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Reactions of 6-Alkoxy(alkylthio)carbonylamino-4-hydroxy-2*H*-pyran-2-ones with Some Electrophilic Reagents

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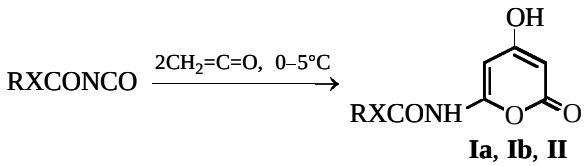
Abstract—Alkoxy(alkylthio)-4-hydroxy-2*H*-pyran-2-ones readily react with electrophiles to give substitution products at C^3. Hard electrophilic reagents replace hydrogen both in position 3 and in position 5 of the pyran ring. Methylation of 6-alkoxy(alkylthio)-4-hydroxy-2*H*-pyran-2-ones with diazomethane leads to formation of *O*- and *N*-methyl derivatives.

There are very limited published data on chemical properties of 4-hydroxy-2*H*-pyran-2-ones. The available information is concerned mainly with halogenation, alkylation, and acylation of 6-alkyl(aryl)-4-hydroxy-2*H*-pyran-2-ones [1–3]. However, some 2-pyranone derivatives, in particular 6-alkoxy(alkylthio)-4-hydroxy-2*H*-pyran-2-ones which were synthesized by us for the first time [4], remain poorly studied. Therefore, it seemed important to examine reactions of these compounds with electrophilic reagents with the goal of obtaining new 2-pyranone derivatives. It is known that a number of compounds having a pyran ring exhibit pronounced biological activity over a wide range [5–10].

Scheme 1.



Ia, **Ib**, **II**

X = O, R = Me (**Ia**), Et (**Ib**); X = S, R = Et (**II**).

Initial compounds **Ia**, **Ib**, and **II** were obtained by reaction of the corresponding acyl isocyanates with ketene in ether at 0–5°C (Scheme 1). Alkylation of pyranones **Ia**, **Ib**, and **II** with diazomethane in ether at room temperature involves the hydroxy group in position 4 and the amino group in position 6. As a result, products **IVa** and **IVb** (**V**) are formed (Scheme 2). The reaction at low temperature (on cooling with ice) gave 4-methoxy-2-pyranones **IIIa** and **IIIb** as the sole products. *N*-Methyl derivatives were not detected under these conditions. According to published data [11], methylation of 6-aryl-4-hydroxy-2-pyranones with diazomethane yields mixtures of the corresponding 4-methoxy-2-pyranones and 2-methoxy-4-pyranones. No such products were formed from 4-hydroxypyranones **Ia**, **Ib**, and **II**. A possible explanation will be given below. The bromination of **Ib** with bromine in methylene chloride at room temperature or in glacial acetic acid at 40–50°C afforded 3-bromo-4-hydroxy-6-ethoxycarbonylamino-2*H*-pyran-2-one (**VI**) (Scheme 2). The reaction of **Ib** with benzenediazonium chloride in alkaline medium (pH ~10) yieds 4-hydroxy-3-phenylazo-6-ethoxycarbonylamino-2-pyranone (**VII**) (Scheme 2).

Several methods are known for introduction of a formyl group into the pyran ring. Poulton and Cyr [12, 13] used methyl dichloromethyl ether in the presence of titanium tetrachloride as formylating agents. The same authors failed to obtain the desired 3-formylpyranone by the Vilsmeier–Haack reaction even at 90–100°C. We have found that 6-ethoxycarbonylamino-4-hydroxy-2*H*-pyran-2-one (**Ib**) readily reacts with $POCl_3$–DMF in dioxane at room temperature, yielding 3-formyl-6-ethoxycarbonylamino-4-hydroxy-2*H*-pyran-2-one (**VIII**) (Scheme 2).

The nitration of compound **Ib** with a mixture of fuming nitric acid and acetic acid in methylene chloride was not selective. The reaction gave a mixture of 5- and 3-nitro-6-ethoxycarbonylamino-4-hydroxy-2*H*-pyran-2-ones **IXa** and **IXb** (Scheme 2). We succeeded in isolating only 5-nitro derivative **IXa** in the pure state. The ^{1}H NMR spectra of compounds **Ia**, **Ib**, and **II** in DMSO-d_6 contain signals from protons in positions 3 (δ 5.0 ppm) and 5 of the pyran ring (δ 6.4 ppm), and downfield singlets from the

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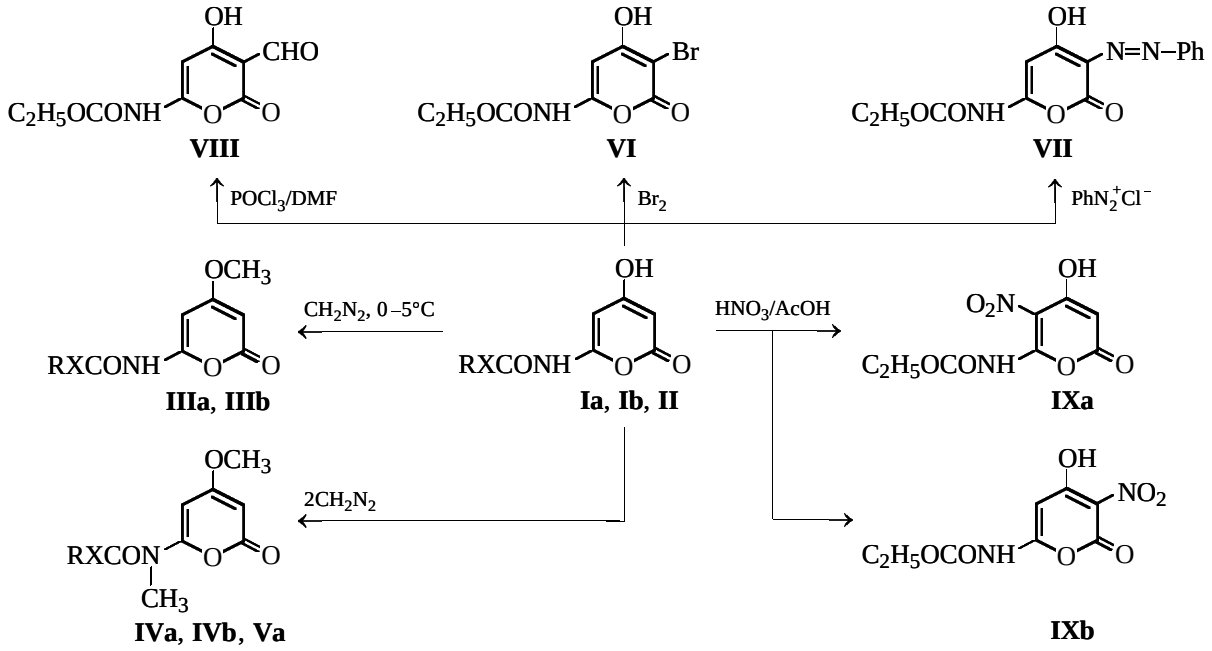
Scheme 2.



amino group (δ 10.8–11.5 ppm) and hydroxy group (δ 11.7–12.6 ppm) (Table 1). The position of the latter depends on the substituent at C^6: in the spectrum of 6-ethylthiocarbonyl derivative **II** these signals are displaced downfield by 0.7 and 1 ppm, respectively. The ^{1}H NMR spectra of methylated products **IVa**, **IVb**, and **V** lack signals from amino and hydroxy protons, but singlets from methyl groups appear at δ 3.2 and 3.8 ppm. The corresponding carbon atoms give signals at δ_C 62.53 (OCH_3) and 56.58 ppm (NCH_3) in the ^{13}C NMR spectra. The structure of products **IIIa** and **IIIb** as *O*-methyl derivatives follows from the absence of hydroxy proton signal and the presence of NH signal, as well as of a singlet at δ 3.8 ppm which was assigned to methoxy group in position 4 of the pyran ring. In addition, compounds **IIIa** and **IIIb** showed in the IR spectra an absorption band at 3150 cm^{-1}, belonging to the NH group; no such band was observed in the IR spectra of **IVa**, **IVb**, and **V**. The ^{1}H NMR spectrum of **VI** in DMSO-d_6 contained no 3-H signal, whereas signals from 5-H, OH, and NH protons were observed in a weaker field (by 0.3–0.5 ppm), as compared to the unsubstituted analog. The signal at δ_C 79.23 ppm in the ^{13}C NMR spectrum belongs to the carbon atom attached to bromine. The long-wave absorption band in the UV spectrum of **VI** is displaced by 12 nm to the short-wave region relative to the absorption maximum of initial compound **Ib**, which is located at λ 310 nm. In the ^{1}H NMR spectrum of **VII** the multiplet signal at δ 7.48 ppm was assigned to the phenyl group. No 3-H signal was present in the spectrum. The OH and NH proton signals appear, respectively, 0.4 and 4.3 ppm downfield relative to the corresponding signals in the spectrum of the parent compound. The red shift of the long-wave absorption band in the UV spectrum of **VII** is 100 nm.

The aldehyde group in compound **VIII** gives rise to a characteristic singlet at δ 9.78 ppm. Signal from 3-H is absent, and that from the hydroxy proton shifts downfield by 3 ppm. In the ^{13}C NMR spectrum, the signal at δ_C 189.66 ppm belongs to the carbonyl carbon atom.

The result of the nitration of compound **Ib** is illustrated best by comparison of the ^{1}H NMR spectra of the mixture of products and pure 5-nitro derivative **IXa**. The latter contains a singlet from the 3-H proton at δ 5.82 ppm. This signal is also present in the spectrum of the product mixture which also contains a singlet at δ 6.47 ppm, which belongs to 5-H; signals from all other protons have a double intensity (Fig. 1).

Our experimental data are consistent with the results of quantum-chemical calculations of the electronic structure of pyranones by the MNDO and MINDO/3 semiempirical methods (HyperChem 3.0 for Windows); the choice of these procedures was substantiated in [14]. As noted above, methylation of 6-aryl-4-hydroxy-2-pyranones gives mixtures of

Table 1. ^{1}H and ^{13}C NMR, IR, and UV spectra of pyranones **I**–**IX**

Comp. no.	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	^{1}H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
Ia	3260, 3135, 2750–2450, 1730, 1650, 1550	215 (4.32), 306 (4.01)	11.60 s (1H), 10.88 s (1H), 6.32 s (1H), 5.05 s (1H), 3.70 s (3H)	173.13, 161.49, 155.41, 152.49, 84.21, 52.73
Ib	3270, 3127, 2700–2400, 1720, 1672 sh, 1645, 1530	215 (4.36), 305 (4.11)	11.75 s (1H), 10.95 s (1H), 6.42 s (1H), 5.10 s (1H), 4.20 q (2H), 1.20 t (3H)	172.84, 161.24, 155.17, 151.76, 84.04, 61.33, 14.12
IIa	3370–3070, 1690, 1655, 1641, 1557	235 (4.17), 315 (4.23)	11.80 s (1H), 11.50 s (1H), 6.48 s (1H), 5.10 s (1H), 2.82 q (2H), 1.18 t (2H)	151.20, 154.62, 161.04, 172.49, 83.65, 60.87, 13.50
IIIa	2750–2450, 1730, 1650, 1550	212 (4.22), 306 (4.03)	10.88 s (1H), 6.32 s (1H), 5.05 s (1H), 3.84 s (3H), 3.70 s (3H)	173.13, 161.49, 155.41, 152.49, 89.35, 85.12, 63.46, 53.73
IIIb	2760, 1750, 1730, 1660, 1580, 1547, 1249	213 (4.33), 306 (4.10)	10.88 s (1H), 6.22 s (1H), 5.33 s (1H), 4.20 q (2H), 3.80 s (3H), 1.20 t (3H)	172.50, 161.33, 154.60, 152.93, 92.48, 85.08, 62.53, 33.73, 14.03
IVa	1730, 1650, 1550	209 (4.25), 306 (4.04)	6.32 s (1H), 5.05 s (1H), 3.84 s (3H), 3.70 s (3H), 3.20 s (3H)	173.13, 161.49, 155.41, 152.49, 89.35, 85.12, 63.46, 58.13, 53.73
IVb	1750, 1730, 1660, 1580, 1547, 1249	210 (4.31), 306 (4.08)	6.22 s (1H), 5.33 s (1H), 4.20 q (2H), 3.80 s (3H), 3.20 s (3H), 1.20 t (3H)	172.50, 161.33, 154.60, 152.93, 92.48, 85.08, 62.53, 56.58, 33.73, 14.03
V	1690, 1655, 1641, 1557	230 (4.10), 315 (4.23)	6.40 s (1H), 5.67 s (1H), 3.48 s (3H), 3.09 s (3H), 2.87 q (2H), 1.21 m (1H)	161.20, 164.62, 171.04, 178.49, 83.65, 70.65, 60.87, 53.16, 13.50
VI	3125, 1725, 1688, 1596, 1570, 1277	224 (4.44), 298 (4.10)	12.60 s (1H), 11.00 s (1H), 6.60 s (1H), 4.15 q (2H), 1.22 s (3H)	168.93, 157.77, 153.79, 151.67, 83.65, 79.23, 61.52, 14.09
VII	3430, 3200, 1745, 1730, 1635, 1604, 1563, 1280	220 (4.12), 416 (4.19), 246 sh (3.72)	11.25 s (1H), 15.90 s (1H), 6.30–7.62 m (5H), 6.27 s (1H), 4.18 q (2H), 1.23 s (3H)	175.62, 156.81, 151.78, 140.85, 129.74, 127.02, 121.24, 117.13, 90.06, 81.87, 61.83, 14.07
VIII	3100–3200, 1755, 1720, 1715, 1640, 1590, 1220	236 (4.15), 306 (4.18), 327 sh (4.01)	14.57 s (1H), 9.78 s (1H), 7.55 s (1H), 6.62 s (1H), 4.29 q (2H), 1.34 s (3H)	189.66, 178.92, 160.43, 159.13, 151.41, 97.31, 83.48, 62.12, 13.99
IXa	3125, 1725, 1688, 1596, 1570	330 (3.75), 300 sh (3.63)	10.87 s (1H), 5.83 s (1H), 4.10 q (2H), 3.88 s (1H), 1.20 m (3H)	169.44, 156.31, 153.90, 151.52, 83.80, 61.65, 48.98, 14.01

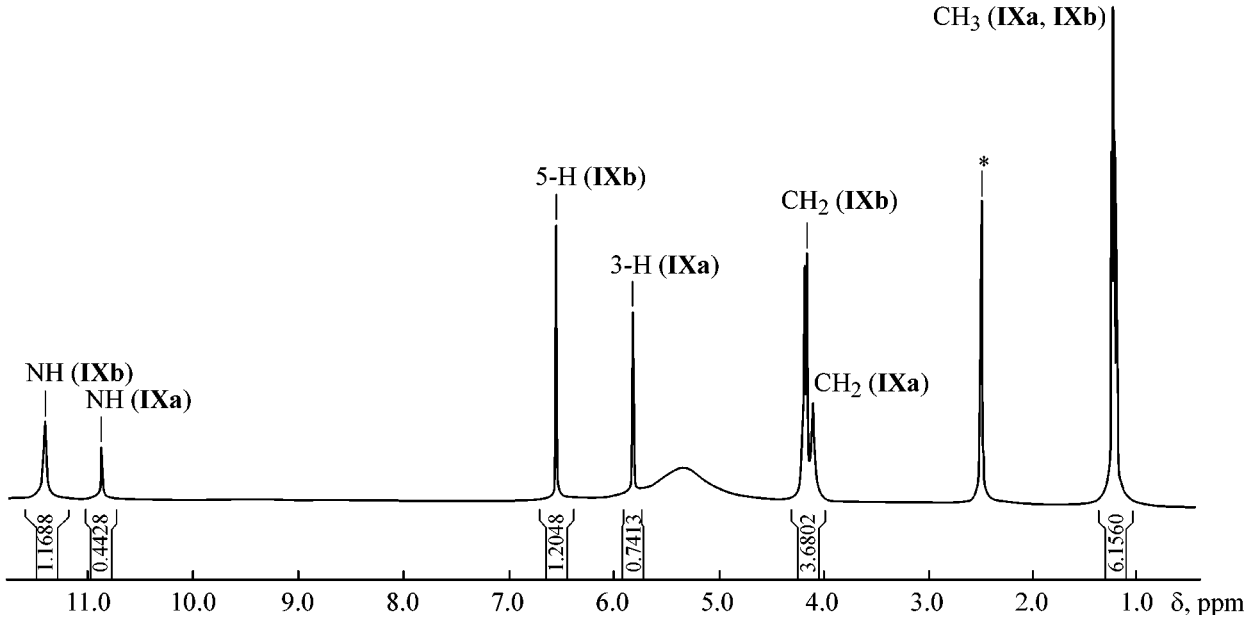
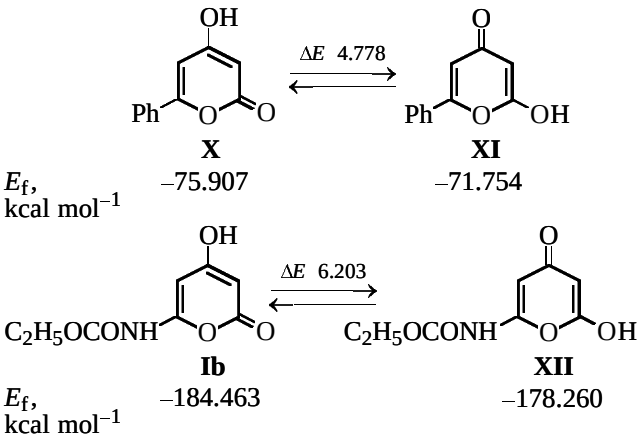


Fig. 1. ^{1}H NMR spectrum of a mixture of 5- and 3-nitro-6-ethoxycarbonylamino-4-hydroxy-2-pyranones **IXa** and **IXb** in DMSO-d_6.

4- and 2-methoxy derivatives [11] which were not formed in the reactions with compounds **Ia**, **Ib**, and **II**. We presumed that the differences in the energy of formation of tautomers **X**/**XI** and **Ib**/**XII** (Scheme 3) are not similar. In fact, the calculated difference in the energy of formation of 4-hydroxy-2-oxo and 2-hydroxy-4-oxo tautomers of 6-phenyl derivatives is by a factor of ~1.5 lower than the corresponding difference for 6-ethoxycarbonylaminopyranones.

Scheme 3.



The results of quantum-chemical calculations of the electronic structures of compound **Ib** and 4-hydroxy-6-methyl-2-pyranone (**XIII**) (the latter was selected as the most studied reperesentative of this series of heterocycles) provide a plausible explanation for the ready Vilsmeier reaction of 6-alkoxycarbonylamino-4-hydroxy-2-pyranones, in contrast to 4-hydroxy-6-methyl-2-pyranone. According to our previous data [15], the possibility of formylation with $POCl_3$–DMF (which is a relatively weak electrophile) and its direction are determined by the charge on the reaction center, the energy of the highest occupied molecular orbital (HOMO), and contribution of the corresponding atomic orbital of the substrate to the HOMO. As follows from Table 2 and Fig. 2, the electron density on C^3 in molecule **XIII** is considerably smaller than in **Ib**. Obviously, this factor facilitates formylation of the latter. The result of the nitration reaction can also be interpreted in terms of the calculation data which show a relatively small difference in the charges on C^3 and C^5 (Table 2). Therefore, nitronium cation, being a hard electrophile, readily attacks both C^3 and C^5 atoms of the pyran ring. Nevertheless, this difference is sufficient for softer reagents to attack only the carbon atom in position 3.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrometer in mineral oil. The UV spectra were measured on an SF-56 spectrophotometer in methanol. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-500 instrument (500 and 125 MHz, respectively) in DMSO-d_6. The purity of the products was checked by TLC on Silufol UV-254 plates (eluent ethyl acetate, development with UV light or iodine vapor). The melting points, R_f values, and elemental analyses of compounds **I**–**IX** are given in Table 3.

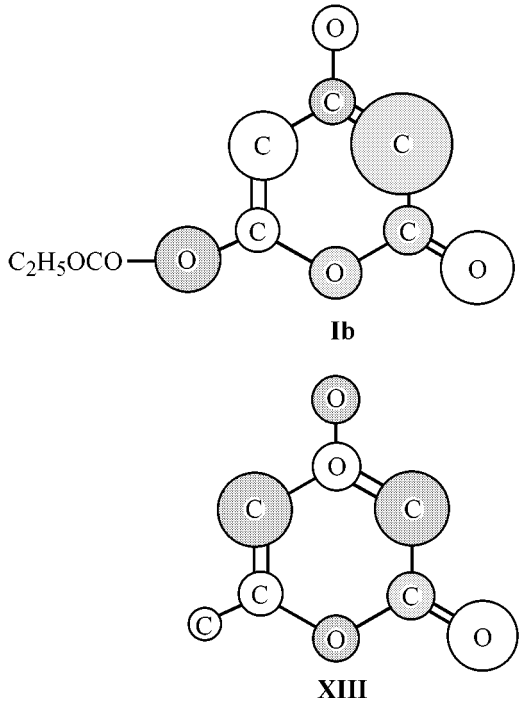


Fig. 2. Electron density distribution in the molecules of 6-ethoxycarbonylamino-4-hydroxy-2*H*-pyran-2-one (**Ib**) and 4-hydroxy-6-methyl-2*H*-pyran-2-one (**XIII**).

Table 2. Calculated energies of the highest occupied molecular orbital and charges on C^3 in molecules **Ib** and **X**–**XIII**

Comp. no.	HOMO energy, eV		Charge on C^3, au	
	MNDO	MINDO/3	MNDO	MINDO/3
Ib	–9.21	–8.52	–0.32 (–0.25)[a]	–0.46 (–0.44)[a]
X	–9.95	–8.43	–0.24	–0.47
XI	–9.86	–8.86	–0.25	–0.44
XII	–9.68	–9.13	–0.31	–0.45
XIII	–9.39	–8.79	–0.29	–0.47

[a] Charge on C^5.

Table 3. Melting points, R_f values, and elemental analyses of compounds **I**–**IX**

Comp. no.	mp, °C	R_f	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
Ia	203–204	0.42	45.2	3.9	7.4	$C_7H_7NO_5$	45.4	3.8	7.6
Ib	160–162 (decomp.)	0.38	48.3	4.8	6.8	$C_8H_9NO_5$	48.2	4.5	7.0
II	159–160	0.48	44.7	4.1	6.6	$C_8H_9NO_4S$[a]	44.6	4.2	6.5
IIIa	183–185	0.46	48.3	4.8	6.8	$C_8H_9NO_5$	48.5	4.7	6.7
IIIb	135–137 (decomp.)	0.44	50.7	5.2	6.6	$C_9H_{11}NO_5$	50.5	5.4	6.5
IVa	113–115	0.51	50.7	5.2	6.6	$C_9H_{11}NO_5$	50.8	5.1	6.4
IVb	92–94	0.47	52.9	5.7	6.2	$C_{10}H_{13}NO_5$	53.0	5.5	6.3
V	133–135 (decomp.)	0.59	49.4	5.3	5.8	$C_{10}H_{13}NO_4S$[b]	49.3	5.3	5.7
VI	131–132 (decomp.)	0.66	34.5	2.9	1.4	$C_8H_8BrNO_5$[c]	34.7	3.0	1.3
VII	168–169 (decomp.)	0.70	55.4	4.3	13.9	$C_{14}H_{13}N_3O_5$	55.2	4.4	14.0
VIII	168–170 (decomp.)	0.45	47.6	4.0	6.2	$C_9H_9NO_6$	47.7	4.1	6.3
IXa	121–123	0.57	42.1	3.5	12.3	$C_8H_8N_2O_6$	42.2	3.4	12.1

[a] Found S, %: 15.0. Calculated S, %: 14.9. [b] Found S, %: 13.2. Calculated S, %: 14.9. [c] Found Br, %: 28.8. Calculated Br, %: 28.5.

Acyl isocyanates were prepared from the corresponding amides by treatment with oxalyl chloride. The solvents were purified and dehydrated by standard procedures. Ketene was generated by pyrolysis of acetone at 650–750°C in a 200 × 22-mm quartz tube packed with crushed quartz.

4-Hydroxy-6-methoxycarbonylamino-2*H*-pyran-2-one (Ia). Ketene, 6.3–10.5 g, was passed through a solution of 4.7 g of methoxycarbonyl isocyanate in 50 ml of dry diethyl ether, maintained at 0–5°C. The mixture was left to stand for 48 h, and the precipitate was filtered off and recrystallized from acetonitrile–water (4 : 1). Yield 2 g (24%).

6-Ethoxycarbonylamino-4-hydroxy-2*H*-pyran-2-one (Ib). Ketene, ~21 g, was passed through a solution of 11.1 g of ethoxycarbonyl isocyanate in 120 ml of dry diethyl ether, maintained at 0–5°C. The precipitate was filtered off. Yield 12.4 g (65%).

6-Ethylthiocarbonylamino-4-hydroxy-2*H*-pyran-2-one (II). Ketene, ~6.3 g, was passed through a solution of 4 g of ethylthiocarbonyl isocyanate in 50 ml of dry diethyl ether, maintained at 0–5°C. The mixture was left overnight at 15–20°C, the most part of the solvent (~80%) was removed under reduced pressure, and the precipitate (3.5 g) was filtered off. The crude product was recrystallized first from chloroform and then from aqueous alcohol (1 : 1). Yield 2.3 g (35%).

4-Methoxy-6-methoxycarbonylamino-2*H*-pyran-2-one (IIIa). A solution of diazomethane in ether was added at 0–5°C to a suspension of 1 g of pyranone **Ia** in 7 ml of ether, and the mixture was left overnight. The solvent was removed under reduced pressure, and the residue was recrystallized from dichloroethane. Yield 0.7 g (65%).

6-Ethoxycarbonylamino-4-methoxy-2*H*-pyran-2-one (IIIb) was synthesized as described above for compound **IIIa**. Yield 6 g (56%).

4-Methoxy-6-[methyl(methoxycarbonyl)amino]-2*H*-pyran-2-one (IVa). A solution of diazomethane in diethyl ether was added to 1 g of pyranone **Ia**, and the mixture was left overnight. The solvent was removed under reduced pressure, and the residue was recrystallized from dichloroethane. Yield 0.4 g (34%).

4-Methoxy-6-[ethoxycarbonyl(methyl)amino]-2*H*-pyran-2-one (IVb) was synthesized as described above for compound **IVa**. Yield 0.7 g (61%).

4-Methoxy-6-[ethylthiocarbonyl(methyl)amino]-2*H*-pyran-2-one (IVb) was synthesized as described above for compound **IVa**. Yield 0.5 g (44%).

3-Bromo-6-ethoxycarbonylamino-4-hydroxy-2*H*-pyran-2-one (VI). Bromine, 0.79 ml, was added dropwise with stirring over a period of 10 min to a suspension of 2 g of 6-ethoxycarbonylamino-4-hydroxy-2*H*-pyran-2-one (**Ib**) in methylene chloride. The mixture was stirred for 1 h and was left overnight. The solvent was removed under reduced pressure, and the residue was recrystallized from acetone. Yield 1.33 g (48%).

6-Ethoxycarbonylamino-4-hydroxy-3-phenylazo-2*H*-pyran-2-one (VII). An aqueous solution of benzenediazonium chloride was added in portions under stirring to a solution of 1 g of pyranone **Ib** in aqueous alkali (pH ~10), cooled to 0–5°C. The mixture was

stirred for 1 h, and the precipitate was filtered off and recrystallized from methanol–water (4 : 1). Yield 0.7 g (50%).

6-Ethoxycarbonylamino-3-formyl-4-hydroxy-2*H*-pyran-2-one (VIII). A mixture of 1.4 ml of dimethylformamide and 0.6 ml of phosphoryl chloride was added to a solution of 1 g of compound **Ib** in 10 ml of anhydrous dioxane. The mixture was stirred for 1.5 h and diluted with 50 ml of water, and the precipitate was filtered off, dried, and recrystallized from dichloroethane–ethyl acetate (4 : 1). Yield 0.6 g (52%).

6-Ethoxycarbonylamino-4-hydroxy-5-nitro-2*H*-pyran-2-one (IXa). Glacial acetic acid, 0.3 ml, and fuming nitric acid (d = 1.51 g cm^{-3}), 0.2 ml, were added to a suspension of 1 g of compound **Ib** in 7 ml of methylene chloride, cooled to 0–5°C. The mixture was stirred for 1 h and was left overnight. The solvent was removed under reduced pressure, and the residue was treated with ice. The precipitate was filtered off and recrystallized twice from methanol. Yield 0.3 g (24%).

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