Nucleophilic Displacement of Aromatic Fluorine, Part II (1). Indazoles, Indazolo[2,3-*c*]quinazolines, Indazolo[2,3-*d*][1,4]benzodiazepines and Indazolo[2,3-*c*]benzo-1,2,3-triazenes

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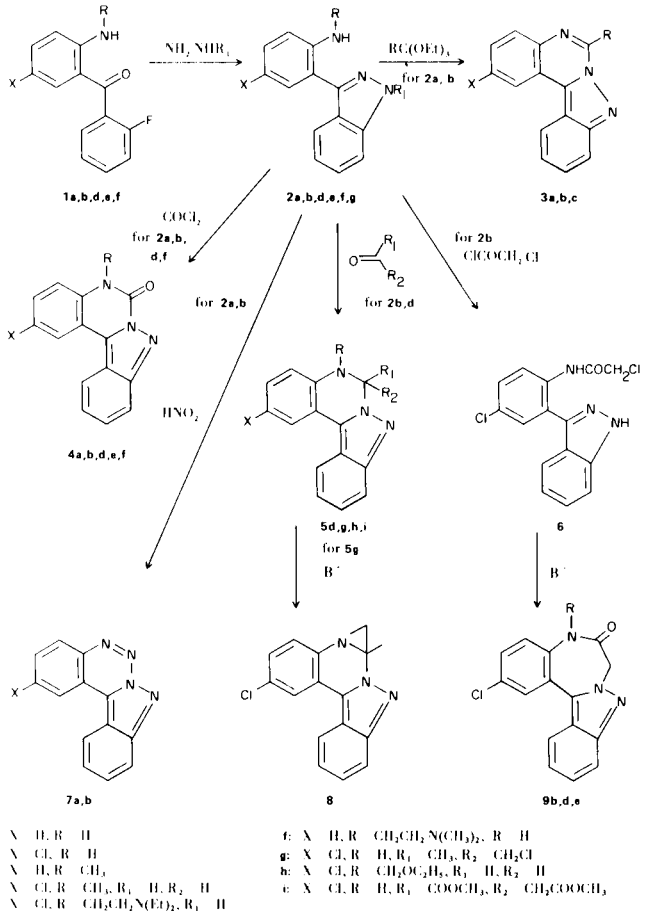
3-(2-Aminophenyl)indazoles **2** were prepared by the reaction of the *o*-fluorobenzophenones **1** with hydrazines. These indazoles were converted to the tetracyclic title compounds by conventional methods.

The reactivity of the fluorine in *ortho*-fluorobenzophenones toward nucleophiles have been documented in earlier publications (2). Utilizing this property of the fluorine we found that indazoles of structure **2** are easily accessible by the reaction of the fluorosubstituted benzophenones **1** with hydrazines. The 3-(2-aminophenyl)-indazoles **2** thus prepared were then used as starting materials for the synthesis of the title compounds. These heterocycles represent a variety of compounds with potential pharmacological interest.



Reaction of the indazoles **2** with orthoesters yielded the indazolo[2,3-*c*]quinazolines **3**. Condensation of **2** with phosgene led to the indazolo[2,3-*c*]quinazolin-6(5*H*)-ones **4**. Compound **4a** has recently been disclosed in the literature (3). While the difficultly soluble indazolo[2,3-*c*]quinazolinones could be alkylated in the 5-position, it was preferable to prepare these compounds by starting with the properly *N*-alkylated benzophenones **1**.

Reaction of the 3-(2-methylaminophenyl)indazole **2d** with formaldehyde afforded the 5,6-dihydroindazolo-[2,3-*c*]quinazoline **5d**. Acid catalysed condensation of the indazole **2b** with formaldehyde in ethanol gave the corresponding ethoxymethyl derivative **5h**. Chloroacetone added to **2b** in the presence of glacial acetic acid and produced the 2-chloro-6-chloromethyl-5,6-dihydro-6-methyl-indazolo[2,3-*c*]quinazoline **5g** in good yield. Treatment of this compound with potassium *t*-butoxide in tetrahydrofuran afforded the aziridine **8**. The protons of the aziridine ring of **8** appear in the nmr spectrum as two sharp singlets, a degenerate AB-system with zero coupling. Field *et al.* (4) have reported on the same observation made with similar quinazolines.

The addition of dimethyl acetylene dicarboxylate to the indazole **2b** gave compound **5i** the structure of which was clearly evident from the spectral data. The chloroacetamide **6**, which was obtained by standard chloroacetylation of **2b**, ring closed to the indazolo[2,3-*d*][1,4]-benzodiazepine **9b** upon treatment with potassium t-butoxide. Alkylation of the potassium salt of **9b** with methyliodide or 2-(diethylamino)ethyl chloride led to the 5-substituted derivatives **9d** and **9e** respectively. Nitrosation of the indazoles **2a,b** with nitrite in glacial acetic acid afforded the stable indazolo[2,3-*c*]benzo-1,2,3-triazenes **7a,b** in good yields.

EXPERIMENTAL

Melting points were determined in a capillary melting point apparatus or a Reichert hot stage microscope. The uv spectra were measured in 2-proponal on a Cary Model 14 spectrophotometer. Nmr spectra were recorded with a Varian T-60 instrument with TMS as internal standard. Ir spectra were determined on a Beckman ir -9 spectrometer. Silica gel Merck (70-325 mesh) was used for chromatography and anhydrous sodium sulfate for drying purposes.

3-(2-Aminophenyl)indazole (**2a**) (3).

A mixture of 107.5 g. (0.5 mole) of 2-(2-fluorobenzoyl)aniline (**1a**) (5) and 220 ml. of hydrazine (97%) was stirred and heated to reflux for 3 hours. After cooling, the product was precipitated by addition of water and was collected. It was washed with water and dried *in vacuo* at 80° to leave 102.5 g. (98%) of off-white material with m.p. 179-182°. Recrystallization from ethyl acetate yielded needles with m.p. 187-189°.

3-(2-Amino-5-chlorophenyl)indazole (**2b**).

Treatment of 100 g. of 4-chloro-2-(2-fluorobenzoyl)aniline (**1b**) (5) with 200 ml. of hydrazine produced similarly 94.4 g. (98%) of crude product with m.p. 182-184°. The analytical sample was recrystallized from ethanol, m.p. 191-192°; uv: λ max 217 mμ (ε = 30,200) 255 (14,500) 303 (5,700) 334 (6,800); nmr (DMSO): δ 6.2 ppm (broad s, 2, NH_2) 6.8-8.2 (m, 7, aromatic H) 13.3 (broad s, 1, NH).

Anal. Calcd. for $C_{13}H_{10}ClN_3$: C, 65.2; H, 4.7; N, 16.3. Found: C, 65.3; H, 4.6; N, 16.4.

3-(5-Chloro-2-methylaminophenyl)indazole (**2d**).

Reaction of 8 g. of 4-chloro-2-(2-fluorobenzoyl)-*N*-methylaniline (**1d**) (5) with 16 ml. of hydrazine under the same conditions yielded 7.3 g. (94%) of product with m.p. 132-134°. For analysis it was recrystallized from methylene chloride/hexane to give off-white prisms, m.p. 148-151°; uv: λ max 260 mμ (ε = 17,450) 296 (5,000) sh 307 (4,600) 351 (7,000).

Anal. Calcd. for $C_{14}H_{12}ClN_3$: C, 65.2; H, 4.7; N, 16.3. Found: C, 65.3; H, 4.6; N, 16.4.

3-[5-Chloro-2-(2-diethylaminoethyl)aminophenyl]indazole (**2e**).

Heating a mixture of 10 g. of 4-chloro-2-(2-fluorobenzoyl)-*N*-(2-diethylaminoethyl)aniline (**1e**) (6) and 30 ml. of hydrazine for 4.5 hours yielded 9 g. (91%) of crude product which was recrystallized from methanol, m.p. 140-142°; uv: λ infl 225 mμ (ε = 26,600) max 261 (18,450) sh 297 (4,900) 348 (6,100).

Anal. Calcd. for $C_{19}H_{23}ClN_4$: C, 66.6; H, 6.8; N, 16.3. Found: C, 66.6; H, 6.8; N, 16.5.

3-[2-(2-Dimethylaminoethyl)aminophenyl]indazole (**2f**).

Reaction of 8.5 g. of *N*-(2-dimethylaminoethyl)-2-(2-fluorobenzoyl)aniline (**1f**) (7) with 30 ml. of hydrazine gave 7.2 g. (86%) of product with m.p. 131-135°. The analytical sample was recrystallized from 2-propanol, m.p. 135-137°.

Anal. Calcd. for $C_{17}H_{20}N_4$: C, 72.8; H, 7.2; N, 20.0. Found: C, 73.0; H, 7.5; N, 20.1.

3-(2-Amino-5-chlorophenyl)-1-methylindazole (**2g**).

A solution of 25 g. of 4-chloro-2-(2-fluorobenzoyl)aniline (**1b**) (5) in 100 ml. of methylhydrazine was stirred and refluxed for 2 hours. The usual workup and recrystallization from methanol gave 23 g. (89%) of light tan crystals, m.p. 124-126°.

Anal. Calcd. for $C_{14}H_{12}ClN_3$: C, 65.2; H, 4.7; N, 16.2. Found: C, 65.0; H, 4.6; N, 16.4.

Indazolo[2,3-*c*]quinazoline (**3a**).

A mixture of 20.9 g. (0.1 mole) of **2a**, 22 g. (0.15 mole) of triethyl orthoformate, 2 g. of *p*-toluenesulfonic acid and 500 ml. of ethanol was stirred and refluxed for 30 minutes. The crystals separated from the cooled reaction mixture were collected, washed with ethanol and ether to leave 16 g. (73%) of pale yellow needles with m.p. 167-169°; uv: λ max 212 mμ (ε = 24,580) 247 (19,180) 259 (16,800) 287 (24,400) 295 (22,850) 311 (9,220) 363 (5,900) 380 (7,200) 398 (5,000).

Anal. Calcd. for $C_{14}H_9N_3$: C, 76.7; H, 4.1; N, 19.2. Found: C, 76.8; H, 4.1; N, 19.3.

2-Chloro[2,3-*c*]quinazoline (**3b**).

The same reaction of 2.4 g. of 2b with 2.2 g. of triethyl orthoformate and 0.2 g. of *p*-toluenesulfonic acid in 50 ml. of ethanol yielded 2 g. (80%) of yellow needles with m.p. 220-225°. For analysis, the product was recrystallized from dimethylformamide, m.p. 227-229°; uv: λ max 212 mμ (ε = 27,800) 251 (19,800) 273 (23,000) 287 (27,800) 297 (26,900) 316 (9,350) 334 (6,950) 366 (6,700) 382 (7,800) 402 (5,500).

Anal. Calcd. for $C_{14}H_8ClN_3$: C, 66.3; H, 3.2; N, 16.6. Found: C, 66.5; H, 3.0; N, 16.8.

6-Methylindazolo[2,3-*c*]quinazoline (**3c**).

Heating of 20.9 g. (0.1 mole) of **2a**, 22 g. of triethylorthoacetate and 2 g. of *p*-toluenesulfonic acid in 500 ml. of ethanol to reflux for 1 hour yielded 17.5 g. (75%) of off-white product with m.p. 163-165°. For analysis it was recrystallized from 2-propanol; uv: λ max 211 mμ (ε = 29,050) 246 (22,600) 278 (27,500) 287 (26,900) 311 (8,300) 325 (5,600) 359 (7,100) 377 (9,400) 396 (6,750).

Anal. Calcd. for $C_{15}H_{11}N_3$: C, 77.2; H, 4.7; N, 18.0. Found: C, 77.2; H, 4.5; N, 18.1.

Indazolo[2,3-*c*]quinazolin-6(5*H*)one (**4a**) (3).

Pyridine, 16 g. (0.2 mole) and 109 g. (0.11 mole) of a solution of 12.5% phosgene in benzene were added to a stirred suspension of 20.9 g. (0.1 mole) of **2a** in 100 ml. of methylene chloride. After stirring over night, the product was collected, washed with water and methanol to leave 19.5 g. (83%) of tan product with m.p. 338-340° dec. For analysis it was recrystallized from dimethylformamide, m.p. 340-342° dec.; uv: λ max 213 mμ (ε = 31,300) 238 (30,500) 267 (18,100) 293 (2,650) 306 (3,500) 319 (4,600) 344 (14,100) 360 (21,000) 378 (17,000).

2-Chloroindazolo[2,3-*c*]quinazolin-6(5*H*)one (**4b**).

Similarly, reaction of 2.4 g. (0.01 mole) of **2b** in 100 ml. of methylene chloride with 10.9 g. of phosgene solution (12.5% in benzene) and 1.6 g. of pyridine yielded within 1 hour 2.5 g. (93%) of product with m.p. 350°. The analytical sample was recrystallized from dimethylformamide, m.p. > 350°; uv: λ max 215 mμ (ε = 24,300) sh 227 (20,000) 243 (25,300) 267 (13,700) 276 (14,000) 300 (2,700) 312 (3,500) sh 328 (5,000) 347 (11,000) 363 (18,000) 381 (16,400).

Anal. Calcd. for $C_{14}H_8ClN_3O$: C, 62.3; H, 3.0; N, 15.9. Found: C, 62.2; H, 3.0; N, 15.8.

2-Chloro-5-methylindazolo[2,3-*c*]quinazolin-6(5*H*)one (**4d**).

A solution of 2.6 g. (0.01 mole) of **2d** in methylene chloride was reacted with phosgene and pyridine. After two hours at room temperature the precipitated product was collected, washed with water and ethanol to leave 2.4 g. (85%) of product with m.p. 310-312°. For analysis it was recrystallized from dimethylformamide; uv: λ max 215 mμ (ε = 28,000) 227 (24,600) 244

(32,400) 268 (18.900) 277 (20,100) 301 (3,750) 316 (4,750) sh 330 (7,100) 350 (14,750) 366 (23,000) 384 (20,500).

Anal. Calcd. for $C_{15}H_{10}ClN_3O$: C, 63.5; H, 3.5; N, 14.8. Found: C, 63.4; H, 3.5; N, 15.0.

2-Chloro-5-(2-diethylaminoethyl)indazolo[2,3-*c*]quinazolin-6-(5*H*)one (**4e**).

Potassium *t*-butoxide, 1.3 g. (0.011 mole) was added to a solution of 2.7 g. (0.01 mole) of **4b** in 150 ml. of dimethylformamide warmed to 100°. After stirring for 10 minutes 3.4 g. (0.011 mole of 43.9% solution of 2-diethylaminoethylchloride in toluene was added and the mixture was kept at 80-85° for 5 hours. the product was precipitated from the cooled solution by addition of water. It was collected, washed with water and recrystallized from 2-propanol to leave 2.4 g. (65%) of yellow crystals with m.p. 209-210°; uv: λ max 213 mμ (ε = 30,900) 244 (30,400) 267 (19,350) 276 (20,400) 300 (3,900) 314 (5,000) sh 330 (7,500) 349 (14,500) 365 (22,500) 383 (19,600); ir (chloroform): 1720 cm^{-1} (C=O).

Anal. Calcd. for $C_{20}H_{21}ClN_4O$: C, 65.1; H, 5.7; N, 15.2. Found: C, 65.0; H, 5.6; N, 15.1.

5-(2-Dimethylaminoethyl)indazolo[2,3-*c*]quinazolin-6(5*H*)one (**4f**).

A solution of 5.6 g. (0.02 mole) of **2f** in 200 ml. of methylene chloride was reacted with 21.8 g. of phosgene solution (12.5% in benzene) and 3.2 g. of pyridine. After stirring for 2 hours at room temperature the reaction mixture was partitioned between methylene chloride and 10% aqueous sodium carbonate. The organic phase was washed with water, dried and evaporated. Crystallization from ether yielded 3.8 g. (62%) of product with m.p. 159-162°. For analysis it was recrystallized from ethyl acetate, m.p. 161-162°; uv: λ max 214 mμ (ε = 29,600) 240 (29,400) 265 (20,400) 271 (30,350) 297 (3,440) 310 (4,460) 324 (5,820) 348 (14,700) 363 (20,800) 381 (16,500); ir (chloroform): 1720 cm^{-1} (C=O).

Anal. Calcd. for $C_{18}H_{10}N_4O$: C, 70.6; H, 5.9; N, 18.3. Found: C, 70.7; H, 6.1; N, 18.3.

2-Chloro-5,6-dihydro-5-methylindazolo[2,3-*c*]quinazoline (**5d**).

Aqueous formaldehyde (37%), 6 ml. was added to a warm solution of 12.9 g. (0.05 mole) of **2d** and 0.3 g. of *p*-toluenesulfonic acid in 250 ml. of ethanol. After standing at 50° for 15 minutes, the solution was chilled in ice and the precipitated crystals were collected to yield 11.8 g. (96%) of pale yellow needles with m.p. 156-159°. The analytical sample was recrystallized from methanol, m.p. 157-159°; uv: λ max 230 mμ (ε = 26,400) 270 (16,300) 308 (8,200) 322 (10,200) 366 (9,500); nmr (deuteriochloroform): δ 3.00 ppm (s, 3, NCH_3) 5.41 (s, 2, C_6-H) 6.7 (d, 1, J = 8.5 Hz, C_4-H) 7-8.1 (m, 6, aromatic H).

Anal. Calcd. for $C_{15}H_{12}ClN_3$: C, 66.8; H, 4.5; N, 15.6. Found: C, 66.9; H, 4.5; N, 15.7.

2-Chloro-6-chloromethyl-5,6-dihydro-6-methylindazolo[2,3-*c*]quinazoline (**5g**).

A mixture of 29.2 g. (0.12 mole) of **2b**, 13.6 g. (0.144 mole) of chloroacetone and 500 ml. of glacial acetic acid was stirred at room temperature for 1 hour. It was then partitioned between water and methylene chloride. The methylene chloride layer was washed with water and saturated aqueous sodium bicarbonate. The crude product obtained upon evaporation was purified by passing over a bed of silica gel using ethyl acetate/methylene chloride (1:1). The combined eluates were evaporated and the residue was crystallized from ethyl acetate/hexane to yield 20.5 g. (59%) of off-white prisms with m.p. 145-147° dec.; uv: λ max 230 mμ (ε = 29,500) 271 (15,700) 308 (7,000) 322 (7,600) 372 (9,600); ir (chloroform): 3400 cm^{-1} (NH).

Anal. Calcd. for $C_{16}H_{13}Cl_2N_3$: C, 60.4; H, 4.1; N, 13.2. Found: C, 60.6; H, 4.1; N, 13.1.

2-Chloro-5,6-dihydro-5-ethoxymethylindazolo[2,3-*c*]quinazoline (**5h**).

A mixture of 2.4 g. (0.01 mole) of **2b**, 1 ml. of aqueous formaldehyde (37%), a few crystals of *p*-toluenesulfonic acid and 75 ml. of ethanol was heated to reflux for 15 minutes. The crystals that precipitated upon cooling were collected to yield 1.8 g. (58%) of needles with m.p. 128-132°. The analytical sample was recrystallized from ethanol, m.p. 130-132°; uv: λ max 216 mμ (ε = 24,900) 230 (27,300) 268 (17,200) 305 (7,950) 318 (10,500) 353 (12,500); nmr (deuteriochloroform): δ 1.22 ppm (t, 3, J = 7 Hz, CH_3) 3.57 (q, 2, OCH_2) 4.81 (s, 2, OCH_2N) 5.71 (s, 2, C_6-H) 6.9-8.1 (m, 7, aromatic H).

Anal. Calcd. for $C_{17}H_{16}ClN_3O$: C, 65.1; H, 5.1; N, 13.4. Found: C, 65.2; H, 5.0; N, 13.6.

2-Chloro-5,6-dihydro-6-methoxycarbonylindazolo[2,3-*c*]quinazoline-6-acetic Acid Methyl Ester (**5i**).

A solution of 1.2 g. (0.005 mole) of **2b**, 0.9 g. (0.006 mole) dimethyl acetylenedicarboxylate and 25 ml. of ethanol was heated under reflux for 2 hours. The solution was cooled and concentrated to dryness *in vacuo* giving a residue which crystallized from ethyl acetate leaving 0.7 g. (37%) of off-white needles, m.p. 190-195°. Recrystallization from ethyl acetate afforded white needles, m.p. 197-198°; uv: λ max 230 mμ (ε = 31,100) 270 (15,600) 307 (6,700) 322 (7,350) 369 (9,950); ir (chloroform): 3400 cm^{-1} (NH) 1740 cm^{-1} (COOMe); nmr (deuteriochloroform); δ 3.24 (d, 1) and 4.30 (d, 1) (AB-system, J = 16.5 Hz, $-CH_2-$) 3.56 (s, 3, $COOCH_3$) 3.78 (s, 3, $COOCH_3$) 6.2 (broad s, 1, NH) 6.74 (d, 1, J = 8.5 Hz, C_4-H) 6.9-8.2 (m, 6, aromatic H).

Anal. Calcd. for $C_{19}H_{10}ClN_3O_4$: C, 59.1; H, 4.2; N, 10.9. Found: C, 59.1; H, 4.2; N, 10.9.

3-[2-(2-Chloroacetamido)-5-chlorophenyl]indazole (**6**).

Chloracetylchloride, 7.7 g. (0.06 mole) was added to a solution of 4.8 g. (0.02 mole) of **2b** in 60 ml. of methylene chloride and 20 ml. of ethanol. A saturated aqueous solution of sodium bicarbonate, 60 ml., was then added and the mixture was stirred for 3 hours at room temperature. The organic phase was separated, washed with bicarbonate and dried. The crude product obtained upon evaporation was chromatographed over 200 g. of silica gel using 5% ethyl acetate in methylene chloride. The pure fractions were combined and evaporated. Crystallization of the residue from methylene chloride/hexane yielded 5 g. (78%) of off-white prisms, m.p. 176-177°; uv: λ max 213 mμ (ε = 29,700) infl 233 (13,500) 258 (20,700) 305 (11,900).

Anal. Calcd. for $C_{15}H_{11}Cl_2N_3O$: C, 56.3; H, 3.5; N, 13.1. Found: C, 56.0; H, 3.3; N, 13.1.

Indazolo[2,3-*c*]benzo-1,2,3-triazene (**7a**).

Sodium nitrite, 11.7 g. (0.17 mole) was added to a solution of 20.9 g. (0.1 mole) of **2a** in 150 ml. of glacial acetic acid. After stirring at room temperature for 1.5 hours, the mixture was diluted with water and the precipitated yellow product was collected, washed and dried to leave 19 g. (86%). For analysis it was recrystallized from ethyl acetate, yellow needles, m.p. 246-247° dec.; uv: δ max 228 mμ (ε = 21,000) sh 242 (13,500) 264 (13,700) 297 (34,000) 307 (43,000) sh 330 (12,600) infl 347 (5,500) 430 (1,200).

Anal. Calcd. for $C_{13}H_8N_4$: C, 70.9; H, 3.7; N, 25.4. Found: C, 70.9; H, 3.5; N, 25.2.

2-Chloroindazolo[2,3-*c*]benzo-1,2,3-triazene (**7b**).

Reaction of 2.4 g. (0.01 mole) of **2b** with 1.2 g. of sodium nitrite in 20 ml. of glacial acetic acid yielded in the same manner 2.2 g. (88%) of orange product which after recrystallization from ethyl acetate had m.p. 246-248°; uv: λ max 228 mμ (ε = 21,000) sh 242 (13,500) 264 (13,700) 297 (34,000) 307 (43,000) sh 330 (12,600) infl 347 (5,500) 430 (1,200).

Anal. Calcd. for $C_{13}H_7Cl_1N_4$: C, 61.3; H, 2.8; N, 22.0. Found: C, 61.6; H, 2.6; N, 22.2.

2-Chloro-6-methyl-5,6-dihydro-5,6-methanoindazolo[2,3-*c*]quinazoline (**8**).

Potassium *t*-butoxide, 7.8 g. (0.07 mole) was added to a solution of 20.5 g. (0.064 mole) of **5g** in 250 ml. of dry tetrahydrofuran. After stirring at room temperature for 2 hours, the reaction mixture was filtered through a bed of celite and the filtrate was evaporated. Crystallization of the residue from ethyl acetate/hexane yielded 16 g. (89%) of product which was recrystallized from the same solvents for analysis, m.p. 146-148°; uv: λ max 228 mμ (ε = 25,300) 265 (15,000) 305 (7,000) 318 (11,350) 342 (15,900) 359 (14,900); nmr (deuteriochloroform): δ 1.93 ppm (s, 1) and 2.83 (s, 1) AB-system with J = 0 Hz, aziridine protons) (4) 2.12 (s, 3, CH_3) 7-8.2 (m, 7, aromatic H).

Anal. Calcd. for $C_{16}H_{12}ClN_3$: C, 68.2; H, 4.3; N, 14.9. Found: C, 67.9; H, 4.1; N, 14.8.

2-Chloro-5,7-dihydro-6*H*-indazolo[2,3-*d*][1,4]benxodiazepin-6-one (**9b**).

Potassium *t*-butoxide, 40.9 g. (0.37 mole) was added to a solution of 55.7 g. (0.174 mole) of **6** in 500 ml. of dry tetrahydrofuran. After stirring at room temperature for 1 hour, the solvent was evaporated under reduced pressure after being neutralized by addition of glacial acetic acid. The residue was partitioned between ether and water. The precipitated crystals were collected to leave 29.6 g. (60%) of off-white needles with m.p. 332-335° dec. The analytical sample was recrystallized from dimethylformamide/water, m.p. 339-340° dec.; uv: λ max 225 mμ (ε = 31,900) 262 (17,400) 325 (15,400), ir (potassium bromide): 3200 cm^{-1} (NH) 1700 (CO); nmr (DMSO) δ 5.12 ppm (s, 2, CH_2) 7-8.1 (m, 7, aromatic H) 10.8 (broad s, 1, NH).

Anal. Calcd. for $C_{15}H_{10}ClN_3O$: C, 63.6; H, 3.5; N, 14.8. Found: C, 63.3; H, 3.4; N, 14.9.

2-Chloro-5,7-dihydro-5-methyl-6*H*-indazolo[2,3-*d*][1,4]benzodiazepin-6-one (**9d**).

Potassium *t*-butoxide, 4.2 g. (0.038 mole) was added to a solution of 10 g. (0.035 mole) of **9b** in 125 ml. of dimethylformamide. The mixture was stirred at room temperature under nitrogen for 15 minutes when 5.4 g. (0.038 mole) of methyl iodide was added. After stirring for 1 hour, the mixture was diluted with water and was extracted with methylene chloride. The extracts were washed with water, dried and evaporated. The oily residue crystallized from methylene chloride/hexane and left 6.3 g. (61%) of product after recrystallization from ethyl acetate/hexane, m.p. 225-230°. The analytical sample was recrystallized again from methylene chloride/hexane, m.p. 232-235°; uv: λ max 228 mμ (ε = 29,500) 356 (18,000) 321 (15,800) infl 332 (14,000); ir (chloroform): 1690 cm^{-1} (CO).

Anal. Calcd. for $C_{16}H_{12}ClN_3O$: C, 64.5; H, 4.1; N, 14.1. Found: C, 64.7; H, 4.0; N, 14.1.

2-Chloro-5,7-dihydro-5-(2-diethylaminoethyl)-6*H*-indazolo[2,3-*d*]-[1,4]benzodiazepin-6-one Hydrochloride (**9e**).

Potassium *t*-butoxide, 1.2 g. (0.011 mole), was added to a solution of 2.8 g. (0.01 mole) of **9b** in 50 ml. of dimethylformamide. After stirring at room temperature under nitrogen for 30 minutes, 3.4 ml. (0.011 mole) a 44% solution of 2-diethylaminoethylchloride in toluene was added. The reaction mixture was stirred overnight, was diluted with water and extracted with methylene chloride. The combined extracts were washed with water, dried and evaporated. The oily residue was dissolved in ethanol and treated with ethanolic hydrogen chloride. The hydrochloride was crystallized by addition of ether to yield 2.1 g. (50%) of tan prism, m.p. 225-228° dec. For analysis it was recrystallized from ethanol/ether to afford off-white crystals, m.p. 231-233° dec.; ir (potassium bromide): 2400 cm^{-1}(NH^+) 1680 (CO).

Anal. Calcd. for $C_{21}H_{24}Cl_2N_4O$: C, 60.1; H, 5.8; N, 13.4. Found: C, 60.0; H, 6.0; N, 13.3.

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