

Synthesis of 1-(*N*-Arylaminomethyl)-3-methyl-1,8-dihydrocycloheptapyrazol-8-ones

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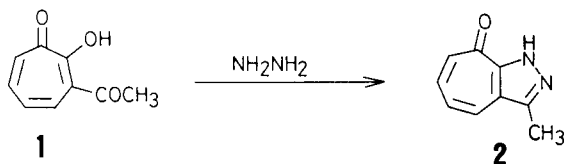
Dedicated to the memory of Dr. Roland K. Robins

Reactions of 3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**2**) with arylamines in the presence of formaldehyde gave 1-(*N*-arylaminomethyl)-3-methyl-1,8-dihydrocycloheptapyrazol-8-ones **5a-l** in good yields. 1,3,5-Tris(phenyl- and 4-methoxyphenyl)hexahydro-1,3,5-triazines or bis(3-nitroanilino)methane, which were condensation products of arylamines and formaldehyde, also reacted with compound **2** to afford **5a,c,j**, respectively.

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In 3-acetyltropolone chemistry, a variety of heterocycle-fused troponoid compounds have been prepared by utilizing positional feature of its acetyl group [1-4]. As an example, 3-acetyltropolone (**1**) reacted with hydrazine to afford 3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**2**) in a good yield [5] (Scheme 1).

Scheme 1



Compound **2** reacted with diazomethane, dialkyl sulfates, or alkyl halides to give isomeric 1-alkyl- and 2-alkyl-substituted products because of its tautomerism [6]. For the purpose of evaluating biological activities, compound **2** was converted to various *N*-alkyl-substituted 3-methyl-1,8-dihydrocycloheptapyrazol-8-ones [7]. It was found that some of them have pharmacological activities.

On the other hand, Mannich reaction is very useful for introduction of alkylaminomethyl or arylaminomethyl groups. It was reported that indole, 1*H*-indazole, benzimidazole, and benzotriazole were treated with cyclic secondary amines and formaldehyde to give 1-aminomethyl-substituted products [8], while treatment of benzimidazole with arylamines in the presence of formaldehyde gave 1-(arylaminomethyl)benzimidazoles [9].

As an extension of the previous work [7], this paper deals with synthesis of 1-arylaminomethyl-substituted 3-methyl-1,8-dihydrocycloheptapyrazol-8-ones by Mannich reaction.

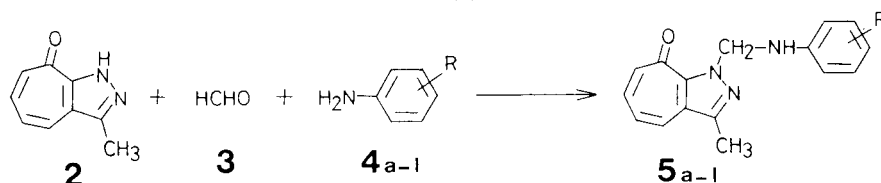
Results and Discussion.

When an ethanolic solution of 3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**2**), formaldehyde (**3**), and aniline (**4a**) was refluxed for 3 hours, 3-methyl-1-(*N*-phenylaminomethyl)-1,8-dihydrocycloheptapyrazol-8-one (**5a**) was obtained as yellow needles in a 84% yield. Its structure was determined on the basis of the spectral data as well as an elemental analysis (C₁₆H₁₅N₃O). The ir spectrum shows two characteristic absorption bands at 3330 (NH) and 1632 cm⁻¹ (C=O). In the ¹H nmr spectrum, ten isolated signals are observed at δ 7.40 (1H, d, J = 10.8 Hz) for 4-H, 6.74 (1H, dd, J = 10.8, 8.0 Hz) for 5-H, 7.26 (1H, dd, J = 12.4, 8.0 Hz) for 6-H, and 7.04 (1H, d, J = 12.4 Hz) for 7-H in the seven-membered ring, at 6.91 (2H, d, J = 8.0 Hz) for 2'- and 6'-H, 7.15 (2H, t, J = 8.0, 8.0 Hz) for 3'- and 5'-H, and 6.72 (1H, t, J = 8.0 Hz) for 4'-H in the benzene ring, and at 2.51 (3H, s) for CH₃, 6.02 (2H, d, J = 8.0 Hz) for CH₂, and 5.61 (1H, t, J = 8.0 Hz) for NH group.

In a similar manner, reaction of compound **2** with arylamines **4b-k** gave the corresponding 1-(*N*-arylaminomethyl)-3-methyl-1,8-dihydrocycloheptapyrazol-8-ones **5b-k** in 47-84% yields. These structures were also determined from the spectral data and elemental analyses (see: Experimental). The compound **2** also reacted with 4-aminoazobenzene (**4l**) to afford 3-methyl-1-[*N*-[4-(phenylazo)phenyl]aminomethyl]-1,8-dihydrocycloheptapyrazol-8-one (**5l**) as orange crystals in a 54% yield.

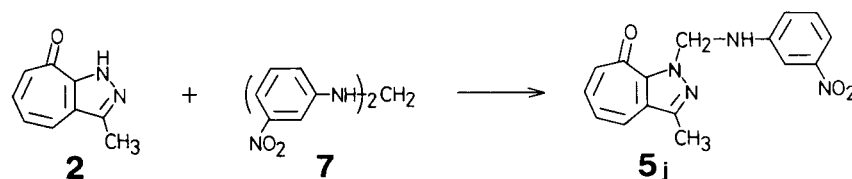
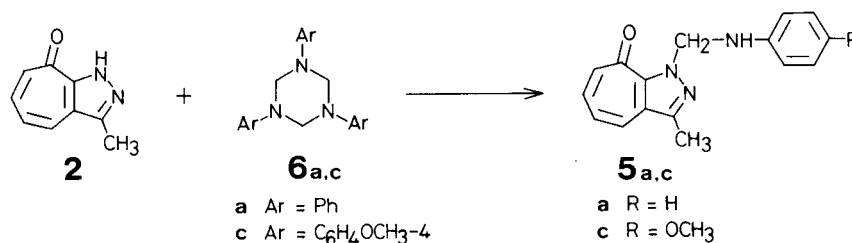
It is known that arylamines reacted with formaldehyde to condensation products, 1,3,5-triarylhexahydro-1,3,5-triazines or bis(arylamino)methane [10]. These condensation products were applied to the reactions. Compound **2** was treated with 1,3,5-tris(phenyl- or 4-methoxyphenyl)hexahydro-1,3,5-triazine **6a,c** to give the 1-(*N*-arylaminomethyl)-

Scheme 2



- | | |
|----------------------------------|----------------------------------|
| a R = H | g R = 2,4-Cl ₂ |
| b R = 2-CH ₃ | h R = 2-Br |
| c R = 4-OCH ₃ | i R = 4-Br |
| d R = 4-COCH ₃ | j R = 3-NO ₂ |
| e R = 2-Cl | k R = 4-NO ₂ |
| f R = 4-Cl | l R = 4-N=N-Ph |

Scheme 3



substituted products **5a,c** in 71 and 73% yields, respectively. The reaction with bis(3-nitroanilino)methane (**7**) gave the compound **5j** in 56% yield.

In summary, 1-(N-arylaminoethyl)-3-methyl-1,8-dihydrocycloheptapyrazol-8-ones were readily prepared in good yields by Mannich reaction on the nitrogen atom in the pyrazole ring. The percentage yields varied with substituents in arylamines and were higher for electron-donating substituents and lower for electro-withdrawing ones. These results are consistent with mechanism for Mannich base formation. The prepared heterocycle-fused troponoid compounds are expected to be pharmacologically active.

EXPERIMENTAL

The melting points are uncorrected. The ir and uv spectra were taken on a Perkin-Elmer 1730 spectrophotometer and a Shimadzu UV-265 spectrophotometer, respectively. The ¹H nmr spectra were measured with a Varian Unity-400 spectrometer.

Reactions of 3-Methyl-1,8-dihydrocycloheptapyrazol-8-one (**2**) with Arylamines **4a-k** in the Presence of Formaldehyde (**3**).

General Procedure.

A solution of 3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**2**)

(40 mg, 0.25 mmole), 37% formalin (**3**) (24 mg, 0.3 mmole), and arylamine **4a-k** (0.25 mmole) in ethanol (5 ml) was heated for 3 hours on a water bath. After removal of the solvent, the residue was recrystallized to give 1-(N-arylaminoethyl)-3-methyl-1,8-dihydrocycloheptapyrazol-8-ones **5a-k**.

3-Methyl-1-(N-phenylaminomethyl)-1,8-dihydrocycloheptapyrazol-8-one (**5a**).

This compound was obtained from the reaction with aniline (**4a**) in a yield of 56 mg (84%) as yellow needles (from acetone), mp 138-139°; ir (potassium bromide): ν max 3330 (NH), 1632 cm⁻¹ (C=O); uv (95% ethanol): λ max 202 (log ϵ 4.40), 231 (4.44), 291 (3.86), 303 (3.82), 359 nm (3.81); ¹H nmr (deuteriochloroform): δ 2.51 (3H, s, CH₃), 5.61 (1H, t, J = 8.0 Hz, NH), 6.02 (2H, d, J = 8.0 Hz, CH₂), 6.72 (1H, t, J = 8.0 Hz, 4'-H), 6.74 (1H, dd, J = 10.8, 8.0 Hz, 5-H), 6.91 (2H, d, J = 8.0 Hz, 2'-, 6'-H), 7.04 (1H, d, J = 12.4 Hz, 7-H), 7.15 (2H, t, J = 8.0 Hz, 3'-, 5'-H), 7.26 (1H, dd, J = 12.4, 8.0 Hz, 6-H), 7.40 (1H, d, J = 10.8 Hz, 4-H).

Anal. Calcd. for C₁₆H₁₅N₃O: C, 72.43; H, 5.70; N, 15.84. Found: C, 72.17; H, 5.77; N, 15.63.

3-Methyl-1-[N-(2-methylphenyl)aminomethyl]-1,8-dihydrocycloheptapyrazol-8-one (**5b**).

This compound was obtained from the reaction with 2-methylaniline (**4b**) in a yield of 50 mg (72%) as yellow needles (from ethanol-water), mp 121-122°; ir (potassium bromide): ν max 3397

(NH), 1629 cm^{-1} (C=O); uv (95% ethanol): λ max 202 (log ϵ 4.62), 231 (4.52), 291 (3.93), 303 (3.88), 358 nm (3.86); ^1H nmr (deuteriochloroform): δ 2.13 (3H, s, 2'-CH₃), 2.51 (3H, 3-CH₃), 5.66 (1H, t, J = 8.0 Hz, NH), 6.07 (2H, d, J = 8.0 Hz, CH₂), 6.66 (1H, t, J = 8.0 Hz, 4'-H), 6.74 (1H, dd, J = 10.4, 8.0 Hz, 5-H), 7.00 (1H, d, J = 8.0 Hz, 6'-H), 7.04 (1H, d, J = 12.4 Hz, 7-H), 7.10 (1H, t, J = 8.0 Hz, 5'-H), 7.21 (1H, d, J = 8.0 Hz, 3'-H), 7.25 (1H, dd, J = 12.4, 8.0 Hz, 6-H), 7.40 (1H, d, J = 10.4 Hz, 4-H).

Anal. Calcd. for C₁₇H₁₇N₃O: C, 73.09; H, 6.13; N, 15.04. Found: C, 73.36; H, 6.27; N, 14.98.

1-[*N*-(4-Methoxyphenyl)aminomethyl]-3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**5c**).

This compound was obtained from the reaction with 4-methoxyaniline (**4c**) in a yield of 60 mg (81%) as yellow needles (from ethanol-water), mp 135-136°; ir (potassium bromide): ν max 3337 (NH), 1628 cm^{-1} (C=O); uv (95% ethanol): λ max 199 (log ϵ 4.52), 229 (4.54), 291 (4.02), 303 (3.98), 358 nm (3.91); ^1H nmr (deuteriochloroform): δ 2.51 (3H, s, CH₃), 3.70 (3H, s, OCH₃), 5.42 (1H, t, J = 8.0 Hz, NH), 5.98 (2H, d, J = 8.0 Hz, CH₂), 6.73 (2H, d, J = 8.8 Hz, 2'-, 6'-H), 6.74 (1H, dd, J = 10.4, 8.0 Hz, 5-H), 6.85 (2H, d, J = 8.8 Hz, 3'-, 5'-H), 7.04 (1H, d, J = 12.4 Hz, 7-H), 7.26 (1H, dd, J = 12.4, 8.0 Hz, 6-H), 7.40 (1H, d, J = 10.4 Hz, 4-H).

Anal. Calcd. for C₁₇H₁₇N₃O₂: C, 69.13; H, 5.80; N, 14.23. Found: C, 69.32; H, 5.91; N, 13.97.

1-[*N*-(4-Acetylphenyl)aminomethyl]-3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**5d**).

This compound was obtained from the reaction with 4-aminoacetophenone (**4d**) in a yield of 52 mg (58%) as yellow needles (from 95% ethanol), mp 187-188°; ir (potassium bromide): ν max 3316 (NH), 1625 cm^{-1} (C=O); uv (95% ethanol): λ max 199 (log ϵ 4.69), 230 (4.75), 315 nm (4.74); ^1H nmr (deuteriochloroform): δ 2.48 (3H, s, COCH₃), 2.53 (3H, s, CH₃), 5.9-6.1 (3H, m, NH + CH₂), 6.78 (1H, dd, J = 10.4, 8.8 Hz, 5-H), 6.93 (2H, d, J = 8.8 Hz, 2'-, 6'-H), 7.06 (1H, d, J = 12.8 Hz, 7-H), 7.29 (1H, dd, J = 12.8, 8.8 Hz, 6-H), 7.43 (1H, d, J = 10.4 Hz, 4-H), 7.81 (2H, d, J = 8.8 Hz, 3'-, 5'-H).

Anal. Calcd. for C₁₈H₁₇N₃O₂: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.21; H, 5.52; N, 13.53.

1-[*N*-(2-Chlorophenyl)aminomethyl]-3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**5e**).

This compound was obtained from the reaction with 2-chloroaniline (**4e**) in a yield of 44 mg (59%) as yellow needles (from acetone), mp 163-164°; ir (potassium bromide): ν max 3399 (NH), 1629 cm^{-1} (C=O); uv (95% ethanol): λ max 205 (log ϵ 4.64), 232 (4.50), 297 (4.03), 310 (3.94), 362 nm (3.83); ^1H nmr (deuteriochloroform): δ 2.51 (3H, s, CH₃), 6.09 (2H, d, J = 8.0 Hz, CH₂), 6.21 (1H, t, J = 8.0 Hz, NH), 6.65 (1H, t, J = 8.0 Hz, 4'-H), 6.75 (1H, dd, J = 10.8, 8.0 Hz, 5-H), 7.06 (1H, d, J = 12.4 Hz, 7-H), 7.13 (1H, t, J = 8.0 Hz, 5'-H), 7.20 (1H, d, J = 8.0 Hz, 6'-H), 7.26 (1H, dd, J = 12.4, 8.0 Hz, 6-H), 7.31 (1H, d, J = 8.0 Hz, 3'-H), 7.39 (1H, d, J = 10.8 Hz, 4-H).

Anal. Calcd. for C₁₆H₁₄ClN₃O: C, 64.11; H, 4.71; N, 14.02. Found: C, 64.31; H, 4.65; N, 13.85.

1-[*N*-(4-Chlorophenyl)aminomethyl]-3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**5f**).

This compound was obtained from the reaction with 4-chloroaniline (**4f**) in a yield of 60 mg (80%) as yellow needles (from acetone), mp 159-160°; ir (potassium bromide): ν max 3398 (NH),

1629 cm^{-1} (C=O); uv (95% ethanol): λ max 203 (log ϵ 4.46), 234 (4.42), 301 (3.92), 361 nm (3.08); ^1H nmr (deuteriochloroform): δ 2.51 (3H, s, CH₃), 5.62 (1H, t, J = 8.0 Hz, NH), 5.98 (2H, d, J = 8.0 Hz, CH₂), 6.76 (1H, dd, J = 10.8, 8.4 Hz, 5-H), 6.84 (2H, d, J = 8.4 Hz, 2'-, 6'-H), 7.04 (1H, d, J = 12.4 Hz, 7-H), 7.09 (2H, d, J = 8.4 Hz, 3'-, 5'-H), 7.27 (1H, dd, J = 12.4, 8.4 Hz, 6-H), 7.42 (1H, d, J = 10.8 Hz, 4-H).

Anal. Calcd. for C₁₆H₁₄ClN₃O: C, 64.11; H, 4.71; N, 14.02. Found: C, 64.37; H, 4.65; N, 13.81.

1-[*N*-(2,4-Dichlorophenyl)aminomethyl]-3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**5g**).

This compound was obtained from the reaction with 2,4-dichloroaniline (**4g**) in a yield of 40 mg (48%) as yellow needles (from ethanol-water), mp 144-145°; ir (potassium bromide): ν max 3317 (NH), 1632 cm^{-1} (C=O); uv (95% ethanol): λ max 206 (log ϵ 4.54), 232 (4.35), 240 (4.33), 298 (3.92), 363 nm (3.71); ^1H nmr (deuteriochloroform): δ 2.51 (3H, s, CH₃), 6.05 (2H, d, J = 8.0 Hz, CH₂), 6.18 (1H, t, J = 8.0 Hz, NH), 6.77 (1H, dd, J = 10.4, 8.0 Hz, 5-H), 7.07 (1H, d, J = 2.4 Hz, 3'-H), 7.07 (1H, d, J = 12.4 Hz, 7-H), 7.09 (1H, dd, J = 8.8, 2.4 Hz, 5'-H), 7.10 (1H, d, J = 8.8 Hz, 6'-H), 7.28 (1H, dd, J = 12.4, 8.0 Hz, 6-H), 7.41 (1H, d, J = 10.4 Hz, 4-H).

Anal. Calcd. for C₁₆H₁₃Cl₂N₃O: C, 57.50; H, 3.92; N, 12.57. Found: C, 57.28; H, 3.98; N, 12.63.

1-[*N*-(2-Bromophenyl)aminomethyl]-3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**5h**).

This compound was obtained from the reaction with 2-bromoaniline (**4h**) in a yield of 40 mg (47%) as yellow needles (from acetone), mp 163-164°; ir (potassium bromide): ν max 3392 (NH), 1628 cm^{-1} (C=O); uv (95% ethanol): λ max 205 (log ϵ 4.63), 232 (4.48), 298 (4.01), 362 nm (3.79); ^1H nmr (deuteriochloroform): δ 2.51 (3H, s, CH₃), 6.08 (2H, d, J = 8.0 Hz, CH₂), 6.23 (1H, t, J = 8.0 Hz, NH), 6.59 (1H, t, J = 8.0 Hz, 4'-H), 6.75 (1H, dd, J = 10.4, 8.4 Hz, 5-H), 7.07 (1H, d, J = 12.4 Hz, 7-H), 7.17 (1H, t, J = 8.0 Hz, 5'-H), 7.27 (1H, dd, J = 12.4, 8.4 Hz, 6-H), 7.30 (1H, d, J = 8.0 Hz, 6'-H), 7.37 (1H, d, J = 8.0 Hz, 3'-H), 7.40 (1H, d, J = 10.4 Hz, 4-H).

Anal. Calcd. for C₁₆H₁₄BrN₃O: C, 55.83; H, 4.10; N, 12.21. Found: C, 55.69; H, 4.09; N, 11.94.

1-[*N*-(4-Bromophenyl)aminomethyl]-3-methyl-1,8-dihydrocycloheptapyrazol-8-one (**5i**).

This compound was obtained from the reaction with 4-bromoaniline (**4i**) in a yield of 62 mg (72%) as yellow needles (from ethanol-water), mp 166-167°; ir (potassium bromide): ν max 3349 (NH), 1630 cm^{-1} (C=O); uv (95% ethanol): λ max 206 (log ϵ 4.49), 235 (4.51), 300 (4.04), 362 nm (3.85); ^1H nmr (deuteriochloroform): δ 2.51 (3H, s, CH₃), 5.63 (1H, t, J = 8.0 Hz, NH), 5.97 (2H, d, J = 8.0 Hz, CH₂), 6.76 (1H, dd, J = 10.8, 8.4 Hz, 5-H), 6.79 (2H, d, J = 8.4 Hz, 2'-, 6'-H), 7.04 (1H, d, J = 12.4 Hz, 7-H), 7.22 (2H, d, J = 8.4 Hz, 3'-, 5'-H), 7.27 (1H, dd, J = 12.4, 8.4 Hz, 6-H), 7.41 (1H, d, J = 10.8 Hz, 4-H).

Anal. Calcd. for C₁₆H₁₄BrN₃O: C, 55.83; H, 4.10; N, 12.21. Found: C, 55.64; H, 4.06; N, 11.96.

3-Methyl-1-[*N*-(3-nitrophenyl)aminomethyl]-1,8-dihydrocycloheptapyrazol-8-one (**5j**).

This compound was obtained from the reaction with 3-nitroaniline (**4j**) in a yield of 50 mg (65%) as yellow needles (from acetic acid), mp 197-198°; ir (potassium bromide): ν max 3306 (NH),

1627 cm^{-1} (C=O); uv (95% ethanol): λ max 198 ($\log \epsilon$ 3.25), 232 (3.45), 300 (2.84), 313 (2.79), 364 nm (2.72); ^1H nmr (deuteriochloroform): δ 2.53 (3H, s, CH_3), 5.92 (1H, t, $J = 8.0$ Hz, NH), 6.05 (2H, d, $J = 8.0$ Hz, CH_2), 6.79 (1H, dd, $J = 10.8, 8.4$ Hz, 5-H), 7.07 (1H, d, $J = 12.4$ Hz, 7-H), 7.19 (1H, d, $J = 8.0$ Hz, 6'-H), 7.27 (1H, t, $J = 8.0$ Hz, 5'-H), 7.30 (1H, dd, $J = 12.4, 8.4$ Hz, 6-H), 7.44 (1H, d, $J = 10.4$ Hz, 4-H), 7.55 (1H, d, $J = 8.0$ Hz, 4'-H), 7.80 (1H, t, $J = 2.4$ Hz, 2'-H).

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_3$: C, 61.93; H, 4.55; N, 18.06. Found: C, 61.77; H, 4.60; N, 17.93.

3-Methyl-1-[*N*-(4-nitrophenyl)aminomethyl]-1,8-dihydrocycloheptapyrazol-8-one (**5k**).

This compound was obtained from the reaction with 4-nitroaniline (**4k**) in a yield of 45 mg (58%) as yellow needles (from ethanol), mp 183-184 $^\circ$; ir (potassium bromide): ν max 3312 (NH), 1628 cm^{-1} (C=O); uv (95% ethanol): λ max 200 ($\log \epsilon$ 4.70), 231 (4.76), 314 (3.63), 362 nm (4.66); ^1H nmr (deuteriochloroform): δ 2.54 (3H, s, CH_3), 6.05 (2H, d, $J = 8.0$ Hz, CH_2), 6.24 (1H, t, $J = 8.0$ Hz, NH), 6.81 (1H, dd, $J = 10.8, 8.4$ Hz, 5-H), 6.93 (2H, d, $J = 8.0$ Hz, 2'-, 6'-H), 7.07 (1H, d, $J = 12.4$ Hz, 7-H), 7.32 (1H, dd, $J = 12.4, 8.4$ Hz, 6-H), 7.45 (1H, d, $J = 10.8$ Hz, 4-H), 8.07 (2H, d, $J = 8.0$ Hz, 3'-, 5'-H).

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_3$: C, 61.93; H, 4.55; N, 18.06. Found: C, 62.11; H, 4.38; N, 18.21.

3-Methyl-1-[*N*-(4-phenylazophenyl)aminomethyl]-1,8-dihydrocycloheptapyrazol-8-one (**5l**).

This compound was obtained from the reaction with 4-aminobenzene (**4l**) in a yield of 50 mg (54%) as orange crystals (from acetone-water), mp 161.5-162.5 $^\circ$; ir (potassium bromide): ν max 3323 (NH), 1632 cm^{-1} (C=O); uv (95% ethanol): λ max 199 ($\log \epsilon$ 4.57), 231 (4.51), 298 (4.06), 309 (4.07), 373 nm (4.44); ^1H nmr (deuteriochloroform): δ 2.54 (3H, s, CH_3), 5.98 (1H, t, $J = 8.0$ Hz, NH), 6.08 (2H, d, $J = 8.0$ Hz, CH_2), 6.78 (1H, dd, $J = 10.8, 8.8$ Hz, 5-H), 7.01 (2H, d, $J = 8.4$ Hz, 2'-, 6'-H), 7.06 (1H, d, $J = 12.4$ Hz, 7-H), 7.29 (1H, dd, $J = 12.4, 8.8$ Hz, 6-H), 7.39 (1H, t, $J = 7.6$ Hz, 4''-H), 7.43 (1H, d, $J = 10.8$ Hz, 4-H), 7.46 (2H, dd, $J = 8.8, 7.6$ Hz, 3''-, 5''-H), 7.80 (2H, d, $J = 8.8$ Hz, 2''-, 6''-H),

7.81 (2H, d, $J = 8.4$ Hz, 3'-, 5'-H).

Anal. Calcd. for $\text{C}_{22}\text{H}_{19}\text{N}_5\text{O}$: C, 71.53; H, 5.18; N, 18.96. Found: C, 71.72; H, 5.22; N, 18.75.

Reaction of 3-Methyl-1,8-dihydrocycloheptapyrazol-8-one (**2**) with 1,3,5-Triarylhexahydro-1,3,5-triazines **6a,c**.

A solution of the compound **2** (40 mg, 0.25 mmole) and the reagent **6a,c** (0.25 mmole) in ethanol (4 ml) was heated for 3 hours on a water bath. After cooling, the precipitate was collected and recrystallized to give the compound **5a,c**.

Compound **5a** was obtained in a yield of 47 mg (71%), mp 138-139 $^\circ$.

Compound **5c** was obtained in a yield of 54 mg (73%), mp 135-136 $^\circ$.

Reaction of 3-Methyl-1,8-dihydrocycloheptapyrazol-8-one (**2**) with Bis(3-nitroanilino)methane (**7**).

A solution of the compound **2** (40 mg, 0.25 mmole) and the reagent **7** (72 mg, 0.25 mmole) in ethanol (4 ml) was refluxed for 3 hours and worked up, as described above, to afford the compound **5j** in a yield of 43 mg (56%).

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