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Nuclear magnetic resonance spectroscopy and the structures of the regioisomeric products of the cycloaddition of *C*-ethoxycarbonyl-*N*-arylnitrilimines to α,β-unsaturated ketones

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Abstract—^{1}H NMR chemical shifts were used to assign the structures of the regioisomeric products obtained from the reactions of *C*-ethoxycarbonyl-*N*-arylnitrilimines **2A–E** to α,β-unsaturated ketones **3a–j**. The assignments were based on the large observed difference between chemical shifts of the H-4 and H-5 of the 2-pyrazoline ring residue. Values of 1.29 ± 0.06 and 0.34 ± 0.03 ppm were found for $\Delta\delta_{4,5}$ for the 5-aroyl- and 4-aroyl-2-pyrazoline regioisomers **4** and **5**, respectively. The regioselectivity in the studied cycloaddition reactions is interpreted in terms of FMO method.

INTRODUCTION

THE present work is concerned with the study of ^{1}H NMR spectra of the extensive series of 3-ethoxycarbonyl-1,4-diaryl-5-aroyl-2-pyrazolines **4** and their regioisomers, namely 3-ethoxycarbonyl-1,5-diaryl-4-aroyl-2-pyrazolines **5** (Scheme 1). Our interest in these compounds resulted from the divergence in the regiochemical assignment of the structures of the cycloaddition products obtained from the reaction of some nitrilimines with α,β-enones. For example, whereas the reaction of benzalacetophenone **3a** with diphenylnitrilimine **6** was reported to give 1,3,4-triphenyl-5-benzoyl-2-pyrazoline **7** [1] (Scheme 2), the cycloadditions of **2D** to **3a** and **3h** and of **2B** to **3h** were reported to yield exclusively the 4-aroyl-2-pyrazoline derivatives **5Da**, **5Dh** and **5Bh**, respectively [2]. Furthermore, the cycloaddition of **2A** to **3a** was reported to give an unseparable mixture of the two regioisomers **4Aa** and **5Aa** in a ratio of 3:2, respectively [3]. This divergence seems to be a result of the fact that only few spectral data of the isomeric 2-pyrazoline derivatives of type **4** and **5** are available and the lack of definite assignments of resonances to H-4 and H-5 in such derivatives. To unravel this problem the cycloaddition of **2A–E** to a wide range of substituted benzalacetophenones **3a–j** was studied and the ^{1}H NMR spectra of the products were investigated. This is because the previously studied enomes are either unsubstituted or substituted with only electron-donating groups [2].

EXPERIMENTAL

All melting points were determined on Bockmonoscop apparatus (hot stage type) and are uncorrected. ^{1}H NMR spectra were recorded on a Varian EM 390-90 MHz spectrometer. All chemical shifts are given in ppm downfield from tetramethylsilane. Microanalyses were performed with a Perkin–Elmer elemental analyzer, model 240-B at King Abdulaziz University. The hydrazonyl chlorides **1A–E** were prepared according to a known procedure [4]. Benzalacetophenone **3a** was obtained from Merck and the other substituted derivatives **3b–j** were prepared by condensation of the appropriate aldehyde with acetophenone following a known procedure [5]. Reaction mixtures were analyzed on Fluka silica gel with fluorescent indicator 254

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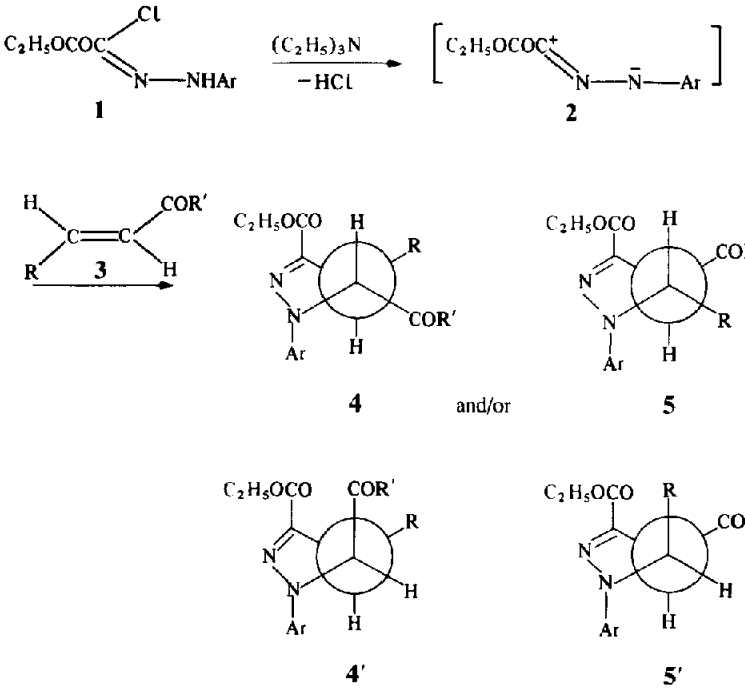


Ar=XC_6H_4

	X
A	H
B	4-CH_3
C	4-Cl
D	4-Br
E	3-Cl

R=YC_6H_4

	Y/Z
a	H/H
b	4-CH_3O/H
c	4-CH_3/H
d	4-Cl/H
e	3-NO_2/H

R'=ZC_6H_4

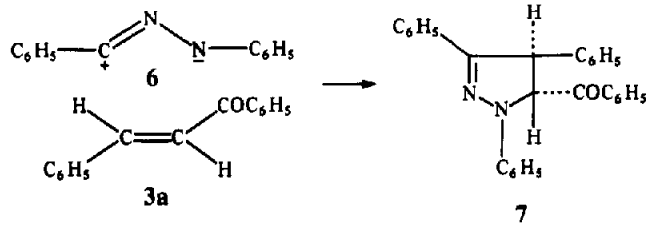
	Y/Z
f	4-NO_2/H
g	4-CH_3O/4-CH_3O
h	3,4-$(CH_3O)_2$/4-CH_3O
i	3,4-CH_2O_2/4-CH_3O
j	4-CH_3O/4-Br

Scheme 1.

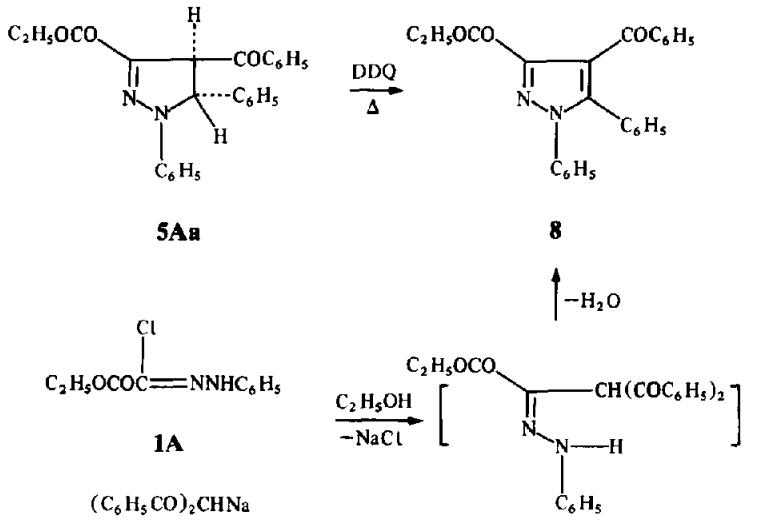
on aluminum cards, and the spots were detected under UV light of 254 nm. The preparative thin layer chromatographic separation was carried out on glass plates (20 × 20 cm) covered with Fluka silica gel G with 13% gypsum and using a mixture of carbon tetrachloride and chloroform in ratio of 5:1.5 (v/v) as eluent.

Reaction of C-ethoxycarbonyl-N-arylnitrilimines with α,β-unsaturated ketones

General method. Triethylamine (0.7 ml, 5 mmol) was added to a chloroform solution (50 ml) of **1** (5 mmol) and the appropriate benzalacetophenone **3** (5 mmol) at room temperature. The mixture was refluxed until the complete disappearance of the reactants **1** and **3** as indicated by thin layer chromatographic analysis. The mixture was cooled, washed with water three times, and the chloroform layer was collected, dried over anhydrous sodium sulphate, then filtered. The solvent in the filtrate was evaporated under reduced pressure and the residue left was triturated with methanol when it solidified. The crude solid was collected and its ^1H NMR spectrum was recorded. When the spectrum showed the presence of only one regioisomer, the product was crystallized



Scheme 2.



Scheme 3.

directly from ethanol–chloroform as indicated in Table 2. When the reaction yielded a mixture of two cycloadducts as indicated by ^{1}H NMR analysis, they were separated by preparative thin layer chromatography in the usual way and were fully characterized by spectral and elemental analyses. The results are summarized in Tables 1 and 2.

Dehydrogenation of the cycloadducts

General method. A mixture of the appropriate cycloadduct **4** (or **5**) (5.4 mmol) in toluene (50 ml) was refluxed with dichlorodicyanobenzoquinone (DDQ) (1.3 g, 5.7 mmol) for 20 h. The solution was diluted with ether, washed with dilute aqueous sodium hydroxide solution and water, dried over anhydrous sodium sulphate, then filtered. The solvent was evaporated under reduced pressure and the crude solid left was crystallized from methanol or ethanol.

Dehydrogenation of **4Aa** gives ethyl 1,4-diphenyl-5-benzoylpyrazole-3-carboxylate, m.p. 142–143°C (methanol), 62% yield, anal. calcd for $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.08; N, 7.07. Found: C, 75.77; H, 4.10; N, 6.98%; IR (KBr): ν(C=O) 1720, 1660 cm^{-1}; ^{1}H ^{1}NMR ($CDCl_3$): δ 1.1 (t, 3H, CH_3CH_2, $J = 7$ Hz), 4.2 (q, 2H, CH_3CH_2, $J = 7$ Hz), 7.1–8.2 (m, 15H, ArH) ppm.

Dehydrogenation of **5Aa** yields ethyl 1,5-diphenyl-4-benzoylpyrazole-3-carboxylate, **8**, m.p. 159–160°C (ethanol), 50% yield (lit. m.p. 159–160°C [5]). This product was found identical in all respects with an authentic sample prepared by a literature method [6].

Results and Discussion

The reactions of the nitrilimines **2A–E**, generated *in situ* by treatment of the corresponding *C*-ethoxycarbonyl-*N*-arylformohydrazonyl chlorides **1** with triethylamine [7], with benzalacetophenone **3a** and its substituted derivatives **3b–i** were carried out in refluxing chloroform. Thin layer chromatographic analysis of the crude cycloaddition product showed in some cases the presence of only one cycloaddition product, whereas in others, two cycloadducts were produced. In the latter cases the formation ratios of the two cycloadducts produced were determined by ^{1}H NMR analysis of the crude reaction product. The results are summarized in Table 1. Next, the cycloadducts were separated by preparative thin layer chromatography using a mixture of carbon tetrachloride and chloroform in ratio 5:1.5 (v/v) respectively as eluent.

The two cycloadducts isolated can be either regioisomeric (**4** and **5** or **4′** and **5′**) or diastereomeric (**4** and **4′** or **5** and **5′**) (Scheme 1). In order to resolve this question we have investigated the chemical behaviour and ^{1}H NMR characteristics of the adducts obtained from the reaction of **2A** with **3a** taken as typical examples of the reaction series studied. Thus, dehydrogenation of the cycloadduct with the higher R_f value and which

represents the minor product of such a reaction gave a product identified as ethyl 1,5-diphenyl-4-benzoylpyrazole-3-carboxylate **8** by comparison with an authentic sample prepared by treatment of **1A** with dibenzoylmethane in ethanol in the presence of sodium ethoxide [6] (Scheme 3). Similar dehydrogenation of the major product obtained from the reaction of **2A** with **3a** and which has the lower R_f value yielded, however, ethyl 1,4-diphenyl-5-benzoylpyrazole-3-carboxylate (see the Experimental section). These findings substantiate the regioisomeric nature of the cycloadducts isolated.

The two regioisomeric structures **4'** and **5'** were discarded on the basis of the observation that the coupling constant between H-4 and H-5 was 6 Hz in the spectra of both cycloadducts. This is because the coupling constants between *trans*- and *cis*-4- and 5-protons of 2-pyrazoline derivatives were reported to be 6 and 12 Hz, respectively [8]. Accordingly it is reasonable to assign structure **4** for the major cycloadduct with the lower R_f value and structure **5** for the minor cycloadduct with the higher R_f value.

The ^{1}H NMR spectra of **4** and **5** each in deuterated chloroform showed, in each case, two doublets assignable to the 4- and 5-ring protons (Table 3). On the basis of the reported substituent effects of the groups Ar–, ArCO– and R_2N– on the chemical shift of the methine proton [9] and application of Shoolery's rules [10], the H-5 would be expected to be more deshielded than H-4 in both regioisomers **4** and **5**. Accordingly the

Table 1. Cycloadducts from the reactions of nitrilimines **2A–E** with enones **3a–j**

Entry	Reactants	Reaction time (h)	Product(s) (Yield)*	Ratio (4:5)†
1	**2A** + **3a**	24	**4Aa** (45) + **5Aa** (20)	3:2
2	**2A** + **3b**	24	**4Ab** (93)	1:0
3	**2A** + **3c**	25	**4Ac** (72)	1:0
4	**2A** + **3d**	20	**4Ad** (85)	1:0
5	**2A** + **3e**	26	**4Ae** (72)	1:0
6	**2A** + **3f**	21	**4Af** (88)	1:0
7	**2A** + **3g**	24	**4Ag** (84)	1:0
8	**2B** + **3a**	27	**4Ba** (70) + **5Ba** (15)	4:1
9	**2B** + **3b**	24	**4Bb** (85)	1:0
10	**2B** + **3c**	25	**4Bc** (70)	1:0
11	**2B** + **3d**	20	**4Bd** (80)	1:0
12	**2B** + **3e**	24	**4Be** (45)	1:0
13	**2B** + **3f**	21	**4Bf** (78)	1:0
14	**2B** + **3g**	27	**4Bg** (46)	1:0
15	**2B** + **3i**	30	**4Bi** (62)	1:0
16	**2B** + **3j**	30	**4Bj** (70)	1:0
17	**2C** + **3a**	28	**4Ca** (50) + **5Ca** (20)	3:2
18	**2C** + **3b**	17	**4Cb** (46)	1:0
19	**2C** + **3c**	25	**4Cc** (38) + **5Cc** (22)	3:2
20	**2C** + **3d**	20	**4Cd** (80)	1:0
21	**2C** + **3f**	24	**4Cf** (78)	1:0
22	**2C** + **3g**	27	**4Cg** (46)	1:0
23	**2C** + **3i**	30	**4Ci** (55)	1:0
24	**2C** + **3j**	30	**4Cj** (70)	1:0
25	**2D** + **3a**	19	**4Da** (65) + **5Da** (20)	3:1
26	**2D** + **3c**	30	**4Dc** (50) + **5Dc** (18)	2:1
27	**2D** + **3e**	24	**4De** (70)	1:0
28	**2D** + **3j**	30	**4Dj** (50)	1:0
29	**2E** + **3a**	20	**4Ea** (83)	1:0
30	**2E** + **3b**	17	**4Eb** (67)	1:0
31	**2E** + **3c**	25	**4Ec** (55)	1:0
32	**2E** + **3d**	14	**4Ed** (47)	1:0
33	**2E** + **3e**	24	**4Ee** (47)	1:0
34	**2E** + **3f**	26	**4Ef** (65)	1:0
35	**2E** + **3g**	12	**4Eg** (52) + **5Eg** (19)	7:3

* Isolated yield.

† The ratio was determined by ^{1}H NMR analysis.

Table 2. Melting points and elemental analyses of cycloadducts **4** and **5**

Compound no.	M.p. (°C)*	Molecular formula	Anal. Calcd (Found) C (%)	H (%)	N (%)
4Aa	139	$C_{25}H_{22}N_2O_3$	75.36 (75.23)	5.56 (5.67)	7.03 (7.00)
4Ab	162	$C_{26}H_{24}N_2O_4$	72.88 (72.64)	5.64 (5.58)	6.53 (6.63)
4Ac	163	$C_{26}H_{24}N_2O_3$	75.71 (75.87)	5.86 (5.79)	6.79 (6.81)
4Ad	191	$C_{25}H_{21}ClN_2O_3$	69.36 (69.93)	4.89 (4.81)	6.47 (6.50)
4Ae	161	$C_{25}H_{21}N_3O_5$	67.71 (67.88)	4.77 (4.66)	9.47 (9.17)
4Af	173†	$C_{25}H_{21}N_3O_5$	67.71 (68.06)	4.77 (4.80)	9.47 (9.54)
4Ag	156	$C_{27}H_{26}N_2O_5$	70.72 (70.61)	5.71 (5.86)	6.11 (6.12)
4Ba	135	$C_{26}H_{24}N_2O_3$	75.71 (74.96)	5.86 (5.92)	6.79 (6.60)
4Bb	143	$C_{27}H_{26}N_2O_4$	73.28 (73.70)	5.92 (5.90)	6.33 (6.36)
4Bc	170	$C_{27}H_{26}N_2O_3$	76.03 (75.84)	6.14 (6.05)	6.56 (6.66)
4Bd	159	$C_{26}H_{23}ClN_2O_3$	69.87 (69.46)	5.18 (5.22)	6.26 (6.20)
4Be	181†	$C_{26}H_{23}N_3O_5$	68.60 (68.37)	5.06 (4.96)	9.18 (9.01)
4Bf	140	$C_{26}H_{23}N_3O_5$	68.60 (68.97)	5.06 (4.95)	9.18 (8.97)
4Bg	132‡	$C_{28}H_{28}N_2O_5$	71.77 (72.30)	5.97 (6.07)	5.93 (5.81)
4Bi	152	$C_{28}H_{26}N_2O_6$	69.12 (68.85)	5.38 (5.34)	5.76 (5.62)
4Bj	172	$C_{27}H_{25}BrN_2O_4$	62.19 (61.92)	4.83 (4.83)	5.37 (5.11)
4Ca	129	$C_{25}H_{21}ClN_2O_3$	69.36 (69.42)	4.89 (4.93)	6.47 (6.72)
4Cb	173	$C_{26}H_{23}ClN_2O_4$	67.45 (67.42)	5.01 (5.03)	6.05 (5.94)
4Cc	176	$C_{26}H_{23}ClN_2O_3$	69.87 (69.31)	5.18 (5.17)	6.26 (6.06)
4Cd	176	$C_{25}H_{20}Cl_2N_2O_3$	64.25 (64.42)	4.31 (4.32)	5.99 (6.06)
4Cf	229†	$C_{25}H_{20}ClN_3O_5$	62.83 (62.64)	4.21 (4.15)	8.79 (8.67)
4Cg	170†	$C_{27}H_{25}ClN_2O_5$	65.78 (65.67)	5.11 (5.13)	5.67 (6.04)
4Ci	185	$C_{27}H_{23}ClN_2O_6$	63.97 (63.64)	4.57 (4.57)	5.52 (5.53)
4Cj	182	$C_{26}H_{22}BrClN_2O_4$	57.63 (57.32)	4.09 (4.02)	5.17 (5.12)
4Da	147	$C_{25}H_{21}BrN_2O_3$	62.90 (66.87)	4.43 (4.38)	5.87 (5.87)
4Dc	164	$C_{26}H_{23}BrN_2O_3$	63.55 (63.60)	4.72 (4.67)	5.70 (5.62)
4De	175	$C_{25}H_{20}BrN_3O_5$	57.48 (56.98)	3.86 (3.84)	8.04 (8.02)
4Dj	183	$C_{26}H_{22}Br_2N_2O_4$	53.26 (53.06)	3.78 (3.81)	4.78 (4.87)
4Ea	123	$C_{25}H_{21}ClN_2O_3$	69.36 (68.91)	4.89 (4.87)	6.47 (6.52)
4Eb	127	$C_{26}H_{23}ClN_2O_4$	67.45 (67.57)	5.01 (5.00)	6.05 (6.22)
4Ec	142	$C_{26}H_{23}ClN_2O_3$	69.87 (69.20)	5.18 (5.11)	6.26 (6.29)
4Ed	133	$C_{25}H_{20}Cl_2N_2O_3$	64.25 (63.87)	4.31 (4.22)	5.99 (5.95)
4Ee	198†	$C_{25}H_{20}ClN_3O_5$	62.83 (62.92)	4.21 (4.11)	8.79 (8.72)
4Ef	186	$C_{25}H_{20}ClN_3O_5$	62.83 (62.41)	4.21 (4.11)	8.79 (8.83)
4Eg	118	$C_{27}H_{25}ClN_2O_5$	65.78 (65.59)	5.11 (5.01)	5.67 (5.80)
5Aa	122	$C_{25}H_{22}N_2O_3$	75.36 (75.66)	5.56 (5.35)	7.03 (6.98)
5Ba	123	$C_{26}H_{24}N_2O_3$	75.71 (74.91)	5.86 (5.91)	6.79 (6.70)
5Ca	137	$C_{25}H_{21}ClN_2O_3$	69.36 (69.40)	4.89 (4.92)	6.47 (6.72)
5Cc	156	$C_{26}H_{23}ClN_2O_3$	69.87 (69.52)	5.18 (5.10)	6.26 (6.12)
5Da	137	$C_{25}H_{21}BrN_2O_3$	62.90 (62.55)	4.43 (4.42)	5.87 (5.82)
5Dc	165	$C_{26}H_{23}BrN_2O_3$	63.55 (63.59)	4.72 (4.66)	5.70 (5.62)
5Eg	156	$C_{27}H_{25}ClN_2O_5$	65.78 (65.35)	5.11 (5.05)	5.67 (5.75)

* All compounds were crystallized from ethanol except otherwise specified.
† Crystallized from ethanol–chloroform mixture.
‡ Crystallized from methanol.

doublets with higher and lower chemical shift values were assigned to H-5 and H-4, respectively, in both regioisomers **4** and **5** as shown in Table 3. This assignment was confirmed by comparison of the spectral data of **5Aa** with those of 1,3,5-triphenyl-5-benzoyl-2-pyrazoline. The latter was reported to exhibit two doublets at 5.61 and 4.61 ppm ($J = 5$ Hz) assignable to H-5 and H-4, respectively [8]. Both substituents, phenyl and ethoxycarbonyl at 3-position, were reported to have roughly the same effects on the chemical shift of H-4 [3].

Statistical treatment of the data in Table 3 revealed that the mean values of the chemical shifts for such protons in **4** are 5.71 and 4.45 with standard deviations of ±0.05 and ±0.06 ppm for H-5 and H-4, respectively. Similar treatment of the spectral data of the regioisomer **5** indicated that the mean values of the chemical shifts of H-5 and H-4 are 5.42 and 5.08 with standard deviations of ±0.04 and ±0.02 ppm, respectively.

As can be seen from these data the difference $(\delta_5-\delta_4)=\Delta\delta_{4,5}$ between the chemical shift values of the pair of doublets of **4** is almost four times that of $\Delta\delta_{4,5}$ of **5**. For example, statistical calculations showed that the mean values of $\Delta\delta_{4,5}$ for the two regioisomers **4** and **5** are 1.29 ± 0.06 and 0.34 ± 0.03 ppm, respectively. This large difference in $\Delta\delta_{4,5}$ values suggests that the latter parameter can be used as a probe for distinction between the regioisomeric cycloadducts of type **4** and **5**. On this basis, the reported ^{1}H NMR data ($\Delta\delta_{4,5}$ 1.33, 1.29 and 1.31 ppm) for the products isolated from the reactions of **1D** with **3a** and **3h** and of **1B** with **3h** agree with the structures **4Da**, **4Dh** and **4Bh**, respectively, contrary to what had already been reported [2].

Table 3. ^{1} NMR spectral data of the cycloadducts **4** and **5**

Compound no.	δ [ppm (multiplicity)] 4-H*	5-H*	Other hydrogens†
4Aa	4.45 (d)	5.75 (d)	1.20 (t, 3H), 4.20 (q, 2H), 7.0–8.0 (m, 15H)
4Ab	4.43 (d)	5.75 (d)	1.20 (t, 3H), 3.85 (s, 3H), 4.25 (q, 2H), 6.8–8.0 (m, 14H)
4Ac	4.42 (d)	5.75 (d)	1.20 (t, 3H), 2.40 (s, 3H), 4.19 (q, 2H), 6.7–8.0 (m, 14H)
4Ad	4.40 (d)	5.71 (d)	1.25 (t, 3H), 4.20 (q, 2H), 6.9–7.9 (m, 14H)
4Ae	4.55 (d)	5.75 (d)	1.20 (t, 3H), 4.20 (q, 2H), 7.0–8.4 (m, 14H)
4Af	4.55 (d)	5.78 (d)	1.20 (t, 3H), 4.20 (q, 2H), 7.4 (d, 2H), 7.5–8.1 (m, 12H), 8.25 (d, 2H)
4Ag	4.40 (d)	5.67 (d)	1.29 (t, 3H), 3.80 (s, 3H), 3.9 (s, 3H), 4.20 (q, 2H), 6.8–7.9 (m, 13H)
4Ba	4.42 (d)	5.72 (d)	1.19 (t, 3H), 2.25 (s, 3H), 4.15 (q, 2H), 7.0–8.0 (m, 14H)
4Bb	4.40 (d)	5.70 (d)	1.20 (t, 3H), 2.20 (s, 3H), 3.80 (s, 3H), 4.18 (q, 2H), 6.8–8.0 (m, 13H)
4Bc	4.40 (d)	5.73 (d)	1.20 (t, 3H), 2.26 (s, 3H), 2.36 (s, 3H), 4.20 (q, 2H), 6.9–8.0 (m, 13H)
4Bd	4.40 (d)	5.70 (d)	1.20 (t, 3H), 2.26 (s, 3H), 4.20 (q, 2H), 7.0–8.1 (m, 13H)
4Be	4.55 (d)	5.70 (d)	1.20 (t, 3H), 2.32 (s, 3H), 4.20 (q, 2H), 7.0–8.3 (m, 13H)
4Bf	4.53 (d)	5.77 (d)	1.20 (t, 3H), 2.26 (s, 3H), 4.20 (q, 2H), 7.0–8.25 (m, 13H)
4Bg	4.40 (d)	5.65 (d)	1.20 (t, 3H), 2.25 (s, 3H), 3.80 (s, 3H), 3.90 (s, 6H), 4.20 (q, 2H), 6.8–8.0 (m, 12H)
4Bi	4.35 (d)	5.65 (d)	1.25 (t, 3H), 2.27 (s, 3H), 4.15 (q, 2H), 5.95 (s, 2H), 6.7–8.0 (m, 11H)
4Bg	4.40 (d)	5.67 (d)	1.20 (t, 3H), 2.30 (s, 3H), 3.82 (s, 3H), 4.20 (q, 2H), 6.8–8.0 (m, 12H)
4Ca	4.45 (d)	5.75 (d)	1.20 (t, 3H), 4.19 (q, 2H), 6.9–8.0 (m, 14H)
4Cb	4.45 (d)	5.73 (d)	1.20 (t, 3H), 3.83 (s, 3H), 4.20 (q, 2H), 6.8–8.0 (m, 13H)
4Cc	4.40 (d)	5.70 (d)	1.20 (t, 3H), 3.5 (s, 3H), 4.15 (q, 2H), 6.9–8.0 (m, 13H)
4Cd	4.47 (d)	5.70 (d)	1.25 (t, 3H), 4.20 (q, 2H), 6.9–8.0 (m, 13H)
4Cf	4.60 (d)	5.78 (d)	1.20 (t, 3H), 4.20 (q, 2H), 7.0–8.3 (m, 13H)
4Cd	4.40 (d)	5.68 (d)	1.20 (t, 3H), 3.80 (s, 3H), 3.88 (s, 3H), 4.20 (q, 2H), 6.8–8.0 (m, 12H)
4Ci	4.45 (d)	5.60 (d)	1.20 (t, 3H), 3.88 (s, 3H), 4.20 (q, 2H), 5.98 (s, 2H), 6.7–8.0 (m, 11H)
4Cj	4.40 (d)	5.60 (d)	1.20 (t, 3H), 3.84 (s, 3H), 4.20 (q, 2H), 6.8–8.0 (m, 12H)
4Da	4.44 (d)	5.72 (d)	1.21 (t, 3H), 4.20 (q, 2H), 6.8–8.0 (m, 14H)
4Dc	4.40 (d)	5.70 (d)	1.20 (t, 3H), 2.35 (s, 3H), 4.20 (q, 2H), 6.9–8.0 (m, 13H)
4De	4.55 (d)	5.67 (d)	1.19 (t, 3H), 4.18 (q, 2H), 6.9–8.2 (m, 13H)
4Dj	4.42 (d)	5.65 (d)	1.25 (t, 3H), 3.85 (s, 3H), 4.20 (q, 2H), 6.8–7.8 (m, 12H)
4Ea	4.47 (d)	5.73 (d)	1.21 (t, 3H), 4.20 (q, 2H), 6.8–8.0 (m, 14H)
4Eb	4.42 (d)	5.70 (d)	1.22 (t, 3H), 3.80 (s, 3H), 4.20 (q, 2H), 6.8–8.0 (m, 13H)
4Ec	4.45 (d)	5.74 (d)	1.25 (t, 3H), 2.40 (s, 3H), 4.20 (q, 2H), 6.8–8.0 (m, 13H)
4Ed	4.45 (d)	5.70 (d)	1.24 (t, 3H), 4.20 (q, 2H), 6.8–8.0 (m, 13H)
4Ee	4.60 (d)	5.76 (d)	1.23 (t, 3H), 4.20 (q, 2H), 6.7–8.2 (m, 13H)
4Ef	4.58 (d)	5.76 (d)	1.25 (t, 3H), 4.20 (q, 2H), 6.8–8.2 (m, 13H)
4Eg	4.43 (d)	5.65 (d)	1.25 (t, 3H), 3.80 (s, 3H), 3.92 (s, 3H), 4.20 (q, 2H), 6.7–8.0 (m, 12H)
5Aa	5.01 (d)	5.49 (d)	1.20 (t, 3H), 4.20 (q, 2H), 7.0–8.0 (m, 15H)
5Ba	5.10 (d)	5.47 (d)	1.19 (t, 3H), 2.20 (s, 3H), 4.20 (q, 2H), 7.0–8.0 (m, 14H)
5Ca	5.10 (d)	5.40 (d)	1.20 (t, 3H), 2.20 (s, 3H), 4.20 (q, 2H), 7.0–8.0 (m, 14H)
5Cc	5.07 (d)	5.39 (d)	1.20 (t, 3H), 2.30 (s, 3H), 4.19 (q, 2H), 6.9–8.0 (m, 13H)
5Da	5.10 (d)	5.40 (d)	1.20 (t, 3H), 4.20 (q, 2H), 6.9–8.0 (m, 14H)
5Dc	5.08 (d)	5.40 (d)	1.20 (t, 3H), 2.30 (s, 3H), 4.20 (q, 2H), 6.9–8.0 (m, 13H)
5Eg	5.05 (d)	5.40 (d)	1.20 (t, 3H), 3.85 (s, 3H), 3.90 (s, 3H), 4.20 (q, 2H), 6.7–8.0 (m, 12H)

* $J_{4,5}=6$ Hz.

† The value of the coupling constant J for the triplet (t) and quartet (q) signals is 7 Hz.

The regioselectivity observed in the cycloaddition studied can be interpreted in terms of the Frontier Molecular Orbital (FMO) method [11, 12]. The nitrilimine **2** being an electron rich species, like diphenylnitrilimine, its reaction with electron deficient α,β-unsaturated ketones **3** would be expected to be controlled by HOMO(nitrilimine)–LUMO(enone) interaction [3]. Molecular orbital calculations on **3** revealed that the oribital coefficient at the β-carbon is larger than that at the α-carbon atom in both HOMO and LUMO with the difference in coefficient magnitudes much larger in the LUMO [1]. Also on the basis of *ab initio* molecular orbital calculations, it was shown that the biggest orbital coefficient is to be found on the carbon atom in both HOMO and LUMO of **2** [3]. Thus, the overlap of orbitals with comparable terminal coefficients, i.e. orbitals of the nitrogen and carbon atoms of **2** with the orbitals of the α- and β-carbon atoms, respectively, of the enone **3**, will lead to the 5-aroyl-4-aryl-2-pyrazoline derivative **4** as the major cycloadduct.

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