,0	4,4	6,9	80
Ie	CH <sub>3</sub> O	139-140		60,4	4,1	6,5	C <sub>11</sub> H <sub>9</sub> NO <sub>4</sub>	60,3	4,1	6,4	25
IIb .	NO <sub>2</sub>	215	0,63	53,4	3,1	11,5	$C_{11}H_8N_2O_5$	53,2	3,2	11,3	85
llc	CI	201-203	0,57	55,4	3,0	6,0	C <sub>11</sub> H <sub>8</sub> CINO <sub>3</sub>	55,6	3,4	5,9	74
						(15,0)		1		(15,0)	
IIe	CH₃O	202 - 204	0,53	62,0	4,8	6,2	$C_{12}H_{11}NO_{4}$	61,8	4,7	6,0	78
Пf	$(CH_3)_{9}N$	202-203	0,48	63,4	5,8	11,2	$C_{13}H_{14}N_2O_3$	63,1	5,7	11,4	71
1V	Ĥ	152-154		66,3	5,2	6,2	$C_{12}H_{11}NO_3$	66,4	5,1	6,4	47
V	Н	104-105	0,17	65,2	4,4	7,1	C <sub>H</sub> H <sub>9</sub> NO <sub>3</sub>	65,0	4,4	6,9	68
VI	н	124-126	0,57	59,6	5,2	6,3	C <sub>11</sub> H <sub>11</sub> NO <sub>4</sub>	59,7	5,0	6,3	100 (A);
											92 (B)
VII	H	105-106	0,56	65,1	4,3	6,8	C <sub>11</sub> H <sub>9</sub> NO <sub>3</sub>	65,0	4,4	6,9	55
VIII	Н	127-129	0,60	66,5	5,3	6,4	C <sub>12</sub> H <sub>11</sub> NO <sub>3</sub>	66,4	5,1	6.4	61

TABLE 1. Physicochemical Properties of Compounds I, II, IV-VIII

\*Solvent for IIb, e, dioxane; for IIc, 1:2 dioxane:dichloroethane; for V, 1:1 chloroform:hexane; for VI, 1:1 benzene:hexane; for VII and VIII, 1:1 acetonitrile:water. Compounds Id, e, IIb, c, e, f, and IV melt with decomposition. \*\*On Silufol UV-254 plates, ethyl acetate eluen.

total tautomer energies calculated by CNDO/2 (248 and 36 kcal/mole).

Since the theoretical calculation of the thermodynamic stability of the potential tautomers, the 2-aryl-1,3-oxazine-4,6-diones, must not be applied to their solutions unequivocally, it became necessary to carry out a comprehensive investigation of the structure of these compounds. For this purpose we synthesized materials of fixed structure that simulated the possible tautomeric forms.



2-Phenyl-5,5-dimethyl-1,3-oxazine-4,6-dione (III) (the model for dicarbonyl form A) was synthesized by the addition of dimethylketene to benzoyl isocyanate [3]; 2-phenyl-3,5dimethyl-6-oxo-1,3-oxazin-3-ium-4-olate (IV) (the model for bipolar ion form D), by the reaction of methylmalonyl dichloride and N-methyl-benzamide by analogy with [7]; and 2phenyl-6-methoxy-4H-1,3-oxazin-4-one (V) (the model of the 6-hydroxy-4-oxo form C), by addition of methoxyacetylene to benzoyl isocyanate [8]. This reaction can give either 5methoxy-4-oxo-1,3-oxazine (Va) or the required 6-methoxy-4-oxo-1,3-oxazine (V). The structure of the substance obtained was confirmed by hydrolyzing it in aqueous acetonitrile to form methyl-N-benzoylmalonamate (VI) which is identical with the methanolysis product of oxazinedione Ia. From alkylation of Ia with diazomethane we might expect O-, N-, and Cmethyl derivatives. The location of the methyl singlet in the PMR spectrum of the compound

TABLE 2. Location of Signals in <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Solutions of 2-Aryl-1,3-oxazin-4,6-diones (I, II) and Model Substances III-V, VII, and VIII in DMSO

Com-	R	R1		δ <sup>13</sup> C	δ 'H*, ppm			
роина			C <sub>(2)</sub>	C <sub>(4)</sub>	C <sub>(6)</sub>	C <sub>(5)</sub>	5-Н <b>ог</b> 5-СН₃	4-OH <b>OI</b> 4(6)-OCH <sub>3</sub>
Ia Ib Ic Id Ie IIa Ib IIC IIe Ilf III V VII VIII	H NO <sub>2</sub> Cl CH <sub>3</sub> O H NO <sub>2</sub> Cl Cl CH <sub>3</sub> O (CH <sub>3</sub> ) <sub>2</sub> N H H H H	Н Н Н СН₃ СН₃ СН₃ СН₃ СН₃ Н Н Н СН₃	$\begin{array}{c} 160,53\\ 160,02\\ 160,58\\ 160,80\\ 160,65\\ 160,98\\ 159,04\\ 159,94\\ 160,98\\ 161,94\\ 163,48\\ 156,93\\ 159,83\\ 160,29\\ 161,29\\ \end{array}$	$\begin{array}{c} 163,56\\ 162,36\\ 163,53\\ 164,50\\ 164,27\\ 161,95\\ 161,37\\ 161,49\\ 162,05\\ 162,34\\ 169,83\\ 156,93\\ 156,93\\ 166,97\\ 163,81\\ 161,29 \end{array}$	$\begin{array}{c} 170,30\\ 169,97\\ 170,40\\ 170,55\\ 170,43\\ 165,57\\ 164,99\\ 165,11\\ 165,66\\ 166,05\\ 180,77\\ 167,96\\ 168,71\\ 170,74\\ 165,00\\ \end{array}$	81,34 82,27 81,70 81,17 80,38 89,99 91,35 90,12 89,10 87,54 49,04 78,12 82,38 81,82 92,35	5.22 5.25 5.24 5.14 1.75 1.73 1.71 1.73 1.45 1.79 5.62 5.58 1.90	12,8 12,9 12,8 12,7 12,5 12,2 12,4 12,1 11,9 

\*For VII, values were obtained in CDCl<sub>3</sub>. \*\*\* $\delta_3$ -CH<sub>3</sub>.

VII thus obtained ( $\delta$  3.96 ppm) is evidence that specifically the product of O-methylation is formed; the properties of the latter are quite different from those of the 6-methoxyoxazinone V mentioned above. Thus, VII can be recrystallized from aqueous acetonitrile (under these conditions, V is cleaved), and it is converted to N-benzoylmalonamic acid only when heated in the presence of mineral acid [1]. In the IR spectrum of crystalline VII the carbonyl band has a frequency of 1745 cm<sup>-1</sup>, which is expected for lactone carbonyl, whereas in the spectrum of 6-methoxyoxazine V (cyclic amide)  $v_{C=0}$  has a frequency of 1660 cm<sup>-1</sup>. Thus the product of methylation of Ia with diazomethane has the structure of 2-phenyl-4methoxy-6H-1,3-oxazin-6-one (VII), molecule B. 2-Phenyl-5-methyl-4-methoxy-6H-1,3-oxazin-6-one (VIII) was synthesized analogously (Table 1).

The choice of solvent for studying the spectral characteristics of oxazinediones I that do not have a substituent at position 5 is limited by their sensitivity to nucleophilic reagents and their low solubility in nonpolar solvents. In this connection we investigated the <sup>1</sup>H and <sup>13</sup>C NMR and the IR spectra of their solutions in THF. It turned out that oxazinediones I are also unstable in DMSO. The conversion product of Ia in DMSO was separated (mp 212-213°). Although its structure was not specially studied, its spectra were recorded in order to avoid any confusion in interpreting the spectra of the stating substances I.

The PMR spectra of freshly prepared solutions of compound I in DMSO (Table 2), in addition to the benzene ring proton signals located (depending on type of substitution) in the 7.0-8.3 ppm region, contain an olefinic proton signal (5.14-5.25 ppm) and a weak-field proton signal (12.5-12.9 ppm). The presence of the two latter indicates that we are dealing with one of the enolic B, C, or the zwitterion form of D. To choose among these on the basis of these data cannot be done, because the 5-H proton shifts of methoxyoxazines V and VII are very close together (5.62 and 5.58 ppm, respectively) and differ substantially from the 5-H proton shift of oxazinedione Ia (5.22 ppm). This situation is probably related to the intermolecular association or the ionization of the enol form of Ia in DMSO. With time the PMR spectrum of Ia shows signals at 3.7 and 11.2 ppm that belong to N-benzoylmalonamic acid (which forms in the presence of traces of water), and 6.90 and 12.05 ppm that belong to the conversion product. The intensity of these signals increases, whereas the signal at 5.22 ppm disappears completely. Consequently the signal at 3.7 ppm cannot be assigned to the CH<sub>2</sub> of dicarbonyl form A.

Besides the aromatic proton signals, the spectra of solutions of 5-methyloxazinediones II in DMSO (which are stable) show only a methyl singlet (1.71-1.76 ppm) and the signal of an OH (or NH) proton (11.9-12.4 ppm). Thus the PMR spectroscopy of dimethyl sulfoxide solutions enables us to exclude only the dicarbonyl form A from consideration. The <sup>13</sup>C NMR spectra are more informative in the weak field region, where the heterocyclic  $C_{(2)}$ ,  $C_{(4)}$ ,



Fig. 1. IR spectra of DMSO solutions of oxazindiones Ia, IIa, and model compounds III-V, VII, VIII.

> TABLE 3. Total Charges (q) on Heterocyclic Carbons of 2-Aryl-1,3-oxazine-4,6-diones (Ia-e) in the 4-Hydroxy-6-oxo Form, Calculated by CNDO/2

Com-	q					
pound	C(2)	C <sub>(4)</sub>	C <sub>(6)</sub>	C <sub>(5)</sub>		
Ia Ib Ic Id Ie	0,338 0,327 0,332 0,338 0,338 0,341	0,350 0,363 0,364 0,351 0,352	0,427 0,425 0,425 0,426 0,427	-0,246 -0,249 -0,255 -0,260 -0,262		

and  $C_{(6)}$  signals are located. Satisfactory results are obtained for compound I only when the spectra of freshly prepared sampled (~25% solution in DMSO) are recorded, provided accumulation time at 20-25° does not exceed 20-30 min. Signals were assigned on the basis of quantum chemical calculation of charge values on the heterocyclic atoms by the CNDO/2 method (Table 3).

As Table 2 shows, the locations of the  $C_{(2)}$ ,  $C_{(4)}$ , and  $C_{(6)}$  signals in the spectra of oxazinedione Ia and compound VII that models the 4-hydroxy-6-oxo form B are almost identical. The differences do not exceed 0.5 ppm, whereas when compared with the models of the other forms III-V they are substantial. The chemical shifts of  $C_{(2)}$ ,  $C_{(4)}$ ,  $C_{(6)}$  of 5-methyloxazine IIa and its 4-methoxy derivative VIII are also close together. Thus the <sup>13</sup>C MMR data are evidence for the predominance in DMSO of the 4-hydroxy-6-oxo form B. Increase of the electron acceptor strength of the substituent at the para position of the benzene ring causes a small shift of the  $C_{(2)}$ ,  $C_{(4)}$ , and  $C_{(6)}$  signals toward the strong field (no more than 2 ppm). The  $C_{(5)}$  signal shifts toward the weak field by a somewhat larger amount (4 ppm in going from dimethylamino to nitro). The overall picture of the spectrum remains the same, i.e., substitution in the benzene ring does not change the structure of the pre-

In the IR spectra of DMSO solutions of the test compounds the most typical feature is the 1500-1800 cm<sup>-1</sup> region (Fig. 1), where the C=O, C=N, and C=C valence vibration bands are

TABLE 4. Frequencies of C=O, C=C, and C=N Stretching Vibrations in IR Spectra of Compounds Ib-e, IIb, c, e, f in DMSO

Com-	v. cm <sup>-1</sup>								
pound	C = 0	C=C	C = N	C=C(ary!)					
Ib Ic Id Ie IIb IIc If If	1753, 1740 1753, 1737 1745, 1734 1752, 1737 1729 1720 1730 1730 1722	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1560 1553 1551 1548 1568 1545 1560 1558	1596, 1521 (NO <sub>2</sub> ) 1593, 1570 1575, 1512 1570, 1505 1604, 1524 (NO <sub>2</sub> ) 1587, 1574 1611, 1584, 1517 1610, 1518					

located. The spectrum of model dicarbonyl form III contains two carbonyl bands, at 1805 and 1722 cm<sup>-1</sup>, that belong to the  $C_{(6)}=0$  and  $C_{(4)}=0$  stretching vibrations, respectively. The band at 1610 cm<sup>-1</sup> belongs to the C=N bond vibrations. The spectra of 4-methoxy oxazinones VII and VIII show a strong low-frequency shift of  $v_{C(6, C)}$  relative to the dicarbonyl form (from 1805 to 1755 and 1730 cm<sup>-1</sup>), due to conjugation with the  $C_{(4)}=C_{(5)}$  double bond. Moreover, replacement of the C(s) hydrogen by methyl decreases  $v_{C(s)=0}$  and increases  $v_{C=C}$  (1612 and 1620 cm<sup>-1</sup>). The bands around 1560 cm<sup>-1</sup> belong to  $v_{C=N}$ . In the spectrum of 6methoxyoxazine V the amidic carbonyl band also shifts strongly toward lower frequencies relative to the corresponding band in the spectrum of the model dicarbonyl form ( $\Delta v = 66$ cm<sup>-1</sup>). At the same time  $v_{C=C}$  has a higher frequency relative to the 6-oxo compounds VII and VIII, due to the proximity of the more electronegative heteroatom, and falls in the region of  $C_{(4)}=0$  absorption. The valence vibration of the C=N bond has approximately the same frequency as that of model form B. The spectrum of betaine IV is characterized by two intense bands. The band at 1740 cm<sup>-1</sup> belongs to  $v_{C(6)=0}$ , and its position is evidence that the carbonyl takes practically no part in the delocalization of the negative charge. The broad band with maximum at 1660 cm<sup>-1</sup> belongs to the vibrations of the  $-^{\delta}O \simeq C_{(4)} \simeq C_{(5)}^{\delta-1}$ . segment. In the frequency region studied the spectra of all the model compounds and the oxazinediones Ia and IIa have bands close to 1600 and 1580 cm<sup>-1</sup> that belong to the benzene ring vibrations. The latter as a rule is more intense, and the former is often masked by heterocyclic C=C absorption.

It is easy to see that the spectra of the compounds that simulate the various tautomers differ sharply from one another, and have characteristic bands by which we can estimate the presence of a particular tautomeric form in the tautomer mixture. Comparison of the spectra of potentially tautomeric oxazinediones Iaand IIa with those of the model substances gives unequivocal evidence in favor of the 4-hydroxy-6-oxo form B. The spectra lack the absorption close to 1800 cm<sup>-1</sup> that is typical of dicarbonyl form A, and around 1660 cm<sup>-1</sup> that is typical of forms C and D. Compound Ia shows some broadening of the  $v_{C(6)=0}$  band as compared with model VII and 5-methyloxazine IIa. The C=C vibrations appear as two bands at 1630 and 1610 cm<sup>-1</sup>; this is apparently due to the formation of a different type of associate.

Introduction of substituents into the benzene ring (Table 4) does not change the overall picture of the spectrum, except for the bands belonging to the aryl vibrations. Changes in the  $v_{C=0}$ ,  $v_{C=C}$ , and  $v_{C=N}$  frequencies do not exceed 10-15 cm<sup>-1</sup>. Thus the IR spectra confirm our conclusion concerning the predominance of form B in DMSO.

The electron spectra of THF solutions of the oxazinediones that simulate the various tautomeric forms are evidence for substantial differences in their electronic structure (Fig. 2). The spectroscopic data were interpreted on the basis of quantum chemical calculations using the SSO MO LCAO approximation by the CNO method. The wave functions and excited state energies were calculated with allowance for the interaction of all configurations corresponding to electron transfers from seven higher occupied levels to seven lower free levels.

The experimental spectrum of 4-hydroxy-6-oxo model VII shows two intense absorption bands with maxima at 308 (log  $\varepsilon$  3.93) and 238 nm (log  $\varepsilon$  4.08) and a sharply defined shoulder at 250 nm (log  $\varepsilon$  3.93). They correspond to the first, fourth, and third  $\pi-\pi^*$  type excited singlet states; the calculated energies are 3.67, 5.32, and 4.95 eV and the respective wave-



Fig. 2. Electron spectra of THF solutions of oxazinediones Ia, IIa, and model compounds III-V, VII, VIII.

lengths of their absorption bands are 339 (F = 0.44), 233 (F = 0.37), and 250.4 nm (F = 0.31). The long wave absorption band is due to the transfer of electron density from the oxazine ring to the benzene ring, which amounts to 0.2 e. The absorption in the shorter wave region corresponding to the third and fourth excited states, is due to charge transfer (0.03 and 0.28 e, respectively) from the benzene ring to the heterocyclic segment.

The experimental spectrum of 6-methoxy-4-oxooxazine V shows one intense absorption band with maximum at 256 nm (log  $\epsilon$  4.13) that corresponds to the third  $\pi$ - $\pi$ \* excited singlet state (calculated energy 4.72 eV) and is due to a charge transfer of 1.6 e from the benzene ring to the heterocycle. The transition from the long wave at 263 nm (F = 0.44) corresponds to it. The absorption bands corresponding to the first and second excited singlet states with transition energies 3.88 and 4.57 eV respectively do not appear under the experimental spectral recording conditions, due to their low intensity (F = 0.075 and 0.063).

Finally, the spectrum of 5,5-dimethyl-4,6-dioxooxazine (III) is characterized by an absorption band with maximum at 272 nm (log  $\varepsilon$  4.14); this corresponds to the second  $\pi-\pi^*$  excited singlet state with 4.53 eV transition energy at 273 nm (F = 0.70). This band is due to an electron density transfer of 0.22 e from the benzene segment to the oxazine.

As Fig. 2 shows, the locations of the bands in the spectrum of oxazinedione Ia coincide with the spectrum of VII (the form B model). It is hard to compare absorption intensities because the sensitivity of the material to traces of water makes it impossible to obtain accurate extinction values. The spectra of oxazinedione IIa and its 4-methoxy derivative are also extremely close together both in band location and band intensity. Unfortunately it is not possible to judge from the electron spectra concerning the presence of other tautomers, because their absorption curves are overlapped by the spectrum of model form B.

It should also be noted that the introduction of both electron donor and electron acceptor substituents at the para position of the benzene ring and the replacement of C(s) hydrogen by methyl causes a substantial bathochromic shift of the long wave absorption band in the experimental spectra of such compounds (Table 5). In all cases this is apparently related to the expansion of the conjugation system in 2-aryl-1,3-oxazinediones.

Thus, the NMR, IR, and UV spectroscopic data are evidence that in DMSO and THF solutions the type I and II compounds exist predominantly as 2-ary1-4-hydroxy-6H-1,3-oxazin-6ones, regardless of the substituent at the para position of the benzene ring.

## EXPERIMENTAL

IR spectra of 1 or 5% solutions of materials in DMSO were recorded with a IKS-29 spectrometer in  $CaF_2$  cuvettes 250 or 35 µm thick, respectively. PMR spectra were recorded

TABLE 5. Electron Spectra of THF\* Solutions of Compounds Ib-e, IIb, c, e, f

Com- pound	$\lambda_{\max}$ , nm (log $\varepsilon$ )		$\lambda_{\max}$ , nm (log $\epsilon$ )
Ib	260 (4,1); 315 (3,8); 330 sh	IIb IIC	260 (4,07); 355 (3,89) 242 (4,08): 258 inf (3,91):
Ic	245 (4,0); 314 (3,7)		327 (3,94)
la le	258 (3,7); 313 (3,7) = 270 (3,7); 275 sh (3,7); 322	ne	(4,05); 327 (4,27)
	(3,8)	IIe	246 (3,76); 315 inf (3,64); 368 (4,31)

\*For compounds Ib-e approximate extinction values are shown; accurate values can not be obtained because of the high sensitivity of these substances to hydrolysis.

with a Tesla BS-487 C spectrometer (80 MHz), HMDS internal standard. <sup>13</sup>C NMR spectra were recorded with Varian CFT-20 and Tesla BS-567 A spectrometers (compounds Ia-e). UV spectra were recorded with a SF-20 spectrophotometer in cuvettes of 1 cm thickness. All preparation of solutions of compounds Ia-e for spectral study and fi'ing of cuvettes and ampoules for NMR were carried out in a moisture-free atmosphere.

Quantum chemical calculations by CNDO/2 and MPNDO/3 were carried out using a set of Viking programs [9]. Calculation of compounds by CNO with special  $\sigma, \pi$ -parametrization was carried out at the M. A. Suslov Scientific-Research Institute of Physical and Organic Chemistry of Rostov State University. The authors are grateful to Professor V. I. Minkin for kindly making possible the CNO calculations.

The physicochemical properties of compounds I, II, and IV-VIII are shown in Table 1.

<u>2-Phenyl-5,6-dihydro-4H-1,3-oxazine-4,6-dione (Ia)</u>. Into a solution of 14.7 g (100 mmole) of benzoyl isocyanate [10] in 150 ml of dry ether at 0° was passed 12.6-21.0 g (300-500 mmole) of ketene. The precipitate was filtered off, washed in ether, and stored in a box over  $P_2O_5$ . mp 165-166° [1].

Compounds Ic, d were obtained similarly.

<u>2-p-Nitrophenyl-5,6-dihydro-4H-1,3-oxazine-4,6-dione (Ib)</u>. Into a solution of 11.9 g (62 mmole) of p-nitrobenzoyl isocyanate in 120 ml of dry THF at temperatures between -20 and -10° was passed 4.2-6.3 f (100-150 mmole) of ketene. The solution was left for 12 h at 15°, then most of the solvent was distilled off in vacuum. The residue was stirred with 100 ml of dry dichloroethane for 15 min. The precipitate was filtered off, washed with dichloroethane and ether and stored in a box over  $P_2O_5$ . mp 207-208° [1].

Compound Ie was obtained similarly.

<u>2-Phenyl-5-methyl-1,3-oxazine-4,6-dione (IIa)</u>. To a suspension of 3.45 g (28 mmole) of benzamide in 20 ml of dry dichloroethane was added 5.3 g (34 mmole) of methylmalonyl dichloride. The mixture was boiled for 4 h, then cooled, and the precipitate was filtered off and washed with dichloroethane. mp 196-197° [2].

Compounds IIb, c, e were obtained similarly. Compound IId was separated as the hydrochloride with mp 175-177°; this was treated with an equimolar amount of methanolic triethylamine; the precipitate was filtered off and washed with methanol.

<u>2-Phenyl-3,5-dimethyl-6-oxo-1,3-oxazin-3-ium-4-olate (IV).</u> To a solution of 4 g (30 mmole) of N-methylbenzamide in 40 ml of dry benzene was added 5.8 g (37 mmole) of methylmalonyl dichloride in 20 ml of benzene at 80-90°. The mixture was stirred for 2 h at 80-90°, then 12 h at 15-17°. The solution was decanted from the oily residue and evaporated in vacuum. To the residue was added 2 ml of triethylamine in 20 ml of dichlorethane, the mixture was stirred for 15 min, and the yellow crystals were filtered off.

<u>2-Phenyl-6-methoxy-4H-1,3-oxazin-4-one (V).</u> To a solution of 7 g (120 mmole) of methoxyacetylene [11] in 50 ml of dry benzene was added 14.7 g (100 mmole) of benzoyl isocyanate with stirring at 5-7°. The mixture was stirred for 5 h at 18°, then the solvent was removed in vacuum. Methyl N-benzoylmalonamate (VI). A. To 2 g (10 mmole) of Ia was added 10 ml of absolute methanol and the mixture was let stand for 10-15 min. Excess methanol was removed in vacuum.

<u>B.</u> Compound V, 2 g (10 mmole) was dissolved with heating in 20 ml of 1:1 aqueous acetonitrile. The precipitate that formed after cooling was filtered off. IR spectrum (mineral oil), v: 3280 (N-H); 1745, 1705, 1680 (C=O); 1599, 1583 cm<sup>-1</sup>(C···C). PMR spectrum (DMSO-D<sub>6</sub>),  $\delta$ : 11.2 (s, 1H, NH), 7.48-7.88 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 3.78 (s, 2H, CH<sub>2</sub>), 3.58 ppm (s, 3H, OCH<sub>3</sub>).

<u>2-Phenyl-4-methoxy-6H-1,3-oxazin-6-one (VII)</u>. To 1.9 g (10 mmole) of Ia was added a solution of 1.26 g (30 mmole) of diazomethane in 50 ml of ether at 0°. A turbulent reaction took place that finished adter several minutes. The mixture was kept for another 1-2 h and the precipitate was filtered off.

Compound VIII was obtained similarly.

Hydrolysis of VII. A solution of 1.1 g (5.4 mmole) of VII in a mixture of 15 ml of water, 5 ml of acetonitrile, and 1 ml of concentrated HCl was stirred at 50° for 1 h, then filtered. The cooled filtrate was concentrated in vacuum and the precipitate that formed was filtered off. Yield 0.7 g (63%); mp 122-123° (with decomposition) [1].

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