1,3-Dipolar Cycloaddition Reactions of Nitrilimines with 1-Aroyl-4,5-dihydro-3,4,4-trimethyl-5-methylene-1*H*-pyrazoles. Synthesis of 6-Aroyl-8,9,9-trimethyl-1,2,6,7-tetrazaspiro[4.4]nona-2,7-dienes

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From the 1,3-dipolar cycloaddition reactions of 5-methylene-1*H*-pyrazoles **3** with *N*-arylnitrilimines the novel spiro-cycloadducts **4** were isolated, in addition to the corresponding 5-(2-aroylhydrazono-1,1-dimethylpropyl)-1*H*-pyrazoles **5**. These pyrazoles **5** were the only products from the reactions of **3** with *N*-methylnitrilimine **2d**. The chemical behaviour of the spiro-cycloadducts **4** was also examined.

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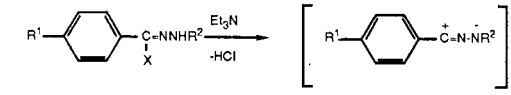
Nitrilimines have been known to react with various types of monosubstituted olefins to give predominantly 5-substituted 2-pyrazolines [1]. On the other hand considerably few reactions between nitrilimines and methylene-substituted cyclic systems [2-4] have been investigated.

Our interest in the chemistry of pyrazoles [5,6] prompted us to examine the cycloaddition reactions of various nitrilimines with 5-methylenepyrazoles **3** and to investigate the regioselectivity of these cycloadducts.

The 1-aroyl-4,5-dihydro-3,4,4-trimethyl-5-methylene-1*H*-pyrazoles (**3**) have been obtained in 50-55% yield by heating the corresponding 1-aroyl-4,5-dihydro-5-hydroxy-3,4,4,5-tetramethyl-1*H*-pyrazoles for 30 minutes at 150-170° [5,6].

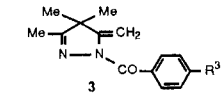
The 1,3-dipolar cycloaddition reactions of 5-methylenepyrazoles **3** to nitrilimines **2**, prepared *in situ* from the corresponding *N*-aryl- or *N*-methylarylhydrazidoyl halides **1** in benzene in the presence of triethylethylamine, were carried out at 80° for 30 hours. From the reactions of the 5-methylenepyrazoles **3** with the *N*-arylnitrilimines **2a-c** the expected spiro-cycloadducts were always isolated as the major products (40-50% yield) and were determined to be the 6-aroyl-1,3-diaryl-8,9,9-trimethyl-1,2,6,7-tetrazaspiro[4.4]nona-2,7-dienes **4a-e**. A second product was always isolated (20-40% yield), with only one exception the reaction between 5-methylenepyrazole **3b** and the *N*-(*p*-nitrophenyl)nitrilimine **2c**, and was characterized as a 5-(2-aroylhydrazono-1,1-dimethylpropyl)-1,3-diaryl-1*H*-pyrazole derivative **5a-d**. In contrast from the reactions of compounds **3** with the *N*-methylnitrilimine **2d** the expected spiro-cycloadducts were not isolated and the 5-(2-aroylhydrazono-1,1-dimethylpropyl)-1-methyl-3-phenyl-1*H*-pyrazoles **5f-h** were isolated as the only products in 30-48% yield.

The structure of compounds **4** and **5** was deduced on the basis of analytical and spectral data (Table I and II). The regiochemistry of the cycloadducts **4** was established by a comparison of the nmr shifts of the 4-CH_2 protons with those in literature [2]. The chemical shifts observed at ~ δ 3.50 and 4.14 (AB system, J_{gem} = 17.5 Hz) correspond well with the reported values [2] (δ 3.40 and 4.20, J_{gem} = 18 Hz) for analogous nitrilimine cycloadducts, and also with the values [6] (δ 3.40 and 4.00, J_{gem} = 17 Hz) for analogous nitriloxide cycloadducts.



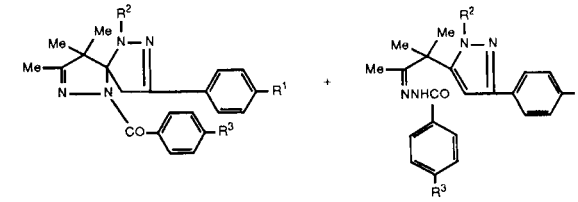
1 2

a, R^1 = H, R^2 = Ph, X = Cl
b, R^1 = Me, R^2 = Ph, X = Cl
c, R^1 = H, R^2 = $C_6H_4NO_2$ (-p), X = Cl
d, R^1 = H, R^2 = Me, X = Br



3

a, R^3 = H
b, R^3 = Me
c, R^3 = Cl



4 5

a, R^1 = R^3 = H, R^2 = Ph
b, R^1 = H, R^2 = Ph, R^3 = Me
c, R^1 = H, R^2 = Ph, R^3 = Cl
d, R^1 = Me, R^2 = Ph, R^3 = H
e, R^1 = H, R^2 = $C_6H_4NO_2$ (-p), R^3 = Me
f, R^1 = Ph, R^2 = Me, R^3 = H
g, R^1 = Ph, R^2 = R^3 = Me
h, R^1 = Ph, R^2 = Me, R^3 = Cl

Table I

Yield and Spectroscopic Data of Compounds **4**

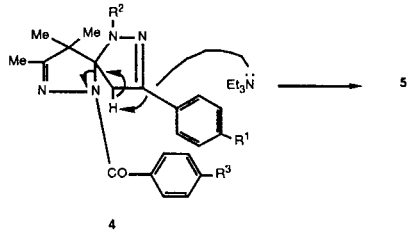
Compound	Yield (%)	^{1}H-NMR (deuteriochloroform), δ (ppm) Me_2C	MeCN	CH_2	other protons	MS, m/e (Relative Intensity %)
4a	40	1.29 (s), 1.36 (s)	2.04 (s)	3.52, 4.14 (AB pattern, J_{AB} 17.5 Hz)	7.00-7.95 (m, 15H)	422 (M^+, 9), 317 (7), 276 (4), 262 (100), 260 (60), 161 (5), 105 (35)
4b	49	1.28 (s), 1.35 (s)	2.02 (s)	3.50, 4.14 (AB pattern, J_{AB} 17.5 Hz)	2.36 (s, 3H), 6.83-7.81 (m, 14H)	436 (M^+, 3), 317 (5), 276 (3), 262 (78), 260 (61), 175 (16), 91 (100)
4c	45	1.29 (s), 1.37 (s)	2.06 (s)	3.51, 4.14 (AB pattern, J_{AB} 17.5 Hz)	6.90-7.92 (m, 14H)	456/458 (M^+, 3), 317 (4), 276 (3), 262 (100), 260 (16), 195/197 (7), 139/141 (99)
4d	44	1.29 (s), 1.36 (s)	2.05 (s)	3.50, 4.16 (AB pattern, J_{AB} 17.0 Hz)	2.48 (s, 3H), 6.90-8.00 (m, 14H)	436 (M^+, 2), 331 (2), 290 (1), 276 (29), 274 (47), 161 (2), 103 (100)
4e	41	1.26 (s), 1.37 (s)	2.16 (s)	3.73, 4.14 (AB pattern, J_{AB} 17.5 Hz)	2.33 (s, 3H), 6.98-8.22 (m, 13H)	481 (M^+, 2), 361 (3), 307 (35), 305 (66), 244 (23), 91 (100)

Table II

Yield and Spectroscopic Data of Compounds **5**

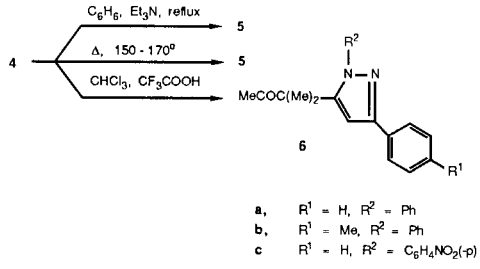
Compound	Yield (%)	^{1}H-NMR (deuteriochloroform), δ (ppm) Me_2C	MeCN	NMe	4-H	other protons	MS, m/e (Relative Intensity %)
5a	32	1.48 (s)	1.75 (s)	– – –	6.68 (s)	7.15-8.10 (m, 15H)	422 (M^+, 2), 317 (3), 262 (78), 260 (17), 161 (45), 105 (100)
5b	19	1.47 (s)	1.73 (s)	– – –	6.69 (s)	2.35 (s, 3H), 7.02-8.00 (m, 14H)	436 (M^+, 1), 317 (2), 262 (100), 175 (55), 119 (75)
5c	25	1.43 (s)	1.78 (s)	– – –	6.67 (s)	6.90-7.98 (m, 14H)	456/458 (M^+, 1), 317 (1), 262 (44), 260 (100), 195/197 (9)
5d	39	1.44 (s)	1.74 (s)	– – –	6.65 (s)	2.36 (s, 3H), 6.90-7.90 (m, 14H)	436 (M^+, 1), 331 (1), 276 (11), 274 (23), 103 (100)
5f	30	1.58 (s)	1.78 (s)	3.74 (s)	6.48 (s)	7.20-7.55 (m, 6H), 7.68-7.15 (m, 4H)	360 (M^+, 11), 255 (4), 200 (74), 198 (47), 161 (37), 105 (100)
5g	48	1.63 (s)	1.78 (s)	3.78 (s)	6.50 (s)	2.40 (s, 3H), 7.05-7.50 (m, 5H), 7.68-7.98 (m, 4H)	374 (M^+, 6), 254 (5), 200 (100), 198 (81), 175 (48), 119 (80)
5h	44	1.58 (s)	1.78 (s)	3.76 (s)	6.52 (s)	7.20-7.53 (m, 5H), 7.63-8.00 (m, 4H)	394/396 (M^+, 14), 254 (5), 199 (100), 161 (19), 139 (54)

The formation of the 5-(2-aroylhydrazono-1,1-dimethylpropyl)-1*H*-pyrazoles **5** can be explained by assuming a nucleophilic attack of the excess of triethylamine and elimination of a hydrogen of the 4-CH_2 group followed by cleavage of the trimethylpyrazole ring. Additional proof for this mechanism was provided by the observation that the spiro-cycloadducts **4** can be cleaved almost quantitatively to the same pyrazoles **5** by refluxing in benzene with triethylamine for 30-40 hours, with exception of the nitro-substituted compound **4e** which remained unchanged after refluxing for 50 hours. The behaviour of this cycloadduct **4e** is in agreement with the non-isolation of the corresponding 2-aroylhydrazonopyrazole **5e** from the reaction between the 5-methylenepyrazole **3b** and the *N*-(*p*-nitrophenyl)nitrilimine **2c**.



4

The spiro-cycloadducts **4** can also be cleaved, again with exception of **4e**, which remains unchanged, almost quantitatively to pyrazoles **5** by heating at 150-170° for 30-60 minutes. Cleavage of **4** can also be effected under acidic conditions, namely by refluxing a chloroform solution containing trifluoroacetic acid for 10 hours. In this case the 5-(1,1-dimethyl-2-oxopropyl)-1*H*-pyrazoles **6** were isolated in good yield (80-85%).



The spiro-cycloadducts **4**, the 5-(2-aroylhydrazono-1,1-dimethylpropyl)-1*H*-pyrazoles **5** and the 5-(1,1-dimethyl-2-oxopropyl)-1*H*-pyrazoles **6** are new compounds and their spectral and experimental data are given in Tables I and II and in the Experimental.

EXPERIMENTAL

All melting points are uncorrected and were obtained with a Kofler hot stage apparatus. Ir spectra were determined on a Perkin-Elmer 297 spectrometer. The ^{1}H nmr spectra were measured on a Varian A-60A instrument with TMS as internal reference. The mass spectra were determined using a Hitachi-Perkin-Elmer RMU-6L spectrometer with ionization energy 70eV and analysis were performed with a Perkin-Elmer Model 240B CHN Analyzer. Literature procedures were followed in the preparation of 1-(α-chlorobenzal)-2-phenylhydrazine (**1a**) [7], 1-(α-chlorobenzal)-2-(*p*-nitrophenyl)hydrazine (**1c**) [8], 1-(α-bromobenzal)-2-methylhydrazine (**1d**) [9] and 1-aroyl-4,5-dihydro-3,4,4-trimethyl-5-methylene-1*H*-pyrazoles (**3**) [6]. 1-(α-Chloro-*p*-tolual)-2-phenylhydrazine (**1b**) was prepared according to the method similar to that of **1a**.

The Reaction of 1-(α-Chlorobenzal)-2-phenylhydrazine (**1a**) with 1-Benzoyl-4,5-dihydro-3,4,4-trimethyl-5-methylene-1*H*-pyrazole (**3a**).

A general procedure is described. To a solution of 1.2 mmoles of 1-(α-chlorobenzal)-2-phenylhydrazine (**1a**) and 1 mmole of 5-methylenepyrazole **3a** in 15 ml dry benzene, 2 mmoles of triethylamine was added and the reaction mixture was stirred and refluxed for 20 hours. Then a second amount (1.2 mmoles) of **1a** and 2 mmoles of triethylamine was added and the mixture was stirred and refluxed for another 20 hours. The benzene solution was washed with water several times, dried (calcium sulfate) and evaporated. The residue was chromatographed on silica gel (petroleum ether-ethyl acetate 15:1) to give the 6-benzoyl-8,9,9-trimethyl-1,3-diphenyl-1,2,6,7-tetrazaspiro[4.4]nona-2,7-diene (**4a**) in 40% yield, mp 170-172° (ethanol); ir (nujol): 1660 (C=O) cm^{-1}.

Anal. Calcd. for $C_{27}H_{26}N_4O$: C, 76.75; H, 6.20; N, 13.26. Found: C, 76.79; H, 6.12; N, 13.29.

5-[2-(Benzoylhydrazono)-1,1-dimethylpropyl]-1,3-diphenyl-1*H*-pyrazole (**5a**).

This compound was also isolated in 32% yield, mp 186-188° (aqueous ethanol); ir (nujol): 3290 (NH), 1660 (C=O) cm^{-1}.

Anal. Calcd. for $C_{27}H_{26}N_4O$: C, 76.75; H, 6.20; N, 13.26. Found: C, 76.89; H, 6.36; N, 13.34.

The Reaction of 1-(α-Chlorobenzal)-2-phenylhydrazine (**1a**) with 4,5-Dihydro-3,4,4-trimethyl-5-methylene-1-(*p*-toluoyl)-1*H*-pyrazole (**3b**).

As described above, 8,9,9-trimethyl-1,3-diphenyl-6-(*p*-toluoyl)-1,2,6,7-tetrazaspiro[4.4]nona-2,7-diene (**4b**) was isolated in 49% yield, mp 158-160° (ethanol); ir (nujol): 1650 (C=O) cm^{-1}.

Anal. Calcd. for $C_{28}H_{28}N_4O$: C, 77.03; H, 6.47; N, 12.84. Found: C, 76.92; H, 6.26; N, 12.59.

5-[1,1-Dimethyl-2-(*p*-toluoylhydrazono)-propyl]-1,3-diphenyl-1*H*-pyrazole (**5b**).

This compound was also obtained in 19% yield, mp 149-150° (aqueous ethanol); ir (nujol): 3180 (NH), 1660 (C=O) cm^{-1}.

Anal. Calcd. for $C_{28}H_{28}N_4O$: C, 77.03; H, 6.47; N, 12.84. Found: C, 77.24; N, 6.31; H, 12.99.

The Reaction of 1-(α-Chlorobenzal)-2-phenylhydrazine (**1a**) with 1-(*p*-Chlorobenzoyl-4,5-dihydro-3,4,4-trimethyl-5-methylene-1*H*-pyrazole (**3c**).

6-(*p*-Chlorobenzoyl)-8,9,9-trimethyl-1,3-diphenyl-1,2,6,7-tetrazaspiro-[4.4]nona-2,7-diene (**4c**).

This compound was isolated as described above in 45% yield, mp 176-178° (ethanol); ir (nujol): 1650 (C=O) cm^{-1}.

Anal. Calcd. for $C_{27}H_{25}ClN_4O$: C, 70.96; H, 5.51; N, 12.26. Found: C, 70.75; H, 5.68; N, 12.44.

5-[2-(*p*-Chlorobenzoylhydrazono)-1,1-dimethylpropyl]-1,3-diphenyl-1*H*-pyrazole (**5c**).

This compound was also isolated in 25% yield, mp 165-167° (aqueous ethanol); ir (nujol): 3310 (NH), 1660 (C=O) cm^{-1}.

Anal. Calcd. for $C_{27}H_{25}ClN_4O$: C, 70.96; H, 5.51; N, 12.26. Found: C, 70.88; H, 5.68; N, 12.37.

The Reaction of 1-(α-Chloro-*p*-tolual)-2-phenylhydrazine (**1b**) with 1-Benzoyl-4,5-dihydro-3,4,4-trimethyl-5-methylene-1*H*-pyrazole (**3a**).

6-Benzoyl-8,9,9-trimethyl-1-phenyl-3-(*p*-tolyl)-1,2,6,7-tetrazaspiro[4.4]-nona-2,7-diene (**4d**).

This compound was isolated as described above in 44% yield, mp 180-181° (ethanol); ir (nujol): 1660 (C=O) cm^{-1}.

Anal. Calcd. for $C_{28}H_{28}N_4O$: C, 77.03; H, 6.47; N, 12.84. Found: C, 77.31; H, 6.61; N, 13.01.

5-[2-(Benzoylhydrazono)-1,1-dimethylpropyl]-1-phenyl-3-(*p*-tolyl)-1*H*-pyrazole (**5d**).

This compound was also isolated in 39% yield, mp 174-175° (aqueous ethanol); ir (nujol): 3200 (NH), 1660 (C=O) cm^{-1}.

Anal. Calcd. for $C_{28}H_{28}N_4O$: C, 77.03; H, 6.47; N, 12.84. Found: C, 77.23; H, 6.55; N, 12.70.

The Reaction of 1-(α-Chlorobenzal)-2-(*p*-nitrophenyl)hydrazine (**1c**) with 4,5-Dihydro-3,4,4-trimethyl-5-methylene-1-(*p*-toluoyl)-1*H*-pyrazole (**3b**).

1-(*p*-Nitrophenyl)-8,9,9-trimethyl-3-phenyl-6-(*p*-toluoyl)-1,2,6,7-tetraza-spiro[4.4]nona-2,7-diene (**4e**).

This compound was isolated as described in 41% yield, mp 222-224° (ethanol); ir (nujol): 1655 (C=O) cm^{-1}.

Anal. Calcd. for $C_{28}H_{27}N_5O_3$: C, 69.83; H, 5.65; N, 14.55. Found: C, 69.58; H, 5.80; N, 14.36.

The Reaction of 1-(α-Bromobenzal)-2-methylhydrazine (**1d**) with 1-Benzoyl-4,5-dihydro-3,4,4-trimethyl-5-methylene-1*H*-pyrazole (**3a**).

To a solution of 2 mmoles of 1-(α-bromobenzal)-2-methylhydrazine (**1d**) and 1.5 mmoles of 5-methylenepyrazole **3a** in 15 ml of dry benzene, 12 mmoles of triethylamine was added slowly. The reaction mixture was stirred and refluxed for 20 hours. Then a second amount of 2 mmoles of **1d** and 12 mmoles of triethylamine was added and the mixture was stirred and refluxed for another 20 hours. The benzene solution was washed with water several times, dried (calcium sulfate) and evaporated. The residue was chromatographed on silica gel (petroleum ether-ethyl acetate 7:1) to give the 5-[2-(benzoylhydrazono)-1,1-dimethylpropyl]-1-methyl-3-phenyl-1*H*-pyrazole (**5f**) in 30% yield, mp 190-192° (aqueous ethanol); ir (nujol): 3300 (NH), 1670 (C=O) cm^{-1}.

Anal. Calcd. for $C_{22}H_{24}N_4O$: C, 73.31; H, 6.71; N, 15.54. Found: C, 73.44; H, 6.85; N, 15.68.

The Reaction of 1-(α-Bromobenzal)-2-methylhydrazine (**1d**) with 4,5-Dihydro-3,4,4-trimethyl-5-methylene-1-(*p*-toluoyl)-1*H*-pyrazole (**3b**).

5-[1,1-Dimethyl-2-(*p*-toluoylhydrazono)-propyl]-1-methyl-3-phenyl-1*H*-pyrazole (**5g**).

This compound was isolated in 48% yield as described above, mp 174-176° (aqueous ethanol); ir (nujol): 3280 (NH), 1655 (C=O) cm^{-1}.

Anal. Calcd. for $C_{23}H_{26}N_4O$: C, 73.77; H, 7.00; N, 14.96. Found: C, 73.55; H, 6.92; N, 14.75.

The Reaction of 1-(α-Bromobenzal)-2-methylhydrazine (**1d**) with 1-(*p*-Chlorobenzoyl)-4,5-dihydro-3,4,4-trimethyl-5-methylene-1H-pyrazole (**3c**).

5-[2-(*p*-Chlorobenzoylhydrazono)-1,1-dimethylpropyl]-1-methyl-3-phenyl-1*H*-pyrazole (**5h**).

This compound was isolated in 44% yield as described above, mp 185-187° (aqueous ethanol); ir (nujol): 3310 (NH), 1650 (C=O) cm^{-1}.

Anal. Calcd. for $C_{22}H_{23}ClN_4O$: C, 66.91; H, 5.87; N, 14.19. Found: C, 67.00; H, 5.84; N, 13.94.

Thermolysis of **4a**.

A sample of 84 mg, 0.2 mmole of **4a** was heated in an oil bath at 150° for 40 minutes. Crystallization (aqueous ethanol) gave 69 mg (82%) of **5a**.

Base Treatment of **4a**.

To a solution of 84 mg, 0.2 mmole of **4a** in 2 ml dry benzene 0.33 mmole of triethylamine was added and the mixture was refluxed for 35 hours, to give **5a** in almost quantitative yield.

Acid Treatment of **4a**.

To 211 mg, 0.5 mmole of the spiro-cycloadduct **4a**, dissolved in 5 ml of chloroform, 1 ml of trifluoroacetic acid was added and the mixture was refluxed for 10 hours. The chloroform layer was separated, washed with water and dried (sodium sulfate). The chloroform was evaporated and the remainder was crystallized by addition of ether containing a few drops petroleum ether to give the 5-(1,1-dimethyl-2-oxopropyl)-1,3-diphenyl-1*H*-pyrazole (**6a**), 114 mg (75%), mp 97-99° (aqueous ethanol); ir (nujol): 1710 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.35 (s, 6H), 2.03 (s, 3H), 6.72 (s, 1H), 7.10-7.55 (m, 8H), 7.70-8.05 (m, 2H); ms: (70 eV, electron impact) m/e (relative intensity) 304 (M^+, 35), 261 (100).

Anal. Calcd. for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 79.08; H, 6.69; N, 9.38.

Thermolysis of **4b**.

As described above, after heating **4b** at 150° for 40 minutes, **5b** was obtained in 85% yield.

Base Treatment of **4b**.

As described above, after refluxing **4b** for 40 hours, **5b** was obtained in quantitative yield.

Acid Treatment of **4b**.

As described above **6a** was obtained in 75% yield.

Thermolysis of **4c**.

As described above, after heating **4c** at 170° for 1 hour, **5c** was obtained in 89% yield.

Base Treatment of **4c**.

As described above, after refluxing **4c** for 30 hours, **5c** was obtained in quantitative yield.

Acid Treatment of **4c**.

As described above, **6a** was obtained in 72% yield.

Thermolysis of **4d**.

As described above, after heating **4d** at 170° for 40 minutes, **5d** was obtained in 79% yield.

Base Treatment of **4d**.

As described above, after refluxing **4d** for 30 hours, **5d** was obtained in quantitative yield.

Acid Treatment of **4d**.

5-(1,1-Dimethyl-2-oxopropyl)-1-phenyl-3-(*p*-tolyl)-1*H*-pyrazole (**6b**).

This compound was isolated in 71% yield, mp 93-95° (aqueous ethanol); ir (nujol): 1705 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.37 (s, 6H), 2.09 (s, 3H), 2.40 (s, 3H), 6.70 (s, 1H), 7.10-7.70 (m, 5H), 7.25 and 7.78 (d, AA'BB' pattern, 4H, J = 8.5 Hz); ms: (70 eV, electron impact) m/e (relative intensity) 318 (M^+, 25), 275 (100).

Anal. Calcd. for $C_{21}H_{22}N_2O$: C, 79.21; H, 6.96; N, 8.80. Found: C, 79.03; H, 6.80; N, 9.01.

Thermolysis of **4e**.

The starting material **4e** remained unchanged after heating at 170° for 2 hours.

Base Treatment of **4e**.

The starting material **4e** remained unchanged after 50 hours reflux.

Acid Treatment of **4e**.

5-(1,1-Dimethyl-2-oxopropyl)-1-(*p*-nitrophenyl)-3-phenyl-1*H*-pyrazole (**6c**).

As described above this compound was isolated in 70% yield, mp 109-111° (aqueous ethanol); ir (nujol): 1710 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.43 (s, 6H), 2.12 (s, 3H), 6.76 (s, 1H), 7.15-8.42 (m, 9H); ms: (70 eV, electron impact) m/e (relative intensity) 349 (M^+, 39), 303 (100).

Anal. Calcd. for $C_{20}H_{19}N_3O_3$: C, 68.75; H, 5.48; N, 12.03. Found: C, 68.59; H, 5.61; N, 11.89.

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