Monatshefte für Chemie 122, 537 – 544 (1991)

Monatshefte für Chemie
Chemical Monthly

Reaction of 1,2-Diarylhydrazines with Acetic Anhydride Catalyzed by 4-(Dimethylamino)pyridine

Gertraud Chiste, Helmut Egg*, Klemens Kraus, Elisabeth Pipitz, and **Elisabeth Spanyar**

Institut für Organische und Pharmazeutische Chemie, Universität Innsbruck, Innrain 52 a, A-6020 Innsbruck, Austria

Summary. A new method for the synthesis of 1,2-diaryl-1,2-dihydro-5-methyl-3*H*-pyrazol-3-ones **3** and 4-acetyl-1,2-diaryl-1,2-dihydro-5-methyl-3*H*-pyrazol-3-ones **5** is presented. The reaction of 4,4′-disubstituted 1,2-diarylhydrazines **1** with acetic anhydride in the presence of an equimolar amount of 4-(dimethylamino)pyridine leads to mixtures of the corresponding acetyl derivatives **2** and **3**. Under the same conditions, 2,2′-disubstituted 1,2-diarylhydrazines yield mixtures of **3** and **5**.

Keywords. Catalysis by 4-(Dimethylamino)pyridine; 1,2-Diaryl-1,2-dihydro-5-methyl-3*H*-pyrazol-3-ones; 4-Acetyl-1,2-diaryl-1,2-dihydro-5-methyl-3*H*-pyrazol-3-ones.

4-(Dimethylamino)pyridin-katalysierte Reaktion von 1,2-Diarylhydrazinen mit Essigsäureanhydrid

Zusammenfassung. Eine neue Methode zur Synthese von 1,2-Diaryl-1,2-dihydro-5-methyl-3*H*-pyrazol-3-onen **3** und 4-Acetyl-1,2-diaryl-1,2-dihydro-5-methyl-3*H*-pyrazol-3-onen **5** wird beschrieben. Die Reaktion von 4,4′-disubstituierten 1,2-Diaryl-hydrazinen **1** mit Essigsäureanhydrid führt in Gegenwart eines Äquivalentes 4-(Dimethylamino)pyridin zu Gemischen der entsprechenden Acetylderivate **2** und **3**. Unter den gleichen Bedingungen werden aus 2,2′-disubstituierten 1,2-Diarylhydrazinen Gemische aus **3** und **5** erhalten.

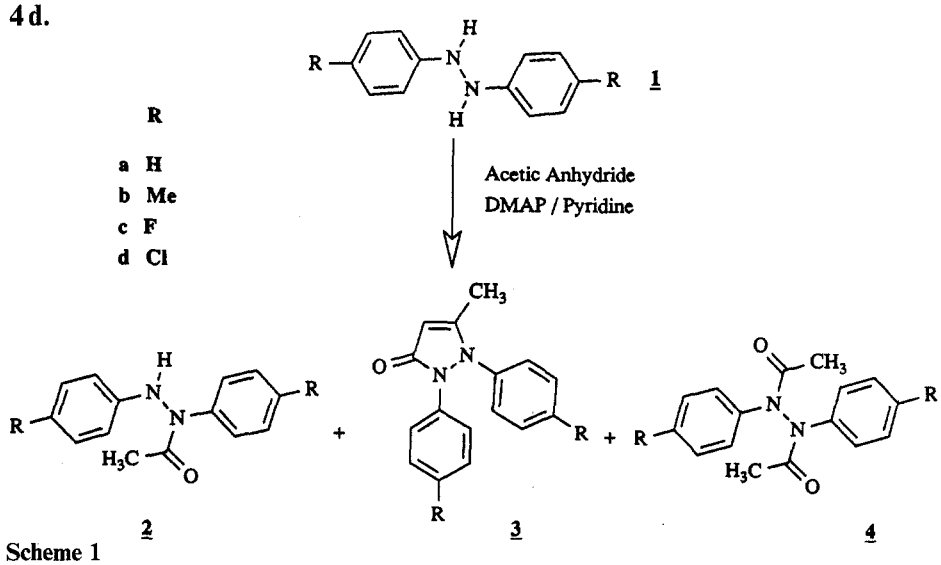
Introduction

In a previous communication [1] we have described the reaction of symmetrically disubstituted ureas with acetic and propanoic anhydride which was catalyzed by 4-(dimethylamino)pyridine (*DMAP*) and yielded 1,3-dialkyl-6-methyluracils and 1,3-dialkyl-6-ethylthymines. Continuing our investigations in this area, we now wish to report the reaction of a variety of symmetrically disubstituted 1,2-diarylhydrazines **1 a–i** with acetic anhydride/*DMAP*.

Results and Discussion

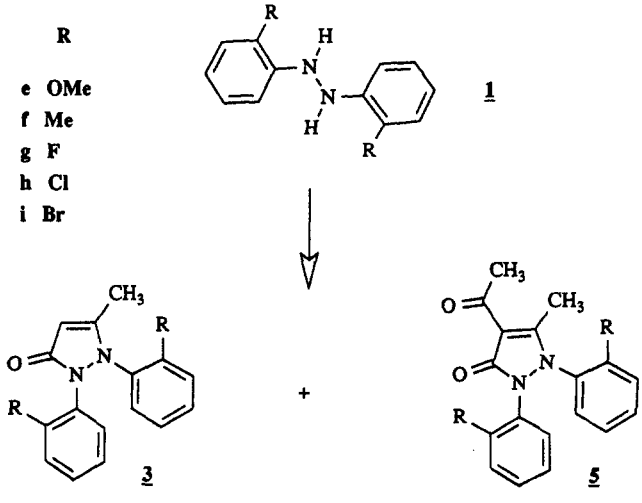
Treatment of **1** with 3 equivalents of acetic anhydride in dry pyridine at room temperature generally furnishes the monoacetyl derivatives **2** in good yields. Exceptions are 2,2′-dichloro- (**1 h**) and 2,2′-dibromohydrazobenzene (**1 i**) which, probably due to steric hindrance, do not react under these conditions.

If the reaction is performed in the presence of an equimolar amount of *DMAP*, cyclization occurs to some extent. Thus, from **1a–c** mixtures of **2** and the dihydropyrazolones **3** are obtained which are separated by preparative liquid chromatography (Scheme 1). **1d** affords a mixture of **2d, 3d**, and the diacetyl derivative **4d.**



Scheme 1

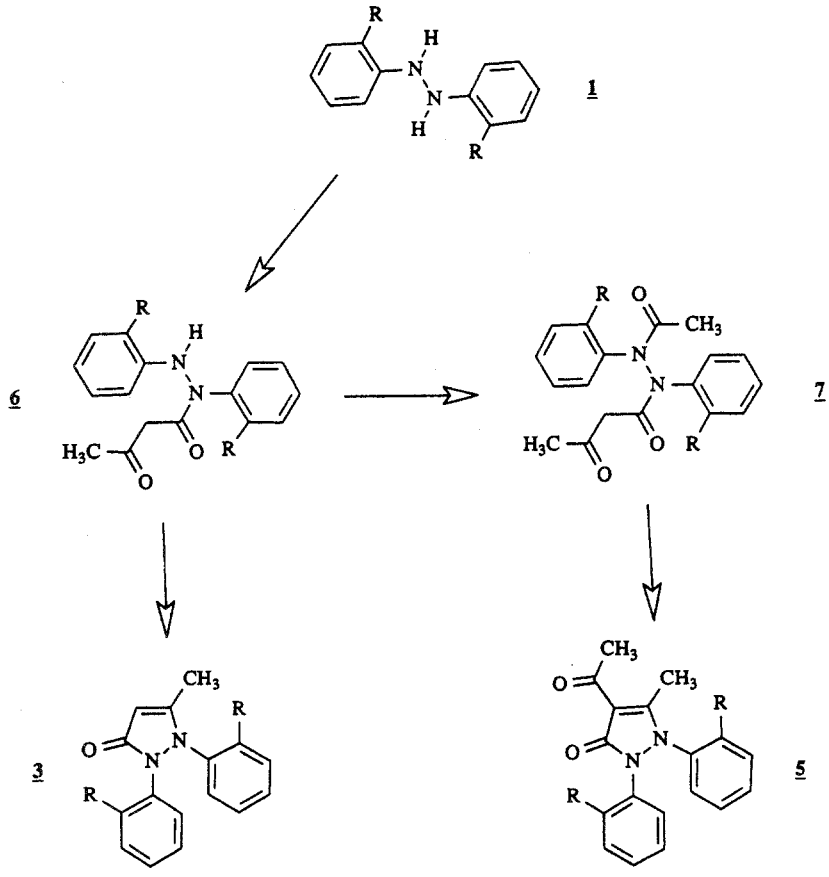
Unexpected results were observed with the 2,2′-disubstituted 1,2-diarylhydrazines **1e–i**. The resulting mixtures consisted of **3** and the hitherto unknown 4-acetyldihydropyrazolones **5**; practically no acetyl derivatives were formed (Scheme 2). The ratio of products was significantly affected by the size and the electronegativity of the *o*-substituents. In the series CH_3, F, Cl, and Br, a decrease of **3** and, simultaneously, an increase of **5** was observed. In the case of the dibromo compound **1i, 5i** the main product was only contaminated by traces of the corresponding dihydropyrazolone **3i.**



Scheme 2

All structures were confirmed either by comparison with data from literature or elemental analysis and spectral evidence (data are given in the experimental section).

The formation of **3** and **5** appears to proceed by a mechanism depicted in Scheme 3. Presumably, the reaction starts with autocondensation of acetic anhydride followed by N-acetoacetylation of **1**. The 2,2′-unsubstituted N-acetoacetyl derivatives **6 a–d** cyclize spontaneously to the dihydropyrazolones **3 a–d**. In contrast, the cyclization of the 2,2′-disubstituted N-acetoacetyl derivatives **6 e–i** seems to be slow, probably due to steric hindrance. Thus, acetylation of **6** on the other nitrogen atom can – and in fact does – occur, leading to **7**, which finally condenses to **5**.



Scheme 3

This mechanism is supported by the findings of Kato et al. [2], who have studied the reaction of hydrazobenzenes with diketene. They observed that 2,2′-disubstituted hydrazobenzenes form considerable amounts of N-acetoacetyl derivatives, which only upon prolonged heating cyclize to the corresponding pyrazolones. In contrast 4,4′-disubstituted hydrazobenzenes yield directly pyrazolones.

The distinct steric hindrance exerted by the 2,2′-substituents is directly evidenced by the NMR spectra of compounds **3 a–h** and **5 e–i**. This steric hindrance results in a restricted rotation about the N-aryl bonds exhibiting rotamers in the NMR spectra recorded at room temperature. Representative examples are the spectra of **3 f** and **5 f.**

Fig. 1 shows the methyl and H-4 region of the 300 MHz ^{1}H-NMR spectrum of **3 f** in *DMSO-d_6* at different temperatures. In the presumed two rotamers, the two *o*-methyl groups and the hydrogen in position 4 show different chemical shifts, thus leading to two signals of almost the same intensity. The protons of the 5-

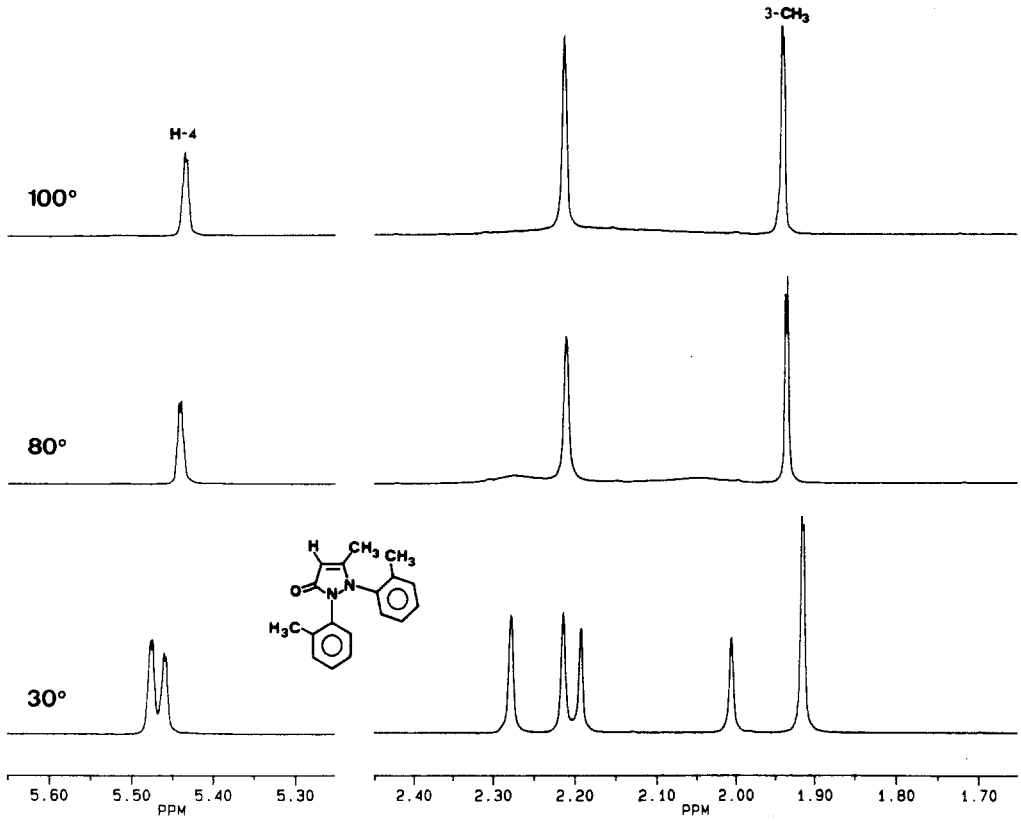


Fig. 1. Methyl and H-4 region of the 300 MHz ^{1}H-NMR spectrum of **3f** in *DMSO-d_6* at different temperatures

methyl group are isochronous, but their signal is split into a doublet by coupling with H-4. When heated, the two signals of the *o*-methyl groups and of H-4 are coalescing. At 80°C, the 2 pairs at 2.19/2.21 ppm (one *o*-methyl group) and 5.46/5.48 ppm (H-4) have merged into a sharp singlet at 2.21 ppm and a hardly resolved, but sharp quadruplet at 5.44 ppm, whereas the 2 signals at 2.01 and 2.28 ppm (other *o*-methyl group) are broadened but still separated. At 100°C, these 2 signals also have merged into one broad signal from 2.0 to 2.4 ppm. The splitting due to rotamers is even more pronounced in the 75 MHz ^{13}C-{^{1}H}-NMR spectrum: all signals being doubled. In Fig. 2, the temperature dependence of the aromatic region is shown. The two aromatic nuclei give rise to 12 pairs of signals coalescing at temperatures below 80°C. The ^{1}H- and ^{13}C-NMR spectra obtained after recooling to 30°C are identical with the ones recorded before heating. This is another indication that the splitting is due to rotamers. Likewise, most of the signals of **5f** in the 300 MHz ^{1}H- and the 75 MHz ^{13}C-{^{1}H}-NMR spectra are doubled. However, upon heating the spectra remain almost unchanged. Up to 100°C, no coalescence is observed.

Experimental

Melting points: uncorrected, Reichert-Kofler hot-stage microscope. IR spectra (KBr; cm^{-1}): Shimadzu IR-470; only selected absorptions are reported. NMR spectra: Bruker AM 300; δ-values

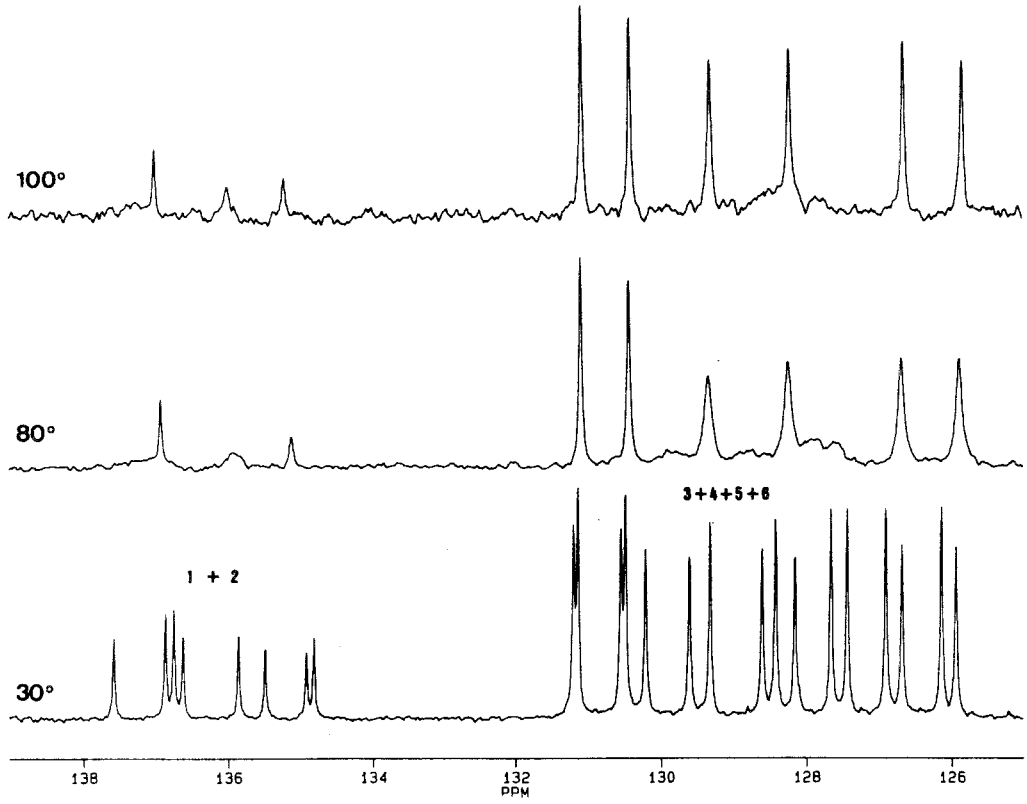


Fig. 2. Aromatic region of the 75 MHz ^{13}C-{^1H}-NMR spectrum of **3f** in *DMSO-d_6* at different temperatures

in ppm using *TMS* as internal standard or solvent signals ($CDCl_3$ or *DMSO-d_6*) as indirect internal standard, J in Hz. Microanalyses: Institut für Physikalische Chemie, Universität Wien.

General Procedure

0.033 mol of acetic anhydride were added to a solution of 0.01 mol of **1** and *DMAP* in 10 ml dry pyridine under ice cooling and stirring. The mixture was kept at room temperature for 12 h, then poured into 100 ml 2*N* HCl and extracted three times with 50 ml portions of methylene chloride each. The combined methylene chloride extract yielded an oily mixture, which was separated by preparative medium pressure LC [3] on silica (Kieselgel Merck, corn size 0.040–0.063 mm, eluting agents given below).

1-Acetyl 1,2-diphenylhydrazine (**2a**) *and 1,2-Dihydro-5-methyl-1,2-diphenyl-3 H-pyrazol-3-one* (**3a**)

Eluting agent: Ether.

2a: Yield 0.82 g (36%); m.p. = 161–162° (Ref. [4] 161–162°). IR: 3270 (N−H), 1650 (C=O). ^1H-NMR ($CDCl_3$): 7.5–6.5 (m, 11 H, aromat. and NH), 2.23 (s, 3 H, CH_3).

3a: Yield 0.55 g (22%); m.p. = 128° (Ref. [2] 131°). IR: 1673 (C=O). ^1H-NMR ($CDCl_3$): 7.4–7.0 (m, 10 H, aromat.), 5.55 (q, 1 H, J = 0.8, H-4), 2.06 (d, 3 H, J = 0.8, CH_3). ^{13}C-NMR ($CDCl_3$): 166.62 (C-3), 156.42 (C-5), 139.21, and 135.91 (C-1′ and C-1″), 129.39 and 128.67 (C-3′/5′ and C-3″/5″), 128.05 and 125.91 (C-4′ and C-4″), 125.60 and 123.65 (C-2′/6′ and C-2″/6″), 99.38 (C-4), 13.69 (CH_3).

1-Acetyl-1,2-bis(4-methylphenyl)hydrazine (**2b**) *and*
1,2-Dihydro-5-methyl-1,2-bis(4-methylphenyl)-3 H-pyrazol-3-one (**3b**)

Eluting agent: Methylene chloride – methanol (95 + 5).

2b: Yield 1.59 g (62%); m.p. = 118–119° (Ref. [5] 120°). IR: 3295 (N – H), 1650 (C = O). ^{1}H-NMR ($CDCl_3$): 7.3–6.7 (m, 9H, aromat. and NH), 2.30 (s, 6H, 2 CH_3-*Ar*), 2.24 (s, 3H, CH_3 – CO).

3b: Yield 0.59 g (21%); m.p. = 145–146° (Ref. [2] 143°). IR: 1668 (C = O). ^{1}H-NMR ($CDCl_3$): 7.3–7.0 (m, 8H, aromat.), 5.51 (q, 1H, J = 0.9, H-4), 2.28 (s, 3H, CH_3-*Ar*), 2.24 (s, 3H, CH_3-*Ar*), 2.03 (d, 3H, J = 0.9, CH_3). ^{13}C-NMR ($CDCl_3$): 166.73 (C-3), 155.95 (C-5), 138.19, 136.52, 135.93, and 133.43 (C-1′, C-1″, C-4′, and C-4″), 130.01, 129.36, 125.78, and 124.12 (C-2′/6′, C-2″/6″, C-3′/5′, and C3″/5″), 98.96 (C-4), 21.04, and 20.95 (2 CH_3-*Ar*), 13.64 (CH_3).

1-Acetyl-1,2-bis(4-fluorophenyl)hydrazine (**2c**) *and*
1,2-Bis(4-fluorophenyl)-1,2-dihydro-5-methyl-3 H-pyrazol-3-one (**3c**)

Eluting agent: Ether.

2c: Yield 1.55 g (59%); m.p. = 107°. $C_{14}H_{12}F_2N_2O$ (262.26). Calcd. C 64.12, H 4.61, N 10.68; found C 64.03, H 4.64, N 10.72. IR: 3290 (N – H), 1654 (C = O). ^{1}H-NMR ($CDCl_3$): 7.5–6.5 (m, 9H, aromat. and NH), 2.15 (s, 3H, CH_3).

3c: Yield 0.52 g (18%); m.p. = 127°. $C_{16}H_{12}F_2N_2O$ (286.28). Calcd. C 67.13, H 4.23, N 9.79; found C 67.18, H 4.22, N 9.77. IR: 1667 (C = O). ^{1}H-NMR ($CDCl_3$): 7.3–6.9 (m, 8H, aromat.), 5.56 (q, 1H, J = 0.9, H-4), 2.05 (d, 3H, J = 0.9, CH_3). ^{13}C-NMR ($CDCl_3$): 166.58 (C-3), 161.82, and 160.69 (sd, J = 249.1 and 246.2, C-4′ and C-4″), 156.83 (C-5), 134.86 and 131.68 (sd, J = 2.9, C-1′ and C-1″), 127.65 and 125.73 (dd, J = 9.1 and 8.4, C-2′/6′ and C-2″/6″), 116.50 and 115.68 (dd, J = 23.2 and 22.9, C-3′/5′ and C-3″/5″), 99.54 (C-4), 13.49 (CH_3).

1-Acetyl-1,2-bis(4-chlorophenyl)hydrazine (**2d**),
1,2-Bis(4-chlorophenyl)-1,2-dihydro-5-methyl-3 H-pyrazol-3-one (**3d**) *and*
1,2-Diacetyl-1,2-bis(4-chlorophenyl)hydrazine (**4d**)

Eluting agent: Ether.

2d: Yield 0.86 g (29%); m.p. = 87°. $C_{14}H_2Cl_2N_2O$ (295.17). Calcd. C 56.97, H 4.10, N 9.49; found C 57.05, H 4.20, N 9.52. IR: 3230 (N – H), 1662 (C = O). ^{1}H-NMR ($CDCl_3$): 7.5–6.5 (m, 9H, aromat. and NH), 219 (s, 3H, CH_3).

3d: Yield 1.27 g (40%); m.p. = 135–136° (Ref. [2] 142°). IR: 1675 (C = O). ^{1}H-NMR ($CDCl_3$): 7.3–6.8 (m, 8H, aromat.), 5.56 (q, 1H, J = 0.8, H-4), 2.06 (d, 3H, J = 0.8, CH_3). ^{13}C-NMR ($CDCl_3$): 166.54 (C-3), 157.29 (C-5), 137.82 and 134.37 (C-1′ and C-1″), 134.18 and 131.70 (C-4′ and C-4″), 129.91 and 129.06 (C-3′/5′ and C-3″/5″), 126.76 and 124.58 (C-2′/6′ and C-2′/6″), 100.21 (C-4), 13.75 (CH_3).

4d: Yield 0.24 g (7%), m.p. = 129–131°. $C_{16}H_{14}Cl_2N_2O_2$ (337.21). Calcd. C 56.99, H 4.18, N 8.31; found C 57.03, H 4.29, N 8.24. IR: 1704 and 1670 (C = O). ^{1}H-NMR ($CDCl_3$): 7.6–7.2 (m, 8H, aromat.), 2.07 (s, 6H, CH_3).

1,2-Dihydro-1,2-bis(2-methoxyphenyl)-5-methyl-3 H-pyrazol-3-one (**3e**) *and*
4-Acetyl-1,2-dihydro-1,2-bis(2-methoxy-phenyl)-5-methyl-3 H-pyrazol-3-one (**5e**)

Eluting agent: Ether – methanol (85 + 15).

3e: Yield 1.06 g (34%); m.p. = 149–150° (Ref. [2] 127°). $C_{18}H_{18}N_2O_3$ (310.35). Calcd. C 69.66, H 5.85, N 9.03; found C 69.55, H 5.93, N 9.31. IR: 1635 (C = O). ^{1}H-NMR ($CDCl_3$): 7.3–6.8 (m, 8H, aromat.), 5.47 (q, 1H, J = 0.7, H-4), 3.75 (s, 6H, 2 CH_3O), 1.99 (d, 3H, J = 0.7, CH_3). ^{13}C-NMR

($CDCl_3$): 166.03 (C-3), 156.73 and 156.27 (C-5), 151.72 (C-2′ and C-2″), 131.11, 130.91, 130.49 and 130.40 (C-4′, C-4″, C-6′ and C-6″), 124.77 and 123.72 (C-1′ and C-1″), 120.43 and 120.28 (C-5′ and C-5″), 112.15 and 111.74 (C-3′ and C-3″), 95.61 (C-4), 55.81 and 55.58 ($2\,CH_3O$), 12.73 (CH_3).

5e: Yield 1.06 g (30%); m.p. = 175°. $C_{20}H_{20}N_2O_4$ (352.39). Calcd. C 68.17; H 5.72, N 7.95; found C 68.15, H 5.70, N 7.96. IR: 1668 and 1643 (C=O). ^{1}H-NMR ($CDCl_3$): 7.3–6.8 (m, 8H, aromat.), 3.77 (s, 6H, CH_3O), 2.65 (s, 3H, CH_3CO), 2.37 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): 195.26 (C=O, 163.61 (C-3), 156.34 and 156.15 (C-5), 152.82 (C-2′ and C-2″), 132.23, 131.58, 131.41 and 130.42 (C-4′, C-4″, C-6′ and C-6″), 122.18 and 121.69 (C-1′ and C-1″), 120.44 and 120.37 (C-5′ and C-5″), 111.81 and 111.72 (C-3′ and C-3″), 106.27 (C-4), 55.66 (CH_3O), 29.62 (CH_3CO), 13.09 (CH_3).

1,2-Dihydro-5-methyl-1,2-bis(2-methylphenyl)-3 H-pyrazol-3-one (**3f**) *and*
4-Acetyl-1,2-dihydro-5-methyl-1,2-bis(2-methylphenyl)-3 H-pyrazol-3-one (**5f**)

Eluting agent: Ether – methanol (80 + 20).

3f: Yield 1.65 g (59%); m.p. = 137–138° (Ref. [2] 141°). IR: 1654 (C=O). ^{1}H-NMR (*DMSO-d*$_6$): 7.4–7.0 (m, 8H, aromat.), 5.47 and 5.46 (2q, 1H, J = 0.7, H-4), 2.28, 2.21, 2.19 and 2.01 (4s, 6H, $2\,CH_3$-*Ar*), 1.91 (d, 3H, J = 0.7, CH_3). ^{13}C-NMR (*DMSO-d*$_6$): 166.19 and 165.65 (C-3), 155.47 and 155.05 (C-5), 137.58, 136.86, 136.74, 136.62, 135.85, 135.48, 134.91 and 134.81 (C-1′, C-1″, C-2′ and C-2″), 131.19, 131.13, 130.54, 130.48, 130.20, 129.60, 129.32, 128.60, 128.42, 128.15, 127.65, 127.43, 126.91, 126.68, 126.13 and 125.93 (C-3′, C-3″, C-4′, C-4″, C-5′, C-5″, C-6′ and C-6″), 95.94 and 95.30 (C-4), 17.47, 17.43, 16.73 and 16.10 (CH_3-*Ar*), 12.52 and 12.33 (CH_3).

5f: Yield 1.04 g (33%); m.p. = 153–155°. $C_{20}H_{20}N_2O_2$ (320.39). Calcd. C 74.98, H 6.29, N 8.74; found C 75.19, H 6.32, N 8.94. IR: 1655 and 1640 (C=O). ^{1}H-NMR (*DMSO-d*$_6$): 7.3–7.0 (m, 8H, aromat.), 2.48 and 2.47 (2s, 3H, CH_3CO), 2.27 (s, 3H, CH_3), 2.22, 2.20 and 2.01 (3s, 6H, CH_3-*Ar*). ^{13}C-NMR (*DMSO-d*$_6$): 192.98 (C=O), 163.44 and 162.95 (C-3), 155.28 and 153.88 (C-5), 137.77, 137.18 and 137.08 (C-1′ and C-1″), 133.26, 133.06, 132.39 and 132.23 (C-2′ and C-2″), 131.31, 131.25, 131.05, 130.65, 129.66, 129.28, 129.10, 128.91, 128.51, 127.07, 126.79, 126.38 and 126.07 (C-3′, C-3″, C-4′, C-4″, C-5′, C-5″, C-6′ and C-6″), 105.14 and 104.74 (C-4), 29.10 (CH_3CO), 17.55, 17.30, 16.72 and 16.32 (CH_3-*Ar*), 12.85 and 12.72 (CH_3).

1,2-Bis(2-fluorophenyl)-1,2-dihydro-5-methyl-3 H-pyrazol-3-one (**3g**) *and*
4-Acetyl-1,2-bis(2-fluorophenyl)-1,2-dihydro-5-methyl-3 H-pyrazol-3-one (**5g**)

Eluting agent: Methylene chloride – methanol (95 + 5).

3g: Yield 0.54 g (19%); m.p. = 122–123°. $C_{16}H_{12}F_2N_2O$ (286.28). Calcd. C 67.13, H 4.23, N 9.79; found C 67.18, H 4.23, N 9.81. IR: 1676 (C=O). ^{1}H-NMR ($CDCl_3$): 7.4–7.0 (m, 8H, aromat.), 5.57 (q, 1H, J = 0.9, H-4), 2.07 and 2.06 (2d, 3H, J = 0.9, CH_3). ^{13}C-NMR ($CDCl_3$): 166.69 (C-3), 158.53 and 157.94 (sd, J = 253.5 and 254, C-2′ and C-2″), 155.75 (C-5), 131.08 and 130.22 (dd, J = 7.8 and 7.9, C-4′ and C-4″), 129.36 and 129.18 (C-5′ and C-5″), 125.15 and 123.15 (sd, J = 11.4 and 12.3, C-1′ and C-1″), 124.94 and 124.46 (dd, J = 4 and 3.9, C-6′ and C-6″), 116.83 and 116.67 (dd, J = 19.5, C-3′ and C-3″), 98.09 (C-4), 12.88 and 12.86 (CH_3).

5g: Yield 1.25 g (38%); m.p. = 153°. $C_{18}H_{14}F_2N_2O_2$ (328.32). Calcd. C 65.85, H 4.30, N 8.53; found C 65.96, H 4.30, N 8.51. IR: 1683 and 1646 (C=O). ^{1}H-NMR ($CDCl_3$): 7.5–7.0 (m, 8H, aromat.), 2.64 (s, 3H, CH_3CO), 2.47 and 2.46 (2s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): 194.54 (C=O), 163.88 (C-3), 158.24 and 158.18 (sd, J = 254.1 and 255.1, C-2′ and C-2″), 156.06 (C-5), 132.48 and 131.41 (dd, J = 8.0 and 7.9, C-4′ and C-4″), 130.45 and 129.85 (C-5′ and C-5″), 125.00 and 124.53 (dd, J = 4.0 and 3.9, C-6′ and C-6″), 121.59 and 121.44 (sd, J = 12.0 and 11.7, C-1′ and C-1″), 116.91 and 116.48 (dd, J = 19.2 and 19.4, C-3′ and C-3″), 106.93 (C-4), 29.61 (CH_3CO), 12.94 (CH_3).

1,2-Bis(2-chlorophenyl)-1,2-dihydro-5-methyl-3 H-pyrazol-3-one (**3h**) *and*
4-Acetyl-1,2-bis(2-chlorophenyl)-1,2-dihydro-5-methyl-3 H-pyrazol-3-one (**5h**)

Eluting agent: Methylene chloride – methanol (9.25 + 7.5).

3h: Yield 0.16 g (5%); m.p. = 154° (Ref. [2] 159°). IR: 1 660 (C = O). ^{1}H-NMR ($CDCl_3$): 7.4–7.1 (m, 8 H, aromat.), 5.57 (s, 1 H, H-4), 2.05 (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): 166.35 (C-3), 155.10 (C-5), 134.77, 133.82, 133.53 and 133.16 (C-1′ and C-1″), 131.84, 130.90, 130.81, 130.74, 130.53, 130.36, 130.09, 130.05 and 129.99 (C-2′, C-2″, C-3′, C-3″, C-4′, C-4″, C-5′ and C-5″), 127.93, 127.55, 127.44 and 126.99 (C-6′ and C-6″), 98.53 and 97.80 (C-4), 13.04 and 12.82 (CH_3).

5h: Yield 1.54 g (43%); m.p. = 165°. $C_{18}H_{14}Cl_2N_2O_2$ (361.23). Calcd. C 59.85, H 3.91, Cl 19.63, N 7.76; found C 59.87, H 3.92, Cl 19.41, N 7.82. IR: 1 666 and 1 650 (C = O). ^{1}H-NMR ($CDCl_3$): 7.5–7.1 (m, 8 H, aromat.), 2.66 (s, 3 H, CH_3CO), 2.43 and 2.42 (2 s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): 195.06 (C = O), 165.08 and 163.83 (C-3), 158.05 and 155.79 (C-5), 135.35, 134.81, 134.42 and 134.24 (C-1′ and C-1″), 132.40, 132.16, 131.99, 131.82, 131.54, 131.36, 131.30, 131.17, 131.09, 130.80, 130.77 and 130.38 (C-2′, C-2″, C-3′, C-3″, C-4′, C-4″, C-5′ and C-5″), 128.10, 127.70, 127.66 and 127.22 (C-6′ and C-6″), 107.51 and 107.03 (C-4), 29.84 and 29.80 (CH_3CO), 13.41 and 13.14 (CH_3).

4-Acetyl-1,2-bis(2-bromophenyl)-1,2-dihydro-5-methyl-3 H-pyrazol-3-one (**5i**)

Eluting agent: Ether – methanol (95 + 5).

Yield 2.80 g (62%); m.p. = 161–162°. $C_{18}H_{14}Br_2N_2O_2$ (450.14). Calcd. C 48.03, H 3.13, N 6.22; found C 47.92, H 3.18, N 6.12. IR: 1 659 and 1 624 (C = O). ^{1}H-NMR ($CDCl_3$): 7.6–7.2 (m, 8 H, aromat.), 2.66 (s, 3 H, CH_3CO), 2.44 and 2.43 (2 s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): 195.09 (C = O), 163.66 (C-3), 155.46 (C-5), 134.45, 134.10, 134.01, 133.58, 133.37, 133.08, 132.33, 132.09, 132.03, 131.94, 131.58, 131.28, 131.22, 128.70, 128.32, 127.85, 124.60 and 124.14 (aromat.), 107.07 (C-4), 29.82 and 29.79 (CH_3CO), 13.64 and 13.28 (CH_3).

Acknowledgement

The authors are indebted to E. P. Müller for recording the NMR spectra and for many helpful discussions.

References

[1] Egg H., Volgger I. (1982) Synthesis: 1071
[2] Kato T., Kato M., Tabei K., Kawashima E. (1975) Chem. Pharm. Bull. **23**: 456
[3] Loibner H., Seidl G. (1979) Chromatogr. **12**: 600
[4] Pongratz A., Böhmert-Süß S., Scholtis K. (1944) Chem. Ber. **77**: 651
[5] Goldschmidt S., Euler K. (1922) Chem. Ber. **55**: 616

Received October 15, 1990. Accepted December 5, 1990