

N. R. El-Rayyes* and N. H. Bahtiti

Department of Chemistry, Kuwait University,
Kuwait

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Aryl aldehydes **I** reacted with 1-benzosuberone to yield the corresponding 2-arylidene-1-benzosuberones **II**. Condensation of **II** with hydrazine and its derivatives provided the substituted 2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazoles **III-VI** respectively. The structures of all products were assigned by chemical and spectroscopic methods.

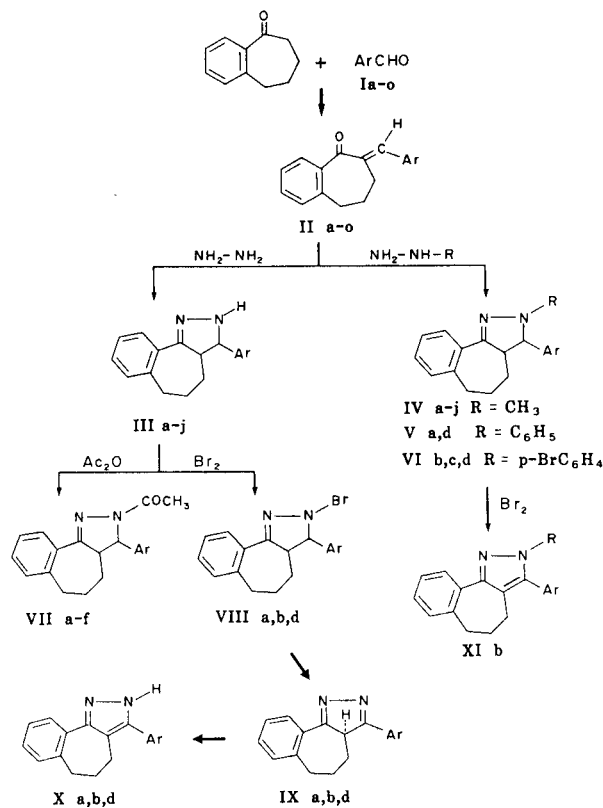
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The reaction of hydrazines with different chalcones was previously reported [1-4]. In the present work different aryl aldehydes **Ia-o** were condensed with 1-benzosuberone to give the corresponding 2-arylidene-1-benzosuberones **IIa-o**. The structure of these chalcones is evident from the infrared, electronic and ¹H nmr spectral data [5].

The chalcones **IIa-m** were condensed with hydrazine, methylhydrazine, phenylhydrazine, and *p*-bromophenylhydrazine to provide the corresponding 3-aryl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazoles **III**, 2-methyl-3-aryl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazoles **IV**, 2-phenyl-3-aryl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazoles **V**, and 2-(*p*-bromophenyl)-3-aryl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazoles **VI** (Scheme 1). The structures of the products were assigned from their spectral and chemical properties. Thus the infrared spectra show stretching vibrations characteristic for C=N and NH groups [4,6]. The electronic spectra of compounds **III-VI** show absorption maxima ascribed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The latter can be correlated to the Ar-C=N-N-X chromophores [1,4,7]. The long wavelength band is affected by the nature of both Ar and X. A bathochromic shift can be detected by going from compound **III** to **VI** [1].

The nmr-spectra of **III-VI** revealed four main chemical shifts. The (-CH₂CH₂CH₂CH-) moieties were represented by multiplets in the range of δ 1.66-3.00 ppm. The doublets representing H₃ appeared in the region δ 3.30-5.41 ppm (*J* = 12-14 Hz). The N-H protons of compounds **III** showed one signal in the range of δ 4.66-5.86 ppm, which disappeared upon deuteration. However, the N-CH₃ groups of compounds **IV** were represented by 3H singlets in the range of δ 2.20-2.86 ppm. The aromatic hydrogens showed multiplets in the range of δ 5.83-8.43 ppm [4,8,9]. The mass spectra is also in good accord with the structure of compounds **III**. Thus **IIIb,c,d,h** show *m/e* at 307 (100%), 312 (100%), 296 (100%) and 306 (100%), respectively representing both molecular ion and base peaks [4,10].

Scheme 1



Compound	Ar
I-Xa	<i>p</i> -OCH ₃ -C ₆ H ₄
I-IV, VII-XIb	<i>p</i> -NO ₂ -C ₆ H ₄
I-VIIc	C ₁₀ H ₇ (1-naphthyl)
I, IV, Vd, VIb	C ₆ H ₅
I-IV, VIIe	2,6-Cl ₂ -C ₆ H ₃
I-IVf	C ₄ H ₃ S (2-thienyl)
I, II, IVg	C ₈ H ₇ (3-indolyl)
I-IVh	C ₇ H ₆ O ₂ (3,4-methylenedioxy-phenyl-)
I-II, IVi	C ₅ H ₄ N (3-pyridyl)
I-IVj	C ₄ H ₃ S (3-thienyl)

I-III, III, VI-VII, Xd	<i>p</i> -Cl-C ₆ H ₄
I-III, IIIg, VIII	C ₆ H ₇ N 2-(1-methyl-pyrrolyl)
I, II, III	<i>m</i> -NO ₂ -C ₆ H ₄
I-II	2,4-(OCH ₃) ₂ C ₆ H ₃
I-IIo	<i>p</i> -Br-C ₆ H ₄

The chemical reactivity of compounds **III** can serve as a tool for their structural elucidation. Thus acetylation led to the formation of the corresponding 2-acetyl-3-aryl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazoles **VIIa-f**. The structure of these products can be predicted by their chemical and spectral analyses. Thus, the infrared spectra of compounds **VII** show absorption bands in the regions 1600 cm⁻¹ and 1670 cm⁻¹ attributed to C=N and C=O of the acetyl group [9]. The electronic spectra revealed absorptions that can be assigned to $\pi \rightarrow \pi^*$ transitions of the *N*-acetyl chromophores [7]. The nmr-spectra were void of signals representing the N-H protons, and showed 3H singlets which stand for the protons of the *N*-acetyl groups. The mass spectrum of **VIIb** showed a molecular ion peak at *m/e* 305 (100%) which stands also for the base peak.

The condensed pyrazoles **IIIa,b** were also reacted with bromine to produce the *N*-bromo derivatives **VIIIa,b**. Dehydrobromination of these products gave the condensed pyrazoles **Xa,b**. The structure of compounds **VIII** and **X** was deduced by chemical and spectral analyses. The formation of the pyrazoles **Xa,b** seems to proceed *via* the formation of the intermediates **IXa,b** followed by 1,3-intramolecular proton shift [11]. It is noteworthy to mention that the bromination of **IIIc** and **IVb** gave directly the corresponding condensed tetrahydropyrazole **Xd** and *N*-methyl analog **XIb** *via* bromination, [12].

The formation of the compounds **III-VI** seems to proceed by 1,2-addition of the hydrazines to chalcones to produce the corresponding hydrazones, followed by cyclization [1-4,7,13,14].

EXPERIMENTAL

General Procedure for the Preparation of 2-Arylidene-1-benzosuberones **IIa-o**.

Equimolar amounts of the aldehydes **Ia-o** (0.03 mole) and 1-benzosuberone (0.03 mole) were dissolved in 50 ml ethanol. The mixture was treated with 1.0 g of potassium hydroxide and stirred for 1-2 hours by room temperature. The product was filtered and recrystallized from ethanol.

2-*p*-Nitrobenzylidene-1-benzosuberone (**IIb**).

This compound was obtained in 96% yield as yellowish needles (ethanol), mp 140-141°; ir (potassium bromide): C=O 1660, C=C 1610, 1595 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.60-3.00 (bm, 6H, CH₂CH₂CH₂), 7.13-8.26 ppm (bm, 9H, ArH + CH); uv (ethanol): λ max 271 nm (ϵ 20040).

Anal. Calcd. for C₁₈H₁₅NO₂ (293.32): C, 73.70; H, 5.15; N, 4.77. Found: C, 73.64; H, 5.23; N, 4.72.

2-(2,6-Dichlorobenzylidene)-1-benzosuberone (**IIe**).

This compound was obtained in 78% yield as colourless needles from ethanol, mp 136°; ir (potassium bromide): C=O 1660, C=C 1600 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.60-3.07 (bm, 6H, CH₂CH₂CH₂), 7.25-7.90 ppm (bm, 8H, Ar-H + CH); uv (ethanol): λ max 262 nm (ϵ 10525).

Anal. Calcd. for C₁₈H₁₄Cl₂O (317.30): C, 68.13; H, 4.44. Found: C, 67.76; H, 4.48.

2-(3,4-Methylenedioxybenzylidene)-1-benzosuberone (**IIh**).

This compound was obtained as colourless needles from ethanol (98%) mp 124°; ir (potassium bromide): C=O 1670, C=C 1600 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.73-3.13 (bm, 6H, CH₂CH₂CH₂), 6.00 (s, 2H, OCH₂O), 6.72-7.80 ppm (bm, 8H, Ar-H + CH); uv (ethanol): λ max 344 nm (ϵ 8510), 300 nm (ϵ 5130), 259 nm (ϵ 12265).

Anal. Calcd. for C₁₉H₁₆O₃ (292.34): C, 78.06; H, 5.51. Found: C, 78.23; H, 5.56.

2-(*m*-Nitrobenzylidene)-1-benzosuberone (**IIm**).

This compound was obtained as yellow needles from ethanol (96%) mp 98°; ir (potassium bromide): C=O 1668, C=C 1610 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.00-3.10 (bm, 6H, CH₂CH₂CH₂), 7.20-8.40 ppm (bm, 9H, ArH + CH); uv (ethanol): λ max 268 nm (ϵ 18520).

Anal. Calcd. for C₁₈H₁₅NO₂ (293.32): C, 73.70; H, 5.15; N, 4.77. Found: C, 73.54; H, 5.18; N, 4.78.

2-(2,4-Dimethoxybenzylidene)-1-benzosuberone (**IIn**).

This compound was obtained as colourless needles from ethanol (80%) mp 106°; ir (potassium bromide): C=O 1660, C=C 1605 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.86-3.10 (bm, 6H, CH₂CH₂CH₂), 3.95 (d, 6H, 2-OCH₃), 6.46-8.13 ppm (bm, 8H, ArH + CH); uv (ethanol): λ max 348 nm (ϵ 11740), 300 nm (ϵ 6070), 254 nm (ϵ 14000).

Anal. Calcd. for C₂₀H₂₀O₃ (308.38): C, 77.89; H, 6.54. Found: C, 77.75; H, 6.61.

2-*p*-Bromobenzylidene-1-benzosuberone (**IIo**).

This compound was obtained as white needles from ethanol (96%) mp 99°; ir (potassium bromide): C=O 1660, C=C 1590 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.80-3.00 (bm, 6H, CH₂CH₂CH₂), 7.03-7.87 ppm (bm, 9H, ArH + CH); uv (ethanol): λ max 303 nm (ϵ 19700).

Anal. Calcd. for C₁₈H₁₅BrO (327.22): C, 66.07; H, 4.62; Br, 24.42. Found: C, 65.95; H, 4.62; Br, 24.59.

General Procedure for the Preparation of 3-Aryl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazoles **IIIa-j**.

To a solution of 0.02 mole of 2-arylidene-1-benzosuberone **II** in 50 ml ethanol, 0.06 mole of hydrazine hydrate were added. The mixture was refluxed for 3-4 hours. The product was obtained after concentration of the solution and crystallized from cyclohexane.

3-(*p*-Methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**IIIa**).

This compound was obtained as white needles from cyclohexane (88%) mp 114-115°; ir (potassium bromide): N-H 3340, C=N 1620 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.70-3.00 (bm, 7H, CH₂CH₂CH₂CH), 3.76 (s, 3H, OCH₃) 4.26 (d, 1H, CH, J_H, 12), 4.73 (d, 1H, NH), 6.66-7.80 ppm (bm, 8H, ArH + CH); uv (ethanol): λ max 278 nm (ϵ 11520).

Anal. Calcd. for C₁₉H₂₀N₂O (292.38): C, 78.05; H, 6.90; N, 9.58. Found: C, 77.91; H, 7.00; N, 9.62.

3-(*p*-Nitrophenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**IIIb**).

This compound was obtained as yellow prisms from cyclohexane (74%) mp 162°; ir (potassium bromide): N-H 1668, C=N 1609 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.73-2.90 (bm, 7H, CH₂CH₂CH₂CH), 4.56 (d,

1H, CH, J_{H} , 12), 5.03 (s, 1H, N-H), 7.06-8.26 ppm (bm, 8H, Ar-H); (ethanol): λ max 277 nm (ϵ 16770); ms: m/e 307 (M^+), 185 ($C_{12}H_{12}N_2$).

Anal. Calcd. for $C_{18}H_{17}N_3O_2$ (307.35): C, 70.35; H, 5.54; N, 13.73. Found: C, 70.52; H, 5.65; N, 13.79.

3-(α -Naphthyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (IIIc).

This compound was obtained as white needles from cyclohexane (85%) mp 116-117°; ir (potassium bromide): N-H 3340, C=N 1605 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.60-3.20 (bm, 7H, $CH_2CH_2CH_2CH$), 5.2 (d, 1H, CH, J_{H} , 12), 5.61 (s, 1H, N-H), 6.46-8.26 ppm (bm, 11H, Ar-H); uv (ethanol): λ max 288 nm (ϵ 132.94); ms: (m/e) 312 (M^+), 185 ($C_{12}H_{12}N_2$).

Anal. Calcd. for $C_{22}H_{20}N_2$ (312.54): C, 84.55; H, 6.41; N, 9.00. Found: C, 84.43; H, 6.45; N, 8.92.

3-(*p*-Chlorophenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (III d).

This compound was obtained as white prisms from cyclohexane (96%) mp 111°; ir (potassium bromide): N-H 3360, C=N 1600 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.32-4.00 (bm, 7H, $CH_2CH_2CH_2CH$), 4.66 (d, 1H, CH, J_{H} , 12), 5.86 (s, 1H, N-H), 7.4-8.53 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 277 nm (ϵ 10420); ms: (m/e) 296 (M^+), 185 ($C_{12}H_{12}N_2$).

Anal. Calcd. for $C_{17}H_{17}ClN_2$ (298.89): C, 72.80; H, 5.74; N, 9.50; Cl, 11.94. Found: C, 72.70; H, 5.83; N, 9.42; Cl, 12.13.

3-(2,6-Dichlorophenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (III e).

This compound was obtained as white prisms from cyclohexane (71%) mp 149-150°; ir (potassium bromide): N-H 3310, C=N 1588 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.76-3.53 (bm, 7H, $CH_2CH_2CH_2CH$), 5.41 (d, 1H, CH, J_{H} , 12), 5.73 (s, 1H, N-H), 7.0-7.90 ppm (bm, 7H, Ar-H); uv (ethanol): λ max 282 nm (ϵ 6010).

Anal. Calcd. for $C_{15}H_{14}Cl_2N_2$ (331.27): C, 65.20; H, 4.80; N, 8.50; Cl, 21.40. Found: C, 65.15; H, 4.90; N, 8.56; Cl, 21.32.

3-(2-Thienyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (III f).

This compound was obtained as brown prisms from cyclohexane (93%) mp 82°; ir N-H 3320, C=N 1604, C=C 1580 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.66-3.00 (bm, 7H, $CH_2CH_2CH_2CH$), 4.7 (d, 1H, CH, J_{H} , 12), 5.66 (s, 1H, N-H), 6.90-8.00 ppm (bm, 7H, Ar-H); uv (ethanol): λ max 282 nm (ϵ 15480); λ max 215 nm (ϵ 20810).

Anal. Calcd. for $C_{15}H_{14}N_2S$ (268.37): C, 71.60; H, 6.00; N, 10.43; S, 11.95. Found: C, 71.40; H, 5.95; N, 10.26; S, 11.90.

3-(1-Methylpyrrol-2-yl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (III g).

This compound was obtained as white needles from cyclohexane (94%) mp 98°; ir (potassium bromide): N-H 3310, C=N 1615 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.80-3.20 (bm, 7H, $CH_2CH_2CH_2CH$), 3.66 (s, 3H, N-CH₃), 4.45 (d, 1H, CH, J_{H} , 12), 5.16 (s, 1H, N-H), 5.83-7.80 ppm (bm, 7H, Ar-H); uv (ethanol): λ max 277 nm (ϵ 9840), 215 nm (ϵ 15290).

Anal. Calcd. for $C_{17}H_{19}N_3$ (265.36): C, 76.94; H, 7.21; N, 15.83. Found: C, 76.81; H, 7.30; N, 15.89.

3-(3,4-Methylenedioxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (III h).

This compound was obtained as colourless prisms from cyclohexane (82%) mp 95°; ir (potassium bromide): N-H 3330, C=N 1600 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.66-2.93 (bm, 7H, $CH_2CH_2CH_2CH$), 4.30 (d, 1H, CH, J_{H} , 12), 5.97 (s, 2H, OCH₂), 4.66 (s, 1H, N-H), 6.80-7.93 ppm (bm, 7H, Ar-H); uv (ethanol): λ max 286 nm (ϵ 12930), 222 nm (ϵ 10960); ms: (m/e), 306 (M^+), 185 ($C_{12}H_{12}N_2$).

Anal. Calcd. for $C_{19}H_{18}N_2O_2$ (306.40): C, 74.55; H, 5.92; N, 9.14. Found: C, 74.95; H, 6.10; N, 8.70.

3-(*m*-Nitrophenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (III i).

This compound was obtained as yellow needles from cyclohexane

(62%) mp 144°; ir (potassium bromide): N-H 3340, C=N 1600 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.76-3.26 (bm, 7H, $CH_2CH_2CH_2CH$), 4.63 (d, 1H, CH, J_{H} , 13), 5.53 (s, 1H, N-H), 7.26-8.43 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 266 nm (ϵ 16585).

Anal. Calcd. for $C_{18}H_{17}N_3O_2$ (307.35): C, 70.35; H, 5.54; N, 13.73. Found: C, 70.25; H, 5.63; N, 13.51.

3-(3-Thienyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (III j).

This compound was obtained as yellow needles from cyclohexane (86%) mp 71°; ir (potassium bromide): N-H 3340, C=N 1600 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.66-3.13 (bm, 7H, $CH_2CH_2CH_2CH$), 4.5 (d, 1H, CH, J_{H} , 12), 5.8 (s, 1H, N-H), 7.03-7.93 ppm (bm, 11H, Ar-H); uv (ethanol): λ max 280 nm (ϵ 10480), 218 nm (ϵ 13420).

Anal. Calcd. for $C_{16}H_{16}N_2S$ (268.37): C, 71.60; H, 6.00; N, 10.43; S, 11.95. Found: C, 71.45; H, 6.11; N, 10.28; S, 11.83.

General Procedure for the Preparation of 3-Aryl-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazoles IV a-j.

To a solution of 0.02 mole of 2-arylidene-1-benzosuberone in 50 ml of ethanol, 0.06 mole of methyl hydrazine was added and stirred at cold for a period of 10 minutes, and the mixture was then refluxed for 3-4 hours. The solid product obtained was recrystallised from methanol.

3-(*p*-Methoxyphenyl)-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (IV a).

This compound was obtained as white needles from methanol (85%) mp 113-115°; ir (potassium bromide): C=N 1612, C=C 1588 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.60-2.10 (bm, 7H, $CH_2CH_2CH_2CH$), 2.76 (s, 3H, N-CH₃), 3.36 (s, 3H, OCH₃), 3.55 (d, CH, J_{H} , 14), 6.66-7.96 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 290 nm (ϵ 13240), 221 nm (ϵ 18650).

Anal. Calcd. for $C_{20}H_{22}N_2O$ (306.41): C, 78.40; H, 7.20; N, 9.20. Found: C, 78.34; H, 7.42; N, 9.19.

3-(*p*-Nitrophenyl)-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (IV b).

This compound was obtained as yellow prisms (82%) mp 182°; ir (potassium bromide): C=N 1608 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.66-2.33 (bm, 7H, $CH_2CH_2CH_2CH$), 2.76 (s, 3H, N-CH₃), 3.55 (d, 1H, CH, J_{H} , 14), 7.10-8.26 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 287 nm (ϵ 68240), 215 nm (ϵ 4960).

Anal. Calcd. for $C_{15}H_{14}N_2O_2$ (321.46): C, 70.90; H, 5.92; N, 13.12. Found: C, 71.27; H, 5.97; N, 13.30.

3-(1-Naphthyl)-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (IV c).

This compound was obtained as white prisms (70%) mp 117°; ir (potassium bromide): C=N 1600 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.66-2.03 (bm, 7H, $CH_2CH_2CH_2CH$), 2.76 (s, 3H, N-CH₃), 4.36 (d, 1H, CH, J_{H} , 14), 7.00-8.26 ppm (bm, 11H, Ar-H); uv (ethanol): λ max 290 nm (ϵ 5540); ms: (m/e) 326 (M^+), 199 ($C_{12}H_{12}N_2$).

Anal. Calcd. for $C_{22}H_{22}N_2$ (326.54): C, 84.60; H, 6.75; N, 8.60. Found: C, 84.52; H, 6.88; N, 8.62.

3-Phenyl-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (IV d).

This compound was obtained as white prisms from methanol (75%) mp 80-81°; ir (potassium bromide): C=N 1600, C=C 1575 cm^{-1} ; 1H nmr (deuteriochloroform): δ 1.56-2.30 (bm, 7H, $CH_2CH_2CH_2CH$), 2.83 (s, 3H, N-CH₃), 3.66 (d, 1H, CH, J_{H} , 14), 7.10-8.06 ppm (bm, 9H, Ar-H); uv (ethanol): λ max 297 nm (ϵ 11360), 222 nm (ϵ 9340).

Anal. Calcd. for $C_{19}H_{20}N_2$ (276.381): C, 82.58; H, 7.36; N, 10.18. Found: C, 82.34; H, 7.44; N, 10.24.

3-(2,6-Dichlorophenyl)-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (IV e).

This compound was obtained as white needles from methanol (71%) mp 149-150°; ir (potassium bromide): C=N 1580 cm^{-1} ; 1H nmr (deu-

teriochloroform): δ 1.66-2.20 (bm, 7H, CH₂CH₂CH₂CH), 2.66 (s, 3H, N-CH₃), 4.66 (d, 1H, CH, J_H, 12), 7.13-7.80 ppm (bm, 7H, Ar-H); uv (ethanol): λ max 294 nm (ϵ 1200).

Anal. Calcd. for C₁₅H₁₈Cl₂N₂ (331.27): C, 66.09; H, 5.25; N, 8.11; Cl, 20.53. Found: C, 66.04; H, 5.28; N, 8.07; Cl, 20.70.

3-(2-Thienyl)-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**IVf**).

This compound was obtained as yellow prisms from methanol (76%) mp 75-76°; ir (potassium bromide): C=O 1600 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.60-2.13 (bm, 7H, CH₂CH₂CH₂CH), 2.80 (s, 3H, N-CH₃), 3.73 (d, 1H, CH, J_H, 14), 7.06-7.96 ppm (bm, 7H, Ar-H); uv (ethanol): λ max 297 nm (ϵ 11420), 215 nm (ϵ 14010).

Anal. Calcd. for C₁₇H₁₈N₂S (282.26): C, 72.34; H, 6.42; N, 9.92; S, 11.36. Found: C, 72.27; H, 6.48; N, 9.83; S, 11.48.

3-(3-Indolyl)-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**IVg**).

This compound was obtained as white prisms from methanol (90%) mp 172°; ir (potassium bromide): C=N 1580 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.63-2.70 (bm, 7H, CH₂CH₂CH₂CH), 2.83 (s, 3H, N-CH₃), 3.56 (s, 1H, N-H), 3.85 (d, 1H, CH, J_H, 14), 7.0-8.0 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 286 nm (ϵ 13690), 224 nm (ϵ 42860).

Anal. Calcd. for C₂₁H₂₀N₃ (315.60): C, 79.92; H, 6.45; N, 13.37. Found: C, 79.88; H, 6.21; N, 13.29.

3-(3,4-Methylenedioxyphenyl)-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**IVh**).

This compound was obtained as white prisms from methanol (75%) mp 126°; ir (potassium bromide): C=N 1600 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.86-2.60 (bm, 7H, CH₂CH₂CH₂CH), 2.86 (s, 3H, N-CH₃), 3.50 (d, 1H, CH, J_H, 14), 5.86 (s, 2H, OCH₂O), 6.86-8.13 ppm (bm, 7H, Ar-H); uv (ethanol): λ max 288 nm (ϵ 5040), 225 nm (ϵ 4220).

Anal. Calcd. for C₂₀H₂₀N₂O₂ (320.40): C, 75.00; H, 6.20; N, 8.80. Found: C, 75.00; H, 6.54; N, 8.76.

3-(3-Pyridyl)-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**VII**).

This compound was obtained as white needles from methanol (60%) mp 95-96°; ir (potassium bromide): C=N 1602 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.20-1.92 (bm, 7H, CH₂CH₂CH₂CH), 2.23 (s, 3H, N-CH₃), 3.3 (d, 1H, CH, J_H, 14), 6.80-8.26 ppm (bm, 7H, Ar-H); uv (ethanol): λ max 295 nm (ϵ 5250); ms: (m/e) 277 (M⁺), 199 (C₁₃H₁₅N₂⁺), 183 (C₁₂H₁₀N₂⁺).

Anal. Calcd. for C₁₈H₁₉N₃ (277.37): C, 77.95; H, 6.42; N, 15.20. Found: C, 77.86; H, 6.80; N, 15.25.

3-(2-Thienyl)-2-methyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**IVj**).

This compound was obtained as brown prisms from ethanol (84%) mp 64-65°; ir (potassium bromide): C=N 1610 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.60-2.13 (bm, 7H, CH₂CH₂CH₂CH), 2.83 (s, 3H, N-CH₃), 3.9 (d, 1H, CH, J_H, 14), 6.86-8.00 ppm (bm, 7H, Ar-H); uv (ethanol): λ max 292 nm (ϵ 11140), 224 nm (ϵ 15150); ms: (m/e) 282 M⁺, 199 (C₁₃H₁₅N₂⁺).

Anal. Calcd. for C₁₇H₁₈N₂S (282.34): C, 72.34; H, 6.42; N, 9.92; S, 11.36. Found: C, 72.28; H, 6.48; N, 9.82; S, 11.50.

General Procedure for the Preparation of 2-Acetyl-3-aryl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazoles **VIIa-f**.

To a solution of 0.005 mole of 3-aryl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazoles **IIIa-f** in 20-30 ml of ethanol was added 0.01 mole of acetic anhydride (1 ml). The mixture was refluxed for 2 hours and poured on a mixture of methanol/water (5:5 ml). The product was recrystallized from methanol.

2-Acetyl-3-(*p*-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**VIIa**).

White prisms of this compound were obtained from methanol (82%) mp 137°; ir (potassium bromide): C=O 1675, C=N 1620, C=C 1595 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.76-3.06 (bm, 7H, CH₂CH₂CH₂CH), 2.40 (s, 3H, COCH₃), 3.9 (d, 1H, CH, J_H, 7), 6.33-7.30 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 274 nm (ϵ 14140), 218 nm (ϵ 13545).

Anal. Calcd. for C₂₁H₂₂O₂N₂ (334.59): C, 75.39; H, 6.63; N, 8.40. Found: C, 75.38; H, 6.78; N, 8.50.

2-Acetyl-3-(*p*-nitrophenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**VIIb**).

Yellow needles of this compound were obtained from methanol (99%) mp 197°; ir (potassium bromide): C=O 1670, C=N 1610 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.70-3.26 (bm, 7H, CH₂CH₂CH₂CH), 2.30 (s, 3H, COCH₃), 5.26 (d, 1H, CH, J_H, 7), 7.06-8.33 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 270 nm (ϵ 22200), 214 nm (ϵ 13545); ms: (m/e) 349 (M⁺), 307 (C₁₈H₁₆N₃O₂⁺), 185 (C₁₂H₁₂N₂⁺).

Anal. Calcd. for C₂₀H₁₉N₃O₃ (349.39): C, 68.89; H, 5.50; N, 12.00. Found: C, 68.82; H, 5.60; N, 12.06.

2-Acetyl-3-(1-naphthyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**VIIc**).

This compound was obtained as white needles from methanol (92%) mp 186-187°; ir (potassium bromide): C=O 1675, C=N 1600, cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.70-3.26 (bm, 7H, CH₂CH₂CH₂CH), 2.50 (s, 3H, COCH₃), 5.9 (d, 1H, CH, J_H, 7), 7.10-8.06 ppm (bm, 11H, Ar-H); uv (ethanol): λ max 278 nm (ϵ 7095), 218 nm (ϵ 26350); ms: (m/e) 312 (M⁺), 185 (C₁₂H₁₂N₂⁺).

Anal. Calcd. for C₂₄H₂₂N₂O₂ (354.45): C, 81.30; H, 6.30; N, 7.90. Found: C, 81.29; H, 6.27; N, 7.90.

2-Acetyl-3-(*p*-chlorophenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**VIIId**).

This compound was obtained as white prisms from methanol (96%) mp 136°; ir (potassium bromide): C=O 1676 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.66-3.06 (bm, 7H, CH₂CH₂CH₂CH), 2.36 (s, 3H, COCH₃), 5.8 (d, 1H, CH, J_H, 7), 7.00-8.00 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 277 nm (ϵ 20530).

Anal. Calcd. for C₂₀H₁₈Cl₂N₂O (338.83): C, 70.89; H, 5.60; N, 8.26; Cl, 10.46. Found: C, 70.82; H, 5.71; N, 8.23; Cl, 10.59.

2-Acetyl-3-(2,6-dichlorophenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**VIIe**).

White prisms of this compound were obtained from methanol (83%) mp 222°; ir (potassium bromide): C=O 1670, C=N 1600 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.70-3.66 (bm, 7H, CH₂CH₂CH₂CH), 2.36 (s, 3H, COCH₃), 5.80 (d, 1H, CH, J_H, 8), 7.00-8.00 ppm (bm, 7H, Ar-H); uv (ethanol): λ max 277 nm (ϵ 19780), 212 nm (ϵ 29120).

Anal. Calcd. for C₂₀H₁₆Cl₂N₂O (373.30): C, 64.35; H, 4.90; N, 7.50; Cl, 19.00. Found: C, 64.28; H, 4.94; N, 7.52; Cl, 19.12.

2-Acetyl-3-(1-methylpyrrol-2-yl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**VIIIf**).

This compound was obtained as pale yellow prisms from methanol (72%) mp 119°; ir (potassium bromide): C=O 1670, C=N 1600 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.73-3.36 (bm, 7H, CH₂CH₂CH₂CH), 2.23 (s, 3H, N-CH₃), 3.73 (s, 3H, COCH₃), 4.46 (d, 1H, CH, J_H, 7), 5.76-7.76 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 273 nm (ϵ 17910), 210 nm (ϵ 18860).

Anal. Calcd. for C₁₉H₂₁N₃O (307.44): C, 74.23; H, 6.90; N, 13.67. Found: C, 74.09; H, 6.97; N, 13.58.

General Procedure for Bromination of Compounds **IIIa,b,d,IVb**.

To a solution of 1.0 g of compounds **IIIa,b,d** or **IVb** in 20 ml of carbon tetrachloride, bromine (0.4 ml) in 5 ml of carbon tetrachloride was added. The mixture was refluxed for 3 hours and the solution was concentrated. The product was recrystallized from methanol.

2-Bromo-3-(*p*-methoxyphenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-c]pyrazole (**VIIIa**).

This compound was obtained as white prisms from methanol (95%) mp 236-237°; ir (potassium bromide): C=N 1611 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.03-2.90 (bm, 7H, CH₂CH₂CH₂CH), 3.76 (s, 3H, COCH₃), 5.10 (d, 1H, CH, J_H, 7), 6.46-7.90 ppm (bm, 8H, ArH); uv (ethanol): λ max 254 nm (ε 27540).

Anal. Calcd. for C₁₉H₁₉BrN₂O (371.28): C, 61.46; H, 5.16; N, 7.50; Br, 21.50. Found: C, 61.20; H, 5.07; N, 7.50; Br, 21.75.

2-Bromo-3-(*p*-nitrophenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**VIIIb**).

This compound was obtained as yellow prisms from methanol (80%) mp 221°; ir (potassium bromide): C=N 1610 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.46-2.06 (bm, 7H, CH₂CH₂CH₂CH), 4.72 (d, 1H, CH, J_H, 7), 6.46-8.20 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 258 nm (ε 11960).

Anal. Calcd. for C₁₈H₁₆N₂O₂ (386.15): C, 56.00; H, 4.20; N, 10.90. Found: C, 56.28; H, 4.48; N, 10.91.

3-(*p*-Chlorophenyl)-2,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**Xd**).

This compound was obtained as white prisms from methanol (91%) mp 219°; ir (potassium bromide): (N-H) 3250, C=N 1615 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.00-2.96 (bm, 6H, CH₂CH₂CH₂), 5.40 (s, 1H, N-H), 7.10-7.83 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 255 nm (ε 21580).

Anal. Calcd. for C₁₈H₁₅ClN₂ (294.65): C, 73.34; H, 5.10; N, 9.50; Cl, 12.01. Found: C, 73.27; H, 5.10; N, 9.52; Cl, 11.92.

Dehydrobromination of Compounds **VIIIa,b**.

General Procedure.

To a solution of **VIIIa,b** (0.5 g) in 10-20 ml of methanol, 3 ml of pyridine was added. The solution was refluxed for 1.5 hours, and the solid product was obtained and recrystallized from methanol.

3-(*p*-Methoxyphenyl)-2,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**Xa**).

This compound was obtained as white prisms from methanol (72%) mp 154-155°; ir (potassium bromide): N-H 3250, C=N 1618 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.20-2.72 (bm, 6H, CH₂CH₂CH₂), 3.06 (s, 3H, OCH₃), 6.66 (s, 1H, N-H), 6.80-7.86 ppm (bm, 11H, Ar-H); uv (ethanol): λ max 256 nm (ε 30150).

Anal. Calcd. for C₁₉H₁₉N₂O (290.36): C, 78.50; H, 6.24, N, 9.60. Found: C, 78.50; H, 6.32; N, 9.56.

3-(*p*-Nitrophenyl)-2,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**Xb**).

This compound was obtained as yellow prisms from methanol (81%), mp 221°; ir (potassium bromide): N-H 3230, C=N 1600 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.56-3.06 (bm, 6H, CH₂CH₂CH₂), 6.52 (s, 1H, N-H), 7.04-8.32 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 284 nm (ε 454545), 254 nm (ε 519480); ms: (m/e) 305 (M⁺) 258 [C₁₈H₁₆N₂]⁺, 183 [C₁₂H₁₀N₂]⁺.

Anal. Calcd. for C₁₈H₁₅N₂O₂ (305.35): C, 70.80; H, 4.95; N, 13.80. Found: C, 70.40; H, 5.22; N, 13.88.

2-Methyl-3-(*p*-nitrophenyl)-2,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**XIb**).

This compound was obtained as yellow prisms from methanol (82%) mp 145-146°; ir (potassium bromide): C=N 1615 cm⁻¹; ¹H nmr (deuteriochloroform): δ 2.00-2.90 (bm, 6H, CH₂CH₂CH₂), 3.83 (s, 1H, N-CH₃), 7.13-8.4 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 255 nm (ε 9635), 304 nm (ε 4760).

Anal. Calcd. for C₁₉H₁₉N₂O₂ (319.36): C, 71.45; H, 5.36; N, 13.15. Found: C, 71.28; H, 5.41; N, 13.05.

General Procedure for the Preparation of Compounds **Va,d** and **VIb,c,d**.

To a solution of 0.01 mole of 2-arylidene-1-benzosuberone in 50 ml of ethanol, 0.03 mole of phenylhydrazine or *p*-bromophenylhydrazine was added with a few drops of sulphuric acid. The mixture was refluxed for

24 hours, and the solid product was recrystallized from cyclohexane.

3-(*p*-Methoxyphenyl)-2-phenyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**Va**).

This compound was obtained as yellow prisms from cyclohexane (45%) mp 110-112°; ir (potassium bromide): C=N 1620, C=C 1600 cm⁻¹; ¹H nmr (carbon tetrachloride): δ 1.63-3.00 (bm, 7H, CH₂CH₂CH₂CH), 3.66 (s, 3H, OCH₃), 4.5 (d, 1H, CH, J_H, 12), 6.26-7.68 ppm (bm, 13H, Ar-H); uv (ethanol): λ max 342 nm (ε 17800), 229 nm (ε 30000).

Anal. Calcd. for C₂₅H₂₄N₂O (368.50): C, 81.48; H, 6.56. Found: C, 81.75; H, 6.21.

2,3-Diphenyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**Vd**).

This compound was obtained as pink prisms from cyclohexane (40%) mp 188-190°; ir (potassium bromide): C=N 1600 cm⁻¹; ¹H nmr (carbon tetrachloride): δ 1.53-3.00 (bm, 7H, CH₂CH₂CH₂CH), 4.66 (d, 1H, CH, J_H, 7), 6.53-8.00 ppm (bm, 14H, Ar-H); uv (ethanol): λ max 337 nm (ε 56000), 298 nm (ε 30900), 240 nm (49000).

Anal. Calcd. for C₂₄H₂₂N₂O₂ (338.50): C, 85.17; H, 6.55; N, 8.27. Found: C, 85.02; H, 6.82; N, 7.88.

2-(*p*-Bromophenyl)-3-phenyl-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**VIb**).

This compound was obtained as pale yellow prisms from cyclohexane (40%) mp 128-130°; C=N 1590 cm⁻¹; ¹H nmr (deuteriochloroform): δ 1.40-3.00 (bm, 7H, CH₂CH₂CH₂CH), 4.63 (d, 1H, CH, J_H, 7), 6.73-8.00 ppm (bm, 13H, ArH); uv (ethanol): λ max 326 nm (ε 9700), 296 nm (ε 8100), 232 nm (8300).

Anal. Calcd. for C₂₄H₂₁BrN₂ (417.40): C, 69.00; H, 5.07; N, 6.71; Br, 19.14. Found: C, 68.86; H, 5.04; N, 6.66; Br, 19.35.

2-(*p*-Bromophenyl)-3-(1-naphthyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**VIc**).

This compound was obtained as white prisms from cyclohexane (35%) mp 200-201°; ir (potassium bromide): C=N 1590 cm⁻¹; nmr ¹H nmr (carbon tetrachloride): δ 1.03-2.97 (bm, 7H, CH₂CH₂CH₂CH), 5.90 (d, 1H, CH, J_H, 13), 6.67-7.90 ppm (bm, 11H, ArH); uv (ethanol): λ max 328 nm (ε 13400), 285 nm (ε 16000), 262 nm (18000), 226 nm (93000).

Anal. Calcd. for C₂₈H₂₃BrN₂ (467.40): C, 71.95; H, 4.95; N, 5.99; Cl, 17.11. Found: C, 71.68; H, 4.66; N, 5.54; Br, 16.81.

2-(*p*-Bromophenyl)-3-(*p*-chlorophenyl)-2,3,3a,4,5,6-hexahydrobenzo[6,7]cyclohepta[1,2-*c*]pyrazole (**VIId**).

This compound was obtained as white prisms from cyclohexane, (34%), mp 160-162°; ir (potassium bromide): C=N 1590 cm⁻¹; nmr ¹H nmr (carbon tetrachloride): δ 1.33-2.90 (bm, 7H, CH₂CH₂CH₂CH), 4.5 (d, 1H, CH, J_H, 10), 6.13-7.66 ppm (bm, 8H, Ar-H); uv (ethanol): λ max 348 nm (ε 8600), 255 nm (ε 8200), 223 nm (12100).

Anal. Calcd. for C₂₄H₂₀BrClN₂ (451.8): C, 63.80; H, 4.46; N, 6.20; Cl, 7.84; Br, 17.68. Found: C, 63.59; H, 4.17; N, 6.18; Cl, 7.44; Br, 17.46.

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