Synthesis of Some New Bicyclic Pyrazoline Derivatives

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2,6-Diarylidenecyclohexanones react with hydrazine to give the corresponding bicyclic pyrazolines. The synthesis of a series of twenty eight substituted pyrazolines is described. The structure of all products was confirmed by microanalyses, ir and nmr data.

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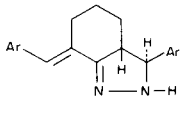
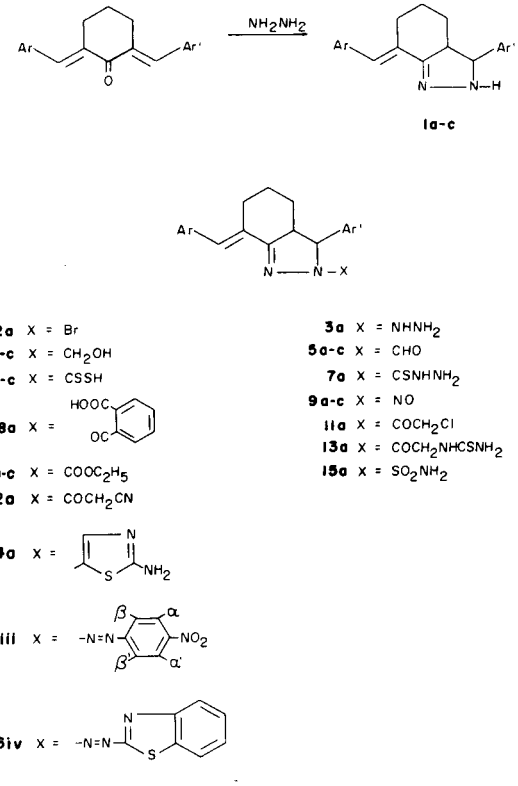
α,β-Unsaturated ketones react with hydrazine or with substituted hydrazines to yield pyrazoline derivatives (1-4). The reaction of mono- and diarylidenecycloalkanones with hydrazine hydrate was studied by Oszbach and Szabo (5) who reported that with 2,6-diarylidenecyclohexanones the reaction afford bicyclic pyrazolines, however, these products were comparatively unstable and were converted into their acetyl derivatives. Since several reports indicated the parmacological importance (6-9) of some bicyclic pyrazoline derivatives we report here the synthesis of a new series of this class of compounds. Our key intermediates **1a-c** (Scheme 1) were obtained by refluxing 2,6-diarylidenecyclohexanones with hydrazine hydrate in methanol. The structure of this product was based on microanalyses, ir and nmr spectral data. Shift reagents and decoupling experiments in deuteriochloroform of some bicyclic pyrazolines (9) showed that C-3 and C-4 protons of the pyrazoline ring are *trans* coupled (J = 13 Hz). The shift reagent study also showed the arylidene proton and the =N- linkage in a *cis* conformation.



A selective *N*-bromination of **1a** using *N*-bromosuccinimide NBS in chloroform gave the bromo pyrazoline **2a** which was converted into the *N*-hydrazino derivative **3a**. Reaction of **1a-c** with formaldehyde in methanol afforded the hydroxymethyl derivatives **4a-c** whereas their reaction with formamide in methanol gave the *N*-formylpyrazolines **5a-c**. The hitherto new reaction of pyrazolines **1a-c** with carbon disulfide produced the *N*-dithio acid derivatives **6a-c**. Reaction of **6a** with hydrazine hydrate gave the *N*-thiohydrazidepyrazoline derivative **7a**. The reaction of pyrazolines with phthalic anhydride was recently reported (10); we apply this reaction to **1a** where we obtained **8a**. The *N*-nitrosopyrazolines **9a-c** were also obtained on treatment **1a-c** with sodium nitrite and hydrochloric acid. The pyrazolines **1a-c** were reacted with ethyl chloroformate in benzene to yield the *N*-carbethoxy derivatives **10a-c**.



In compound **1-15 a**, Ar = Ar' = C_6H_5; **b**, Ar = Ar' = C_6H_4-4-OCH_3; **c**, Ar = Ar' = C_6H_4-4-$N(CH_3)_2$; in compound **16 i**, Ar = C_6H_5, Ar' = C_6H_4-4-NO_2; **ii**, Ar = C_6H_4-4-OCH_3, Ar' = C_6H_4-4-NO_2; **iii**, Ar = C_6H_4-4-$N(CH_3)_2$, Ar' = C_6H_4-4-NO_2; **iv**, Ar = C_6H_5, Ar' = 2-benzthiazolyl.

Acetylation of bicyclic pyrazoline **1a** in dry benzene with chloroacetyl chloride yielded predominantly the *N*-acylated substance **11a** which on reaction with sodium cyanide gave the α-cyanoketo derivative **12a**. The reaction of *N*-acylated derivative **11a** with thiourea in dry benzene was also achieved to produce the condensation product **13a**. The latter compound was converted into the *N*-(2-amino-5-thiazolyl)pyrazoline derivative **14a** by boiling in dry ethanol containing anhydrous sodium acetate.

The *N*-amination of 1,2,3-benzotriazin-4-one was reported by Adamson, *et al* (11) using hydroxylamine-*O*-

sulphonic acid in aqueous potassium carbonate at 3°. On applying these conditions to compound **1a** no reaction occurs however, when **1a** was refluxed in methanolic solution of hydroxylamine-*O*-sulphonic acid we obtained, unexpectedly, the *N*-suphonamide derivative **15a**.

In continuation of our recent study on the synthesis of some *N*-aryl(or heteroaryl)-azo-1,2,3-benzotriazin-4-ones (12) we reported here the reaction of our key bicyclic pyrazolines **1a-c** with a series of aryl or heteroaryl diazonium tetrafluoroborates where we obtained the corresponding coupling products **16i-iv**. The solid diazonium reagents used in this reaction were obtained by the diazotization of aryl or heteroaryl amines using sodium nitrite-fluoroboric acid (50%) at 3°.

EXPERIMENTAL

All melting points were determined on a Kofler bank and are uncorrected; ir spectra were recorded (potassium bromide) on a Pye Unicam Sp-1200 spectrometer. The ^{1}H-nmr spectra were obtained on a Varian EM 360 A or NV 14 spectrometer at 60 MHz or at 100 MHz, using TMS (tetramethylsilane) as an internal standard and chemical shifts were expressed as δ, parts per million (ppm).

7-Benzylidene-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**1a**).

General Procedure.

A mixture of 0.01 mole (2.74 g) of dibenzylidenecyclohexanone and 0.05 mole (2.50 g) of hydrazine hydrate (98%) in methanol (100 ml) was stirred under reflux for 1.5 hours. The reaction mixture was then allowed to cool and was kept at 0° for 24 hours. The precipitated product was filtered off, washed with methanol then with petroleum ether 60-80° and was recrystallized from a mixture (30:1) by volume of methanol-hydrazine hydrate to yield 2.16 g (75%). The pure product was conserved in a dark bottle in the refrigerator, mp 84-86°; ir (potassium bromide): ν cm^{-1} 3290 (N-H), 1660 (C=N); ^{1}H-nmr (deuteriochloroform): δ ppm 7.7-7.0 (m, 10H, Ar), 6.9 (s, 1H, =CH), 6.0 (s, 1H, NH), 5.0 (d, 1H, N-CH), 3.3-0.9 (m, 7H, aliphatic).

Anal. Calcd. for $C_{20}H_{20}N_2$: C, 83.33; H, 6.94; N, 9.72. Found: C, 83.29; H, 7.03; N, 9.80.

Compound **1b**.

The general procedure was employed using (3.34 g, 0.01 mole) of di-*p*-anisylidenecyclohexanone, yield 2.83 g (81.5%), mp 93-95°; ir (potassium bromide): ν cm^{-1} 3220 (N-H), 1660 (C=N).

Anal. Calcd. for $C_{22}H_{24}N_2O_2$: C, 75.86; H, 6.89; N, 8.04. Found: C, 75.73; H, 7.00; N, 8.16.

Compound **1c**.

The general procedure was employed using (3.60 g, 0.01 mole) of di-*p*-*N*-dimethylaminobenzylidenecyclohexanone, yield 2.67 g (71.6%), mp 110°; ir (potassium bromide): ν cm^{-1} 3320 (N-H), 1670 (C=N).

Anal. Calcd. for $C_{24}H_{30}N_4$: C, 77.00; H, 8.02; N, 14.97. Found: C, 77.09; H, 8.13; N, 15.08.

7-Benzylidene-2-bromo-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**2a**).

An equimolar mixture (0.005 mole) of **1a** (1.44 g) and *N*-bromosuccinimide (0.89 g) in 30 ml of chloroform was stirred in direct sunlight for 2 hours. The precipitated product **2a** was filtered off, washed throughly with water then with benzene, air-dried and recrystallized from benzene to yield 0.94 g (52%), mp 226-228°; ir (potassium bromide): ν cm^{-1} 1650 (C=N), 710 (N-Br); ^{1}H-nmr (deuteriochloroform): δ ppm 7.8-7.2 (m, 10H, Ar), 7.0 (s, 1H, =CH), 5.1 (d, 1H, N-CH), 3.5-1.2 (m, 7H, aliphatic).

Anal. Calcd. for $C_{20}H_{19}BrN_2$: C, 65.39; H, 5.17; N, 7.62. Found: C, 65.48; H, 5.26; N, 7.69.

7-Benzylidene-2-hydrazino-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**3a**).

An equimolar mixture (0.005 mole) of both **2a** 1.83 g and hydrazine hydrate 0.25 g in 30 ml of ethanol was heated at reflux for ½ hour. The reaction solution was cooled and the resulting solid was collected, washed with dilute ammonia, air-dried and recrystallized from benzene to afford 1.39 g (88%), mp 218°; ir (potassium bromide): ν cm^{-1} 3400, 3220 ($NHNH_2$), 1650 (C=N); ^{1}H-nmr (deuteriochloroform): δ ppm 7.5-7.0 (m, 10H , Ar), 6.9 (s, 1H, =CH), 6.2 (s, 1H, NH), 4.95 (d, 1H, N-CH), 4.68 (s, 2H, NH_2), 3.2-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{20}H_{22}N_4$: C, 75.47; H, 6.91; N, 17.61. Found: C, 75.56; H, 6.77; N, 17.80.

Hydroxymethylation of Pyrazoline Derivatives. Synthesis of 7-Benzylidene-2-hydroxymethyl-3-phenyl-3,3a,4,5,6,7,-hexahydro-2*H*-indazole (**4a-c**).

General Procedure

A mixture of 0.005 mole of **1a** (1.44 g) and 2 ml of formaldehyde (40%) in 30 ml of methanol was stirred at room temperature (26°) for 1 hour. The reaction mixture was kept at 0° for 12 hours whereby the desired product **4a** was precipitated, collected by filtration and recrystallizated from methanol to yield 0.72 g (45%), mp 143°; ir (potassium bromide): ν cm^{-1} 3450 (O-H), 1660 (C=N); ^{1}H-nmr (deuteriochloroform): δ ppm 7.50-7.15 (m, 10H, Ar), 7.0 (s, 1H, =CH), 4.8 (d, 1H, N-CH), 4.45 (m, 2H, CH_2) 3.5 (s, 1H, OH), 3.0-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{21}H_{22}N_2O$: C, 79.24; H, 6.91; N, 8.80. Found: C, 79.15; H, 6.78; N, 9.00.

Compound **4b**.

The general procedure was employed using (1.74 g, 0.005 mole) of **1b** and the reaction time was 2.5 hours, yield 1.69 g (90%) from methanol, mp 109°.

Anal. Calcd. for $C_{23}H_{26}N_2O_3$: C, 73.01; H, 6.87; N, 7.40. Found: C, 72.89; H, 6.96; N, 7.27.

Compound **4c**.

The general procedure was realized using (1.87 g, 0.005 mole) of **1c**, time of reaction was 4 hours, yield 1.69 g (84%) from methanol-petroleum ether 60-80°, mp 208-209°.

Anal. Calcd. for $C_{25}H_{32}N_4O$: C, 74.25; H, 7.92; N, 13.86. Found: C, 74.33; H, 7.82; N, 13.72.

Formylation of Pyrazoline Derivatives. Synthesis of 7-Benzylidene-2-formyl-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**5a**).

General Procedure.

Compound **1a** (1.44 g, 0.005 mole) was suspended in a mixture of 30 ml of formaldehyde and 20 ml methanol. The reaction mixture was stirred under relux for ½ hour and was then cooled to 0°. The desired product **5a** was collected by filtration and recrystallized from methanol, yield 0.95 g (60%), mp 145°; ir (potassium bromide): ν cm^{-1} 1665 (C=O); ^{1}H-nmr (deuteriochloroform): δ ppm 8.85 (s, 1H, CHO), 7.35-7.0 (m, 10H, Ar), 6.85 (s, 1H, =CH), 4.8 (d, 1H, N-CH), 3.0-1.3 (m, 7H, aliphatic).

Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.74; H, 6.32; N, 8.86. Found: C, 79.88; H, 6.23; N, 8.71.

Compound **5b**.

The general procedure was employed using (1.74 g, 0.005 mole) of **1b** and the time of reaction was 2 hours, yield 1.07 g (57%) from methanol, mp 128°; ir (potassium bromide): ν cm^{-1} 1670 (C=O).

Anal. Calcd. for $C_{23}H_{24}N_2O_3$: C, 73.40; H, 6.38; N, 7.44. Found: C, 73.33; H, 6.50; N, 7.60.

Compound **5c**.

The general procedure was utilized using (1.87 g, 0.005 mole) of **1c** where the time of reaction was 5 hours, yield 1.96 g (98%) from methanol

-petroleum ether 60-80°, mp 170°; ir (potassium bromide): ν cm^{-1} 1670 (C=O).

Anal. Calcd. for $C_{25}H_{30}N_4O$: C, 74.62; H, 7.46; N, 13.93. Found: C, 74.75; H, 7.28; N, 13.79.

7-Benzylidene-2-dithioacid-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**6a**).

General Procedure.

Pyrazoline derivative **1a** (1.44 g, 0.005 mole) was added to an excess amount (20 ml) of cold dry carbon disulphide. A clear solution was developed which was kept at 0° for 48 hours. The reaction mixture was evaporated *in vacuo*. The solid substance was triturated with petroleum ether 60-80° and recrystallized from benzene, yeild 1.79 g (99%), mp 140°; ir (potassium bromide): ν cm^{-1} 1130 (C=S), 2570 (S-H); ^{1}H-nmr (deuteriochloroform): δ ppm 7.65-7.0 (m, 10H, Ar + 1H =CH), 5.30 (s, 1H, SH), 5.0 (d, 1H, N-CH), 2.9-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{21}H_{20}N_2S_2$: C, 69.23; H, 5.49; N, 7.69. Found: C, 69.40; H, 5.35; N, 7.80.

Compound **6b**.

This compound was obtained by applying the general procedure using (1.74 g, 0.005 mole) of **1b**, yield 1.8 g (85%), mp 122°.

Anal. Calcd. for $C_{23}H_{24}N_2S_2O_2$:C, 65.09; H, 5.66; N, 6.60. Found: C, 64.89; H, 5.77; N, 6.54.

Compound **6c**.

The general procedure was realized using (1.87 g, 0.005 mole) of **1c**, yield 2.14 g (95%), mp 134°.

Anal. Calcd. for $C_{25}H_{30}N_4S_2$: C, 66.66; H, 6.66; N, 12.44. Found: C, 66.61; H, 6.51; N, 12.54.

7-Benzylidene-2-thiohydrazide-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**7a**).

Compound **6a** (1.82 g, 0.005 mole) with hydrazine hydrate (98%) (0.3 g, 0.006 mole) in 30 ml of absolute ethanol was heated at reflux until all hydrogen sulphide evolution was ceased (3.5 hours). The reaction mixture was filtered while hot and the filtrate was concentrated *in vacuo*, the solid product was obtained by suction and recrystallized from ethanol, yield 1.09 g (56%), mp 154°; ir (potassium bromide): ν cm^{-1} 3450, 3250 ($NHNH_2$), 1150 (C=S); ^{1}H-nmr (deuteriochloroform): δ ppm 7.7-7.1 (m, 10H, Ar), 7.0 (s, 1H, =CH), 6.7 (s, 1H, NH), 5.0 (d, 1H, N-CH), 4.7 (s, 2H, NH_2), 3.0-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{21}H_{22}N_4S$: C, 69.61; H, 6.07; N, 15.46. Found: C, 69.58; H, 5.89; N, 15.33.

7-Benzylidene-2-(*o*-carboxybenzoyl)-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H* indazole (**8a**).

To a solution of pyrazoline derivative **1a** (0.86 g, 0.003 mole) in dry benzene (50 ml), phthalic anhydride (0.44 g, 0.003 mole) and few drops of triethylamine were added. The mixture was stirred at room temperature (26°) for 4 hours. The solid product which separated out was recrystallized from benzene, yield, 0.54 g (41%), mp 210°; ir (potassium bromide): ν cm^{-1} 3030, 2940 (O-H), 1695, 1665 (C=O); ^{1}H-nmr (deuteriochloroform): δ ppm 11.2 (s, 1H, COOH), 8.0-7.5 (m, 4H, CO-C_4H_4), 7.45-6.95 (m, 10H, Ar), 6.9 (s, 1H, =CH), 5.05 (d, 1H, N-CH), 3.1-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{28}H_{24}N_2O_3$: C, 77.06; H, 5.50; N, 6.42. Found: C. 77.18; H, 5.41; N, 6.55.

7-Benzylidene-2-nitroso-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**9a**).

General Procedure.

A solution of **1a** (1.44 g, 0.005 mole) in 1:1 hydrochloric acid (20 ml) was treated at 3° with a cooled concentrated solution of sodium nitrite (1.38 g , 0.02 mole in 10 ml of water). The mixture was stirred in cold for one hour and left in the refrigerator for 3 hours. The separated solid was recrystallized from methanol-petroleum ether 60-80°, yield 1.45 g (92%), mp 131-133°; ir (potassium bromide): ν cm^{-1} 1580 (N=O); ^{1}H-nmr (deuteriochloroform): δ ppm 7.65-7.0 (m, 10H, Ar), 6.9 (s, 1H, =CH), 5.1 (d, 1H, N-CH), 3.2-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{20}H_{19}N_3O$: C, 75.70; H, 5.99; N, 13.24. Found: C, 75.58; H, 5.84; N, 13.29.

Compound **9b**.

The general procedure was employed using (1.74 g, 0.005 mole) of **1b**, yield 1.84 g (97.8%), mp 115-117°; ir (potassium bromide): ν cm^{-1} 1585 (N=O).

Anal. Calcd. for $C_{22}H_{23}N_3O_3$: C, 70.02; H, 6.10; N, 11.14. Found: C, 69.91; H, 6.00; N, 11.23.

Compound **9c**.

This compound was obtained by applying the general procedure using (1.87 g, 0.005 mole) of **1c**, yield 1.97 g (98%), mp 113°; ir (potassium bromide): ν cm^{-1} 1585 (N=O).

Anal. Calcd. for $C_{24}H_{29}N_5O$: C, 71.46; H, 7.19; N, 17.36. Found: C, 71.32; H, 7.29; N, 17.27.

7-Benzylidene-2-carbethoxy-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**10a**).

General Procedure.

Ethyl chloroformate 1.08 g, 0.01 mole in 20 ml of cold dry benzene was added dropwise with stirring to a solution of 2.88 g (0.01 mole) of **1a** in 20 ml of benzene. The mixture was kept at 0° for 24 hours when the *N*-carbethoxypyrazoline derivative **10a** was precipitated, filtered off and recrystallized from methanol-petroleum ether 60-80°, yield 2.39 g (67%), mp 171-172°; ir (potassium bromide): ν cm^{-1} 1710 (C=O); ^{1}H-nmr (deuteriochloroform): δ ppm 7.55-7.15 (m, 10H, Ar), 7.05 (s, 1H, =CH), 5.0 (d, 1H, N-CH), 4.23 (q, 2H, CH_2), 3.0-1.0 (m, 10H, aliphatic + CH_3).

Anal. Calcd. for $C_{23}H_{24}N_2O_2$: C, 76.66; H, 6.66; N, 7.77. Found: C, 76.73; H, 6.82; N, 7.91.

Compound **10b**.

The general procedure was realized using (3.48 g, 0.01 mole) of **1b**, yield 3 g (72%), mp 120-122° from benzene-petroleum ether 60-80°; ir (potassium bromide): ν cm^{-1} 1715 (C=O).

Anal. Calcd. for $C_{25}H_{28}N_2O_4$: C, 71.42; H, 6.66; N, 6.66. Found: C, 71.30; H, 6.72; N. 6.61.

Compound **10c**.

The general procedure was employed using (3.74 g, 0.01 mole) of **1c**, yield 3.59 g (81%), mp 184-5° from benzene; ir (potassium bromide): ν cm^{-1} 1715 (C=O).

Anal. Calcd. for $C_{27}H_{34}N_4O_2$: C, 72.64; H, 7.62; N, 12.55. Found: C, 72.74; H, 7.70; N, 12.49.

7-Benzylidene-2-chloroacetyl-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**11a**).

To a solution of 2.88 g (0.01 mole) of **1a** in 50 ml of benzene 1.34 g (0.012 mole) of chloroacetyl chloride was added dropwise under efficient stirring, the reaction mixture was stirred for an additional one hour. The benzene layer was evaporated *in vacuo* and the solid mass was triturated with water, filtered off and recrystallized from benzene-petroleum ether 60-80°, yield 3.2 g (88%), mp 151-153°; ir (potassium, bromide): ν cm^{-1} 1710 (C=O); ^{1}H-nmr (deuteriochloroform): δ ppm 7.55-7.10 (m, 10H, Ar), 7.0 (s, 1H, =CH), 5.0 (d, 1H, N-CH), 3.48 (m, 2H, CH_2), 3.0-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{22}H_{21}ClN_2O$: C, 72.42; H, 5.76; N, 7.68. Found: C, 72.60; H, 5.66; N, 7.56.

7-Benzylidene-2-cyanoacetyl-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**12a**).

Compound **11a** (1.82 g, 0.005 mole) in 30 ml ethanol was treated with an equivalent amount of sodium cyanide (0.24 g) dissolved in 3 ml of

water. The mixture was heated at reflux for ½ hour, and was cooled to room temperature. The separated sodium chloride was filtered off and the filtrate was evaporated *in vacuo* to give an oily residue which solidified on washing with petroleum ether 60-80° and recrystallized from benzene, yield 1.59 g (87%), mp 101-102°; ir (potassium bromide): ν cm^{-1} 2280 (C≡N), 1710 (C=O); ^{1}H-nmr (deuteriochloroform): δ ppm 7.6-7.0 (m, 10H, Ar), 6.95 (s, 1H, =CH), 5.0 (d, 1H, N-CH), 3.15 (s, 2H, CH_2), 3.1-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{23}H_{21}N_3O$: C, 77.74; H, 5.91; N, 11.83. Found: C, 77.91; H. 5.80; N, 12.02.

7-Benzylidene-2-acetylthiourea-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**13a**).

To 0.01 mole of thiourea (0.76 g) in 40 ml of absolute ethanol, an equivalent amount of compound **11a** (3.65 g) was added. The reaction mixture was treated with 0.01 mole of triethylamine (1.01 g) and was heated at reflux for one hour, concentrated *in vacuo* and filtered. The solid was washed with water, air-dried and recrystallized from ethanol, yield 2.02 g (50%), mp 205-207°; ir (potassium bromide): ν cm^{-1} 3360, 3250 ($NHNH_2$), 1735 (C=O); ^{1}H-nmr (deuteriochloroform): δ ppm 7.50-7.15 (m, 10H, Ar), 7.0 (s, 1H, =CH), 6.45 (s, 1H, NH), 5.0 (d, 1H, N-CH), 4.85 (s, 2H, NH_2), 4.20 (m, 2H, CH_2), 3.0-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{23}H_{24}N_4SO$: C, 68,31; H, 5.94; N, 13.86. Found: C, 68.22; H, 5.78; N, 14.00.

7-Benzylidene-2-(5'-phenyl-2'-aminothiazolyl-)-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**14a**).

Compounds **13a** (2.02 g, 0.005 mole) was boiled with 2 g of anhydrous sodium acetate in 25 ml of absolute ethanol for 2 hours, the mixture was filtered while hot and the filtrate was concentrated *in vacuo*. The solid was collected by suction, washed throughly with water, air-dried and recrystallized from ethanol, yield 1.07 g (56%), mp 274-276°; ir (potassium bromide): ν cm^{-1} 3430, 3360 (NH_2); ^{1}H-nmr (deuteriochloroform): δ ppm 8.07 (s, 1H, CH-thiazolyl-), 7.45-7.10 (m, 10H, Ar), 6.95 (s, 1H, =CH), 6.0 (s, 2H, NH_2), 5.1 (d, 1H, N-CH), 3.15-1.00 (m, 7H, aliphatic).

Anal. Calcd. for $C_{23}H_{22}N_4S$: C, 71.50; H, 5.69; N, 14.50. Found: C, 71.68; H, 5.74; N, 14.45.

7-Benzylidene-2-sulphonamide-3-phenyl-3,3a-4,5,6,7-hexahydro-2*H*-indazole (**15a**).

An equimolar amounts of **1a** (1.44 g) and hydroxylamine-*O*-sulphonic acid NH_2OSO_3H(0.56 g, 0.005 mole) in 30 ml of ethanol were heated at reflux for ½ hour. The reaction mixture was left to cool in the refrigerator and was then concentrated *in vacuo*. The product was filtered, washed with water and recrystallized from ethanol-water mixture, yield, 0.95 g (52%), mp 131-133°; ir (potassium bromide): ν cm^{-1} 3350, 3200, 1350 (SO_2NH_2); ^{1}H-nmr (deuteriochloroform): δ ppm 7.6-7.0 (m, 10H, Ar), 6.95 (s, 1H, =CH), 6.45 (s, 2H, NH_2), 5.0 (d, 1H, N-CH), 3.0-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{20}H_{21}N_3SO_2$: C, 65.39; H, 5.72; N, 11.44. Found: C, 65.46; H, 5.61; N, 11.27.

7-Benzylidene-2-(*p*-nitrophenylazo)-3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indazole (**16i**).

General Procedure.

The pyrazoline derivatives **1a** (1.44 g, 0.005 mole) was suspended in 30 ml of ethanol, an equivalent amount of *p*-nitrophenyldiazonium tetrafluoroborate (1.18 g) was added gradually under efficient stirring at 5°. The mixture was stirred for 2 hours whereby all the solids were dissolved and was then left in the refrigerator for 6 hours and was then concentrated *in vacuo*. The separated product was collected by suction, washed with water and recrystallized from methanol, yield 1.12 g (51%), mp 162-164°; ir (potassium bromide): ν cm^{-1} 1580 (N=N); ^{1}H-nmr (deuteriochloroform): δ ppm 8.15 (d, 2H, α, α'), 8.0 (d, 2H, β, β'), 7.5-7.15 (m, 10H, Ar), 7.0 (s, 1H, =CH), 5.1 (d, 1H, N-CH), 3.1-1.1 (m, 7H, aliphatic).

Anal. Calcd. for $C_{26}H_{23}N_5O_2$: C, 71.39; H, 5.26; N, 16.01. Found: C, 71.28; H, 5.19; N, 16.11.

Compound **16ii**.

The general procedure was employed starting with **1b** (1.74 g, 0.005 mole), yield 1.84 g (75%) from ethanol, mp 135-136°; ir (potassium bromide): ν cm^{-1} 1585 (N=N).

Anal. Calcd. for $C_{28}H_{27}N_5O_4$: C, 67.60; H, 5.43; N, 14.08. Found: C, 67.52; H, 5.45; N, 14.01.

Compound **16iii**.

The general procedure was realized starting with compound **1c** (1.87 g. 0.005 mole), yield, 2.09 g (80%), mp 143-145° from ethanol; ir (potassium bromide): ν cm^{-1} 1585 (N=N).

Anal. Calcd. for $C_{30}H_{33}N_7O_2$: C, 68.83; H, 6.30; N, 18.73. Found: C, 68.87; H, 6.21; N, 18.61.

Compound **16iv**.

The general procedure was employed starting with an equimolar amounts of **1a** (1.44 g, 0.005 mole) and benzothiazolyldiazonium tetraflouroborate (1.24 g), yield, 0.99 g (45%), mp 193-195° from ethanol-petroleum ether 40-60°; ir (potassium bromide): ν cm^{-1} 1600 (N=N); ^{1}H-nmr (deuteriochloroform): δ ppm 7.7-6.95 (m, 14H, Ar + benzothiazolyl), 6.90 (s, 1H, =CH), 5.05 (d, 1H, N-CH), 3.0-1.0 (m, 7H, aliphatic).

Anal. Calcd. for $C_{27}H_{23}N_5S$: C, 72.16; H, 5.12; N, 15.59. Found: C, 72.31; H, 5.09; N, 15.51.

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