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2H-INDAZOLES FROM 2-AMINOBENZOPHENONES

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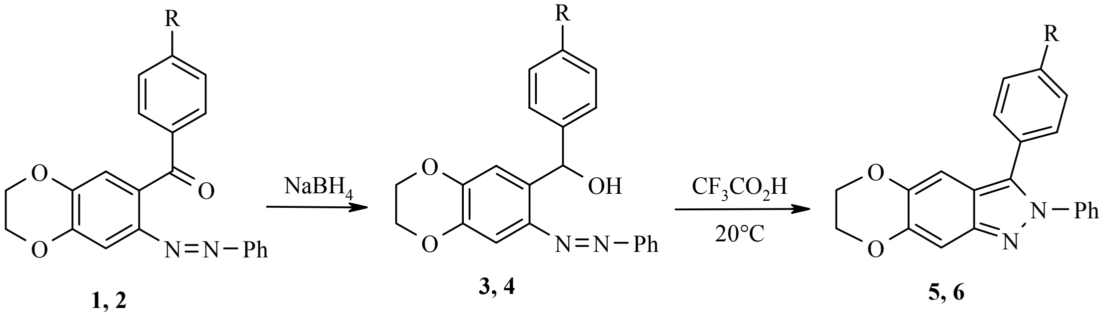
2H-Indazoles have proved difficult to prepare and, hence, have not been studied extensively. Only one general method is known for the preparation of such compounds, which involves the acid-catalyzed rearrangement of 2-arylazophenylcyclopropanes [1].

We are the first to show that 4,5-ethylenedioxy-2-phenylazobenzophenones **1** and **2**, which may be readily synthesized from 2-amino-4,5-ethylenedioxybenzophenones by condensation with nitrosobenzene, are converted by consecutive reduction and acid-catalyzed cyclization to give the corresponding substituted 2H-indazoles **5** and **6** in high yield.

The scope of this transformation as a general method for the synthesis of 2H-indazoles is under investigation.



1, **3**, **5** R = H; **2**, **4**, **6** R = Cl

The ^{1}H NMR spectra were taken on a Varian VX2-400 spectrometer at 400 MHz in $CDCl_3$ with residual $CHCl_3$ as the internal standard.

4,5-Ethylenedioxy-2-phenylazobenzhydrol (3). 4,5-Ethylenedioxy-2-phenylazobenzophenone (**1**) (0.69 g, 2 mmol) was added to a solution of $NaBH_4$ (75 mg, 2 mmol) in ethanol. The reaction mixture was stirred for 3 h at 40°C, cooled to 20°C, and treated with 10% hydrochloric acid until there was no further evolution of hydrogen gas. The ethanolic solution of the reduction product was poured into 150 ml water, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solvent was evaporated off and the residue was subjected to

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chromatography on a column packed with grade-II-activity alumina using 1:1:2 ether–CH_2Cl_2–petroleum ether as the eluent to give compound **3** (0.63 g, 91%), mp 115-116°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.92 (1H, d, *J* = 6.0, OH); 4.29 (4H, m, OCH_2CH_2O); 6.57 (1H, d, *J* = 6.0, CHAr); 6.99 (1H, s); 7.25 (1H, m); 7.35 (2H, m); 7.48 (6H, m); 7.80 (2H, m, Ar). Found, %: C 72.64; H 5.03; N 7.82. $C_{21}H_{18}N_2O_3$. Calculated, %: C 72.82; H 5.24; N 8.09.

4'-Chloro-4,5-ethylenedioxy-2-phenylazobenzhydrol (4) was obtained analogously from 4'-chloro-4,5-ethylenedioxybenzophenone-2-phenylazo (**2**) (0.76 g, 2 mmol) in 86% yield (0.66 g), mp 73-74°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.88 (1H, d, *J* = 5.8, OH); 4.33 (4H, m, OCH_2CH_2O); 6.51 (1H, d, *J* = 5.8, CHAr); 6.95 (1H, s); 7.27 (2H, d, *J* = 7.8); 7.37 (2H, d, *J* = 7.8); 7.44 (1H, s); 7.52 (3H, m, ArH); 7.77 (2H, m, ArH). Found, %: C 65.94; H 4.31; N 7.15. $C_{21}H_{17}ClN_2O_3$. Calculated, %: C 66.23; H 4.50; N 7.36.

5,6-Ethylenedioxy-2,3-diphenyl-2H-indazole (5). Phenylazobenzhydrazol **3** (0.35 g, 1 mmol) was dissolved in trifluoroacetic acid (3 ml). The reaction mixture was maintained for 15 min, poured into a 1:1 mixture of ice and water, and neutralized by adding sodium carbonate. The cyclization product was extracted with chloroform and dried over $MgSO_4$. The solvent was evaporated off and the residue was subjected to chromatography on a column packed with grade-II-activity alumina using 1:1:3 ether–CH_2Cl_2–petroleum ether as the eluent to give compound **5** (0.27 g, 82%), mp 199-200°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 4.33 (4H, m, OCH_2CH_2O); 7.06 and 7.20 (each 1H, 2 s, indazole H-4 and H-7); 7.30-7.45 (10H, m, ArH). Found, %: C 76.53; H 4.71; N 8.22. $C_{21}H_{16}N_2O_2$. Calculated, %: C 76.81; H 4.91; N 8.53.

3-(4-Chlorophenyl)-5,6-ethylenedioxy-2-phenyl-2H-indazole (6) was obtained analogously from phenylazobenzhydrol **4** (0.38 g, 1 mmol) in 86% yield (0.31 g), mp 179-180°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 4.33 (4H, m, OCH_2CH_2O); 7.06 and 7.20 (each 1H, 2 s, indazole H-4 and H-7); 7.25 (2H, d, *J* = 8.2); 7.35 (2H, d, *J* = 8.2); 7.41 (5H, m, ArH). Found, %: C 69.31; H 3.98; N 7.53. $C_{21}H_{15}ClN_2O_2$. Calculated, %: C 69.52; H 4.17; N 7.72.

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