REACTIONS OF ETHYL 2-HYDROXY-4-(4-HYDROXY-6-METHYL-2-PYRON-3-YL)-4-OXO-2-BUTENOATE WITH N-NUCLEOPHILES. SYNTHESIS OF ISOMERIC PYRONYLPYRAZOLES AND PYRANO[4,3-c]PYRAZOLES

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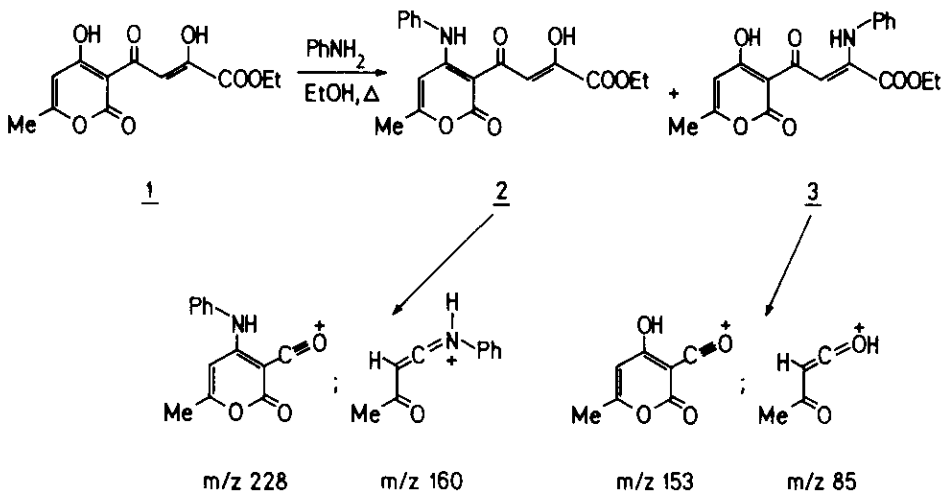
Abstract - Reaction of the title compound **1** with aniline gave two Schiff's bases **2** and **3**, while condensation of **1** with phenylhydrazine afforded four products **4** - **7**. Compounds **4** and **6** were formed after initial nucleophilic attack at the central carbonyl carbon of tricarbonylic moiety, while **5** and **7** were formed after initial attack at the 4-position of the 2-pyrone ring. These structures were confirmed by the selective preparation of **4** - **7** from pyranopyrandiones **12** and **13**, respectively. Pyrazole-4-carboxylic acid derivatives **6** and **7** cyclize in acetic anhydride into fused pyrano[4,3-c]pyrazoles **8** and **9**, respectively. Their structures were compared with that of the parent 3-methyl congeners **14** and **15**, obtained from dehydroacetic acid.

2-Pyrone derivative **1**[1] has been intensively studied as a specific analytical reagent[2-5]. Related to these studies it has been shown that **1** reacts with alkylamines to give exclusively the products of nucleophilic attack at the 4-position of 2-pyrone ring[6], contrasting a similar reaction of **1** with hydroxylamine which yields the products of the initial attack at the side chain carbonyl carbons[7]. Continuing this study we examined reactivity of the parent compound **1** with the simplest arylamine (aniline) and arylhydrazine (phenylhydrazine). The results of synthetic and spectroscopic studies are reported in this paper.

Treatment of **1** with aniline in hot ethanol afforded a mixture of two Schiff's bases, **2** and **3** (Scheme 1), contrasting the formation of a single product in a similar reaction with alkylamines[6]. These two isomers have been assigned as the products of nucleophilic attack at 4-position of 2-pyrone ring and 2-position of side chain, respectively. ^{1}H Nmr spectrum of **2** and **3** revealed two pairs of signals

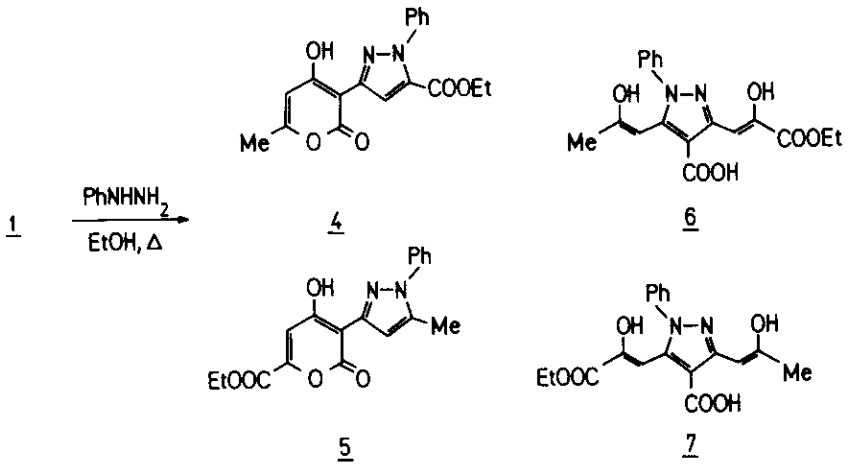
strongly shifted downfield, at δ 18.7 and 12.7 ppm for 2 and at 17.4 and 11.3 ppm for 3, respectively. Their positions correspond with strongly hydrogen bonded protons. The two more downfield shifted sharp signals may be assigned to the hydroxyl protons, and the broad higher field signals to the amino protons[6,18]. Mass spectra of 2 and 3 exhibited rather different fragmentation patterns. The most characteristic ions observed for 2 were those at m/z 228 (19%) and 160 (84%), while 3 exhibited ions at m/z 153 (66%) and 85 (25%); their structures are indicated in Scheme 1.

Scheme 1

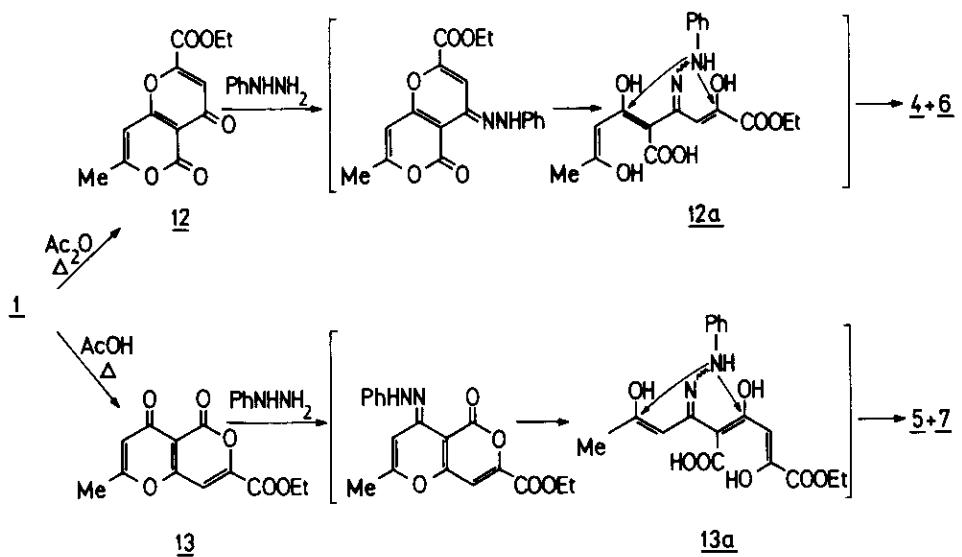


An unexpected absence of site selectivity in reaction of aniline with 1 was also observed in the reaction of phenylhydrazine with the same starting compound affording, however, different structural isomers. Again, a brief heating of the above reaction partners in ethanol led to the formation of four products, as revealed by thin layer chromatography (Scheme 2). A mixture of compounds 4 and 5 was separated from the reaction mixture by fractional crystallization, while the individual fluorescent products 4 and 5 were subsequently separated by preparative thin layer chromatography. From the mother liquors compounds 6 and 7 were extracted with aqueous sodium hydrogen carbonate, followed by precipitation with dilute acid. Compounds 4,5 were obtained in ca. 13% yield as 2.5 : 1 mixture, while compounds 6,7 in ca. 61% yield as a 6 : 1 mixture. The reaction of 1 with

Scheme 2



Scheme 3



phenylhydrazine or its hydrochloride was repeated, e.g. in refluxing ethanol and/or acetic acid. This did not, however, affect the structure of the products but only, though not significantly, their ratio. A somewhat lower yield of **4,5** was obtained in acetic acid. Compound **6**, however, was regularly obtained as the major product. A characteristic example is given under Experimental, some physical and spectroscopic data for **4 - 7** are collated in Tables 1-4.

Additional chemical evidence for the formation of the two pairs of products **4,6** and **5,7**, from **1** was provided by a stepwise approach. In the first step compound 1 was cyclized with acetic acid and acetic anhydride into two isomeric pyrano-pyrandiones 12 and 13[8]. Their subsequent reaction with phenylhydrazine afforded the same two pairs of products, **4,6** and **5,7**, respectively. Scheme 3 outlines the plausible mechanistic pathway[9], which requires ring opening of the intermediate hydrazones into **12a** and **13a**, respectively.

The structures of **4 - 7** were confirmed after detailed spectroscopic study. Compounds **4** and **5** exhibit characteristic ir frequencies at 1728 and 1700 cm^{-1} for **4** and at 1730 and 1710 cm^{-1} for **5**, corresponding to 2-pyrone and ester carbonyl stretching bands. ^{1}H Nmr data for isomer **4** reveal characteristic positions for the signals of methyl group and C(5)-H at δ 2.29 and 6.01 ppm, close to the values observed for starting compound **1**. A corresponding C(5)-H signal in isomer **5** is shifted downfield by ca. 1 ppm, revealing the deshielding effect of ethoxycarbonyl group, as already observed for 6-methoxycarbonyl-2-pyrone[10]. A rather strong hydrogen bond is evidenced for = C(4)-OH proton at δ 12.5 ppm in **4**, and 13.4 ppm in **5**. Both structures allow hydrogen bonding to the heterocyclic nitrogen atom. Conclusive evidence for structures **4** and **5** comes from the ^{13}C nmr spectra (Table 1) and in particular from some of the off resonance decoupling experiments. In the spectrum of pyronylpyrazole **5** downfield shifts were observed for C-3 and C-5 signals and a significant upfield shift for C-6 signal of 2-pyrone ring[10,18]. Similar regularities of α, β and δ effects have been observed on the introduction of the methoxycarbonyl group to the 6-position of 2-pyrone[10].

^{13}C Nmr spectroscopic characteristics of a pyrazole part in isomer **5** are congruent with those of some 3-substituted 5-methyl-1-phenylpyrazoles [11-13]. On the other hand, the ^{13}C chemical shift values for pyrazole part in isomer **4** are also explicable by the influence of ethoxycarbonyl substituent. Namely, the ethoxy-carbonyl group causes an upfield shift at the site of substitution (C-5) and a

downfield shift of the pyrazole C-4 signal.

Finally, it is noteworthy that M^+ - COOEt fragment in the mass spectrum of isomer 5 represents the base peak while it is absent in the spectrum of isomer 4. This feature, together with some other characteristic peaks follows the general fragmentation patterns of 6-substituted 4-hydroxy-2-pyrones[14] as well as those of some N-phenylpyrazoles[15].

Table 1. ^{13}C Nmr Data of Isomers 4 and 5 ($CDCl_3$, δ/ppm)

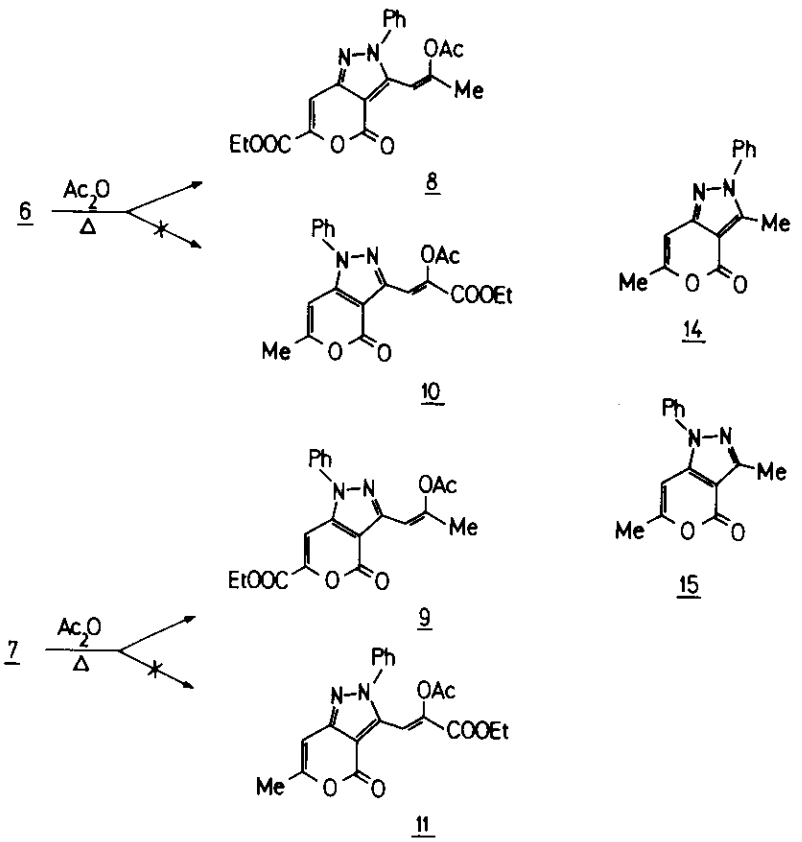
Compd	2-Pyrone ring					Pyrazole ring		
	C-2	C-3	C-4	C-5	C-6	C-3	C-4	C-5
4	162.4	93.3	168.6	101.0	162.2	147.9	111.8	133.9
5	160.4	99.6	166.2	108.2	147.1	147.7	107.7	139.9

The structure assignments of isomeric compounds **6** and **7** are also based on elemental analysis and spectral data. The mass spectrum of each isomer did not show molecular ion, instead M^+-18 ion was observed. However, the elemental analyses fit in well with molecular formula $C_{18}H_{18}N_2O_6$. Ir spectra of both compounds reveal evidence for the presence of the carboxylic group. Besides medium strong hydroxyl stretching band near 3500 cm^{-1}, they exhibit a broad absorption at about 2500 cm^{-1} which is characteristic for the carboxylic acid dimer. Further, ^1H nmr spectra show broad strongly concentration dependent resonance corresponding to the hydroxyl protons. They also reveal ethoxycarbonyl proton signals.

Since structural features of compounds **6** and **7** permit two competitive pathways to the fused pyranopyrazole ring, four products might be expected (Scheme 4). However, in the reaction of each starting compound with acetic anhydride only **8** was obtained from **6** in 81% yield and **9** in 75% yield from **7**.

Alternate methods of cyclization failed to convert **6** or **7** to the fused pyranopyrazole ring. No reaction occurred, e.g. on treatment of **6** with acetic acid under reflux for 6 h. However, product **8** was observed by tlc immediately after adding acetic anhydride into the reaction mixture. On the other hand, any attempt to saponify the acetoxy group in **8** and **9**, e.g. with sodium methoxide or dilute acid, yielded only pyrazole-4-carboxylic acid derivatives **6** and **7**, respectively.

Scheme 4



Thus, it seems plausible that the cyclization cannot proceed without parallel O-acylation. The unambiguous evidence for fused structures **8** and **9** was provided by comparison with congeneric structures **14** and **15**[16,17] derived from 3-acetyl-4-hydroxy-6-methyl-2-pyrone(dehydroacetic acid). The most relevant ^{1}H nmr and ^{13}C nmr spectral data are collated in Table 2.

Both products derived from **6** and **7** showed in their ^{1}H nmr spectra signals assignable to C(7)-H of the fused pyranopyrazole moiety and methine protons of the side chain. The observed resonances at δ 6.07 and 7.02 ppm in the spectrum of compound derived from **6** revealed marked shifts as related to C(7)-H resonance of the model compound. Thus, the structure **10** seemed implausible for this product. The ^{1}H nmr spectrum of the product derived form **7** exhibited corresponding signals at δ 6.38 and 7.07 ppm, indicating the structure **11**. Inspection of the methyl signal at δ 2.38 ppm, however, revealed a small downfield shift (ca. 0.1 ppm) with respect to

C(6)-CH_3 of the model compound. Moreover, no discernible splitting was observed, which is to be expected for allylic coupling of C(6)-CH_3 with C(7)-H. These facts suggest that among four possible isomeric structures we may exclude those with a methyl group on the fused pyranopyrazole moiety. To prove this more rigorously we investigated the ^{13}C nmr spectral data. Indeed, the positions of C-7 resonances in the spectra of **8** and **9** exhibited large downfield shifts as compared with appropriate carbon resonances of model substances **14** and **15** (Table 2). Such large downfield shifts (ca. 15.5 ppm) are in accordance with the expected β effect of C(6)-COOEt substituent in **8** and **9**, respectively.

Table 2. Selected ^1H Nmr and ^{13}C Nmr Spectral Data ($CDCl_3$, δ/ppm)[a]

Compd	H(CH_3)	C(7)-H	C-7[b]	C-3a
8	2.28	7.02	112.3 d	104.6 s
9	2.38	7.07	108.5 d	112.9 s
14	2.28 d[c]	6.32 q[c]	96.8 d	106.0 s
15	2.29 d[c]	6.38 q[c]	92.7 d	104.7 s

s - singlet, d - doublet, q - quartet

[a] The complete assignments of ^{13}C nmr spectral data will be published separately; [b] Splittings observed with off resonance decoupling; [c] J=0.7 Hz.

The direction of cyclization is probably determined by the location of the functional groups in the substrates **6,7**, hence the presence of the COOEt group seems to favour formation of the fused pyranopyrazole forms **8** and **9**, but not **10** and **11**. It is also noteworthy that the fragmentation pathways of **8** and **9** exhibit considerable similarity to that of starting compounds **6** and **7**, respectively. Namely, in the mass spectrum of both **6** and **7** molecular ion is absent, M^+-18 ion is generated instead. The fragmentation patterns originating from M^+-18 ions are identical with those obtained for fused compounds **8** and **9**, respectively. This indicated that the electron-impact induced cyclization and/or thermal cyclization of **6** and **7** occurred initially in the mass spectrometer. The unsuccessful attempt of cyclization of compound **6** by prolonged heating in a vacuum ruled out the possibility of thermally

induced cyclization. Further investigations of electron-impact induced cyclization of **6** and **7** in the mass spectrometer are in progress.

EXPERIMENTAL

The melting points were taken on a Kofler micro hot stage, and are uncorrected. The ir spectra were recorded on a Perkin-Elmer infrared spectrophotometer 297, the uv/vis spectra on a Cary 17 spectrophotometer, and the ^{1}H nmr and ^{13}C nmr spectra were recorded on a JEOL FX 90Q spectrometer with TMS as an internal standard. The mass spectra were taken on Varian MAT CH-7 and GCMS-QP 1000 Shimadzu instruments. Silica gel plates (Merck, TLC, 60 F_{254}) were used for thin layer chromatography. Preparative chromatography was performed on silica plates prepared with silica gel (Merck, 60 PF_{254}) and on Al_2O_3 plates (Merck, 150 F_{254}, Type T).

Pyranopyrandiones 12 and **13** were prepared from compound **1** in acetic acid and acetic anhydride by our procedure described previously[8]. **Pyranopyrazole 14** (mp 210°C) was prepared in a two-step reaction from dehydroacetic acid by treatment with $POCl_3$ and PCl_5, followed by reaction with phenylhydrazine, according to published procedure [16]. **Pyranopyrazole 15** (mp 158°C) was prepared from dehydroacetic acid and phenylhydrazine, according to published procedure[17].

Preparation of compound 1 from dehydroacetic acid (3-acetyl-4-hydroxy-6-methyl-2-pyrone)

A suspension of dehydroacetic acid (14.9 g, 0.089 mol) in absolute ether (150 ml) was added to sodium ethoxide prepared from metallic sodium (4.5 g, 0.2 mol) and absolute ethanol (10.5 ml) in ether (50 ml). Diethyl oxalate (12 ml, 0.089 mol) was added to the reaction mixture, stirred for 4 h and kept overnight at room temperature. The sodium salt of **1** was filtered off, dried in the air and dissolved in cold water. When the water solution was acidified with diluted hydrochloric acid, the compound **1** precipitated immediately. The crude **1** (15 g, 63%) was purified for further use by recrystallization from ethanol, affording a pure product with mp 139 - 141°C. For spectroscopic data (ir, ^{1}H nmr and mass spectra) see refs.[5,6].

Ethyl 4-(4-anilino-6-methyl-2-pyron-3-yl)-2-hydroxy-4-oxo-2-butenoate (2) and ethyl 2-anilino-4-(4-hydroxy-6-methyl-2-pyron-3-yl)-4-oxo-2-butenoate (3)

A mixture of compound **1** (0.67 g, 2.5 mmol) and aniline (0.25 ml, 2.5 mmol) in ethanol (20 ml) was refluxed for 1 h. The mixture was cooled, the yellow precipi-

tate was filtered off to yield Schiff's base 2 (0.37 g, 43%). The filtrate was reduced by evaporation, the yellow precipitate formed by cooling the solution was separated to yield Schiff's base 3. (0.25 g, 29%).

Preparation of 4 - 7 from 1, general procedure

A mixture of 1 (1.34 g, 5 mmol) and phenylhydrazine (0.55 g, 5 mmol) in ethanol (20 ml) was refluxed for 15 min. The reaction mixture was cooled overnight. The formed precipitate (0.22 g, 13%), as shown by ^{1}H nmr analysis, was a mixture of 4 and 5 in about 2.5:1 ratio. The pure isomeric **5-ethoxycarbonyl-3-(4-hydroxy-6-methyl-2-pyron-3-yl)-1-phenylpyrazole (4)** and **3-(6-ethoxycarbonyl-4-hydroxy-2-pyron-3-yl)-5-methyl-1-phenylpyrazole (5)** were obtained by preparative chromatography on silica gel with chloroform - petrol ether (1:1).

After removal of 4 and 5 from the reaction mixture the filtrate was evaporated to dryness, the residue was dissolved in methylene chloride and extracted with 10% aqueous sodium hydrogen carbonate solution. The aqueous layer was then acidified with 10% hydrochloric acid and extracted with methylene chloride. After evaporation of the solvent, product (1.1 g, 61%) was obtained, which was shown by ^{1}H nmr analysis to consist of 6 and 7 in about 6:1 ratio.

3-(2-Ethoxycarbonyl-2-hydroxyvinyl)-5-(2-hydroxy-1-propenyl)-1-phenyl-4-pyrazolecarboxylix acid (6) and 5-(2-ethoxycarbonyl-2-hydroxyvinyl)-3-(2-hydroxy-1-propenyl)-1-phenyl-4-pyrazolecarboxylic acid (7) were separated by repeated recrystallizations from ethanol-water. Compound 7 was prepared in the best yield from compound 13 (see procedure below). Compounds 4 - 7 display fluorescence when exposed to long wavelength light (365 nm) on thin layer of silica gel: 4 - yellow, 5 - light blue, 6 - deep blue, and 7 - yellow.

Preparation of 4 and 6 from pyrano[4,3-b]pyrandione (12)

A mixture of compound 12 (0.5 g, 2 mmol) and phenylhydrazine hydrochloride (0.32 g, 2.2 mmol) in ethanol (20 ml) was refluxed for 10 h. After cooling overnight compound 4 (0.21 g, 31%) was obtained. The filtrate was evaporated to dryness, the residue was dissolved in methylene chloride, extracted with 10% aqueous sodium hydrogen carbonate solution. After the usual work-up as described above compound 6 (0.24 g, 33.5%) was obtained.

Preparation of 5 and 7 from pyrano[4,3-b]pyrandione (13)

Method A - A mixture of compound **13** (0.5 g, 2 mmol) and phenylhydrazine hydrochloride (0.32 g, 2.2 mmol) in ethanol (20 ml) was refluxed for 3 h. After cooling overnight, compound **5** (0.1 g, 14.7%) was obtained. The filtrate was evaporated to dryness, the residue was dissolved in methylene chloride and extracted with 10% aqueous sodium hydrogen carbonate solution. From the organic layer an additional yield of compound **5** (45 mg, 6.7%) was obtained by preparative chromatography on silica gel with chloroform-petrol ether (1:1). The aqueous layer was acidified with 10% hydrochloric acid and extracted with methylene chloride. The solvent was evaporated, yielding compound **7** (0.3 g, 42%).

Method B - A mixture of compound **13** (0.5 g, 2 mmol) and phenylhydrazine hydrochloride (0.32 g, 2.2 mmol) in acetic acid (20 ml) was refluxed for 2 h. The solvent was evaporated, the residue was dissolved in methylene chloride and extracted with 10% aqueous sodium hydrogen carbonate solution. Using the procedure described above (see Method A) compound **5** (40 mg, 6%) was obtained from the organic layer, and compound **7** (0.45 g, 63%) from the aqueous layer.

3-(2-Acetoxy-1-propenyl)-6-ethoxycarbonyl-4-oxo-2-phenyl-2H,4H-pyrano[4,3-c]-pyrazole (8)

Compound **6** (0.72 g, 2 mmol) in acetic anhydride (20 ml) was heated under reflux for 1 h. The mixture was concentrated, and crude **8** (0.62 g, 81%) was precipitated with ether.

3-(2-Acetoxy-1-propenyl)-6-ethoxycarbonyl-4-oxo-1-phenyl-1H,4H-pyrano[4,3-c]-pyrazole (9)

Compound **7** (0.72 g, 2 mmol) in acetic anhydride (20 ml) was heated at 80°C for 1 h. The solvent was evaporated to give an oily product, which was dissolved in methylene chloride and washed with 10% aqueous sodium hydrogen carbonate, followed by water. The organic layer gave compound **9** (0.57 g, 74.6%) after evaporation. The crude **9** was purified by preparative chromatography on Al_2O_3 using chloroform - petrol ether (10:1).

Table 3. Physical and Spectral Data of Compounds 2 - 9

Compd	Mp °C (Solvent)	Molecular Formula	Ms, M^+ m/z	Analyses % Calcd./Found C	H	N	Ir(KBr) $\nu_{C=O}$, cm^{-1}	Uv(EtOH) λ_{max}, nm(ε)
2	170-172 (EtOH)	$C_{18}H_{17}NO_6$	343	62.97 63.00	4.99 5.19	4.08 4.23	1730,1715	397 (25700) 297 (9000)
3	145-147 (EtOH)	$C_{18}H_{17}NO_6$	343	62.97 63.24	4.99 4.75	4.08 4.07	1740,1730	389 (30000) 309 (3200)
4	196-197 (EtOH)	$C_{18}H_{16}N_2O_5$	340	63.52 63.40	4.74 4.54	8.23 8.40	1728,1700	316 (13400) 221 (25700)
5	159-160 (EtOH)	$C_{18}H_{16}N_2O_5$	340	63.52 63.35	4.74 4.96	8.23 8.35	1730,1710	356 (13400) 344 (13200) 222 (18800)
6	110-112 (EtOH/H_2O)	$C_{18}H_{18}N_2O_6$	340 (b)	60.33 60.43	5.06 5.17	7.82 8.04	1730,1685	283 (13300) 248sh(16800)
7	120-122 (EtOH/H_2O)	$C_{18}H_{18}N_2O_6$	340 (b)	60.33 60.58	5.06 4.92	7.82 7.75	1735,1690	325 (16300) 245sh(25500) 225 (38600)
8	136-137 (EtOH)	$C_{20}H_{18}N_2O_6$	382	62.82 63.01	4.75 4.51	7.33 7.14	1780,1728 1718	306 (10000) 240sh(12800)
9	59-61 (a)	$C_{20}H_{18}N_2O_6$	382	62.82 62.77	4.75 4.98	7.33 7.55	1785,1745 1730	323 (7600) 237 (12300)

(a) purified by preparative thin layer chromatography (see Experimental).

(b) M^+-18 was observed instead of M^+(358).

Table 4. ^{1}H Nmr Spectroscopic Data ($CDCl_3$, δ/ppm)

2	1.38(t, J=7Hz, 3H, CH_3), 2.18(s, 3H, CH_3-pyrone), 4.40(q, J=7Hz, 2H, CH_2), 6.78(s, 1H, pyrone), 6.88(s, 1H, methine), 7.12-7.45(m, 5H, phenyl), 12.69(s, 1H, NH), 18.69(s, 1H, OH)
3	1.13(t, J=7Hz, 3H, CH_3), 2.26(s, 3H, CH_3-pyrone), 4.20(q, J=7Hz, 2H, CH_2), 5.91(s, 1H, pyrone), 7.15(s, 1H, methine), 7.01-7.35(m, 5H, phenyl), 11.31(s, 1H, NH), 17.37(s, 1H, OH)
4	1.30(t, J=7Hz, 3H, CH_3), 2.29(d, J=0.7Hz, 3H, CH_3-pyrone), 4.28(q, J=7Hz, 2H, CH_2), 6.01(q, J=0.7Hz, 1H, pyrone), 7.46(s, 5H, phenyl), 7.88(s, 1H, pyrazole), 12.5(s, 1H, OH)
5	1.40(t, J=7Hz, 3H, CH_3), 2.40(d, J=0.7Hz, 3H, CH_3-pyrazole), 4.41(q, J=7Hz, 2H, CH_2), 7.08(s, 1H, pyrone), 7.19(q, J=0.7Hz, 1H, pyrazole), 7.48(s, 5H, phenyl), 13.4(s, 1H, OH)
6	1.34(t, J=7Hz, 3H, CH_3), 2.12(s, 3H, CH_3), 4.34(q, J=7Hz, 2H, CH_2), 5.93(s, 1H, propenyl), 6.87(s, 1H, acrylate), 7.27(s, 5H, phenyl), 10-11(br, concentration dependent)
7	1.33(t, J=7Hz, 3H, CH_3), 2.23(s, 3H, CH_3), 4.32(q, J=7Hz, 2H, CH_2), 4-6(br, 3H, concentration dependent), 6.30(s, 1H, propenyl), 6.76(s, 1H, acrylate), 7.22(s, 5H, phenyl)
8	1.41(t, J=7Hz, 3H, CH_3), 2.07(s, 3H, acetyl), 2.28(s, 3H, CH_3), 4.44(q, J=7Hz, 2H, CH_2), 6.07(s, 1H, propenyl), 7.02(s, 1H, pyrone), 7.40(s, 5H, phenyl)
9	1.37(t, J=7Hz, 3H, CH_3), 2.07(s, 3H, acetyl), 2.38(s, 3H, CH_3), 4.38(q, J=7Hz, 2H, CH_2), 6.38(s, 1H, propenyl), 7.07(s, 1H, pyrone), 7.34(s, 5H, phenyl)

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