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THE RING CLOSURE AND REARRANGEMENT OF N-2-AMINOBENZOYL -N-METHYLHYDRAZONES OF β-DICARBONYL COMPOUNDS

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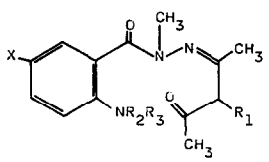
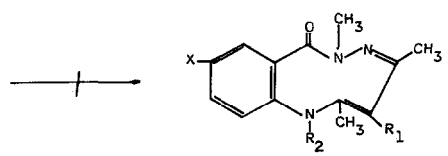
Abstract—A novel rearrangement was observed during the cyclization of N-(2-aminobenzoyl)-N-methylhydrazones of β-dicarbonyl compounds, leading to pyrazole derivatives **2**, **4**, and **5** depending on substituents and the reaction media.

A series of condensed seven-membered ring systems have been synthesized starting with aromatic ortho-diamines and β-dicarbonyl compounds.[1] We have attempted to enlarge the heterocyclic ring from seven to nine atoms because only one representative[2] of the possible benzotriazonine rings had been studied so far.

When N-(2-aminobenzoyl)-N-methylhydrazine was used as diamine in the reaction with 2,4-pentanedione, **1a** was obtained. Structure **1** represents one of the possible tautomers, since **1** type compounds are found to exist as mixtures of keto and enol forms and in certain cases a ring-chain tautomerism was also observed.[3] The N-methyl substituent of **1a** was introduced in order to hinder the reactions at the N-1 nitrogen of the hydrazide moiety[4] and to prevent the known formation of the pyrazole rings.[5]

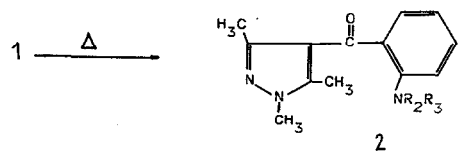


1



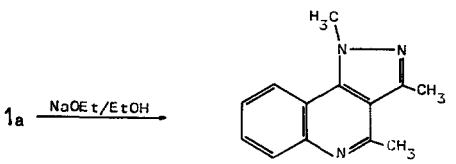
	R_1	R_2	R_3	X
1a	H	H	H	H
1b	CH_3	H	H	H
1c	CH_3	H	H	Cl
1d	H	CH_3	H	H
1e	H	CH_3	CH_3	H
1f	CH_3	CH_3	H	H
1g	CH_3		H	H

On heating **1a** did not afford the expected 1,5,6-benzotriazonin-7-one ring system, but the rearranged pyrazole **2a**. The structure of **2a** was deduced from MS data and was proved by an independent synthesis starting with 3-(2-nitrobenzoyl)-2,4-pentanedione.



2

	R_2	R_3
1a → 2a	H	H
1d → 2d	CH_3	H
1e → 2e	CH_3	CH_3

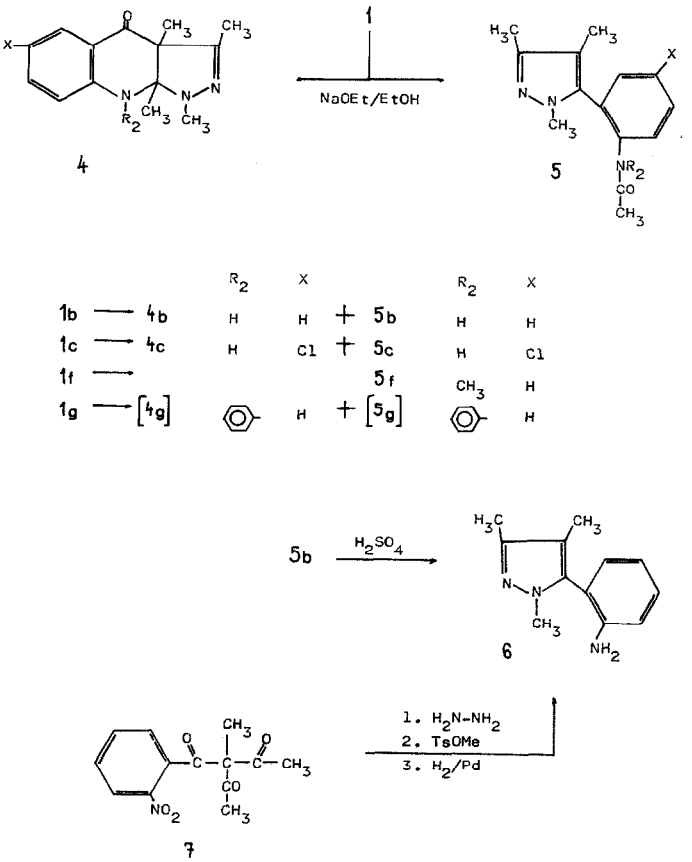


3

On the other hand, boiling of **1a** in ethanolic NaOEt resulted in the desired condensation of the 2-amino and the carbonyl groups, but at the same time a further reaction took place yielding the tricyclic compound **3**, via formation of a C–C bond. The latter transformation is in agreement with the cyclization of N-aroyl-N-phenyl-hydrazones of β-ketoaldehydes into 4-acylpyrazoles reported by von Auwers[6] and re-investigated recently.[7]

To avoid the reactions **1a**→**2a** and **1a**→**3a** a 3-methyl substituent was introduced on 2,4-pentanedione **1b**. Boiling **1b** in ethanolic NaOEt or in dry benzene, however, yielded a mixture of two isomeric products **4b** and **5b**. The structures of **4b** and **5b** deduced from MS data were confirmed by X-ray analysis[8] and by independent synthesis. The hydrolysis product of **5b** (compound **6**) was obtained from **7** in three steps.

The mechanism of the reaction **1a**→**2a** assuming an intermediate of type **8** which rearranges into **10** via 1,3-acyl migration, is similar to the mechanism postulated for the thermal rearrangement of 2,4-diphenyl-2,3-benzodiazocin-1(2H)-one.[9] This reaction path affords **2a**



by ring-opening ($R_1 = H$) or the reaction terminates at **10(4b**, $R_1 = Me$). The formation of **5b** however cannot be explained by this reaction path. More reasonable therefore is the hypothesis, that in alkaline solution the common intermediate **9** may undergo two types of dehydration for **1b** ($R_1 = Me$). The formation of **5b** can be attributed to dehydration C-9b followed by ring opening. The other reaction path, dehydration at C-4 accompanied by rearrangement may lead to **10** = **4b**. The latter seems to be less favorable as the molar ratio of **4b** and **5b** was 1:2 as was determined in the reaction mixture by UV. An electronwithdrawing substituent in position 8 of **9** (**1c**) increased the amount of product **4c** (molar ratio 2:1), which may be due to the promotion of deprotonation at 9b-OH of **9** hindering the reaction leading to **5c**.

The substitution of the 2-amino group (**1d**, **1e**) resulted in no changes in the structure of the products of type **2**; even the 2-unsubstituted benzoyl analogue of **1a** underwent a rearrangement similar to **1a**→**2**, reported recently.[10] Both the yields and the temperatures necessary to complete the reactions showed that the amino group may facilitate the rearrangement.

After the alkaline treatment of **1g** only **11** and **12** were isolated instead of **4g** and **5g**, probably due to further reaction with alkali.

EXPERIMENTAL

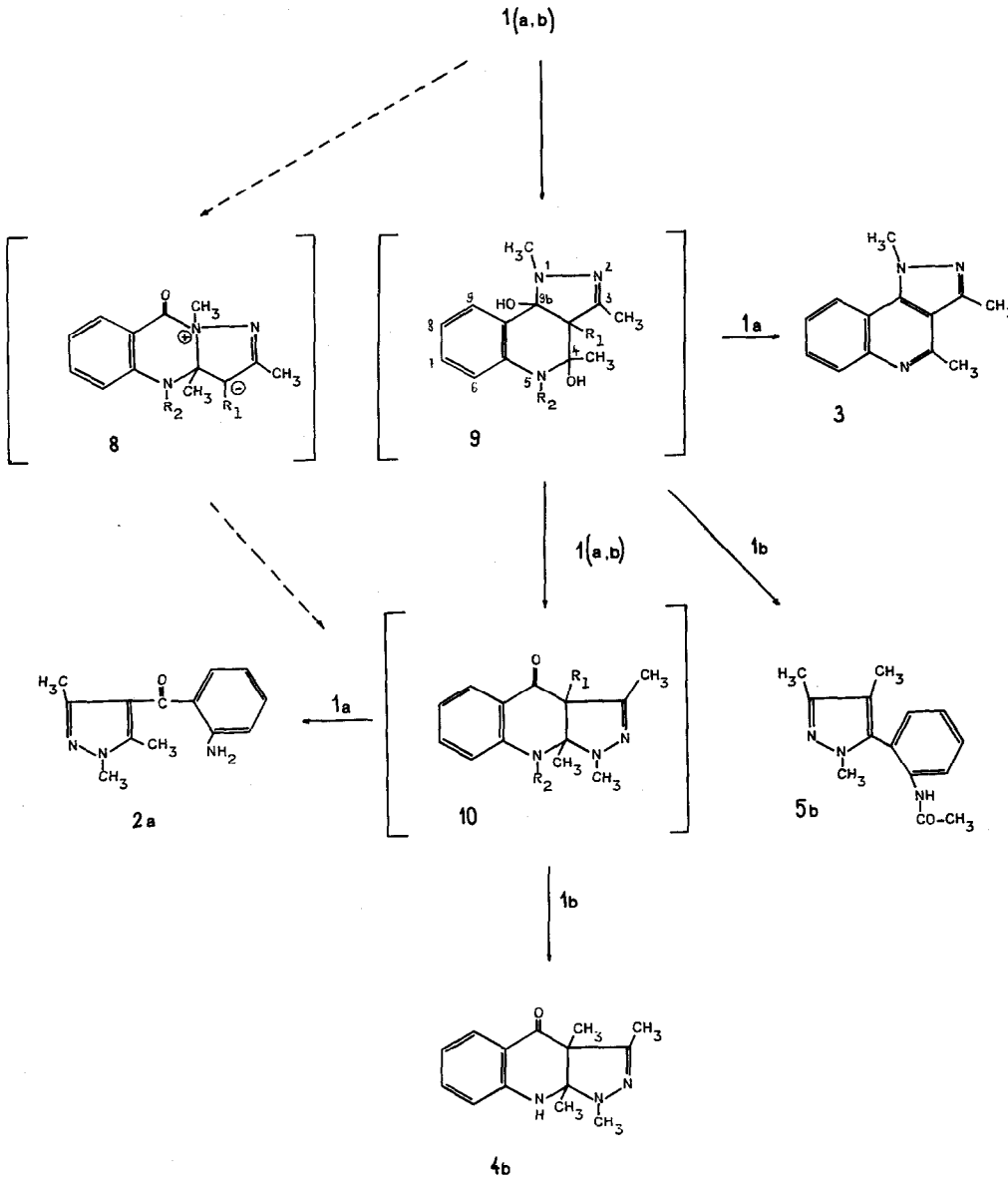
All m.ps are uncorrected. IR spectra were measured using a Perkin Elmer 577 spectrometer. ^1H NMR spectra were obtained at 60 MHz on a Jeol 60 HL spectrometer, using TMS as internal standard. ^{13}C NMR spectra were measured on a Varian XL-100 spectrometer (25.16 MHz). Mass spectra were obtained on a Varian MAT SM-1 instrument at 70 eV and R 1250. High resolution measurements were made at R 10000 using PFK as reference standard.

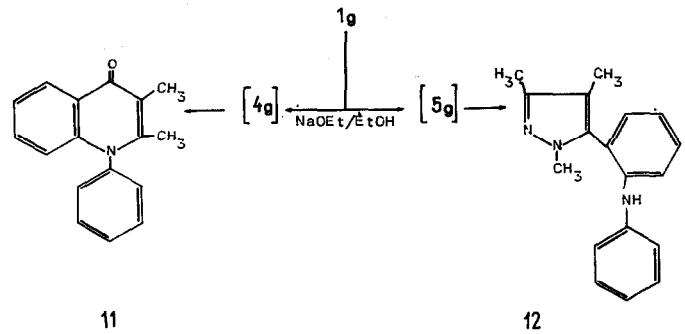
4-[N'-(2-Aminobenzoyl)-N'-methylhydrazino]-4-penten-2-one **1a**

A mixture of 4.95 g (0.03 mole) N-(2-aminobenzoyl)-N-methylhydrazine and 2,4-pentanedione (25 ml) was stirred for 5 h. After evaporation the residue was recrystallised from ethanol to give 5.5 g (74%) of **1a**, m.p. 136–138°. Found: C, 62.85; H, 6.93; N, 16.87. Calc. for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.92; N, 16.92%. IR (KBr) 3430, 3420 (ν_{NH_2}), 1635 ($\nu_{C=O}$), 1550 ($\nu_{C=N}$), 760 ($\nu_{C_{ArH}}$) cm^{-1}. ^1H NMR shows the mixture[5] to be an open chain enol and a ring closed keto form in ratio of 2:3 in $CDCl_3$: enol form: δ 10.6, b, 1H, OH; 6.5–7.4, m, 4H, ArH; 4.85, s, 1H, C=CH–C; 4.6, b, 2H, NH_2; 3.32, s, 3H, N–CH_3; 1.95, s, 3H, C–CH_3; 1.73, s, 3H, N=C–CH_3, keto form: δ 7.8, dd, 1H, ArH; 6.5–7.4, m, 3H, ArH; 2.80, s, 2H, C–CH_2; 2.18, s, 3H, CO–CH_3; 1.34, s, 3H, C–CH_3.

4-[N'-(2-Aminobenzoyl)-N'-methylhydrazino]-3-methyl-4-penten-2-one **1b**

1b was prepared according to the method described above for **1a**. Yield 75.9% m.p. 142–148° (benzene). Found: C, 64.27; H, 7.39; N, 16.19. Calc. for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33; N, 16.03%. IR (KBr): 3360, 3230 (ν_{NH}), 1705 ($\nu_{C=O}$), 1635 ($\nu_{C=O}$), 1595 ($\nu_{C=N}$), 765 (ν_{CArH}) cm^{-1}. ^1H NMR shows the mixture to be an open chain keto compound and a ring closed keto compound in a ratio of 1:5 in $CDCl_3$: open chain keto form: δ 6.5–7.5, m, 4H, ArH; 4.4, b, 2H, NH_2; 3.3, s, 3H, N–CH_3; 3.2, q, 1H, CH; 2.12, s, 3H, CO–CH_3; 1.84, s, 3H, =CCH_3; 1.20, d, 3H, CH–CH_3; ring closed keto form: δ 7.8, dd, 1H, ArH; 6.5–7.5, m, 3H, ArH; 5.1 and 4.3, b, 2×1H, NH; 3.3, s, 3H, N–CH_3; 3.3, q, 1H, CH; 2.28, s, 3H, CO–CH_3; 1.35, d, 3H, CH–CH_3; 1.30, s, 3H, CH_3.


1(a,b)
8
9
3
1a
1(a,b)
1b
2a
1a
10
5b
1b
4b


1g
[4g]
NaOEt/EtOH
[5g]
11
12

4-[N'-2-Amino-5-chlorobenzoyl)-N'-methylhydrazino]-3-methyl-4-penten-2-one **1c**

1c was prepared according to the method described above for **1a**. Yield 66%, m.p. 138–145° (ethanol). Found: C, 56.79; H, 6.20; N, 14.10; Cl, 12.08. Calc. for $C_{14}H_{18}N_3O_2Cl$: C, 56.85; H, 6.13; N, 14.21; Cl, 11.98% IR (KBr): 3380 (ν_{asNH_2}), 3260 (ν_{sNH_2}), 1715 ($\nu_{COketone}$), 1650 ($\nu_{CO(N)}$) cm^{-1}. ^1H NMR shows the mixture to be an open chain and a ring closed keto form in a ratio of 1:3 in $CDCl_3$: open chain keto form: δ 6.5–7.7, m, 3H, ArH; 4.6, b, 2H, NH_2; 3.25, s, 3H, N–CH_3; 3.2, m, 1H, CH; 2.10 and 1.80, 2xs, 2×3H, 2×=C–CH_3; ring closed keto form: δ 6.5–7.7, m, 3H, ArH; 4.2 and 5.0, 2×b, 2×1H, 2×NH; 3.25, s, 3H, N–CH_3; 3.2, m. 1H, CH; 2.27, s, 3H, $COCH_3$; 1.37, d, 3H, CH–CH_3; 1.30, s, 3H, C–CH_3.

4-[N'-(2-Methylaminobenzoyl)-N'-methylhydrazino]-4-penten-2-one **1d**

1d was prepared according to the method described above for **1a**. Yield 54%, m.p. 120–123° (ethanol). Found: C, 64.49; H, 7.55; N, 15.96. Calc. for $C_{14}H_{19}N_3O_2$: C, 64.34; H, 7.32; N, 16.08%. IR (KBr): 3380 (ν_{OH}), 3180 (ν_{NH}), 1630 (ν_{CO}) cm^{-1}. ^1H NMR ($CDCl_3$): 11.8, s, 1H, OH; 7.0–7.3, m, 2H, Ar (4) (6) H; 6.4–6.7, m, 2H, Ar (3) (5) H, 5.4, b, 1H, NH; 4.95, s, 1H, =CH; 3.21, s, 3H, N–NH_3; 2.80, s, 3H, NH–CH_3; 2.0 and 1.78 2×s, 2×3H, 2×CH_3.

4-[N'-(2-Dimethylaminobenzoyl)-N'-methylhydrazino]-4-penten-2-one **1e**

1e was prepared according to the method described above for **1a**. Yield 30%, m.p. 75–78°. Found: C, 65.40; H, 7.78; N, 15.43. Calc. for $C_{15}H_{21}N_3O_2$: C, 65.43; H, 7.68; N, 15.26%. IR (KBr): 1650 ($\nu_{CO(N)}$), 1600, 1490 (ν_{C-CArH}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.6, s, 1H, OH; 6.7–7.4, m, 4H, ArH; 4.72, s, 1H, =CH; 3.28, s, 3H, N–CH_3; 2.8, s, 6H, NMe_2; 1.86 and 1.70, 2×s, 2×3H, 2×CH_3.

4-[N'-(2-Methylaminobenzoyl)-N'-methylhydrazino]-3-methyl-4-penten-2-one **1f**

1f was prepared according to the method described above for **1a**. Yield 57%, oil. Found: C, 65.30; H, 7.58; N, 15.14, Calc. for $C_{15}H_{21}N_3O_2$: C, 65.43; H, 7.68; N, 15.26%. IR (liquid film): 3400 (ν_{NH}), 1720 (ν_{CO}), 1630 ($\nu_{CO(N)}$) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.6–7.5, m, 4H, ArH; 5.7, b, 1H, NH; 3.55, q, 1H, CH; 3.32, s, 3H, N–CH_3; 2.83, s, 3H, $NHCH_3$; 2.16 and 1.84, 2×s, 2×3H, 2×CH_3; 1.25, d, 3H, CH–CH_3.

4-[N'-(2-Phenylaminobenzoyl)-N'-methylhydrazino]-3-methyl-4-penten-2-one **1g**

1g was prepared according to the method described above for **1a**. Yield 68%, m.p. 124–130° (ethanol). Found: C, 70.74; H, 6.91; N, 12.45. Calc. for $C_{20}H_{23}N_3O_2$: C, 71.19; H, 6.87; N, 12.45%. IR (KBr): 3380 (ν_{NH}), 1640 ($\nu_{CO(N)}$) cm^{-1}. ^1H NMR shows the mixture to be an open chain enol and keto form in a ratio of 2:1 in $CDCl_3$: enol form: δ 12.5, s, 1H, OH; 6.6–7.5, m, 9H, ArH; 3.3, s, 3H, N–CH_3; 2.1, s, 3H, CH_3; 1.8, s, 6H, 2×CH_3; keto form: δ 6.66–7.5, m, 9H, ArH; 3.50, q, 1H, CH; 3.3, s, 3H, N–CH_3; 2.1, s, 3H, CH_3; 1.8, s, 3H, CH_3, 1.25, d, 3H, CH–CH_3.

4-(2-Aminobenzoyl)-1,3,5-trimethyl-1H-pyrazole **2a**

Under nitrogen 6 g (0.024 mole) of **1a** was heated for 1 h on an oil bath at 160°. The product was dissolved in ether, filtered, and after evaporation of the solvent recrystallised from water to give 4.2g (76%) of **2a** m.p. 120–122°. Found: C, 68.20; H, 6.80; N, 18.40. Calc. for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33%. MS: *m/z* (%) 229 (100) M^+, 137 (23) $C_7H_9N_2O$, 120 (35) C_7H_6NO, 56 (3.3) C_3H_6N. IR (KBr): 3480, 3460, 3410, 3380, 3360, 3300 (ν_{NH}); 1610 cm^{-1} ($\nu_{C=O}$). ^1H NMR ($CDCl_3$): δ 6.33–7.5, m, 4H, ArH; 6.9, s, 2H, NH_2; 3.75, s, 3H, N–CH_3; 2.25 and 2.20, 2×s, 2×3H, =C–CH_3.

Synthesis of **2a** *from 3-(2-nitrobenzoyl)-2,4-pentanedione*

2 g (0.08 mole) 3-(2-nitrobenzoyl)-2,4-pentanedione (dissolved in 12 ml AcOH) was added to an ethanolic solution (16 ml) of 0.63 ml (0.09 mole) 72% hydrazine hydrate. After the completion of the reaction it was poured into water (40 ml) and extracted with chloroform (3×30 ml). The organic layer was washed with aq $NaHCO_3$ dried ($MgSO_4$) and evaporated. Yield: 1.48 g (76%) of 3,5-dimethyl-4-(2-nitrobenzoyl)-1H-pyrazole m.p. 107–108° (ether). Found: C, 58.39; H, 4.46; N, 17.18. Calc. for $C_{12}H_{11}N_3O_3$: C, 58.77; H, 4.49; N, 17.13%. IR (KBr): 2800–3200 (ν_{NH}), 1640 ($\nu_{C=O}$), 1520 (ν_{asNO_2}), 1340 (ν_{sNO_2}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 10.0, b, 1H, NH; 7.3–8.2, m, 4H, ArH; 2.16, s, 2×3H, 2×CH_3.

3.29 g (0.016 mole) 3,5-dimethyl-4-(2-nitrobenzoyl)-1H-pyrazole was methylated in dry xylene (80 ml) by refluxing it with 3.26 g (0.016 mole) TsOMe and 0.9 g (0.016 mole) NaOMe. The TsONa was filtered off and after evaporation of the solvent 1,3,5-trimethyl-4-(2-nitrobenzoyl)-1H-pyrazole was crystallised. Yield: 3.7 g (89%), m.p. 137–139° (EtOH). Found: C, 60.14, H, 5.14; N, 16.23. Calc for $C_{13}H_{13}N_3O_3$: C, 60.23; H, 5.05; N, 16.21%. IR (KBr): 1630 ($\nu_{C=O}$), 1520 (ν_{asNO_2}), 1350 (ν_{sNO_2}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.3–8.2, m, 4H, ArH; 3.72, s, 3H, N–CH_3; 2.3 and 1.94, 2×s, 2×3H, 2×CH_3.

1.8 g (0.007 mole) 1,3,5-trimethyl-4-(2-nitrobenzoyl)-1H-pyrazole was hydrogenated in methanol (85 ml) over Pd/C (0.36 g). After removal of the catalyst and evaporation of the solvent 1.5 g (94%) of **2a** m.p. 122–123° was isolated.

4-(2-Methylaminobenzoyl)-1,3,5-trimethyl-1H-pyrazole **2d**

Under nitrogen 1.3 g (0.005 mole) of **1d** was heated for 3.5 h on oil bath temperature adjusted to 160°. The residue was triturated with ether (3×5 ml) and the combined etheric solutions were evaporated to give a yellow oil from which **2b** (0.3 g, 25%) with a m.p. 68–71° was separated by chromatography over silica, eluting with benzene-ethyl acetate 1:9. MS; *m/z*(%): 243(100)$M^+\cdot$, 228 (21), 226(12.5), 137(12), 134(18), 133(19), 111(11.5), 105(33), 104(13). IR (KBr): 3360 (ν_{NH}), 1620 (ν_{CO}), 760 (ν_{CArH}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.3, b, 1H, NH; 7.16–7.5 m, 2H, Ar–3, –6H; 6.33–6.83, m, 2H, Ar-4, -5H; 3.75, s, 3H, N–CH_3; 2.95, d, (J = 4Hz) 3H, NH–CH_3; 2.15 and 2.2, 2×s, 2×3H, 2×CH_3.

4-(2-Dimethylaminobenzoyl)-1,3,5-trimethyl-1H-pyrazole **2e**

1.5 g (0.0054 mole) **1e** was refluxed in tetralin for 8 h. The solvent was evaporated and the residue purified by chromatography over silica eluting with a mixture of chloroform-hexane-acetic acid (8:1:1). Yield: 0.23 g of **2e** (16.5%), m.p. 49–50°. Found: C, 69.88; H, 7.67; N, 16.09. Calc. for $C_{15}N_{19}N_3O$: C, 70.01; H, 7.44; N, 16.33%. IR (KBr): 1630 (ν_{CO}), 1590 and 1490 (ν_{CArH}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.7–7.4, m, 4H, ArH; 3.7, s, 3H, N–CH_3; 2.74, s, 6H, NMe_2; 2.23 and 2.06, 2×s, 2×3H, 2×CH_3.

1,3,4-Trimethyl-1H-pyrazolo[4,3-c]quinoline **3**

15 g (0.06 mole) of **1a** and 6.12 g (0.09 mole) of NaOEt were refluxed in 300 ml ethanol for 5 h. After cooling water (300 ml) was added, the solution was neutralised, and the ethanol was evaporated. The product was filtered off and recrystallised from water to give 10.1 g (79.7%) **3** m. p. 150–151°. Found: C, 73.40; H, 6.30; N, 19.92. Calc. for $C_{13}H_{13}N_3$: C, 73.91; H, 6.20; N, 19.89%. IR (KBr): 755 cm^{-1} (ν_{CArH}). ^1H NMR ($CDCl_3$): δ 7.16–8.16, m, 4H, ArH; 4.20, s, 3H, N–CH_3; 2.60 and 2.80, 2×s, 2×3H, =$\overset{|}{C}$–CH_3.

Alkaline cyclization of **1b**

20.9 g (0.08 mole) of **1b** and 8.16 g (0.12 mole) of NaOEt were refluxed in ethanol (400 ml) for 1 h. After cooling the mixture was diluted with water (400 ml) and extracted with chloroform (3×200 ml). The chloroformic solution was washed with water (3×150 ml), dried ($MgSO_4$) and evaporated to give a mixture of **4b** and **5b**, 15.6 g (80%) which was dissolved in hot ethanol. On cooling **5b** (7.9 g, 40.6%) precipitated and was filtered off; m.p. 207–208° (ethanol). The filtrate diluted with water of double volume gave **4b** (4.7 g, 24.2%) m.p. 167–170° (benzene).

3a,9a-dihydro-1,3,3a,9a-tetramethyl-4H-pyrazolo[3,4-b]quinolin-4-one **4b**. Found: C, 69.50; H, 7.18; N, 17.33. Calc. for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27%. MS: *m/z*(%): 243(29)$M^+\cdot$, 228(36), 174(14) $C_{11}H_{12}NO$, 125(100) $C_7H_{13}N_2$, 124(60), 123(43), 119(70), 109(10). UV λ_{max}: 237 nm, $E^{1\%}_{1cm}$ = 1120

λ_{max}: 376 nm, $E^{1\%}_{1cm}$ = 148.2 (ethanol). IR (KBr): 3270 (ν_{NH}), 1660 (ν_{CO}), 760 (ν_{CArH}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.5–7.83, m, 1H, Ar(5)H; 7.0–7.33, m, 1H, Ar(8)H; 6.33–6.83, m, 2H, Ar(6) (7)H; 5.5, s, 1H, NH; 2.7, s, 3H, N–CH_3; 2.05, s, 3H, =C–CH_3; 1.25, s, 2×3H, 2×CH_3.

5-(2-*acetylaminophenyl*)-1,3,4-*trimethyl*-1*H*-*pyrazole* **5b**. Found: C, 69.14; H, 7.10; N, 17.64. Calc. for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27%. MS: *m/z*(%): 243(100)M^+·, 242(4.8), 228(9), 201(13), 200(28), 186(4.3), 159(7), 130(1.8), UV λ_{max}: 203 nm, $E^{1\%}_{1cm}$ = 883; λ_{max}: 227 nm, $E^{1\%}_{1cm}$ = 633 (ethanol). IR (KBr): 3300–2700 (ν_{NH}), 1680 (ν_{NCO}), 775 (ν_{CArH}) cm^{-1}, ^1H NMR (DMSO-d_6): δ 9.1, s, 1H, NH; 3.5, s, 3H, N–CH_3; 2.15, s, 3H, CO–CH_3; 1.95 and 1.75, 2×s, 2×3H, 2×CH_3.

5-(2-*Aminophenyl*)-1,3,4-*trimethyl*-1*H*-*pyrazole* **6**

0.9 g (0.0037 mole) of **5b** was refluxed for 16 h in a mixture of EtOH (18 ml) and 5N H_2SO_4 (1.8 ml). The solution was poured into water (18 ml) ethanol was evaporated, the pH of the aqueous solution was adjusted to 9 with aq NaOH. The reaction mixture was filtered off and the alkaline filtrate was extracted with ether (3×10 ml). The organic layer was washed with water (10 ml), dried ($MgSO_4$) and the ether was evaporated to give 0.46 g (62%) of **6**, m.p. 93–95°. Found: C, 71.79; H, 7.74; N, 20.50. Calc for $C_{12}H_{15}N_3$: C, 71.61; H, 7.51; N, 20.87%. IR (KBr): 3400, 3320, 3210 (ν_{NH}), 750 (ν_{CArH}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.83–7.66, m, 4H, ArH; 3.7, s, 3H, N–CH_3; 2.3 and 1.9 2×s, 2×3H, 2×CH_3.

5-(2-*Aminophenyl*)-1,3,4-*trimethyl*-1*H*-*pyrazole* **6** *from* 3-(2-*nitrobenzoyl*)-3-*methyl*-2,4-*pentanedione* **7**

To a mixture of 1.7 g (0.07 mole) of magnesium and 16 g (0.14 mole) of 3-methyl-2,4-pentanedione in benzene and THF (1:1 mixture, 50 ml) 26 g (0.14 mole) 2-nitro-benzoyl chloride in dry benzene (30 ml) was added at 5° during 45 min. The mixture was allowed to warm to room temperature and was stirred for 1.5 h. The clear solution was poured into ice-water (12.0 g) containing 5N H_2SO_4 (13 ml) and after separation the aqueous layer was extracted with benzene (2×20 ml). The combined organic solutions were washed with 1% aq $NaHCO_3$ and water (2×20 ml), dried ($MgSO_4$) and evaporated. The residue was crystallised from ether to give 9.1 g (25%) of **7** m.p. 95–97°. Found: C, 59.18; H, 4.87; N, 5.41. Calc. for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.97; N, 5.32%. IR (KBr): 1710, 1685 (ν_{CO}), 1515 (ν_{asNO_2}), 1335 (ν_{sNO_2}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.0–8.25, m, 1H, Ar–6H; 7.16–7.83, m, 3H, ArH; 2.35, s, 6H, 2×CO–CH_3; 1.6, s, 3H, CH_3.

3,4-*Dimethyl*-5-(2-*nitrophenyl*)-1*H*-*pyrazole*

To 5.8 g (0.022 mole) of **7** in ethanol (60 ml) 2.3 ml (0.033 mole) 72% hydrazine hydrate in 23 ml ethanol was added dropwise with stirring for 1 h, the mixture was allowed to stand overnight. Ethanol was evaporated and the oil was dissolved in $CHCl_3$ (30 ml) and extracted with water (3×10 ml), dried ($MgSO_4$), evaporated and the residue was crystallised from ether to give a crude product (3.1 g) 4-[N'-(2-nitrobenzoyl)-hydrazino]-3-methyl-4-penten-2-one. Found: C, 56.38; H, 5.41; N, 14.82. Calc. for $C_{13}H_{15}N_3O_4$: C, 56.31; H, 5.45; N, 15.15%. IR (KBr): 3320 (ν_{OH}), 1630 ($\nu_{CO(N)}$), 1520 (ν_{asNO_2}), 1360 (ν_{sNO_2}) cm^{-1} (enolised). ^1H NMR (DMSO-d_6): δ 7.3–7.6, m, 4H, ArH; 6.6, s, 1H, NH; 3.2, m, 1H, CH; 2.05 and 1.96, 2×s, 2×3H, 2×=C–CH_3; 1.12, d, 3H, CH–CH_3. The filtrate was diluted with water (16 ml) to give 2.1 g (44%) 3,4-dimethyl-5-(2-nitrophenyl)-1H-pyrazole. Found: C, 60.95; H, 5.21; N, 19.29. Calc. for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.10; N, 19.34%. IR (KBr): 3300–2500 (ν_{NH}), 1530–15 (ν_{asNO_2}) 1350 (ν_{sNO_2}), 850 ($\nu_{C-N(O_2)}$), 760 (ν_{CArH}) cm^{-1}. ^1H NMR ($CDCl_3$): 7.66–8.0, m, 1H Ar3H; 7.16–7.66, m, 3H, ArH; 2.0 and 1.85, 2×s, 2×3H, 2×CH_3.

1,3,4-*Trimethyl*-5-(2-*nitrophenyl*)-1*H*-*pyrazole* *and* 1,4,5-*Trimethyl*-3-(2-*nitrophenyl*)-1*H*-*pyrazole*

A mixture of 2.17 g (0.01 mole) 3,4-dimethyl-5-(2-nitrophenyl)-1H-pyrazole, 0.54 g (0.01 mole) NaOMe and 1.86 g (0.01 mole) TsOMe were refluxed in 50 ml dry benzene for 12 h. TsONa was filtered off and the filtrate was extracted with water (3×10 ml), dried ($MgSO_4$) and evaporated. The products were separated by chromatography over silica, eluting with a mixture of benzene–methanol (9:1). Yields: 1,4,5-trimethyl-3-(2-nitrophenyl)-1H-pyrazole, (11%), m.p. 101–102°. IR (KBr): 1530, 1365, 860 (ν_{NO_2}); 760 (ν_{CArH}) cm^{-1}. ^1H NMR: 7.66–8.0, m, 1H, Ar(3)H; 7.66–7.16 m, 3H, Ar(4)(5)(6)H; 3.8, s, 3H, N–CH_3; 2.25 and 1.9, 2×s, 2×3H, 2×CH_3. ^{13}C NMR ($CDCl_3$): δ 145.3, C-5; 112.3, C–4; 145.3, C–3; 9.6, 5–CH_3; 8.5, 4–CH_3; 1,3,4-trimethyl-5-(2-nitrophenyl)-1H-pyrazole, (17%), m.p. 89–91°. IR (KBr): 1520, 1360, 860–840 (ν_{NO_2}) 760 (ν_{ArH}) cm^{-1}. ^1H NMR: δ 7.83–8.16 m, 1H, Ar(3)H; 7.16–7.83, m, 3H, Ar(4)(5)(6)H; 3.6, s, 3H, N–CH_3; 2.25 and 1.8, 2×s, 2×3H, 2×CH_3. ^{13}C NMR ($CDCl_3$): 125.8, C–5; 113.6, C–4; 146.4, C–3; 11.7, 3–CH_3; 8.1, 4–CH_3.

5-(2-*Aminophenyl*)-1,3,4-*trimethyl*-1*H*-*pyrazole* **6**

1,3,4-Trimethyl-5-(2-nitrophenyl)-1H-pyrazole (0.2 g) in methanol (3 ml) was hydrogenated over Pd/C. After the completion of the reaction the catalyst was filtered off and the filtrate was evaporated. The product was identical with **6** prepared from **5b**.

Alkaline cyclization of **1c**

1c was cyclised according to the method described above for **1b**. Yields; 6-chloro-3a,9a-dihydro-1,3,3a,9a-tetramethyl-4H-pyrazolo [3,4-b] quinolin-4-one **4c**, 62% m.p. 165–169° (benzene). Found: C, 60.75; H, 6.2; Cl, 12.77, N, 15.39. Calc for $C_{14}H_{16}ClN_3O$: C, 60.54; H, 5.81; Cl 12.76 N, 15.13%. MS: *m/z*(%): 277(31)M^+·, 262(35), 208(3), 153(43), 125(97), 124(100), 123(57), 109(13). UV λ_{max}: 237 mn, $E^{1\%}_{1cm}$ = 984; λ_{max}: 388 mn, $E^{1\%}_{1cm}$ = 115 (ethanol). IR (KBr): 3280 ν_{NH}), 1670 (ν_{CO}), 1610 (ν_{CArH}), 1510 (ν_{CArH}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.75, d, 1H, Ar(5)H; 7.25, dd, 1H, Ar(7)H; 6.68, d, 1H, Ar(8)H; 5.2, b, 1H, NH; 2.73, s, 3H, N–CH_3; 2.06, s, 3H, =C–CH_3; 1.28, s, 6H, 2×CH_3.

5-(2-*acetylamino*-5-*chlorophenyl*)-1,3,4-*trimethyl*-1*H*-*pyrazole* **5c** 9.5%, m.p. 224–226° (benzene-ethyl acetate). Found: C 60.51; H, 6.05; Cl, 12.36; N, 14.89. Calc. for $C_{14}H_{16}ClN_3O$: C, 60.54; 5.81; C, 12.76; N, 15.13%. UV λ_{max}: 203 nm, $E^{1\%}_{1cm}$ = 897; λ_{max}: 234 nm, $E^{1\%}_{1cm}$ = 648 (ethanol). IR (KBr): 3240 (ν_{NH}), 3180 (ν_{NH}), 1690 (ν_{CO}) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.1, b, 1H, NH; 7.8, d, 1H, Ar–3H; 7.52 d, 1H, Ar–6H; 7.28, dd, 1H, Ar–4H; 3.36, s, 3H, N–CH_3; 2.15, 2.00 and 1.80, 3×s, 3×3H, 3×CH_3.

Alkaline cyclization of **1f**

1f was cyclised according to the method described above for **1b**. Yield: **5f**; 5-(2-acetyl-2-methylaminophenyl)-1,3,4-trimethyl-1H-pyrazole (18.5%) m.p. 123–126°. Found: C, 70.15; H, 7.66; N, 16.19. Calc. for $C_{15}H_{19}N_3O$: C, 70.01; H, 7.44; N, 16.33. IR (KBr): 1660 ($\nu_{CO(N)}$) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.1–7.3, m, 4H, ArH; 3.55, s, 3H, N–CH_3; 2.9, broad s, 3H, N–CH_3; 2.2, s, 3H, =C–CH_3; 1.95 and 1.8, 2×s, 2×3H, 2×=C–CH_3.

Alkaline cyclization of **1g**

1g was cyclised according to the method described above for **1b**. Yields: 2,3-dimethyl-1-phenylquinolin-4-one **11** (13%) m.p. 256–257°. Found: C, 81.7, H, 6.41; N, 5.63. Calc. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62%. MS: *m/z*(%): 249(72.5) M^+·, 248(100), 247(5.2), 246(5.5) 234(16), 233(5.3), 204(6.8), 124(5.8). IR (KBr): 1620, 1600, 1575, 1545, 1490, 1470 (ν_{CO} + $\nu_{C=C}$), 760 (ν_{CArH}), 710, 695 ($\nu_{CAr-CAr}$) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.33–8.58, m, 1H, Ar–5H; 7.5–7.75, m, 3H, Ar–8H, 6'H, 2'H; 7.08–7.41, m, 4H, Ar–6H, 7H, 3'H, 5'H; 6.5–6.75, m, 1H, Ar–4'H; 2.2 and 2.1, 2×s, 2×3H, CH_3.

5-[(2-*phenylamino*)*phenyl*]-1,3,4-*trimethyl*-1*H*-*pyrazole*

12(20%) m.p. 130–132°. Found: C, 77.46; H, 6.56; N, 15.03. Calc. for $C_{18}H_{19}N_3$: C, 77.94; H, 6.90 N, 15.15%. MS: *m/z*(%) 277 (100)M^+·, 276(9.2), 262(1.9), 235(2.5), 224(1.2), 207(1.1), 206(0.6), 138.5(2.6). IR (KBr): 3260 (ν_{NH}), 760, 750, and 690 (ν_{CArH}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.83–7.5, m, 9H, ArH; 5.5, s, 1H, NH; 3.6, s, 3H, N–CH_3; 2.25 and 1.85, 2×s, 2×3H, 2×CH_3.

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