Pergamon

Tetrahedron Vol. 50, No. 45, pp. 13023-13036, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00825-6

Regio- and Stereo-Selective 1,3-Dipolar Cycloaddition Reactions of Ethyl Diazoacetate to 3-Substituted 2*H*-1-Benzopyran-2-ones.

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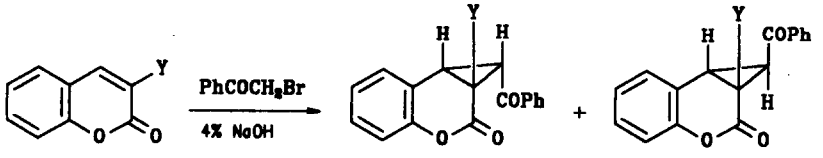
Abstract:. The cycloaddition of ethyl diazoacetate to 3-substituted 2*H*-1-benzopyran-2-ones, **1**, gave the benzopyrano[3,4][2]pyrazolines **11**, the benzopyrano[3,4]cyclopropanes **12**, the benzopyrano[3,4-*c*]pyrazole **13** and the (*o*-hydroxy)phenyl-pyrazoles **14** as the main products. When the cycloaddition was performed in the presence of silica gel the rate of the reaction increased substantially and the yields of the cyclopropane derivatives **12** were more than doubled. Ethyl diazoacetate adds to benzopyran-3,4-double bond *regio*- and *stereo*-selectively giving the *endo*-form of the initial cycloadduct **15**, which being unstable, is then transformed mainly to the above mentioned compounds.

Recently we have studied[1,2] the interaction of phenacyl bromide with 3-substituted 2*H*-1-benzopyran-2-ones (3-substituted coumarins), **1**, (in the presence of a base and under phase transfer catalysed conditions), which resulted in the preparation of a series of cyclopropane derivatives **2** and **3**. The yield and the stereoselectivity of this reaction were found to depend on the experimental conditions (solvent, catalyst, amount of the base used) as well as on the substituent Y at the coumarin 3-position.

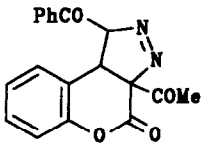


1 2 3

Continuing the above study and aiming to replace the benzoyl group in compounds **2** and **3** by other functional groups, we tried the reaction of 3-acyl-substituted coumarins with ethyl bromoacetate under the same experimental conditions. However the expected cyclopropanation of the coumarin 3,4-double bond did not occur, and this was in agreement with the analogous reaction of methyl chloroacetate with benzylidene acetophenone which did not give the expected cyclopropane derivative[3].

Another approach however to cyclopropane derivatives is the decomposition of pyrazolines, which can be formed by 1,3-dipolar cycloaddition reactions of diazocompounds to an activated with an electron attracting group double bond. Thus it has been reported[4] that the cycloaddition of diazoacetophenone to 3-acetylcoumarin gave the pyrazoline derivative **4**, which upon heating gave the benzopyrano-3,4-cyclopropane derivative **2** (Y = MeCO). Also the cycloaddition of diazoacetaldehyde dimethylacetale to 3- or 4-ethoxycarbonylcoumarin gave

the corresponding pyrazolines **5** and **6** respectively, which on irradiation eliminate nitrogen, giving mainly cyclopropane derivatives[5].



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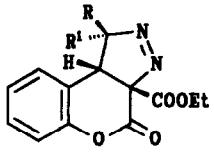

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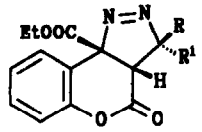
a) R=H, R^1=CH(OMe)$_2$

b) R=CH(OMe)$_2$, R^1=H



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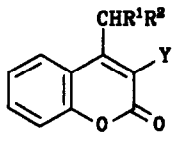
1,3-Dipolar cycloadditions to 2*H*-1-benzopyran-2-ones, **1**, have been performed using nitrilimines[6-8] and diazocompounds[4,5,9-15] as dipoles. In the second case, with the exception of diazoacetophenone[4] and diazoacetaldehyde dimethylacetale[5], only diazoalkanes were used as dipoles and their cycloaddition to 3-substituted or unsub-stituted coumarins has been studied extensively[9-15]. From the reported studies it comes out that in the case of 3- or 4-substituted coumarins the cycloaddition is highly regioselective leading to benzopyrano-pyrazoline derivatives of the type **5** or **6** respectively[4,5,9-12], where the terminal nitrogen of the diazo moiety binds to the carbon atom bearing the electronegative substituent Y. In the unsubstituted coumarin this regioselectivity is lost[15].

Pyrazoline derivatives of the type **5** or **6** are not stable and in the case of diazoalkane cycloadducts, only in a few cases[9-11,15] were isolated. Normally they decompose spontaneously[5,9-13], by heating[4,9-15] or on irradiation[5] to 4-alkylcoumarins **7**, benzoxepinones **8**, 3,4-cyclopropylbenzopyranes **9** and in certain cases[14] to benzopyrano-pyrazoles **10**.



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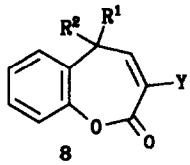

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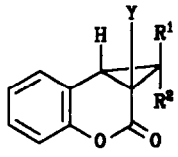

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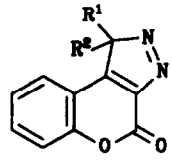

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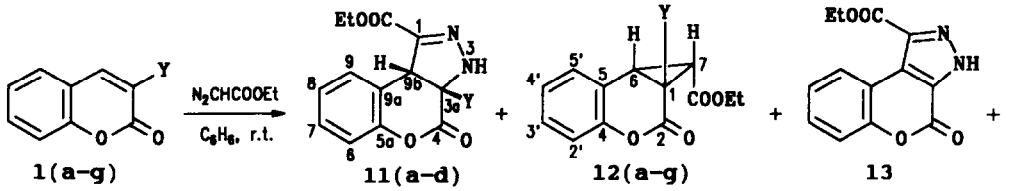
The stability of the pyrazoline derivatives as well as the way they decompose to give the compounds **7-10** depend mainly on the substituents R^1 and R^2 of the diazo moiety and on the substituent Y of the benzopyran ring. It seems likely that the presence of an electron attracting[4,5] or a bulky[11] substituent in the diazo-compound makes the initially formed pyrazoline more stable and tending to decompose mainly to cyclopropane derivatives[4,5,11].

The above mentioned unsuccessful attempts for the reaction of ethyl bromoacetate and 3-substituted coumarins and the possibility of preparing cyclopropane derivatives by decomposition of benzopyrano-pyrazolines[4,5], prompted us to study the 1,3-dipolar cycloaddition of ethyl diazoacetate to 3-substituted coumarins, with the scope to prepare pyrazoline derivatives which then would be transformed into the cyclopropane derivatives of the type **2** or **3**.

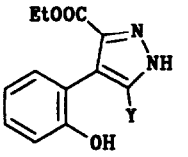
RESULTS AND DISCUSSION

Cycloaddition reactions were performed in benzene solution at room temperature by allowing a mixture of equimolecular amounts of ethyl diazoacetate and the corresponding 3-substituted coumarin **1a-g** to react for several days, until all or most of the starting coumarin **1** was consumed (TLC). In another procedure (method B), an amount of silica gel was added to the reaction mixture, and this resulted in a considerably reduced reaction time, the first observed in 1,3-cycloaddition reactions. Except for the acceleration of the reaction, silica gel also affected the yields and the ratio of the reaction products with an obvious preference in increasing the

yield of the cyclopropane derivatives **12**. The yields of the products isolated from the above reaction without (method A) and with (method B) silica gel are given in Table 1.



a) Y = $COCH_3$ e) Y = COOEt
b) Y = $COCH(CH_3)_2$ f) Y = NO_2
c) Y = $COCH(CH_2)_2$ g) Y = CN
d) Y = COPh



14(a-c)

Table 1. Yields of the Compounds **11-14** Obtained from the Reaction of **1a-g** with Ethyl Diazoacetate under different experimental conditions.

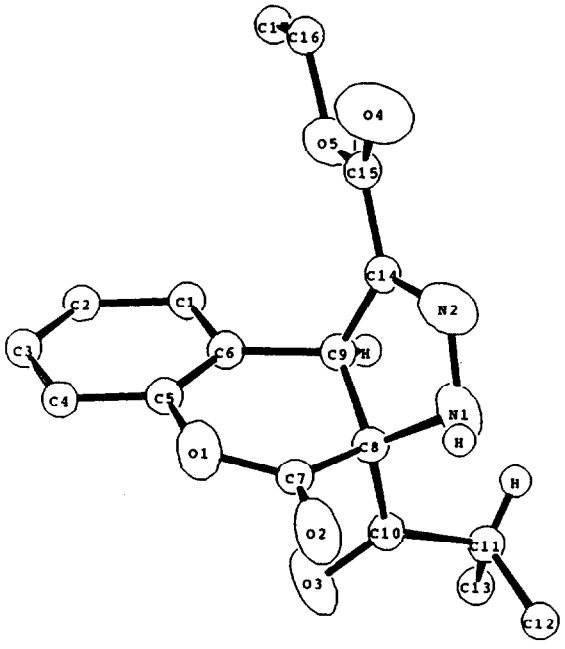
				Yield % [a]				
Comp.	Substituent	Method[b]	Time[c]	1[d]	11	12	13	14
a	COMe	A	30 d	21	50	7	8	-
		B	3 d	-	33	29	8	22
b	$COCHMe_2$	A	34 d	-	52	7	8	23
		B	9 d	-	9	43	31	-
		G[e]	7 d	-	-	27	39	7
c	$COCH(CH_2)_2$	A	21 d	-	40	17	15	17
		B	5 d	-	-	40	8	-
d	COPh	A	90 d	40	36	6	-	-
		B	14 d	30		27	8	-
e	COOEt	B	7 d	-	-	33	-	-
f	NO_2	A	4 d	42	-	25	31	-
		B	12 h	-	-	58	35	-
g	CN	B	4 d	56	-	27	-	-

[a] Yield % of an isolated product
[b] Method A: Reaction in benzene solution at room temperature; Method B: As in method A but with silica gel.
[c] Reaction time: d = day; h = hour.
[d] Unreacted starting coumarin **1**.
[e] As in method B, but with THF as solvent.

A. *Cycloaddition of ethyl diazoacetate to 3-acylsubstituted coumarins* ***1a-d***. Four products in different yields and ratios, depending on the 3-acyl substituent and the method used (A or B) were mainly isolated from the

above reactions, i.e. the pyrazoline derivatives **11**, the cyclopropanes **12**, the benzopyrano[3,4-c]pyrazole **13** and the (*o*-hydroxy)phenyl-pyrazoles **14**.

The structure of compounds **11-14** was revealed by their spectroscopic characteristics, whereas the structure of compound **11b** was confirmed by X-ray analysis (Figure 1).

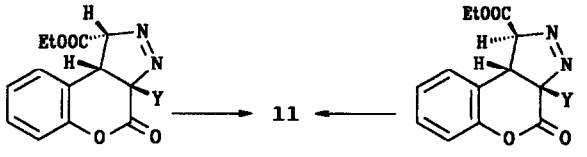


ROTATIONS: 5.0 ABOUT X, 168.0 ABOUT Y, AND 60.0 ABOUT Z

Fig. 1. ORTEP drawing of **11b** with thermal ellipsoids at 50% probability.

The reaction is completely regioselective as evidenced by compounds **11**, **13** and **14**, and this is in agreement with the findings in other analogous 1,3-cycloadditions of diazo compounds to 3- or 4-substituted coumarins, where the terminal nitrogen of the diazomoiety binds to the carbon atom of the benzopyran 3,4-double bond bearing the electronegative substituent[4,5,9-14].

The initially formed cycloadducts **15** or **16** were not isolated however. Instead 2-pyrazoline derivatives **11** were formed and obviously this is due to the acidic character of the proton adjacent to the ethoxycarbonyl group, which can easily undergo a prototropic shift to give the isolated compounds **11**.



15 **16**

There is no direct evidence about the stereoselectivity of these reactions, since the initially formed cycloadducts **15** were not isolated, and if both the *endo*, **15**, and the *exo*, **16**, stereoisomers were formed, they would give the same pyrazoline derivative **11**. An indirect indication about it could however be deduced from

the cyclopropane derivatives **12**, which are formed from the pyrazolines **15** or **16** by extrusion of N_2 and before being transformed to **11**.

All the cyclopropane derivatives isolated from the above reactions have the structure depicted in **12**, i.e. they are *endo* isomers, with the two protons of the cyclopropane ring in a *cis* disposition. This is revealed by their ^{1}H-NMR spectra, where these protons show a large vicinal coupling constant, with a value ranging from 9.4-11.0 Hz, which is accepted[1,2,14b] as an evidence for their *cis* character.

Although the thermal and photochemical decomposition of 1-pyrazolines to give cyclopropane derivatives have been extensively studied[11,12,16-20], a mechanism generally accepted for this process has not been proposed. Concerning the stereochemistry some of the above reactions have been found to be completely stereoselective[10b,15] and others partially so[5,14-15]. The pyrazoline→cyclopropane transformation may proceed either under inversion or under retention of the carbons C-3 and/or C-5 of the 1-pyrazoline ring, depending on the reaction conditions and on the substituents of these carbons[16-20].

In the reactions under investigation, and assuming that the cycloaddition of ethyl diazoacetate to the coumarin 3,4-double bond gives the expected *cis* isomer and that this remains also in the cyclopropane ring, i.e. the Y group stays *cis* to H-4 of the coumarin, compounds **12** could be formed either from **15** under retention or from **16** under inversion of the stereochemistry of the carbon bearing the carboethoxy group (C-5). It seems more or less unreasonable to accept that **15** and **16**, if both they were formed initially, would give exclusively the same stereoisomer as the isolated **12**, more over so that the *endo* disposition of the carboethoxy group, as found in **12**, is sterically rather less favourable comparing to that of the *exo*.

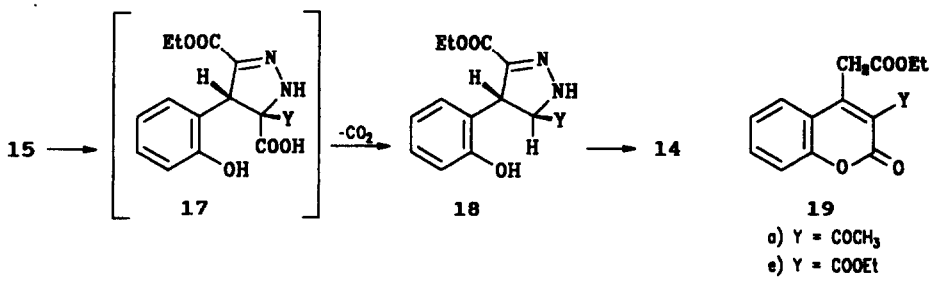
The above reasoning implies that compounds **12** are formed from one stereoisomer, which then should be the main cycloadduct in the cycloadditions under investigation. We tend to accept that this is the *endo* isomer **15**, which by extrusion of N_2 and under retention of C-5 gave compounds **12**. An analogous cyclopropane formation under retention of the corresponding carbon has been observed in thermal decomposition of other condensed pyrazoline systems[15], whereas the photochemical decomposition of compounds **5a** and **5b** gave the corresponding *cis* and *trans* respectively cyclopropane derivatives with a 75% and 80% retention of the carbon bearing the dimethoxymethyl group[5]. The formation stereoselectively of the *endo* isomer **15** is most probably the result of the secondary interaction (during the cycloaddition) between the diazoacetate carbonyl and the aromatic ring of the benzopyran system. The formation of the *exo* derivative **16** from which **12** could be formed by inversion of C-5 can not be excluded however. In any case the cycloaddition of ethyl diazoacetate to 3-substituted coumarins is stereoselective as is also the decomposition of the benzopyrano-pyrazolines to cyclopropanes.

The benzopyrano[3,4-*c*]pyrazole **13** was isolated from the reaction under investigation in yields from 8% to 39%, depending on the acyl substituent Y and the reaction conditions. (It is more likely that the presence of silica gel in the reaction mixture (method B) or in the column affects the formation of **13**).

Although many cycloadditions of the 3-acylcoumarins with diazo compounds have been studied[5,9-13], the isolation of pyrazole derivatives analogous to **13** has never been reported. Only from the reaction of 3-arylsulfenylcoumarin **1** (Y=SOAr) with diazo compounds the corresponding benzopyrano[3,4-*c*]pyrazoles were isolated. Their formation was explained[10,14] by a 1,2 *syn*-elimination of arenesulfenic acid from the initially formed benzopyrano-pyrazoline. The formation of pyrazoles from 1- or 2-pyrazolines by extrusion of a good leaving group has been also reported[21].

In the reaction under investigation it is very difficult to explain the formation of **13** from **15** or **11** by an analogous mechanism, since this would require a 1,2-elimination of an aldehyde, such as acetaldehyde or benzaldehyde, that seems rather unlikely and such an elimination, to our knowledge, has never been reported. In an analogous case 1,3-diaryl-5-benzoyl-pyrazoles were formed from 1,3-diaryl-4,5-dibenzoyl-2-pyrazolines and this transformation was explained by a hydrolytic cleavage of the C-COPh bond caused by water present in the reaction mixture and subsequent dehydrogenation of the formed 1,3-diaryl-4-benzoyl-2-pyrazoline[22]. A similar transformation could be accepted for the formation of **13** from **11** or **15**. Whatever the reaction mechanism however, the aromatization of the system and the re-establishment of the conjugation between the carbonyl and the aromatic ring of the benzopyranone system should be regarded as a driving force for this transformation.

Compounds **14** were isolated only from the reactions of **1a-c**, and their formation could be explained by accepting a hydrolysis of the benzopyran-2-one ring by water present in traces in the reaction mixture and/or on the column to **17**, followed by decarboxylation and subsequent dehydrogenation of the pyrazoline **18**. It is



noted that from the cycloaddition of diethyl diazoacetate to 3-acetylcoumarin **1a**, when carried out in the presence of florisil at ambient temperature, compound **18a** (Y=COMe) was isolated in 36%. When however the same reaction was performed under reflux (benzene as solvent), the decarboxylation-dehydrogenation product **14a** was isolated in 39% yield.

In an attempt to investigate the influence of the reactions conditions such as temperature and solvent as well as the role of the different adsorbents on the course of the cycloaddition and the isolated products, a series of experiments were performed, where the 3-acetylcoumarin **1a** reacted with ethyl diazoacetate in the presence of silica gel, florisil and molecular sieves 4A at room temperature and under refluxing conditions. The results are presented in Table 2.

Table 2. Yields and Compounds Obtained from the Reaction of 3-Acetylcoumarin **1a** with Ethyl Diazoacetate under Different Experimental Conditions.

			Yield % [a]						
Reaction conditions[b]	Method	Time[c]	1[d]	11a	12a	13	14a	18	19a
r.t.	A	30 d	21	50	7	8	-	-	-
Silica gel, r.t.	B	3 d	-	33	29	8	22	-	-
Reflux	C	13 h	-	43	5	8	5	-	6
Florisil, r.t.	D	6 d	-	-	7	-		36	-
Florisil, Reflux	E	7 h	-	8	22	-	39	-	5
Mol. Sieves 4A, Reflux	F	5 h	-	10	55	31	-	-	-

[a] Yield % of an isolated product
[b] Reactions carried out in benzene solutions
[c] Reaction time: d = day; h = hour.
[d] Unreacted starting coumarin 1.

An increase of the temperature besides reducing the reaction time, as expected, led to the isolation of more degradation products of the initially formed 1-pyrazoline **15**. When the reaction was carried out in the presence of florisil and at room temperature (Table 2, method D), the decarboxylated pyrazoline derivative **18** was isolated as already mentioned, whereas at higher temperature (Table 2, method E) the same reaction gave the cyclopropane **12a** and the pyrazole **14a** in yields 22% and 39% respectively. On the other hand the presence of molecular sieves in the reaction mixture resulted in an increase of the isolated cyclopropane **12a** (55%) and

benzopypano[3,4-*c*]pyrazole **13** (31%). The isolation of compound **19a** from the reactions performed at higher temperatures (Table 2, methods C, E) is noteworthy. Compounds of the type **19** are considered as alkylation products of the starting coumarin and are normally isolated from the cycloaddition reactions of diazo compounds[9-13]. They are formed from the initial 1-pyrazoline **15** by extrusion of N_2 and a hydrogen shift, and the mechanism of this transformation is well documented[9-12].

B. *Cycloaddition of ethyl diazoacetate to 3-ethoxycarbonyl coumarin 1e.* This reaction was carried out in the presence of silica gel (method B) and the only product isolated was the cyclopropane derivative **12e** in 33% yield (Table 1). The coupling values of the protons of the cyclopropane ring, $^3J = 9.5$ Hz, indicate their *cis* disposition and consequently the *endo* character of the ethoxycarbonyl group as depicted in **12**. Other products isolated from the above reaction were not identified.

When the same reaction was performed in the presence of molecular sieves 4A while refluxing the reaction mixture, except of a shortening of the reaction time as expected (7 hours instead of 7 days) compound **19e** was isolated in 26% yield. Other products were also isolated as mixtures but their purification and identification was unsuccessful.

C. *Cycloaddition of ethyl diazoacetate to 3-nitro- and 3-cyano-coumarin 1f,g.* As it is seen from Table 1, the cycloaddition of 3-nitrocoumarin gave the cyclopropane derivative **12f** and the benzopyrano[3,4-*c*]pyrazole **13**, in good yields. In the absence of silica gel (method A) the reaction was not completed after 4 days, giving 42% of unreacted starting compound **1f**, whereas the presence of silica gel (method B) resulted in a considerable increase of the yield (58% versus 25%) of the isolated cyclopropane derivative **12f**. In both methods the yields of the isolated benzopyrano-pyrazole **13** were good (30-35%) and this can be explained as an 1,2 *syn*-elimination of the good leaving group HNO_2. This elimination could be proceed either from the cycloadduct **15** or from the 2-pyrazoline **11f**, which however was not isolated from the reaction under investigation. It should be noticed that the cycloaddition of diazoethane to 3-nitro-coumarin gave[10] among others, cyclopropane derivative of the type of **12**, as well as alkylation products and benzoxepinone derivatives of the type **7** and **8** respectively, but not pyrazole derivatives analogous to **13**.

The cycloaddition of ethyl diazoacetate to 3-cyanocoumarin proceeded only in the presence of silica gel and from this reaction only the cyclopropane derivative **12g** was isolated in 27% yield along with the unreacted starting compound **1g** (56%). Alkylation compounds analogous to **7** or **19**, which were the products isolated exclusively and in yields up to 100% from the cycloaddition reactions of diazoalkanes[9,11,13] or diazoacetaldehyde diethylacetale[5] to 3-cyano-coumarin were not isolated from the above reaction.

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus. - IR spectra were recorded with a Specord 71 IR or a Perkin-Elmer 297 spectrometer. - ^{1}H-NMR spectra were obtained either with a Bruker AM 300 (300 MHz) or a Bruker WM 250 (250 MHz). - ^{13}C-NMR spectra were obtained with a Bruker AM 300 (75 MHz) or a Bruker WM 250 (62.9 MHz). All NMR spectra were obtained by using TMS as internal standard in $CDCl_3$ or DMSO-d_6 solutions. - E.I. mass spectra were recorded at 70 eV with a Jeol JMS-D 300 or a VG TS-250 spectrometer. C.I. mass spectra were obtained with a Jeol JMS-D 300 instrument and by using CH_4 as ionising gas. - Column chromatography was carried out on silica gel (Merck 60; 0.063-0.2 mm); eluent: *n*-hexane/EtOAc mixtures of increasing polarity.

***Preparation of the Starting Materials*:** The starting coumarins **1a-g** were prepared according to the literature[23-28] and their spectroscopic characteristics (IR, ^{1}H-NMR and MS) were in agreement with their structure.

***Reaction of Ethyl Diazoacetate with 3-Substituted Coumarins 1a-g. - General Procedure*:** Depending on the reaction conditions (temperature, adsorbent used) the following methods are distinguished:

Method A: To a solution of the corresponding benzopyran **1** (1 mmol) in dry benzene (6-7 ml) ethyl diazoacetate (0.15 g, 1 mmol) were added. The reaction mixture was closed and kept at room temperature for the appropriate time (TLC monitoring). After the reaction was completed or most of the starting coumarin was consumed the solvent was evaporated and the residue was crystallised from the appropriate solvent or was separated on the column.

Method B: The reaction procedure was like in method A but in the presence of silica gel (2.0-2.5 g; Merck 60; 0.063-0.2 mm). The reaction mixture was extracted with hot chloroform (3 x 30 ml) and after evaporation of the solvent it was worked up as above.

Method C: To a refluxing solution of the corresponding benzopyran **1** (10 mmoles) in dry benzene (20 ml) a solution of ethyl diazoacetate (10 mmoles) in dry benzene (10 ml) was added dropwise over a period of 4 h. The reaction mixture was refluxed for 13 h and then worked up as in method A.

Method D: The reaction was carried out in the presence of Florisil (1.5-2.0 g, 60-100 mesh) and worked up as in method B.

Method E: To a solution of **1** (2 mmoles) in benzene (5 ml) Florisil (2 g, 60-100 mesh) was added. To this mixture, brought under reflux, a solution of ethyl diazoacetate (0.3 g, 2 mmoles) in dry benzene (5 ml) was added dropwise under stirring and over a period of 3 h. The reaction mixture was refluxed for another 4 h and then worked up as in method B.

Method F: To a solution of **1** (1 mmol) and ethyl diazoacetate (0.15 g, 1 mmol) in dry benzene (5 ml) molecular sieves 4A were added (1.5 g). The reaction mixture was refluxed for 5 h and then worked up as in method B.

The compounds and the yields obtained from each of the above methods are given in Tables 1 and 2.

3a-Acetyl-3a,9a-dihydro-1-ethoxycarbonyl-1-benzopyrano[3,4-c]pyrazoline-4(3H)-one **(11a)**: From **1a** and ethyl diazoacetate: (yields and methods prepared as in Tables 1 and 2), m.p. 110-112 °C (decomp.) (*n*-hexane/-ether). - IR (nujol): 3150, 1770, 1735, 1580 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ = 1.32 (t, *J*=7.0 Hz; 3H, CH_2CH_3), 2.42 (s; 3H, $COCH_3$), 4.22-4.82 (m; 2H, CH_2CH_3), 4.82 (s; 1H, 9b-H), 7.10 (dd, *J*=8.1 and 1.3 Hz; 1H) 7.23 (ddd, *J* =7.6, 7.5 and 1.3 Hz; 1H), 7.37 (ddd, *J* =8.1, 7.5 and 1.6 Hz; 1H), 7.50 (s; 1H, NH), 7.70 (dd, *J* =7.6 and 1.6 Hz; 1H). - ^{13}C-NMR (62.9 MHz) (DMSO-d_6): δ = 13.4 (CH_3), 26.0 ($COCH_3$), 48.25 (C-9b), 60.9 (OCH_2), 78.4 (C-3a), 115.0 (C-9a), 116.6 (C-6), 124.9 (C-8), 129.7 (C-9), 131.5 (C-7), 139.9 (C-1, C=N), 149.45 (C-5a), 160.9 (C-4, C=O), 165.2 (COOEt). - MS: *m/z* (%) = 303 (M+1, 80), 302 (M^+,6), 285 (12), 275 (13), 261 (33), 260 (82), 259 (37), 238 (36), 229 (16), 228 (11), 213 (41), 190 (14), 189 (82), 188(32) 187 (100), 186 (46), 173 (32), 161 (13), 159 (17), 158 (21), 145 (11), 144 (8), 143 (15), 133 (11), 132 (11), 131 (19), 116 (25), 115 (25), 103 (16), 102 (13), 89 (29), 77 (17), 43 (65).

$C_{15}H_{14}N_2O_5$ (302.28)	Calcd.	C 59.60	H 4.67	N 9.27
	Found	C 60.01	H 4.75	N 9.43

3a,9a-Dihydro-1-ethoxycarbonyl-3a-isobutyryl-1-benzopyrano[3,4-c]pyrazoline-4(3H)-one **(11b)**: From **1b** and ethyl diazoacetate: (yields and methods prepared as in Table 1), m.p. 116-118 °C (decomp.) (*n*-hexane/ether). - IR (nujol): 3140, 1760, 1725, 1705, 1595 cm^{-1}. - ^{1}H-NMR (250 MHz) (DMSO-d_6): δ = 0.98 (d, *J*=6.8 Hz; 3H, $CH(CH_3)_2$), 1.07 (d, *J*=6.8 Hz; 3H, $CH(CH_3)_2$), 1.18 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 3.43 (septet, *J*=6.8 Hz; 1H, $CHMe_2$), 4.14 (q, *J*=7.1 Hz; 2H, CH_2CH_3), 5.17 (s; 1H, 9b-H), 7.14 (dd, *J*=7.9 and 1.0 Hz; 1H), 7.24 (ddd as td, *J*=7.5 and 1.0 Hz; 1H), 7.39 (ddd, *J*=7.9, 7.4 and 1.6 Hz; 1H), 7.61 (dd, *J*=7.6 and 1.2 Hz; 1H), 10.02 (s; 1H, NH). - ^{13}C-NMR (62.9 MHz) (DMSO-d_6): δ = 13.9 (CH_3), 18.5, 18.9 ($CH(CH_3)_2$), 35.3 ($CHMe_2$), 48.6 (C-9b), 60.9 (OCH_2), 78.55 (C-3a), 114.8 (C-9a), 116.6 (C-6), 124.9 (C-8), 129.8 (C-9), 131.7 (C-7), 139.8 (C-1, C=N), 149.6 (C-5a), 160.8 (C-4, C=O), 165.5 (COOEt), 208.5 ($COCHMe_2$). - MS: *m/z* (%) = 331 (2), 330 (M^+, 17), 302 (2), 288 (4), 261 (10), 260 (67), 259 (17), 158 (10), 231 (8), 230 (5), 216 (23), 213 (23), 188 (12), 187 (83), 186 (29), 174 (15), 173 (87), 146 (25), 132 (5), 131 (5), 116 (8), 114 (12), 102 (5), 101 (12), 89 (16), 77 (10), 71 (50), 43 (100).

$C_{17}H_{18}N_2O_5$ (330.33)	Calcd.	C 61.81	H 5.49	N 8.48
	Found	C 61.99	H 5.50	N 8.36

3a-Cyclopropanoyl-3a,9b-dihydro-1-ethoxycarbonyl-1-benzopyrano[3,4-c]pyrazoline-4(3H)-one **(11c)**: From **1c** and ethyl diazoacetate: (yields and methods prepared as in Table 1), m.p. 116-118 °C (decomp.) (*n*-hexane/ether). - IR (nujol): 3170, 1750, 1715, 1595 cm^{-1}. - ^{1}H-NMR (300 MHz) ($CDCl_3$): δ = 1.08-1.21 (m; 4H, H-cyclpr), 1.33 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 2.43 (m, Σ*J*=15 Hz; 1H, H-1 cyclpr), 4.23-4.33 (m; 2H, CH_2CH_3), 4.96 (s; 1H, 9b-H), 7.10 (dd, *J*=8.1 and 1.3 Hz; 1H, 6-H), 7.22 (ddd, *J*=7.9, 7.5 and 1.3 Hz; 1H, 8-H), 7.34 (ddd, *J*=8.1, 7.5 and 1.6 Hz; 1H, 7-H), 7.60 (s; 1H, NH), 7.71 (dd, *J*=7.9 and 1.6 Hz; 1H, 9-H). - ^{13}C-NMR (75 MHz) ($CDCl_3$): δ = 13.45 (*J*=168 Hz), 13.65 (*J*=168 Hz) (C-cyclpr), 14.1 (*J*=127.6 and 2.5 Hz; CH_3), 17.8 (*J*=168 Hz; C-1 cyclpr), 49.5 (*J*=138.0 Hz; C-9b), 62.0 (*J*=148.6 and 4.5 Hz; OCH_2), 78.1 (*J*=1.5 and 3.0 Hz; C-3a), 113.5 (C-9a), 117.3 (C-6), 125.2 (C-8), 130.7 (C-7), 131.6 (C-9), 143.25 (C-1, C=N), 149.8 (C-5a), 161.0 (C-4, C=O), 165.5 (COOEt), 202.0 (CO-cyclpr). - MS: *m/z* (%) = 329 (23), 328 (M^+, 90), 327 (51), 300 (29), 299 (56), 282 (17), 271 (18), 254 (60), 253 (84), 229 (35), 228 (54), 214 (90), 213 (50), 188 (60), 186 (50), 184 (60), 173 (49), 159 (63), 145 (47), 131 (80), 115 (98), 103 (94), 101 (84), 84 (90), 77 (100), 76 (82), 70 (97), 69 (49), 42 (64).

$C_{17}H_{16}N_2O_5$ (328.31)	Calcd.	C 62.19	H 4.91	N 8.53
	Found	C 62.27	H 4.84	N 8.48

3a-Benzoyl-3a,9b-dihydro-1-ethoxycarbonyl-1-benzopyrano[3,4-c]pyrazoline-4(3H)-one **(11d)**: From **1d** and ethyl diazoacetate: (yields and methods prepared as in Table 1), m.p. 190-192 °C (decomp.) (ethanol). - IR (nujol): 3130, 1735, 1700, 1580 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ = 1.35 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 4.33 (q, *J*=7.1 Hz; 2H, CH_2CH_3), 5.13 (s; 1H, 9b-H), 7.20-7.27 (m; 2H), 7.38-7.51 (m; 3H), 7.60-7.71 (m; 3H, arom. + NH), 7.90-7.93 (m; 2H). - ^{13}C-NMR (62.9 MHz) (DMSO-d_6): δ = 13.9 (CH_3), 49.9 (C-9b), 62.6 (OCH_2), 76.3 (C-3a), 113.7 (C-9a), 117.9 (C-6), 125.9 (C-8), 130.27, 130.36 (C-7/C-8), 144.3 (C-1, C=N), 149.6 (C-5a), 161.7, (C-4, C=O), 163.4 (COOEt); PhCO: 129.3 (C-3, C-5), 129.7 (C-2, C-6), 131.4 (C-1), 134.7 (C-4), 191.6 (CO). - MS (C.I): *m/z* (%) = 366 (21), 365 (M+1, 100), 364 (M^+, 2), 338 (19), 337(75), 291 (10), 266 (9), 252 (9), 251 (46), 219 (6), 147 (4), 115 (17), 105 (17).

$C_{20}H_{16}N_2O_5$ (364.34)	Calcd.	C 65.93	H 4.43	N 7.69
	Found	C 66.05	H 4.70	N 7.54

Ethyl 1-Acetyl-4,5-benzo-3-oxa-2-oxo-cis-bicyclo[4.1.0]hept-4-en-endo-1-carboxylate **(12a)**: From **1a** and ethyl diazoacetate (yields and methods prepared as in Tables 1 and 2), m.p. 68-70 °C (decomp.) (*n*-hexane/ether). - IR ($CHCl_3$): 2990, 1755, 1715, 1615, 1595 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ = 1.06 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 2.55 (s; 3H, $COCH_3$), 3.15 (d, *J*=9.6 Hz; 1H, 6-H), 3.22 (d, *J*=9.6 Hz; 1H, 7-H), 3.90-4.04 (m; 2H, CH_2CH_3), 7.07-7.16 (m; 2H), 7.27-7.38 (m; 2H). - ^{13}C-NMR (62.9 MHz) ($CDCl_3$): δ = 13.6 (CH_3), 29.3 ($COCH_3$), 31.8, 32.9 (C-6/C-7), 39.5 (C-1), 61.8 (OCH_2), 114.6 (C-5), 118.5 (C-2'), 124.6 (C-4'), 128.0, 129.6 (C-3'/C-5'), 151.3 (C-4), 163.1 (C-2, C=O), 165.8 (COOEt), 199.4 ($COCH_3$). - MS: *m/z* (%) = 275 (M+1, 37), 274 (M^+, 13), 232 (24), 231 (14), 228 (5), 187 (22), 186 (100), 175 (3), 159 (6), 158 (5), 131 (9), 102 (11), 77 (18), 43 (18).

$C_{15}H_{14}O_5$ (274.26)	Calcd.	C 65.65	H 5.15
	Found	C 65.40	H 5.20

Ethyl 4,5-Benzo-1-isobutyryl-3-oxa-2-oxo-cis-bicyclo[4.1.0]hept-4-en-endo-1-carboxylate **(12b)**: From **1b** and ethyl diazoacetate (yields and methods prepared as in Table 1), liquid. - IR ($CHCl_3$): 1760, 1740, 1715, 1620, 1600, 1570 cm^{-1}. - ^{1}H-NMR (250 MHz) (DMSO-d_6): δ = 0.96 (t, *J*=7.0 Hz; 3H, CH_2CH_3), 1.00 (d, *J*=7.0 Hz; 3H, $CHCH_3$), 1.07 (d, *J*=6.8 Hz; 3H, $CHCH_3$), 3.17 (d, *J*=9.7 Hz; 1H, 6-H), 3.25 (septet, *J*=6.8 Hz; 2H, $CHMe_2$), 3.49 (d, *J*=9.7 Hz; 1H, 7-H), 3.91 (m; 2H, 7.33-7.54 (m; 2H). - ^{13}C-NMR (62.9 MHz) (DMSO-d_6): δ

= 13.6 (CH_3), 17.8 , 18.5 ($CH(CH_3)_2$), 29.3, 31.5, (C-6/C-7), 37.9 ($CHMe_2$), 38.9 (C-1), 61.4 (OCH_2), 114.7 (C-5), 116.0 (C-2'), 124.6 (C-4'), 129.3, 129.6 (C-3'/C-5'), 150.6 (C-4), 162.4 (C-2, C=O), 165.7 (COOEt), 203.9 ($COCHMe_2$).

$C_{17}H_{18}O_5$ (302.31)	Calcd.	C 67.54	H 6.00
	Found	C 68.03	H 5.95

Ethyl 4,5-Benzo-1-cyclopropanoyl-3-oxa-2-oxo-cis-bicyclo[4.1.0]hept-4-en-endo-1-carboxylate **(12c)**: From **1c** and ethyl diazoacetate (yields and methods prepare as in Table 1), m.p. 115-116 °C (decomp.) (*n*-hexane/-ether). - IR ($CHCl_3$): 2900, 1760, 1730, 1690, 1620, 1590 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ = 0.94-1.28 (m; 4H, cyclpr), 1.08 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 2.62 (m, Σ*J*= 15.2 Hz; 1H, 1-H cyclpr), 3.14 (d, *J*=9.5 Hz; 1H, 6-H), 3.28 (d, *J*=9.5 Hz; 1H, 7-H), 3.92-4.07 (m; 2H, CH_2CH_3), 7.11-7.18 (m; 2H), 7.30-7.39 (m; 2H). - ^{13}C-NMR (75 MHz) ($CDCl_3$): δ = 13.68 (*J*=167 Hz), 13.74 (*J*=167 Hz; C-cyclpr), 13.8 (*J*=127.2 and 2.5 Hz; CH_3), 19.7 (*J*=170.0 Hz; C-1 cyclpr), 31.2 (*J*=174.0 and 3.0 Hz; C-7), 33.0 (*J*=172.2 Hz; C-6), 40.05 (t, *J*=2.0 Hz; C-1), 61.9 (*J*=148.5 and 4.5 Hz; OCH_2), 114.7 (C-5), 116.5 (C-2'), 124.5 (C-4'), 128.9, 129.5 (C-3'/C-5'), 151.3 (C-54), 163.1 (C-2, C=O), 165.9 (COOEt), 201.4 (CO-cyclpr). - MS: *m/z* (%) = 300 (M^+, 0.5), 273 (3), 232 (1), 231 (5), 212 (3), 187 (1), 186 (12), 173 (5), 131 (1), 102 (1), 77 (1), 69 (100), 41 (30).

$C_{17}H_{16}O_5$ (300.301)	Calcd.	C 67.99	H 5.37
	Found	C 68.11	H 5.10

Ethyl 4,5-Benzo-1-benzoyl-3-oxa-2-oxo-cis-bicyclo[4.1.0]hept-4-en-endo-1-carboxylate **(12d)**: From **1d** and ethyl diazoacetate (yields and methods prepared as in Table 1), m.p. 145-146 °C (decomp.) (ethanol) . - IR ($CHCl_3$): 1750, 1690, 1615, 1600 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ = 1.11 (t, *J*=7.1 Hz; 3H, CH_2CH_3), = 3.19 (d, *J*=9.4 Hz; 1H, 6-H), 3.49 (d, *J*=9.4 Hz; 1H, 7-H), 3.92-4.12 (m; 2H, CH_2CH_3), 7.20-7.27 (m; 2H), 7.37-7.49 (m; 3H), 7.52-7.64 (m; 2H), 7.76-7.79 (m; 2H). - ^{13}C-NMR (75 MHz) ($CDCl_3$): δ = 13.8 (*J*=127.5 and 2.5 Hz; CH_3), 28.2 (*J*=170.5 and 2 Hz; C-7), 31.6 (*J*=170.0 Hz; C-6), 39.4 (dd as t, *J*=2.0 Hz; C-1), 61.9 (*J*=148.6 and 4.5 Hz; OCH_2), 113.95 (C-5), 117.05 (C-2'), 124.9 (C-4'), 129.3, 129.8 (C-3'/C-5'), 151.3 ((C-4), 162.3 (C-2, C=O), 166.0 (COOEt); PhCO: 128.5, 129.0 (C-2,C-6/C-3,C-5), 133.85 (C-4), 134.95 (C-1), 190.6 (C=O). - MS (C.I.): *m/z* (%) = 338 (21), 337 (M+1, 100), 233 (2), 105 (10).

$C_{20}H_{16}O_5$ (336.33)	Calcd.	C 71.42	H 4.80
	Found	C 71.62	H 4.99

Ethyl 4,5-Benzo-1-ethoxycarbonyl-oxa-2-oxo-cis-bicyclo[4.1.0]hept-4-en-endo-1-carboxylate **(12e)**: From **1e** and ethyl diazoacetate (yields and methods prepared as in Table 1), m.p. 120-122 °C (decomp.) (*n*-hexane/-ether) . - IR ($CHCl_3$): 1760, 1725, 1620, 1595 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ 1.09 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 1.31 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 3.18 (d, *J*=9.5 Hz; 1H, 6-H), 3.25 (d, *J*=9.5 Hz; 1H, 7-H), 3.92-4.11 (m; 2H, CH_2CH_3), 4.22-4.34 (m; 2H, CH_2CH_3), 7.07-7.16 (m; 2H), 7.27-7.39 (m; 2H). - ^{13}C-NMR (75 MHz) ($CDCl_3$): δ = 13.8 (*J*=127.3 and 2.6 Hz, CH_3), 14.0 (*J*=127.3 and 2.6 Hz; CH_3), 30.0 (*J*=173.8 and 2.0 Hz; C-7), 31.2 (*J*=171.0 Hz; C-6), 33.4 (t, *J*=2.0 Hz; C-1), 61.9 (*J*=148.4 and 4.5 Hz; OCH_2), 63.1 (*J*=148.8 and 4.5 Hz; OCH_2), 114.0 (C-5), 116.6 (C-2'), 124.45 (C-4'), 128.9, 129.6 (C-3'/C-5'), 151.4 (C-4), 160.2 (C-2, C=O), 165.7, 166.8 (COOEt). - MS: *m/z* (%) = 305 (27), 304 (M^+, 22), 259 (10), 258 (16), 232 (15), 231 (39), 230 (10), 203 (38), 187 (29), 186 (100), 175 (32), 173 (8), 159 (30), 158 (17), 131 (23), 130 (20), 115 (8), 114 (7), 103 (11), 102 (25), 89 (7), 77 (10).

$C_{16}H_{16}O6$ (304.29)	Calcd.	C 63.15	H 5.30
	Found	C 62.92	H 5.48

Ethyl 4,5-Benzo-1-nitro-3-oxa-2-oxo-cis-bicyclo[4.1.0]hept-4-en-endo-1-carboxylate **(12f)**: From **1f** and ethyl diazoacetate (yields and methods prepared as in Table 1), m.p. 132-133 °C (decomp.) (*n*-hexane/ether). - IR (nujol): 1775, 1730, 1600, 1560 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ = 1.09 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 3.70 (d, *J*=11.0 Hz; 1H, 6-H), 3.82 (d, *J*=11.0Hz; 1H, 7-H), 3.95-4.10 (m; 2H, CH_2CH_3), 7.13-7.27 (m; 2H), 7.36-7.43 (m; 2H). - ^{13}C-NMR (62.9 MHz) ($CDCl_3$): δ = 13.5 (CH_3), 31.6, 32.7 (C-6/C-7), 62.6 (OCH_2), 66.6 (C-1), 112.4 (C-5), 117.1 (C-2'), 125.3 (C-4'), 128.9, 130.6 (C-3'/C-5'), 150.8 (C-4), 155.8 (C-2, C=O), 163.7 (COOEt). - MS: *m/z* (%) = 278 (M+1, 4), 232 (19), 231 (78), 204 (10), 203 (69), 187 (7), 186 (28), 176 (11), 175 (100), 159 (49), 158 (19), 147 (6), 131 (29), 130 (23), 114 (5), 114 (6), 103 (17), 102 (38), 77 (10).

$C_{13}H_{11}NO_6$ (277.23)	Calcd.	C 56.32	H 4.00	N 5.05
	Found	C 56.53	H 4.00	N 4.87

Ethyl 4,5-Benzo-1-cyano-3-oxa-2-oxo-cis-bicyclo[4.1.0]hept-4-en-endo-1-carboxylate **(12g)**: From **1g** and ethyl diazoacetate (yields and methods prepared as in Table 1), m.p. 183-185 °C (decomp.) (*ethanol*). - IR (nujol): 2210, 1740, 1715, 1595 cm^{-1}. - ^{1}H-NMR (300 MHz) ($CDCl_3$): δ = 1.08 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 3.16 (d, *J*=9.9 Hz; 1H, 6-H), 3.58 (d, *J*=9.9 Hz; 1H, 7-H), 3.99, 4.05 (two dq, *J*=7.1 and 10.6 Hz; 2H, $CH_AH_BCH_3$), 7.10 (dd, *J*=8.1 and 1.0 Hz; 1H, 2'-H), 7.21 (ddd as td, *J*=7.5 and 1.0 Hz; 1H, 4'-H), 7.36-7.44 (m; 2H). - ^{13}C-NMR (75 MHz) ($CDCl_3$): δ = 13.7 (*J*=127.5 and 2.6 Hz; CH_3), 21.0 (t, *J*=2.6 Hz; C-1), 31.3 (*J*=175.5 and 5.5 Hz; C-7), 32.3 (*J*=171.8 Hz; C-6), 62.75 (*J*=149.0 and 4.5 Hz; OCH_2), 112.1 (C-5), 115.7 (t, J=5.5 Hz; CN), 117.2 (C-2'), 125.7 (C-4'), 128.8, 130.4 (C-3'/C-5'), 150.2 (C-4), 157.7 (C-2, C=O), 163.7 (COOEt). - MS: *m/z* (%) = 258 (M+1, 33), 257 (M^+, 7), 230 (16), 229 (52), 212 (21), 201 (7), 186 (8), 185 (100), 157 (23), 156 (74), 141 (5), 140 (17), 130 (4), 129 (8), 128 (18), 118 (6), 102 (25), 101 (13), 77 (12), 29 (100).

$C_{14}H_{11}NO_4$ (257.24)	Calcd.	C 65.36	H 4.31	N 5.45
	Found	C 65.87	H 4.50	N 5.21

Ethyl 3,4-Dihydro-4-oxo-1-benzopyrano[3,4-c][2]pyrazole-1-carboxylate **(13)**: The yields of this compound, isolated from the reactions of ethyldiazoacetate and the 3-substituted coumarins **1** under the different proccedures are given in Tables 1 and 2, m.p. 235-237 °C (ether). - IR (nujol): 3100, 1755, 1730, 1640 cm^{-1}. - ^{1}H-NMR (300 MHz) (DMSO-d_6): δ = 1.43 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 4.45 (q, *J*=7.1 Hz; 2H, CH_2CH_3), 7.33 (ddd, *J*=7.8, 7.0 and ~0.5 Hz; 1H, 8-H), 7.39 (dd, *J*=8.0 and ~0.5 Hz; 1H, 6-H), 7.50 (ddd, *J*=8.0, 7.0 and 1.0 Hz; 1H, 7-H), 8.75 (dd, *J*=7.8 and 1.0 Hz; 1H, 9-H), 15.4 (bs; 1H, NH). - ^{13}C-NMR (75 MHz) (DMSO-d_6): δ = 14.0 (*J*=127.2 and 2.6 Hz; CH_3), 61.5 (*J*=149.0 and 4.5 Hz; OCH_2), 114.6 (*J*=9.2 and 4.2 Hz; C-9a), 116.9 (C-6), 122.3 (*J*=5 Hz; C-9b), 124.5 (C-8), 126.5, 129.7 (C-7/C-9), 132.8 (b; C-1), 151.1 (C-5a), 154.0 (b; C-2, C=O), 160.0 (b; COOEt). - MS : *m/z* (%) = 259 (24), 258 (M^+, 100), 230 (11), 214 (6), 213 (39), 212 (16), 187 (4), 186 (33), 158 (24), 157 (10), 131 (3), 129 (11), 128 (21), 114 (3), 103 (8), 102 (11), 101 (10) 76 (10).

$C_{13}H_{10}N_2O_4$ (258.23)	Calcd.	C 60.46	H 3.90	N 10.85
	Found	C 60.62	H 4.26	N 10.55

Ethyl 5-Acetyl-4-(2-hydroxy)phenyl-1H-pyrazole-3-carboxylate **(14a)**: From **1a** and ethyl diazoacetate (yields and methods prepared as in Tables 1 and 2), m.p. 160-162 °C (decomp.) (hexane/ether). - IR (nujol): 3140, 1740, 1730, 1680, 1620, 1585 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$+DMSO-d_6): δ = 1.14 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 2.30 (s; 3H, $COCH_3$), 4.20 (q, *J*=7.1 Hz; 2H, CH_2CH_3), 6.85-6.99 (m; 2H), 7.06-7.14 (m; 1H), 7.20-7.27 (m; 1H). - ^{13}C-NMR (75 MHz) ($CDCl_3$+DMSO-d_6): δ = 13.8 (CH_3), 27.6 ($COCH_3$), 60.6 (OCH_2), 115.8, 117.8, 118.9, 119.1, 121.6, 126.8, 129.4, 131.5, 154.7. - MS: *m/z* (%) = 275 (4), 274 (M^+, 25), 257 (7),

256 (4), 229 (18), 228 (100), 214 (13), 213 (84), 186 (11), 185 (6), 157 (7), 130 (2), 129 (7), 115 (6), 102 (8), 101 (8), 77 (8), 76 (9).

$C_{14}H_{14}N_2O_4$ (274.27)	Calcd.	C 61.31	H 5.15	N 10.21
	Found	C 61.23	H 5.33	N 10.36

Ethyl 4-(2-Hydroxy)phenyl-5-isobutyryl-1H-pyrazole-3-carboxylate **(14b)**: From **1b** and ethyl diazoacetate (yields and methods prepared as in Table 1), m.p. 152-155 °C (decomp.) (hexane/ether). - IR (nujol): 3150, 1720, 1680, 1600, 1565 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$+DMSO-d_6): δ = 1.07 (d, *J*=6.8 Hz; 6H, $CH(CH_3)_2$), 1.13 (t, *J*=7.2 Hz; 3H, CH_2CH_3), 2.54 (m; $CHMe_2$), 4.19 (q, *J*=7.2 Hz; 2H, CH_2CH_3), 4.26-4.57 (m; 2H), 6.86-6.98 (m; 2H), 7.03-7.14 (m; 1H), 7.19-7.27 (m; 1H), 7.75 (bs; NH and OH exchangeable with D_2O). - ^{13}C-NMR (75 MHz) ($CDCl_3$+DMSO-d_6): δ = 13.8 (CH_3), 18.5 ($CH(CH_3)_2$), 37.3 ($CHMe_2$), 60.9 (OCH_2), 116.5, 117.4, 119.3, 119.4, 122.2, 126.8, 129.4, 131.7, 154.6. - MS: *m/z* (%) = 303 (0.1), 302 (M^+, 1), 284 (2), 260 (5), 259 (42), 256 (4), 214 (12), 213 (100), 187 (1), 158 (2), 157 (2), 129 (2), 115 (1), 103 (2), 102 (2), 101 (5), 77 (2), 76 (2), 43 (5), 41 (3).

$C_{16}H_{18}N_2O_4$ (302.32)	Calcd.	C 63.56	H 6.00	N 9.27
	Found	C 63.76	H 6.08	N 9.12

Ethyl 5-Cyclopropanoyl-4-(2-hydroxy)phenyl-1H-pyrazole-3-carboxylate **(14c)**: From **1c** and ethyl diazoacetate (yields and methods prepared as in Table 1), m.p. 170-173 °C (decomp.) (hexane/ether). - IR (nujol): 3190, 3120, 1720, 1700, 1640, 1610, 1590 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ = 0.84 (m; 2H), 1.06-1.27 (m; 2H), 1.14 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 2.70 (m as bs; 1H, cyclpr), 4.19 (q, *J*=7.1 Hz; 2H, CH_2CH_3), 6.81-6.93 (m; 2H), 7.13-7.24 (m; 2H), 8.52 (bs; 1H), 14 (vbs; 1H), (OH and NH exchangeable with D_2O). - ^{13}C-NMR (75 MHz) ($CDCl_3$+DMSO-d_6)): δ = 11.82, 11.81, 13.8 (CH_3), 18.4 (C-1cyclpr), 60.7 (OCH_2), 116.1, 117.4, 119.0, 119.3, 122.8, 129.2, 131.8, 154.9. - MS: *m/z* (%) = 301 (16), 300 (M^+, 58), 259 (10), 255 (27), 255 (100), 236 (12), 214 (10), 213 (62), 208 (6), 207 (9), 186 (5), 158 (8), 157 (12), 129 (12), 128 (10), 115 (12), 103 (16), 102 (12), 101 (20), 77 (10), 76 (16), 69 (46), 41 (67).

$C_{16}H_{16}N_2O_4$ (300.30)	Calcd.	C 63.99	H 5.37	N 9.33
	Found	C 63.56	H 5.62	N 9.87

Ethyl 5-Acetyl-4-(2-hydroxy)phenyl-1H-pyrazoline-3-carboxylate **(18)**: From **1a** and ethyl diazoacetate in the presence of florisil (method D, Table 2), m.p. 142-145 °C (decomp.) (hexane/ether). - IR ($CHCl_3$): 3180, 1740, 1720, 1610, 1540 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ = 1.30 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 2.41 (s; 3H, $COCH_3$), 4.23 (q, *J*=7.1 Hz; 2H, CH_2CH_3), 4.52 (d, *J*=4.0 Hz; 1H), 4.87 (d, *J*=4.0 Hz; 1H), 6.83 (ddd, *J*=7.6, 7.4 and 1.2 Hz; 1H), 6.91 (dd, *J*=8.0 and 1.2 Hz; 1H), 7.03 (dd, *J*=7.6 and 1.7 Hz; 1H), 7.13 (ddd, *J*=8.0, 7.4 and 1.7 Hz; 1H), 7.60 (s; 1H), 8.60 (s, 1H, NH and OH). ^{13}C-NMR (75 MHz) ($CDCl_3$): δ = 14.1 (CH_3), 25.4 ($COCH_3$), 44.9 (C-4pyrz), 62.7 (OCH_2), 69.4 (C-5pyrz), 152.2 (C-3pyrz, C=N), 171.0 (COOEt), 199.0 ($COCH_3$); Ph: 119.1 (C-6), 121.9 (C-4), 126.7 (C-3), 127.0 (C-2), 129.3 (C-5), 153.6 (C-1). - MS: *m/z* (%) = 278 (19), 277 (87), 276 (M^+, 65), 235 (10), 233 (7), 204 (19), 203 (100), 187 (15), 185 (33), 162 (13), 161 (82), 160 (13), 134 (12), 133(19), 131 (9), 118 (5), 116 (17), 115 (5), 106 (10), 103 (6), 102 (10), 77 (12), 43 (62).

$C_{14}H_{16}N_2O_4$ (276.28)	Calcd.	C 60.86	H 5.84	N 10.14
	Found	C 61.29	H 6.03	N 9.87

Ethyl 3-Acetyl-2-oxo-2H-1-benzopyren-4-yl-accetate **(19a)**: From **1a** and ethyl diazoacetate (yields and methods prepared as in Table 2), m.p. 138-140 °C (ethanol). - IR ($CHCl_3$): 1730, 1610, 1560 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ = 1.26 (t, *J*=7.1 Hz; 3H, CH_2CH_3), 2.64 (s; 3H, $COCH_3$), 3.99 (s; 2H, CH_2CO), 4.19 (q, *J*=7.1 Hz; 2H, CH_2CH_3), 7.33-7.40(m; 2H), 7.62 (m; 1H), 7.90 (m; 1H). - ^{13}C-NMR (75 MHz) ($CDCl_3$): δ = 14.1 (*J*=127.3 and 2.6 Hz; CH_3), 31.6 (*J*=129.1 Hz; $COCH_3$), 34.0 (*J*=131.9 Hz; CH_2CO), 61.9 (*J*=148.3 and

4.5 Hz; OCH_2), 117.3 (C-8), 118.9 (C-10), 125.0 (C-6), 125.8 (C-5), 128.4 (C-3), 133.1 (C-7), 146.5 (*J*=5.7 and 5.0 Hz; C-4), 153.3 (C-9), 158.7 (C-2, C=O), 168.4 (*J*=8.5 and 3.2 Hz; COOEt), 200.55 (*J*=6.5 Hz; $COCH_3$). - MS: *m/z* (%) = 274 (M^+, 39), 259 (16), 245 (7), 231 (9), 229 (48), 228 (20), 214 (14), 213 (99), 204 (16), 203 (100), 202 (61), 187 (16), 175 (12), 160 (29), 145 (6), 131 (23), 129 (6), 115 (12), 103 (12), 102 (21), 101 (8), 91 (10), 77 (20), 76 (11), 43 (99).

$C_{15}H_{14}O_5$ (276.28)	Calcd.	C 65.69	H 5.15
	Found	C 65.90	H 5.08

Ethyl 3-Ethoxycarbonyl-2-oxo-2H-1-benzopyren-4-yl-accetate (**19e**): From **1e** and ethyl diazoacetate in the presence of molecular sieves (method F), 0.8 g, (26%), m.p. 100-103 °C (hexane/ether). - IR ($CHCl_3$): 1760-1720, 1610, 1570 cm^{-1}. - ^{1}H-NMR (250 MHz) ($CDCl_3$): δ = 1.23 (t, *J*=7.2 Hz; 3H, CH_2CH_3), 1.40 (t, *J*=7.0 Hz; 3H, CH_2CH_3), 3.95 (s; 2H, CH_2CO), 4.18 (q, *J*=7.2 Hz; 2H, CH_2CH_3),), 4.44 (q, *J*=7.0 Hz; 2H, CH_2CH_3), 7.31-7.39(m; 2H), 7.58-7.69 (m; 2H). - ^{13}C-NMR (62.9MHz) ($CDCl_3$): δ = 13.1, 15.0 (CH_3), 35.2 (CH_2CO), 61.9, 62.3 (OCH_2), 116.3 (C-10), 118.4 (C-8), 124.6 (C-6), 125.8 (C-5), 132.8 (C-7), 146.4 (C-4), 153.3 (C-9), 157.4 (C-2, C=O), 164.2, 167.9 (COOEt). -MS: *m/z* (%) = 305 (10), 304 (M^+, 79), 260 (6), 259 (37), 258 (23), 232 (23), 231 (22), 230 (67), 214 (12), 213 (79), 203 (33), 202 (100), 187 (12), 186 (67), 175 (29), 174 (35), 160 (12), 157 (12), 146 (25), 131 (17), 130 (25), 118 (20), 115 (7), 103 (25), 102 (58), 101 (21), 91 (27), 77 (30), 76 (21).

$C_{16}H_{16}O_6$ (304.28)	Calcd.	C 56.63	H 5.06
	Found	C 65.90	H 5.08

X-ray analysis of **11b**. Compound **11b**, $C_{17}H_{18}N_2O_5$, M = 330.33, crystallises (from hexane/ether) as white prismatic crystals; space group $P2_1/c$, z = 4, a = 12.987 (2), b = 6.6648(12), c = 19.971(3) Å, β = 76.163 (5) Å, V = 1678.5(5) Å^3, D_{measd} = 1.29 Mg.m^{-3}, D_{calcd} = 1.307 Mg.m^{-3}, Mo-Ka, Zr filtered radiation, λ = 0.7107 Å, μ = 0.097 mm^{-1}.

Data were collected using a crystal with *ca* 0.34 x 0.22 x 0.50 mm mounted in air on a Nicolet $P2_1$ diffractometer upgraded by Crystal Logic using Zr-filtered Mo radiation. Unit cell dimensions were determined and refine by using the angular settings of 25 automatically centered reflections in the range 11<2θ<24. Intensity data were recorded using a θ-2θ scan to 2θ(max) = 50deg with scan speed 3.0 deg/min and scan range 2.5 plus $\alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorenz and polarization correction were applied using Crystal Logic software. Symmetry equivalent data were averaged with R = 0.0236 to give 2772 independent reflections from a total 2969 collected.

The structure was solved by direct methods using[29] SHELXS-86 and refined by full-matrix least-squares techniques[30] on F^2 with SHELXL-93 using only 2772 unique reflections and refining 265 parameters. All hydrogen atoms (except those of C12, C13, C16 and C17 which were introduced at calculated positions as riding on bonded atoms) were located by difference maps and their positions were refined isotropically. All non-hydrogen atoms were refined anisotropically.

The final for all data R1, wR2 and GOF values are 0.1456, 0.3741 and 1.045 respectively. The maximum and minimum residual peaks in the final difference map were 0.331 and -0.452 e/Å^3. The largest shift/esd in the final cycle was 0.099. The final atomic co-ordinates with anisotropic thermal parameters and supplementary material have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW, UK, and are available on request.

Acknowledgement.

This work was financially supported by the Bulgarian National Fund for Scientific Investigation. C. P. Raptopoulou is grateful to John Boutari and Son Co. for a financial support.

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(*Received in UK* 17 *August* 1994; *revised* 19 *September* 1994; *accepted* 23 *September* 1994)