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Synthesis of Pyrazolone Derivatives. XXIII.[1] Benzo[5,6]cyclohepta-[1,2-*c*]pyrazole-3,10-dione and Related Compounds[2]

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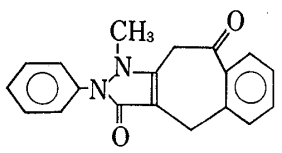
Syntheses of 1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (**3a**) and its aminoalkylidene derivatives (**3b**—**d**) were investigated. Treatment of **3a** with N-bromosuccinimide gave 4(5)-bromo-1-methyl-2-phenyl-1,2,3-trihydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (**13**), while reaction of **3a** with N-chlorosuccinimide produced 2-phenyl-2,3,3a,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta-[1,2-*c*]pyrazole-3,10-dione (**15**). Dehydrogenation of **3a** at 310° with palladium on carbon catalyst afforded 1-methyl-2-phenyl-1,2,3-trihydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (**18**) in a trace.

A previous paper[1] described the synthesis of two new tricyclics: 1-methyl-2-phenyl-1,2,3,9,10-pentahydro-4*H*-benzo[4,5]cyclohepta[1,2-*c*]pyrazole-3,9-dione (**1**) and 1-methyl-2-phenyl-1,2,3,9,10-pentahydro-4*H*-benzo[4,5]cyclohepta[1,2-*c*]pyrazole-3,4-dione (**2**). In this paper we report the synthesis of another new tricycle: 1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (**3a**) and its aminoalkylidene derivatives (**3b**—**d**), expecting pharmacologically interesting properties.



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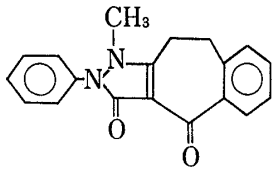

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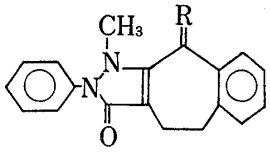

3a : R=O
3b : R=CH(CH$_2$)$_2$N(CH$_3$)$_2$
3c : R=CH(CH$_2$)$_2$N⟨⟩NCH$_3$
3d : R=CH(CH$_2$)$_2$N⟨⟩NCH$_2$CH$_2$OH

Chart 1

The parent compound (**3a**) was prepared as outlined in Chart 2, starting from ethyl α-ethoxalyl-γ-phenylbutyrate[4] (**4**). Condensation of **4** with phenylhydrazine isolated colorless needles ethyl 5-oxo-4-phenethyl-1-phenyl-3-pyrazoline-3-carboxylate (**5**), melted at 78—79° after recrystallization. Careful fractionation of the residue gave colorless prisms, melted at 121—122°. Each compound showed the identical spectral data and the former was easily convertible into the latter by continuous recrystallization from a variety of organic solvents. Consequently these compounds are not tautomer of **5** but polymorphism. Ethyl 2-methyl-5-oxo-4-phenethyl-1-phenyl-3-pyrazoline-3-carboxylate (**6**) was obtained in pure crystalline form by reaction of **5** with dimethyl sulfate, followed by repeated chromatography on silica

1) Part XXII: I. Ito and S. Nagai, *Chem. Pharm. Bull.* (Tokyo), 22, 2131 (1974).
2) A part of this paper was presented at the 92nd Anunal Meeting of Pharmaceutical Society of Japan, Osaka, April 1972.
3) Location: 3-1 *Tanabe-dori, Mizuho-ku, Nagoya.*
4) E.B. Hershberg and L.F. Fieser, "Organic Syntheses," Coll. Vol. II, ed. by A.H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 194.

gel. Treatment of ester (**6**) with 3% methanolic potassium hydroxide led to the formation of 2-methyl-5-oxo-4-phenethyl-1-phenyl-3-pyrazoline-3-carboxylic acid (**7a**). Cyclization was successfully performed to give tricyclic compound (**3a**) in excellent yield when **7a** was heated with polyphosphoric acid under reduced pressure. The Friedel-Crafts reaction of acid chloride (**7b**) was also resulted in preparation of **3a**. The structural assignment of **3a** was made by spectral data as described in the Experimental.

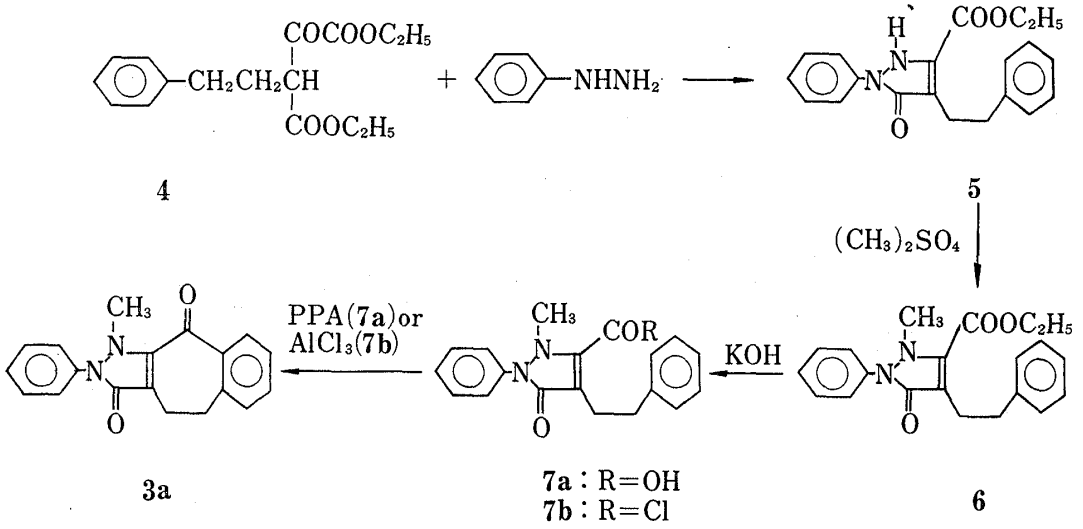

Chart 2

Alkylation of **3a** with dimethylaminopropylmagnesium chloride and heterocyclic aminopropylmagnesium chloride was carried out as shown in Chart 3. Reaction of **3a** with dimethylaminopropylmagnesium chloride in tetrahydrofuran gave 1-methyl-2-phenyl-10-hydroxy-10-(3-dimethylaminopropyl)-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (**8**). Dehydration of **8** was effected by heating in acetic acid-hydrobromic acid to yield 1-methyl-2-phenyl-10-(3-dimethylaminopropylidene)-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]-cyclohepta[1,2-*c*]pyrazol-3-one (**3b**). Attempts to alkylate **3a** with Grignard reagents prepared from 1-methyl-4-chloropiperidine and 1-chloro-3-(4-methylpiperazin-1-yl)propane, however, were resulted in failure and produced a by-product 10-hydroxy-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (**9**), identical with prepared by lithium aluminum hydride reduction of **3a**. This seems due to the reducing capabilities of the particular Grignard reagents which have been often observed[5] when cyclic ketones were involved. An indirect synthetic method was then employed for the preparation of 1-methyl-10-[3-(4-methylpiperazinyl)propylidene]-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (**3c**) and 10-[3-(4-hydroxyethylpiperazinyl)propylidene]-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (**3d**). Treatment of **3a** with Grignard reagent derived from 3-chloro-1-methoxypropane followed by dehydration of the resulting 10-hydroxy-10-(3-methoxypropyl)-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (**10**) with 48% hydrogen bromide afforded corresponding 10-(3-bromopropylidene)-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo-[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (**11**). It has been reported[6] that the olefinic proton of the *trans* 4-(3-methylaminopropylidene)-9,10-dihydro-4*H*-benzo[4,5]cyclohepta[1,2-*b*]thiophene is observed at lower field (τ: 3.90) than that of the corresponding *cis* derivative (τ: 4.35) in nuclear

5) S.O. Winthrop, M.A. Davis, G.S. Myers, J.G. Gavin, R. Thomas and R. Barber, *J. Org. Chem.*, **27**, 230 (1962).
6) J.M. Bastian, A. Ebnöther, E. Jucker, E. Rissi and A.P. Stoll, *Helv. Chim. Acta*, **49**, 214 (1966); *ibid.*, **54**, 293 (1971).

magnetic resonance (NMR) spectrum in dimethyl sulfoxide. The NMR spectrum of compound (**11**) showed the signal due to the olefinic proton at 3.82 τ (dimethyl sulfoxide) which is in the same region as the *trans* derivative described above. This suggests that the olefinic proton is probably in the deshielding area of the pyrazolone ring and shifted down field. Gas liquid chromatography examination (3% Silicon OV-17, 270°) of compound (**11**) showed the existence of only one geometric isomer. In addition, if compound (**11**) is the *cis* isomer, it is difficult to construct molecular models (Dreiding) of the *cis* isomer because of an intense steric interaction between the N-methyl group and the propyl group. On the basis of these data, it seems reasonable to assume that compound (**11**) is the *trans* isomer rather than the *cis* isomer. Compound (**11**) could be used as a common intermediate for the desired **3c** and **3d** which were successfully prepared from the reaction with 4-methylpiperazine and 1-(2-hydroxyethyl)-piperazine respectively.

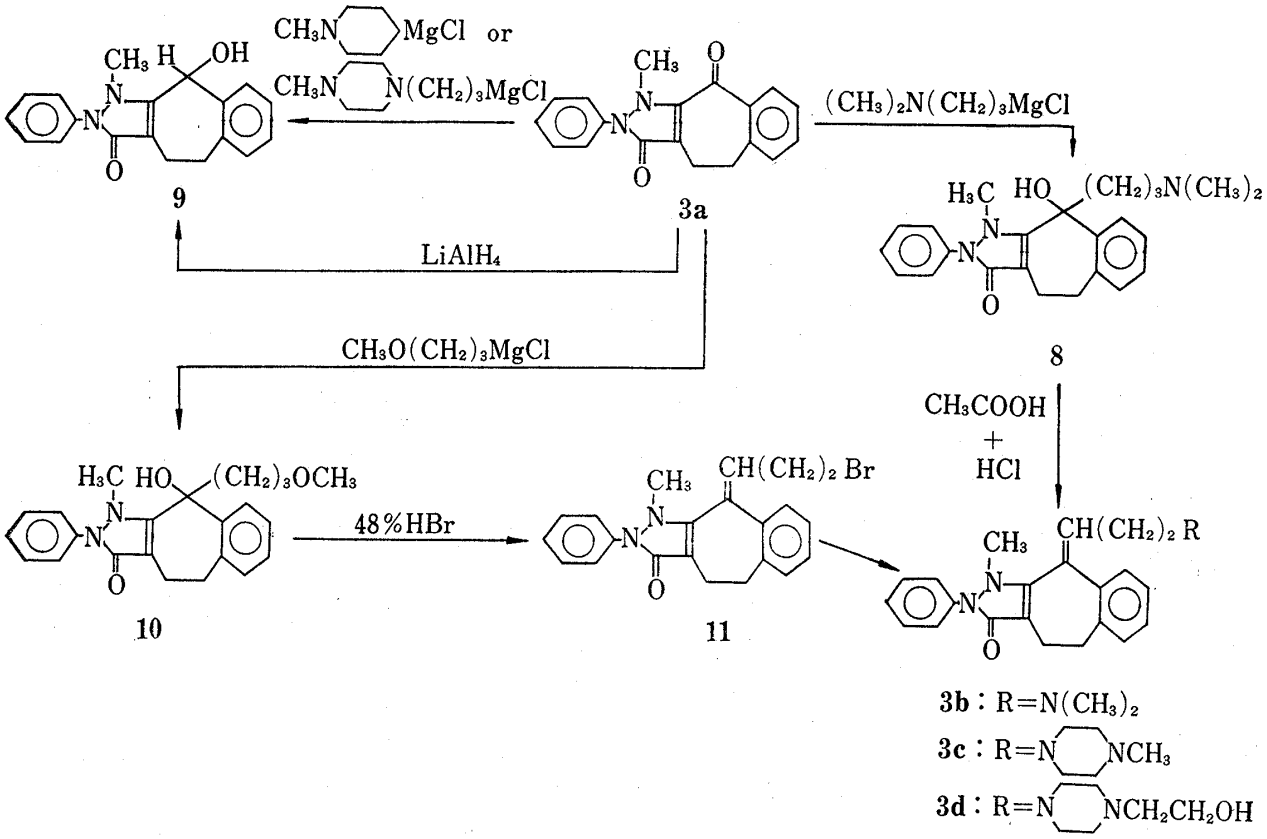

Chart 3

Further attempts were made to prepare 1-methyl-2-phenyl-1,2,3-trihydro-10*H*-benzo-[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (**18**), suitable for subsequent conversion to other derivatives. For the synthesis of **18**, halogenation and dehydrogenation of ethylenic group in the central seven-membered ring of **3a** were carried out as outlined in Chart 4.

Halogenation of **3a** with N-bromosuccinimide (NBS) gave 4(5)-bromo-1-methyl-2-phenyl-1,2,3-trihydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (**13**) in poor yield with recovering the majority of the unchanged starting material. This reaction is recognized to proceed *via* 4,5-dibromo-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta-[1,2-*c*]pyrazole-3,10-dione (**12**), since a remarkable evolution of bromine was observed and bromine apparently arised from the reaction of NBS with hydrogen bromide generated on the thermal decomposition of **12**. The spectral data were fully compatible with the structure assigned to **13**. Continuing efforts to isolate **12** or enhance the yield of **13** consistently gave poor results. Compound (**13**) was converted to 4(5)-cyano-1-methyl-2-phenyl-1,2,3-trihydro-

10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (**14**) on treatment with cuprous cyanide in dimethylformamide. The selective debromination of **13** under hydrogen atmosphere using Raney Nickel failed to obtain desired **18**, with a quantitative amount of **3a** being formed.

Attempted preparation of **18** by halogenation method was unsuccessful as observed above and consequently the direct dehydrogenation using palladium on carbon was investigated under the usual condition. Heating of **3a** with 20% palladium on carbon at the boiling temperature of decalin resulted in reduction of carbonyl group to yield 1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (**16**) in quantitative yield. Characterization of **16** was made by spectral data and also by its conversion to 10-bromo-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (**17**) on treatment with bromine in acetic acid. By a modification of the published method,[7] **3a** was then treated with 20% palladium on carbon at 310° without solvent. The gas chromatography analysis showed the formation of the new product with complete disappearing of the starting material. Repeated purification of the resulting residue by chromatography on silicagel encountered with great difficulty, giving less than 5% of the desired product (**18**) which was very unstable and difficult to purify.

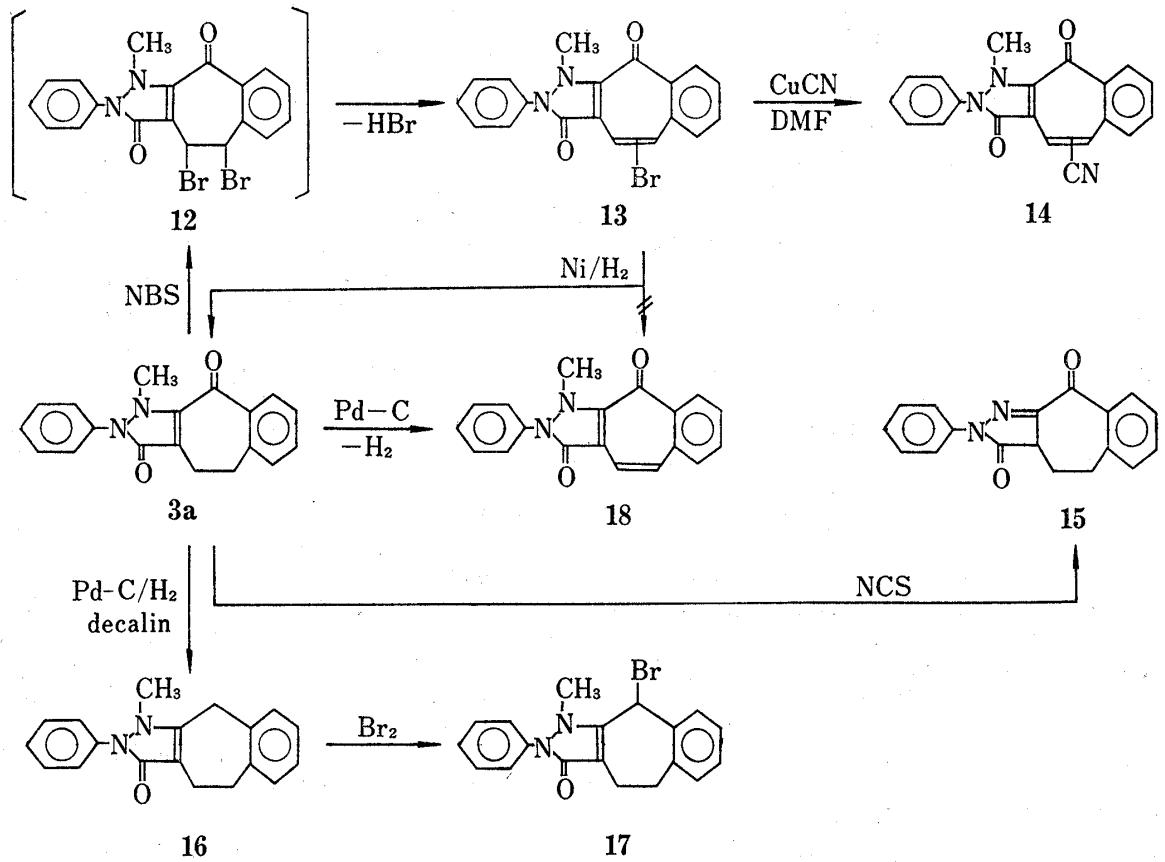

Chart 4

Experimental

Melting points were determined on a Yanagimoto Micro-melting Point apparatus and uncorrected. Infrared (IR) spectra were determined with a Nihon Bunko Model IR-G spectrophotometer. Nuclear magnetic resonance (NMR) spectra were determined on a Japan Electron optics Laboratory Co. JNM-MH-60 spectrometer and all shifts are relative to tetramethylsilane as an internal standard.

Ethyl 5-Oxo-4-phenethyl-1-phenyl-3-pyrazoline-3-carboxylate (**5**)——A mixture of 2 g (0.007 mole) of ethyl α-ethoxalyl-γ-phenylbutylate[4] and 0.74 g (0.007 mole) of phenylhydrazine was heated at 90° for

7) J. Blum and S. Biger, *Tetrahedron Letters*, **1970**, 1825.

3 hr and dissolved in ethyl acetate. After dried over magnesium sulfate, ethyl acetate was evaporated to dryness. The resulting viscous oil was triturated with ether on cooling to give white solid. Recrystallization from ether-petroleum ether gave colorless needles, mp 78—79°. Yield 0.33 g (14%). From the mother liquid were obtained colorless prisms, mp 121—122° after recrystallization from ether–petroleum ether. Yield 1.3 g (55%). The former was convertible into the latter by repeated recrystallization. *Anal.* Calcd. for $C_{20}H_{20}O_3N_2$: C, 71.41; H, 5.99; N, 8.32. Found: C, 71.32; H, 5.94; N, 8.20. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1727 (COO-C_2H_5). NMR ($CDCl_3$) τ: 5.60 (2H, quartet, J=7.5 Hz, $C\underline{H}_2CH_3$), 7.15 (4H, broad singlet, CH_2CH_2), 8.66 (3H, triplet, J=7.5 Hz, $CH_2C\underline{H}_3$).

Ethyl 2-Methyl-5-oxo-4-phenethyl-1-phenyl-3-pyrazoline-3-carboxylate (6)——A suspension of 8.5 g (0.025 mole) of **5** and 12.7 (0.1 mole) of dimethylsulfate was stirred at 110° for 1 hr. To the resulting oil was added 50 ml of dry toluene and the stirring was continued for additional 2 hr. The reaction mixture was neutralized with 10% sodium bicarbonate and extracted with chloroform. Removal of chloroform gave a dark red oil which was chromatographed on silicagel. Elution with chloroform gave yellow solid. Recrystallization from ether–petroleum ether gave pale yellow needles, mp 78—80°. Yield 6.4 g (73%). *Anal.* Calcd. for $C_{21}H_{22}O_3N_2$: C, 71.98; H, 6.33; N, 7.99. Found: C, 71.64; H, 6.03; N, 7.80. NMR ($CDCl_3$) τ: 6.85 (3H, singlet, N–CH_3).

2-Methyl-5-oxo-4-phenethyl-1-phenyl-3-pyrazoline-3-carboxylic Acid (7a)——A mixture of 17 g (0.048 mole) of **6** and 300 ml of 3% methanolic potassium hydroxide was allowed to stand for 24 hr and evaporated *in vacuo*. The resulting residue was dissolved in water and the solution was acidified with 10% hydrochloric acid to afford precipitates. Recrystallization from ethyl acetate gave colorless plates, mp 175—177°. Yield 9 g (58%). *Anal.* Calcd. for $C_{19}H_{18}O_3N_2$: C, 70.79; H, 5.62; N, 8.69. Found: C, 70.51; H, 5.42; N, 8.54. IR ν_{max}^{KBr} cm^{-1}: 1725 (COOH).

1-Methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (3a)——a) A solution of 3 g (0.0093 mole) of **7a** and 66 g of polyphosphoric acid was stirred at 180—190° under reduced pressure. After 6 hr, the mixture was treated with cracked ice and the resulting solution was made alkaline with powdered potassium carbonate. The green solid precipitated was extracted with chloroform. Removal of chloroform left light green powders. Recrystallization from isopropyl ether gave light green needles, mp 170—171°. Yield 2 g (71%). *Anal.* Calcd. for $C_{19}H_{16}O_2N_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 75.07; H, 5.37; N, 9.26. IR ν_{max}^{KBr} cm^{-1}: 1670 (C=O), 1650 (CON<). UV λ_{max}^{EtOH} mμ(log ε): 295 (4.19). NMR ($CDCl_3$) τ: 6.72 (3H, singlet, N–CH_3), 6.95—7.03 (4H, multiplet, CH_2CH_2). Mass Spectrum *m/e*: 304 (M^+).

b) A solution of 0.5 g (0.0016 mole) of **7a** and 0.55 g of thionyl chloride in 10 ml of dry chloroform was refluxed for 2 hr and evaporated to dryness. The residual crude acid chloride (**7b**) was dissolved in 20 ml of dry tetrachloroethane containing 0.63 g (0.0048 mole) of aluminum chloride. The mixture was heated at 120° for 4 hr, treated with water and extracted with chloroform. Removal of extracts left a viscous oil. Chromatography on aluminum oxide with chloroform as an eluent provided green powders which were recrystallized from isopropyl ether to give light green needles, mp 170—171°, identical by IR spectrum and mixture melting point with **3a** obtained in procedure a).

1-Methyl-2-phenyl-10-hydroxy-10-(3-dimethylaminopropyl)-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (8)——To 0.12 g (0.005 mole) of magnesium and 5 ml of dry tetrahydrofuran was added a few crystals of iodine. One milliliter of ethyl bromide was then added, followed by 0.6 g (0.005 mole) of dimethylaminopropyl chloride in 10 ml of dry tetrahydrofuran. The formation of the Grignard reagent started immediately. A solution of 0.5 g (0.002 mole) of **3a** in 10 ml of dry tetrahydrofuran was added dropwise and the mixture was heated under reflux for 20 hr. The Grignard complex was decomposed with 20% ammonium chloride and the resulting solution was extracted with chloroform. The extracts were concentrated to give a brown oil which was chromatographed on silicagel. Elution with chloroform afforded crystals. Recrystallization from ether gave colorless prisms, mp 139—141°. Yield 0.32 g (51%). *Anal.* Calcd. for $C_{24}H_{29}O_2N_3$: C, 73.63; H, 7.47; N, 10.73. Found: C, 73.80; H, 7.47; N, 10.74. IR ν_{max}^{KBr} cm^{-1}: 3240 (OH), 1650 (CON<).

1-Methyl-2-phenyl-10-(3-dimethylaminopropylidene)-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (3b)——A solution of 0.1 g (0.0003 mole) of **8**, 3 ml of concentrated hydrochloric acid and 6 ml of glacial acetic acid was refluxed for 4 hr and evaporated to dryness. The residue was dissolved in water, made alkaline and extracted with chloroform. Removal of chloroform afforded crystals which were recrystallized from ether to give colorless prisms, mp 170—172°. Yield 0.08 g (84%). *Anal.* Calcd. for $C_{24}H_{27}ON_3$: C, 77.18; H, 7.29; N, 11.25. Found: C, 77.25; H, 7.24; N, 11.30. IR ν_{max}^{KBr} cm^{-1}: 1680 (CON<).

Grignard Reaction of 3a with 4-Chloro-1-methylpiperidine and 1-Chloro-3-(4-methylpiperazin-1-yl)-propane——The Grignard reagents derived from 0.005 mole of chlorides and 0.005 mole of magnesium in 10 ml of tetrahydrofuran were reacted with 0.8 g (0.003 mole) of **3a** under reflux for 5 hr and worked up as described in preparation of **8**. Trituration of the work-up residue with ether gave 10-hydroxy-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (**9**). An analytical sample was obtained by recrystallization from methanol–chloroform: colorless prisms, mp 265°. Yield 68—81%. *Anal.* Calcd. for $C_{19}H_{18}O_2N_2$: C, 74.49; H, 5.92; N, 9.14. Found: C, 74.41; H, 6.03; N, 8.98. IR ν_{max}^{KBr} cm^{-1}: 3260 (OH), 1625 (CON<). Mass Spectrum *m/e*: 306 (M^+).

10-Hydroxy-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (9)——A mixture of 0.3 g (0.001 mole) of **3a**, 0.02 g of lithium aluminum hydride and 25 ml of tetrahydrofuran was heated under reflux for 4 hr and decomposed by addition of moist tetrahydrofuran and aqueous acetic acid. The resulting solution was extracted with chloroform. The chloroform layer was washed with water and dried over magnesium sulfate. Evaporation of the solvent yielded a viscous oil which solidified on standing. Recrystallization from methanol gave colorless prisms, mp 265°: identical by IR spectrum and mixture melting point with **9** obtained as a by-product on the reaction of **3a** with Grignard reagents.

10-Hydroxy-10-(3-methoxypropyl)-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (10)——The Grignard reagent derived from 0.57 g (0.005 mole) of 3-chloro-1-methoxypropane and 0.13 g (0.005 mole) of magnesium in 10 ml of dry tetrahydrofuran was treated with 0.8 g (0.003 mole) of **3a** and heated under reflux for 5 hr. After cooling, the mixture was poured into ice water containing an excess of ammonium chloride. The oil was taken up in chloroform and evaporation of chloroform gave a viscous oil. Chromatography on silicagel gave **10** as a colorless oil in 51% yield with **9** in 8% yield. The crude oily **10** was used in the next experiment without further purification.

trans-10-(3-Bromopropylidene)-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]-pyrazol-3-one (11)——A mixture of 0.58 g of crude **10** and 17 ml of 48% hydrobromic acid was refluxed for 2 hr. Water was added and the resulting precipitates were taken up in chloroform which was evaporated *in vacuo*. The residue was recrystallized from ethanol to give colorless prisms, mp 180—182°. Yield 0.5 g. *Anal.* Calcd. for $C_{22}H_{21}ON_2Br$: C, 64.55; H, 5.17; N, 6.84. Found: C, 64.26; H, 5.10; N, 6.83. NMR (DMSO-d_6) τ: 3.82 (1H, broad singlet, *trans* olefinic proton[6]), 6.92—7.04 (8H, multiplet, $2\times CH_2CH_2$); NMR (100 MHz, CF_3COOD–$CDCl_3$) τ: 3.64 (1H, triplet, J=7.5 Hz, *trans* olefinic proton).

1-Methyl-10-[3-(4-methylpiperazinyl) propylidene]-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (3c)——A solution of 0.25 g (0.0006 mole) of **11** and 0.2 g (0.002 mole) of 4-methylpiperazine in 5 ml of dry toluene was refluxed with stirring for 20 hr and evaporated to dryness. The resulting residue was extracted with 10% hydrochloric acid and the acidic layer was made alkaline with sodium hydroxide. The product precipitated was extracted with chloroform. Removal of solvent gave 0.23 g (88%) of a light brown oily product which was treated with hydrochloric acid. The dihydrochloride was recrystallized from isopropyl alcohol to give colorless prisms, mp 269—272° (decomp.). *Anal.* Calcd. for $C_{27}H_{32}ON_4\cdot 2HCl$: C, 64.67; H, 6.83; N, 11.17. Found: C, 64.39; H, 6.86; N, 10.96.

10-{3-[4-(2-Hydroxyethyl)piperazinyl]propylidene}-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (3d)——This material was prepared from 0.25 g (0.0006 mole) of **11** and 0.26 g (0.002 mole) of 1-(2-hydroxyethyl)piperazine by the same procedure described in the preparation of **3c**. Yield 0.19 g (68%). The oily **3d** was treated with maleic acid. Recrystallization from acetone–methanol gave colorless plates, mp 178—179°. *Anal.* Calcd. for $C_{28}H_{34}O_2N_4\cdot 2C_4H_4O_4$: C, 62.60; H, 6.13; N, 8.11. Found: C, 62.45; H, 6.17; N, 7.87.

4(5)-Bromo-1-methyl-2-phenyl-1,2,3-trihydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (13)——A mixture of 0.35 g (0.002 mole) of N-bromosuccinimide, 0.5 g (0.0016 mole) of **3a**, 0.05 g of benzoyl peroxide and 150 ml of carbon tetrachloride was heated under reflux for 4 hr. During the reaction a vigorous evolution of bromine was observed. The mixture was filtered to separate succinimide and the filtrate was washed with water. Removal of solvent gave a viscous oil which was dissolved in chloroform and chromatographed on silica gel. From the first elution was obtained yellow needles, mp 152—153° after recrystallization from isopropyl ether. Yield 0.075 g (12%). *Anal.* Calcd. for $C_{19}H_{13}O_2N_2Br$: C, 59.86; H, 3.44; N, 7.35; Br, 20.96. Found: C, 59.69; H, 3.30; N, 7.32; Br, 20.96. NMR ($CDCl_3$) τ: 2.19 (1H, singlet, olefinic proton). Mass Spectrum *m/e*: 382 (M^++2, 97% intensity of M^+), 380 (M^+). From the second elution was recovered 0.25 g of the unchanged starting material **3a**.

4(5)-Cyano-1-methyl-2-phenyl-1,2,3-trihydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (14)——A mixture of 0.05 g (0.00015 mole) of **13**, 0.02 g (0.0002 mole) of cuprous cyanide and 10 ml of dimethylformamide was refluxed for 4 hr. The reaction mixture was cooled and dissolved in a mixture of chloroform and 10% ammonium hydroxide. The chloroform layer was successively washed with 10% hydrochloric acid and water. The product obtained after evaporation of the solvent was recrystallized from isopropyl ether–methanol to give yellow needles, mp 189—191°. Yield 0.035 g (82%). *Anal.* Calcd. for $C_{20}H_{13}O_2N_3$: C, 73.38; H, 4.00; N, 12.84. Found: C, 73.38; H, 4.02; N, 12.96. IR ν_{max}^{KBr} cm^{-1}: 2210 (CN).

2-Phenyl-2,3,3a,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (15)——To a hot solution of 1 g (0.003 mole) of **3a**, 0.05 g of benzoyl peroxide and 100 ml of dry chloroform was added portionwise 1.3 g (0.009 mole) of N-chlorosuccinimide under irradiation of 350 W mercury lamp. The mixture was refluxed for 5 hr, washed with water and evaporated to dryness. The residue was chromatographed on silica gel. Elution with chloroform gave light brown solid. Recrystallization from methanol–chloroform afforded colorless prisms, mp 197—199° (decomp.). Yield 0.1 g (14%). *Anal.* Calcd. for $C_{18}H_{14}O_2N_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.57; H, 4.68; N, 9.66. IR ν_{max}^{KBr} cm^{-1}: 1730 (C=O), 1670 (CON<). NMR ($CDCl_3$) τ: 6.90—7.68 (5H, multiplet, 3a-position proton and CH_2CH_2). Mass Spectrum *m/e*: 290 (M^+).

1-Methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (16)——A mixture of 0.5 g (0.0016 mole) of **3a**, 0.35 g of 20% palladium on carbon and 30 ml of dry decalin was heated under reflux for 24 hr. The hot mixture was filtered by suction and the filtrate was evaporated to dryness. The residue was recrystallized from acetone to give colorless prisms, mp 226—228°. Yield 0.42 g (88%). *Anal.* Calcd. for $C_{19}H_{18}ON_2$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.77; H, 6.18; N, 9.64. IR ν_{max}^{KBr} cm^{-1}: 1643 (CON<). NMR ($CDCl_3$) τ: 5.97 (2H, broad singlet, benzylic protons). Mass Spectrum *m/e*: 290 (M^+).

10-Bromo-1-methyl-2-phenyl-1,2,3,4,5-pentahydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazol-3-one (17)——To a solution of 0.2 g (0.0006 mole) of **16** and 5 ml of acetic acid was added 0.48 g (0.003 mole) of bromine in 3 ml of acetic acid. The mixture was refluxed for 3 hr and evaporated to dryness. The residue was dissolved in chloroform and washed with 10% sodium carbonate. The chloroform layer was separated and concentrated to give yellow solid. Recrystallization from acetone gave pale yellow plates, mp 207—209° (decomp.). Yield 0.18 g (82%). *Anal.* Calcd. for $C_{19}H_{17}ON_2Br$: C, 61.80; H, 4.64; N, 7.59. Found: C, 61.51; H, 4.68; N, 7.34. NMR (CD_3COOD) τ: 3.69 (1H, singlet, benzylic proton), 6.90—7.28 (4H, multiplet, CH_2CH_2).

1-Methyl-2-phenyl-1,2,3-trihydro-10*H*-benzo[5,6]cyclohepta[1,2-*c*]pyrazole-3,10-dione (18)——A mixture of 0.73 g (0.002 mole) of **3a** and 0.8 g of 30% palladium on carbon heated at 310° for 15 min. The reaction mixture was analyzed by gas chromatography on a 1 m×3 mm vpc column packed with 1.5% Silicon OV-17 on Chromosorb AW. The dehydrogenated compound was isolated from the reaction mixture by chromatography on silicagel: mp 148—151° (decomp.). Yield 0.035 g (4.8%). This material was very labile and recrystallization was unsuccessful. *Anal.* Calcd. for $C_{19}H_{14}O_2N_2$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.02; H, 4.67; N, 9.14. NMR ($CDCl_3$) τ: 2.11—2.57 (11H, multiplet, olefinic protons and aromatic protons), 6.49 (3H, singlet, N–CH_3). Mass Spectrum *m/e*: 302 (M^+).

Hydrogenation of 13——A mixture of 0.02 g (0.00005 mole) of **13**, 0.025 g of Raney nickel and 0.01 g of sodium bicarbonate in 95% ethanol was hydrogenated at room temperature. The catalyst was filtered and the filtrate was evaporated to dryness. The residue was recrystallized from isopropyl ether to give light green needles, mp 170—171°, identical by IR spectrum and mixture melting point with **3a**.

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