The Regioselectivity in the Reactions of *N*-Aryl-*C*-Ethoxycarbonylnitrilimines with Acrylic Acid Derivatives

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Received April 28, 1987

The cycloaddition of a series of *C*-ethoxycarbonyl-*N*-arylnitrilimines **5a-f** to acrylic acid derivatives namely acrylamide, acrylonitrile and ethyl acrylate has been studied. Under thermal conditions 1,3-dipolar cycloadditions proceed with complete regioselectivity to give 5-R substituted 2-pyrazolines **8-10** in high yield. The structures of the cycloadducts **8-10** were confirmed by ^{13}C nmr, ^{1}H nmr and ir spectra. The regioselectivity is interpreted in terms of HOMO(nitrilimine)-LUMO(dipolarophile) interaction.

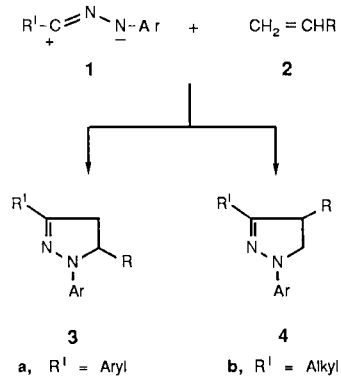
J. Heterocyclic Chem., **25**, 257 (1988).

Introduction.

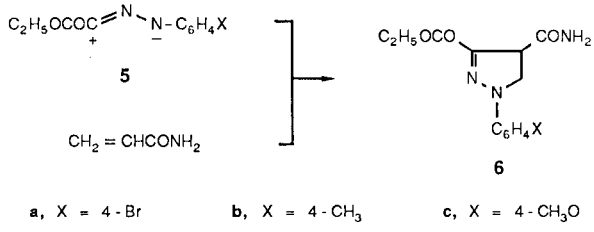
The 1,3-dipolar cycloaddition of nitrilimines **1** to various dipolarophiles **2** has been studied over the past two decennia [2-10]. There is ample evidence that the cycloaddition of **1** to electron deficient dipolarophiles occurs with complete regioselectivity yielding the corresponding 5-R substituted 2-pyrazolines **3** (Scheme 1). Therefore, it is surprizing that 1-aryl-3-ethoxycarbonyl-2-pyrazoline-5-carboxamides **6a-c** were reported to be the exclusive products from the cycloaddition of *C*-ethoxycarbonyl-*N*-arylnitrilimines **5a-c** to acrylamide (Scheme 2) [11-12]. This finding prompted us to undertake a more systematic investigation of the cycloaddition of α-ketonitrilimines to acrylic acid derivatives, with the objective of identifying the effects of the α-carbonyl group on the regiochemistry of this class of 1,3-dipoles.

Recently, one of us reported the kinetics and mechanism of formation of *C*-ethoxycarbonyl-*N*-arylnitrilimines **5a-f** from *C*-ethoxycarbonyl-*N*-arylformohydrazidoyl chlorides **7a-f** [13]. We now report the results of the study of the cycloaddition of a series of **5** with acrylamide, acrylonitrile and ethyl acrylate (Scheme 3).

Scheme 1



Scheme 2



Scheme 3

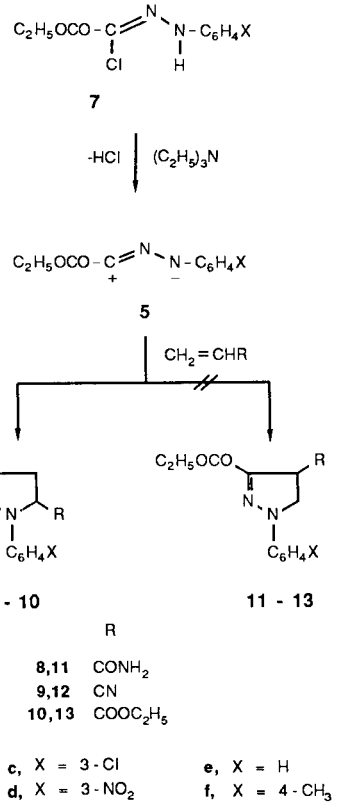
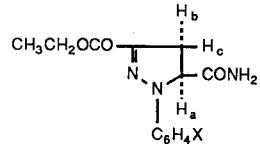


Table I

Infrared and ^1H NMR Spectral Data of the Cycloadducts **8a-f** and **16a,b**

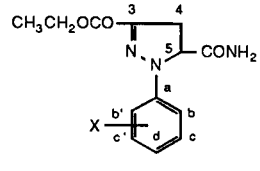


Compound No.	ν, cm^{-1}		6, ppm (multiplicity) [d]				
	NH_2	CO	CH_3 [e]	CH_2O [e]	H_a [f]	H_c [f]	H_b [f]
8a	3400 3220	1700 1670	1.3 (t)	4.28 (q)	4.90 (dd)	3.54 (dd)	3.05 (dd)
8b	3380 3200	1690 1670	1.33 (t)	4.30 (q)	4.84 (dd)	3.60 (dd)	3.20 (dd)
8c	3400 3300	1675 1705 [g]	1.32 (t)	4.30 (q)	4.90 (dd)	3.65 (dd)	3.10 (dd)
8d	3425 3300	1701 [g] 1680	1.30 (t)	4.32 (q)	4.97 (dd)	3.62 (dd)	3.25 (dd)
8e	3370 3180	1690 1640	1.30 (t)	4.28 (q)	4.90 (dd)	3.62 (dd)	3.04 (dd)
8f	3350 3250	1700 1680	1.30 (t) 2.25 (s)	4.28 (q)	4.87 (dd)	3.68 (dd)	3.30 (dd)
16a	3390 3300	1675 1647			4.82 (dd)	3.62 (dd)	3.05 (dd)
16b	3380 3200	1655 1645			4.93 (dd)	3.75 (dd)	3.30 (dd)

[d] All compounds exhibit aromatic proton multiplet in the region 7.0-8.0 ppm. [e] J = 7 Hz. [f] J_{ab} = 8 Hz; J_{ac} = 13 Hz; J_{bc} = 18 Hz. [g] Shoulder.

Table II

^{13}C NMR Data of 1-Aryl-3-ethoxycarbonyl-2-pyrazoline-5-carboxamides **8a-f**



Carbon No.	Compound No., δ ppm					
	8a	**8b**	**8c**	**8d**	**8e**	**8f**
C-3	141.8 (s)	141.4 (s)	143.9 (s)	143.7 (s)	142.5 (s)	140.3 (s)
C-4	37.5 (t)	37.5 (t)	37.7 (t)	38.0 (t)	37.3 (t)	37.1 (t)
C-5	62.3 (d)	62.3 (d)	62.4 (d)	62.4 (d)	62.3 (d)	62.7 (d)
C-a	139.4 (s)	139.2 (s)	139.8 (s)	148.5 (s)	138.3 (s)	137.5 (s)
C-b	115.2 (d)	114.7 (d)	113.2 (d)	107.6 (d)	113.2 (d)	113.3 (d)
C-c	131.6 (d)	128.8 (d)	134.0 (s)	140.9 (s)	128.9 (d)	129.1 (d)
C-d	112.1 (s)	124.3 (s)	120.2 (d)	114.7 (d)	120.6 (d)	129.5 (s)
C-b'	115.2 (d)	114.7 (d)	111.7 (d)	119.1 (d)	113.2 (d)	113.3 (d)
C-c'	131.6 (d)	128.8 (d)	130.2 (d)	129.9 (d)	128.9 (d)	129.1 (d)
CH_3	14.1 (q)	14.0 (q)	14.1 (q)	14.1 (q)	14.0 (q)	13.9 (q)
CH_2O	60.5 (t)	60.5 (t)	60.6 (t)	60.8 (t)	60.3 (t)	60.1 (t)
COO	161.7 (s)	161.2 (s)	161.2 (s)	161.1 (s)	161.3 (s)	161.3 (s)
$CONH_2$	170.9 (s)	170.9 (s)	171.2 (s)	170.9 (s)	171.3 (s)	171.3 (s)
$ArCH_3$						19.8 (q)

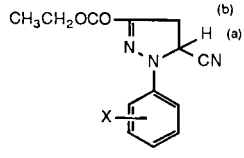
Results and Discussion.

The reflux of a mixture of *N*-*p*-bromophenyl-*C*-ethoxycarbonylformohydrazidoyl chloride **7a** and acrylamide in chloroform in the presence of triethylamine afforded, after work up and purification, 1-*p*-bromophenyl-3-ethoxycarbonyl-2-pyrazoline-5-carboxamide **8a** in 80% yield. Similarly, reactions of **7b-f** with acrylamide gave the corresponding 1,3-dipolar cycloadducts **8b-f** respectively in good yield (Scheme 3). The assigned structures of the latter cycloadducts were based on their analytical and spectral (^{1}H nmr, ^{13}C nmr and ir) data. In ^{1}H nmr spectra each of the cycloadducts **8a-f** exhibited an ABX pattern assignable to the methylene (dd, δ 3.10-3.60 ppm) and methine (dd, δ 4.87-4.97 ppm) protons characteristic of the 5-R substituted 2-pyrazoline ring residue (Table 1). The observed low chemical shift of the methine proton signal is compatible with the 2-pyrazoline-5-carboxamide structure **8**. The value of δ 4.87-4.97 ppm is too low to be assigned to the CH at the 4-position of the regioisomer, 2-pyrazoline-4-carboxamide **11** (Scheme 3). Generally, the chemical shift of the methine proton at the 5-position of 5-substituted 2-pyrazolines appear at lower field than that of the methine proton at the 4-position of 4-substituted 2-pyrazolines [3,14,15]. The ^{13}C nmr spectra of **8a-f** provide additional evidence for their assigned structure (Table 2). Thus, in ^{13}C nmr spectra of **8a-f** each compound exhibited three characteristic signals assignable to C-3 (s, δ 140.3-143.9), C-4 (t, δ 37.1-38.0), and C-5 (d, δ 62.3-62.7) respectively.

Addition of nitrilimines **5a-f** to acrylonitrile took place in the same regiochemical sense as for acrylamide. Thus, the reflux of the chloride **7a-f** with acrylonitrile in the presence of triethylamine afforded the corresponding 1-aryl-3-ethoxycarbonyl-5-cyano-2-pyrazolines **9a-f** in 80-85% yield, respectively (Scheme 3). The tlc and nmr analyses of the reaction product in each case showed that only one regioisomer was formed. The distinction between the two possible regioisomers **9** and **12** was made on the basis of the ^{1}H nmr, ^{13}C nmr and ir spectral data (Tables 3 and 4). For example, each of the cycloadducts **9a-f** exhibited an A_2X pattern in its ^{1}H nmr spectrum: a triplet (δ 5.03-5.07) and a doublet (δ 3.55-3.66 ppm) assignable to the methine and methylene protons of 5-cyano-2-pyrazoline ring residue. These chemical shifts are similar to those reported for 1,3-diphenyl-5-cyano-2-pyrazoline [9]. This similarity suggests that both substituents, phenyl and ethoxycarbonyl, at C-3 of 1-aryl-5-substituted 2-pyrazoline derivatives would have roughly the same effects on the chemical shifts of the 4-CH_2 and 5-CHR protons of 1-aryl-5-R-2-pyrazolines having the same 1-aryl and 5-R substituents. This suggestion seems to be substantiated by the identity of the inductive substituent effects (σ_I) of the phenyl and ethoxycarbonyl groups, the values of σ_I are 0.22 [14] and 0.30 [16] respectively. The ^{13}C nmr spectra of **9a-f** (Table 4) are also in support of their assigned structures. Thus, each compound exhibited three signals: a singlet at 139.5-142.2, a triplet at 37.6-38.3 and a doublet

Table III

IR and ^{1}H NMR Spectral Data of 1-Aryl-5-cyano-2-pyrazoline Derivatives **9a-f** and **17a,b**

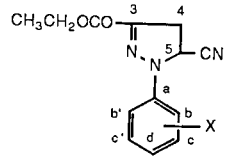


Compound No.	ν, cm^{-1} CO	CN	δ, ppm [a] (multiplicity) CH_3 [b]	OCH_2 [b]	H_a [c]	H_b [c]
9a	1715	[e]	1.40 (t)	4.35 (q)	5.05 (t)	3.58 (d)
9b	1715	[e]	1.35 (t)	4.36 (q)	5.05 (t)	3.57 (d)
9c	1702	[e]	1.38 (t)	4.38 (q)	5.05 (t)	3.60 (d)
9d	1700	[e]	1.48 (t)	4.40 (q)	5.18 (t)	3.67 (d)
9e	1720	2240 [d]	1.38 (t)	4.35 (q)	5.07 (t)	3.55 (d)
9f	1710	[e]	1.35 (t)	4.35 (q)	5.03 (t)	3.50 (d)
17a	1670	[e]			5.05 (t)	3.65 (d)
17b	1665	[e]			5.15 (t)	3.55 (d)

[a] All compounds exhibit aromatic proton multiplet in the region 7.0-8.0 ppm. [b] J = 7 Hz. [c] J = 9 Hz. [d] Very weak. [e] Absent.

Table IV

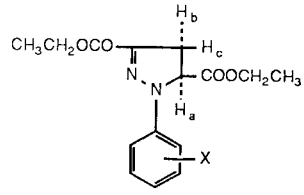
^{13}C NMR Spectral Data of 1-Aryl-3-ethoxycarbonyl-5-cyano-2-pyrazolines **9a-f**



Carbon No.	Compound No./δ ppm					
	9a	**9b**	**9c**	**9d**	**9e**	**9f**
C-3	140.7 (s)	140.5 (s)	142.4 (s)	142.2 (s)	141.3 (s)	139.5 (s)
C-4	37.9 (t)	38.0 (t)	38.0 (t)	38.3 (t)	37.7 (t)	37.6 (t)
C-5	50.1 (d)	50.4 (d)	50.1 (d)	50.1 (d)	50.2 (d)	50.6 (d)
C-a	140.4 (s)	140.0 (s)	140.9 (s)	149.0 (s)	139.8 (s)	139.1 (s)
C-b	115.8 (d)	115.8 (d)	112.6 (d)	109.3 (s)	114.8 (d)	114.9 (d)
C-c	132.3 (d)	129.4 (d)	135.3 (s)	142.4 (s)	129.4 (d)	132.5 (d)
C-d	115.5 (s)	128.2 (s)	115.1 (d)	117.2 (d)	122.9 (d)	129.3 (s)
C-b′	115.8 (d)	115.8 (d)	122.9 (d)	120.3 (d)	114.8 (d)	114.9 (d)
C-c′	132.3 (d)	129.4 (d)	130.4 (d)	130.4 (d)	129.4 (d)	132.5 (d)
CH_3	14.2 (q)	14.3 (q)	14.2 (q)	14.2 (q)	14.2 (q)	14.2 (q)
CH_2O	61.2 (t)	61.9 (t)	61.9 (t)	62.1 (t)	61.7 (t)	61.5 (t)
COO	160.3 (s)	160.9 (s)	160.2 (s)	160.7 (s)	161.1 (s)	161.1 (s)
CN	115.7 (s)	116.1 (s)	115.8 (s)	115.7 (s)	116.1 (s)	116.3 (s)
$ArCH_3$						20.5 (q)

Table V

Infrared and ^1H NMR of 1-Aryl-3,5-diethoxycarbonyl-2-pyrazolines, **10a-f**



Compound No.	ν, cm^{-1}	δ, ppm (multiplicity) [d]				
	CO	CH_3 [e]	OCH_2 [e]	H_a [f]	H_c [f]	H_b [f]
10a	1725	1.15 (t)	4.20 (q)	4.72 (dd)	3.39 (dd)	3.20 (dd)
	1690 [g]	1.32 (t)	4.35 (q)			
10b	1730	1.20 (t)	4.22 (q)	4.90 (dd)	3.56 (dd)	3.28 (dd)
	1690	1.40 (t)	4.40 (q)			
10c	1730	1.20 (t)	4.20 (q)	4.90 (dd)	3.58 (dd)	3.22 (dd)
	1680	1.40 (t)	4.40 (q)			
10d	1740	1.20 (t)	4.20 (q)	5.01 (dd)	3.67 (dd)	3.26 (dd)
	1700	1.40 (t)	4.38 (q)			

[d] All compounds exhibit aromatic proton multiplet in the region 7.0-8.0 ppm. [e] J = 7 Hz. [f] J_{ab} = 9 Hz, J_{ac} = 12 Hz, J_{bc} = 18 Hz. [g] Shoulder.

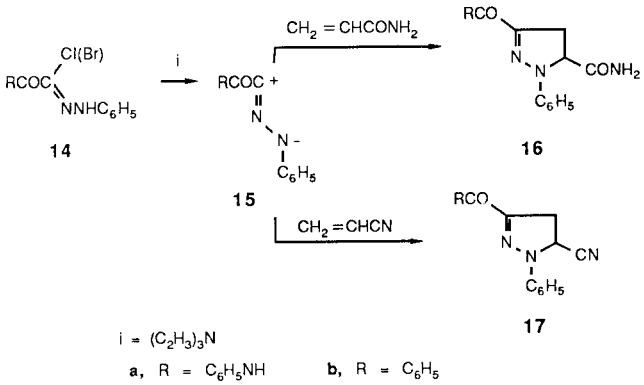
at 50.1-50.6 ppm assignable to C-3, C-4 and C-5 of **9** respectively. That the cycloadducts obtained from the reaction of **5a-f** and acrylonitrile have structure **9** and not **12** is supported further by the observation that the nitrile absorption was absent or very weak, if present, in their IR spectra, as it is the case of aliphatic nitriles activated by a nitrogen or an oxygen atom in the α-position [17-20].

The predominant formation of the 5-substituted 2-pyrazolines was also recognized with regard to ethyl acrylate. Thus, the reaction of **7a-f** with ethyl acrylate in the presence of triethylamine proceeded smoothly to give 1-aryl-3,5-diethoxycarbonyl-2-pyrazolines **10a-f** in 79-85% yield respectively. The structure of the latter cycloadducts was supported by their ^1H nmr, ir spectra and elemental

analyses. For example, the ^{1}H nmr spectra (Table 5) was characterised in each case by ABX pattern assignable to 5-methine and 4-methylene protons. The observed chemical shifts and coupling constants of **10a-f** are comparable to those of **8a-f** (in this work) and of ethyl 1,3-diaryl-2-pyrazoline-5-carboxylates reported in literature [9].

Other α-ketonitrilimines **15a,b** exhibited similar regioselectivity in their reactions with acrylic acid derivatives. Thus, both *C*-phenylcarbamoyl-*N*-phenylnitrilimine **15a** and *C*-benzoyl-*N*-phenylnitrilimine **15b** add acrylamide and yield the cycloadducts **16a** and **16b** respectively. Also, the cycloaddition of **15a** and **15b** to acrylonitrile afforded the cycloadducts **17a** and **17b** respectively (Scheme 4). The structural assignments of **16** and **17** were based on their elemental analyses and their ^{1}H nmr and ir spectra (Tables 1 and 3).

Scheme 4



The foregoing results demonstrate that the cycloaddition of *C*-ethoxycarbonyl-*N*-arylnitrilimines to acrylic acid derivatives occurs in the same regiospecific sense to give exclusively 5-substituted 2-pyrazoline derivatives regardless of the nature of the substituents in the dipolarophile ($CH_2=CHR$) and the *N*-aryl group in the nitrilimine. This regioselectivity can be explained satisfactorily on the basis of HOMO (dipole)-LUMO (dipolarophile) interaction as follows. Recently, Houk and Caramella [21] on the basis of *ab initio* molecular orbital calculations argued that in the non-planar most stable conformation of $H\overset{+}{C}=N\text{-}\overset{-}{N}H$ the biggest HOMO coefficient is to be found on the carbon atom and this is also the case in diphenyl nitrilimine [22]. As both substituents, phenyl and ethoxycarbonyl, would have roughly similar effects on the properties of molecular orbitals of nitrilimines, it could be assumed that the coefficient of carbon atom in HOMO of *C*-ethoxycarbonyl-*N*-arylnitrilimine is larger than that of the nitrogen atom. Furthermore, molecular orbital calculations on electron deficient olefins of type $CH_2=CHR$ (where R is an electron withdrawing substituent) showed that both HOMO and LUMO are always polarized away from the substituent, with the difference in coefficient magnitudes much larger in the LUMO [23] (Figure 1). On this basis, the reaction of the studied *C*-ethoxycarbonyl-*N*-arylnitrilimines with acrylic acid derivatives would be expected to be controlled by dipole HOMO-dipolarophile LUMO interaction,

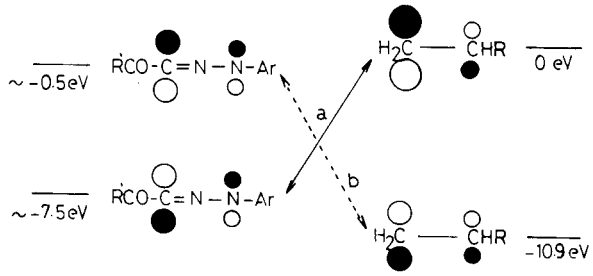


Figure 1

as such pair of addends has a narrow dipole HOMO-dipolarophile LUMO (see interaction a in Figure 1). As the favoured cycloadduct is the one that would be formed by the union of the atoms with the largest coefficients, it is obvious that the predominant dipole HOMO-dipolarophile LUMO interaction in the studied reactions would lead to the exclusive formation of 5-R substituted 2-pyrazolines and this is what is observed experimentally. Such finding substantiates our previous assumption that the relative order of the orbital coefficients of the carbon and terminal nitrogen atoms in the HOMO of **5** is similar to that in diphenylnitrilimine HOMO.

EXPERIMENTAL

All melting points were determined with Bockmonoscop apparatus (hot stage type) and are uncorrected. Infrared spectra of the compounds in potassium bromide were obtained with Zeiss infrarot spectrophotometer model IMT6. ^{1}H nmr spectra were recorded on a Varian EM-390-90MHz spectrometer, while ^{13}C nmr were obtained from 1 *M* deuterated chloroform (or deuterated dimethyl sulfoxide) solutions on Jeol JNM FX 100 spectrometer using tetramethylsilane as internal reference. Measurements of the ^{13}C-H coupling constants were carried out using IRMOD nOe method. All nmr spectral chemical shifts are given in parts per million (δ) downfield from tetramethylsilane. Microanalyses were performed with Perkin-Elmer elemental analyzer, model 240-B at King Abdulaziz University. *C*-Ethyoxycarbonyl-*N*-arylformohydrazidoyl chlorides **7a-f** [24], *C*-phenylcarbamoyl-*N*-phenylformohydrazidoyl chloride **14a** [25] and *C*-benzoyl-*N*-phenylformohydrazidoyl bromide **14b** [6] were prepared according to literature procedures. Acrylamide, acrylonitrile and ethyl acrylate are Aldrich laboratory reagents.

Preparation of 1-Aryl-3-ethoxycarbonyl-2-pyrazoline-5-carboxamides **8a-f**. General Procedure.

To a solution of the approriate *C*-ethoxycarbonyl-*N*-arylformohydrazidoyl chloride **7** (0.005 mole) and acrylamide (0.4 g, 0.005 mole) in chloroform (40 ml) was added triethylamine (0.7 ml, 0.005 mole) at room temperature. The mixture was refluxed until the disappearance of **7** as shown by tlc analysis (10-16 hour). The solvent system used for tlc analysis was a mixture of toluene, acetic acid and acetone in a ratio of 150:5:0.5 (v/v) respectively. The reaction mixture was cooled, extracted three times with water and the chloroform extract was dried over

anhydrous sodium sulfate, then filtered. The solvent was evaporated and the residue left was triturated with little methanol where it solidified. The crude product was collected and crystallized from ethanol. In cases of **8a**, **8b** and **8d**, most of the 2-pyrazoline product precipitated during refluxing. The reaction mixture was filtered prior to work up. In these cases, the products were crystallized from 1:1 mixture of dimethylformamide and ethanol. The results are summarized in Table 6.

Table VI

1-Aryl-3-substituted-2-pyrazoline-5-carboxamides, **8a-f** and **16a,b**

Compound No.	Mp, °C	Yield, %	Molecular formula	*Anal.* Calcd./(Found) C,%	H,%	N,%
8a	221 [a]	75	$C_{13}H_{14}BrN_3O_3$	45.88 (46.39)	4.11 (4.17)	12.35 (12.39)
8b	232	74	$C_{13}H_{14}ClN_3O_3$	52.79 (52.75)	4.77 (4.78)	14.21 (14.20)
8c	209 [b]	86	$C_{13}H_{14}ClN_3O_3$	52.79 (52.63)	4.77 (4.74)	14.21 (14.28)
8d	236 [b]	73	$C_{13}H_{14}N_4O_5$	50.98 (51.27)	4.60 (4.56)	18.29 (18.24)
8e	231 [b]	78	$C_{13}H_{15}N_3O_3$	59.76 (59.18)	5.78 (5.78)	16.08 (15.88)
8f	217	81	$C_{14}H_{17}N_3O_3$	61.09 (61.48)	6.18 (6.19)	15.27 (15.19)
16a	279	83	$C_{17}H_{16}N_4O_2$	66.22 (66.12)	5.23 (5.26)	18.17 (17.98)
16b	242	79	$C_{17}H_{15}N_3O_2$	69.55 (69.67)	5.15 (5.03)	14.32 (14.09)

[a] Lit mp 195° [11]. [b] Sublimes.

1-Phenyl-3-phenylcarbamoyl-2-pyrazoline-5-carboxamide **16a** and 1-phenyl-3-benzoyl-2-pyrazoline-5-carboxamide **16b** were prepared similarly from *C*-phenylcarbamoyl-*N*-phenylformohydrazidoyl chloride **14a** and *C*-benzoyl-*N*-phenylformohydrazidoyl bromide **14b** and acrylamide respectively following the same procedure. The results are given in Table 6.

Table VII

1-Aryl-3-substituted-5-cyano-2-pyrazolines, **9a-f** and **17a,b**

Compound No.	Mp, °C	Yield, %	Molecular formula	*Anal.* Calcd./(Found) C,%	H,%	N,%
9a	78	83	$C_{13}H_{12}BrN_3O_2$	48.47 (48.94)	3.75 (3.73)	13.04 (13.19)
9b	74	77	$C_{13}H_{12}ClN_3O_2$	56.22 (56.71)	4.35 (4.37)	15.13 (15.17)
9c	108	78	$C_{13}H_{12}ClN_3O_2$	56.22 (56.12)	4.35 (4.34)	15.13 (15.12)
9d	161	69	$C_{13}H_{12}N_4O_4$	54.17 (53.97)	4.19 (4.16)	19.44 (19.35)
9e	86	76	$C_{13}H_{13}N_3O_2$	64.18 (64.52)	5.39 (5.41)	17.28 (17.26)
9f	103	80	$C_{14}H_{15}N_3O_2$	65.35 (65.08)	5.87 (5.93)	16.33 (16.30)
17a	154	75	$C_{17}H_{14}N_4O$	70.33 (70.17)	4.86 (4.89)	19.29 (19.25)
17b	140 [a]	84	$C_{17}H_{13}N_3O$	74.17 (73.88)	4.76 (4.54)	15.25 (15.09)

[a] Lit mp 139° [7].

Preparation of 1-Aryl-3-ethoxycarbonyl-5-cyano-2-pyrazolines, **9a-f**. General Procedure.

To a stirred chloroform (40 ml) solution of *C*-ethoxycarbonyl-*N*-arylformohydrazidoyl chloride **7** (0.005 mole), and acrylonitrile (15 ml) was added triethylamine (1.4 ml, 0.01 mole) at room temperature. The mixture was refluxed for 5-6 hours, cooled and extracted with water. The chloroform solutiion was dried over anhydrous sodium sulfate, then filtered. The solvent and excess acrylonitrile were evaporated. The residue left was triturated with little methanol and the crude solid that formed was collected and crystallized from ethanol. The results are summarized in Table 7.

1-Phenyl-3-phenylcarbamoyl-5-cyano-2-pyrazoline **17a** and 1-phenyl-3-benzoyl-5-cyano-2-pyrazoline **17b** were similarly prepared from the corresponding hydrazidoyl halides **14a** and **14b** respectively and acrylonitrile following the same procedure. The compounds prepared together with their physical constants are given in Table 7.

Preparation of 1-Aryl-3,5-diethoxycarbonyl-2-pyrazolines **10a-f**. General Procedure.

These compounds were prepared by the same method described for synthesis of **9a-f** using ethyl acrylate (15 ml, 0.138 mole) in place of acrylonitrile. Work up of the reaction mixture as above yielded viscous liquids which solidified upon standing for two weeks. The solids were collected and crystallized from petroleum ether 40/60°. The results are summarized in Table 8.

Table VIII

1-Aryl-3,5-diethoxycarbonyl-2-pyrazolines, **10a-d**

Compound No.	Mp, °C	Yield, %	Molecular formula	*Anal.* Calcd./(Found) C,%	H,%	N,%
10a	48	80	$C_{15}H_{17}BrN_2O_4$	48.79 (48.39)	4.64 (4.69)	7.58 (7.89)
10b	61	85	$C_{15}H_{17}ClN_2O_4$	55.47 (55.53)	5.27 (5.63)	8.62 (8.42)
10c	39	84	$C_{15}H_{17}ClN_2O_4$	55.47 (55.70)	5.27 (5.46)	8.62 (8.53)
10d	81	79	$C_{15}H_{17}N_3O_6$	53.72 (53.70)	5.11 (5.23)	12.53 (12.74)

Acknowledgement.

The authors wish to express their thanks to King Abdulaziz University for their financial support.

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