Preparation of 4*H*-Pyrazolo[1,5-*a*]indole

Hajime KATAYAMA,* Masahiko SAKURADA, Wasala H. H. HERATH, Noriyuki TAKATSU and Jing-Kang SHEN

Niigata College of Pharmacy, 5–13–2 Kamishin'ei-cho, Niigata 950–21, Japan. *Received January 13, 1992*

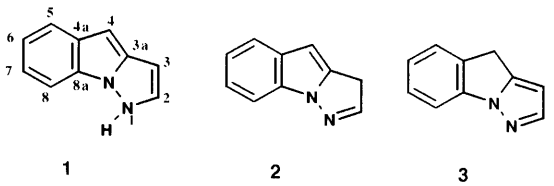
4*H*-Pyrazolo[1,5-*a*]indole was prepared by two pathways employing the decarbonylation of 2-formyl-4*H*-pyrazolo[1,5-*a*]indole and the intramolecular cyclization of 1-(2′-carboethoxyphenyl)pyrazole as key reactions. The latter of approach was found to be more practical than the former one.

Keywords preparation; decarbonylation; Wilkinson catalyst; fragmentation; dehydrogenation; 2-cyanomethylindoline; 2-formyl-4*H*-pyrazolo[1,5-*a*]indole; 4-oxo-4*H*-pyrazolo[1,5-*a*]indole; hydrogenolysis; 4*H*-pyrazolo[1,5-*a*]indole

There are three isomers of pyrazolo[1,5-*a*]indole and they are designated as 1*H*-, 3*H*- and 4*H*-pyrazolo[1,5-*a*]indoles (**1**, **2** and **3**) (Chart 1). Among them registry numbers have been given to **1** (42318-55-8) and **3** (247-75-6) but no report has appeared so far on the preparation of any of these compounds. In this report we would like to present the first synthesis of one of them, 4*H*-pyrazolo[1,5-*a*]indole (**3**).

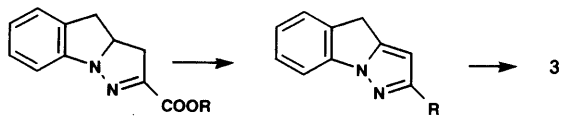
First, **3** was prepared according to the pathway outlined below (Chart 2). The ethyl ester **4a** was prepared by the known method described for the corresponding methyl ester.[1] The ester **4a** was then dehydrogenated with dichlorodicyano-*p*-benzoquinone (DDQ).[2a] The presence of the pyrazole ring in **5a** was supported by the ultraviolet (UV) (λ_{max} 272 nm; log ε 3.21) and proton nuclear magnetic resonance (^{1}H-NMR) spectra (δ 6.84, s).[2,3] The ester **5a** was hydrolyzed into the acid **5b**. Following the literature,[4] the acid **5b** was heated to 270 °C but no decarboxylation was observed.[5] Then **5a** was reduced with lithium aluminum hydride and the resulting alcohol **5c** was oxidized by the Swern procedure[6] to give the aldehyde **5d**, which was then subjected to decarbonylation.[7] An equimolar mixture of **5d** and tris(triphenylphosphine)rhodium chloride (Wilkinson's catalyst) in dry toluene was refluxed for 5 h and the product was recrystallized from pentane under cooling to give **3** in moderate yield. The title compound **3** has mp 41.0—42.5 °C and exhibited characteristic signals at δ 6.25 (1H, m due to long-range couplings) due to H-3 and 7.70 (1H, d, J=1.9 Hz) due to H-2. The drawback of this pathway is the poor reproducibility of the decarbonylation step and the high cost of the catalyst, so the second pathway was explored (*vide infra*). At the same time, two other attempts were made to prepare the dihydro derivative of **3**, 3,3a-dihydro-4*H*-pyrazolo[1,5-*a*]indole (**8**) (Chart 3). Firstly, the acid **4b** was derived from the ester **4a** and heated at 160 °C, resulting in gas evolution. The residue was sublimed *in vacuo* and the nitrile **7** was obtained in 91% yield. The nitrile **7** was identical with 2-cyanomethylindoline derived from 2-cyanomethylindole[8] by reduction with sodium cyanoborohydride.[9] The formation of **7** can be rationalized in terms of a fragmentation reaction[10] as shown for **6**, and this provides a good method for the preparation of **7**. Secondly, ester **4a** was reduced with lithium aluminum hydride and the obtained mixture of aminoalcohols (**9a** and **9b**) was oxidized with periodic acid. No C–C bond cleavage was observed, but the dehydrogenated product **5c** was formed.

Since the above pathway is not practical for a large quantity of **3**, the following pathway was developed (Chart 4). Alley and Shirley have reported that the reaction of 1-phenylpyrazole (**10a**) with 2 eq of butyllithium and subsequent trapping of the organolithium compound with carbon dioxide led to the formation of the cyclized product **11a** (8%) and its 8-carboxylated derivative (26%).[11] Also, Marxer and Siegrist have observed that ethylmagnesium bromide selectively removed the *ortho*-proton of the phenyl ring from **10a** and butyl lithium preferentially abstracted H-5 on the pyrazole ring of **10a**.[12] Based upon these reports,



1 2 3

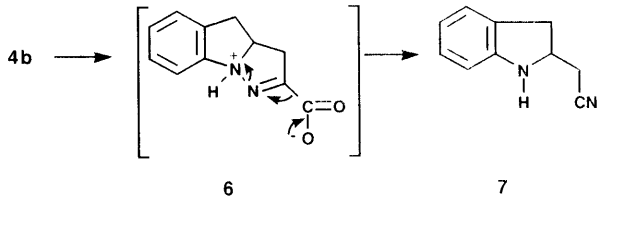
Chart 1



4a: R=Et
4b: R=H

5a: R=COOEt **5c**: R=CH_2OH
5b: R=COOH **5d**: R=CHO

Chart 2

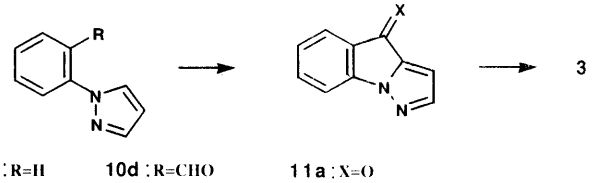


6 7

8

9a: R^1=CH_2OH, R^2=H
9b: R^1=H, R^2=CH_2OH

Chart 3



10a: R=H **10d**: R=CHO
10b: R=COOEt **10e**: R=CH2OH
10c: R=COOH

11a: X=O
11b: X=NNHCONH$_2$
11c: X=H, OH

Chart 4

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the ester **10b** was prepared from anthranilic acid according to the reported procedures,[11,13] and treated with lithium diisopropylamide (LDA). When the reaction was carried out at −78 °C, the tricyclic product **11a** was obtained in 65% yield. The starting material (12%) and the reduced product **11c** (15%) were also isolated. The yield of **11a** became poor when the reaction temperature was higher than −20 °C and when hexamethylphosphoric triamide (HMPA)[14] was added. No **11a** was obtained when lithium 2,2,6,6-tetramethylpiperidide,[15] instead of LDA, was used in order to avoid the reduction of **11a** with LDA. The alcohol **11c** was readily formed by the reduction of **11a** with sodium borohydride in 99% yield and oxidized to the ketone **11a** by pyridinium chlorochromate (PCC)[16] in 97% yield. The ketone **11a** was transformed into the semicarbazone **11b**, Wolff–Kishner reduction[17] of which yielded an intractable mixture. The preparation of **3** was carried out by hydrogenolytic removal of the hydroxy group from **11c** with 10% palladium on charcoal in 77% yield. This procedure is more convenient and practical than the above decarbonylation method, and allows the synthesis of large quantities of 3*H*-pyrazolo[1,5-*a*]indole (**3**).

Experimental

2-Ethoxycarbonyl-4*H*-pyrazolo[1,5-*a*]indole (5a) A solution of 2-ethoxycarbonyl-3a,4-dihydro-3*H*-pyrazolo[1,5-*a*]indole (**4a**)[1] (0.697 g, 3 mmol) and DDQ (1.106 g, 4.5 mmol) in dry benzene (70 ml) was refluxed for 2.5 h. The solvent was evaporated off and the residue was chromatographed repeatedly on silica gel with dichloromethane containing 2% ethyl acetate. The product (613 mg, 88%) thus obtained was recrystallized from methanol to give **5a** (472 mg, 68%), mp 126.0—127.0 °C. MS *m/z* (relative intensity): 228 (M^+, 80.2), 200 (18.8), 183 (88.1), 156 (54.5), 155 (100), 130 (27.2), 128 (28.8). UV λ_{max}^{EtOH} nm (log ε): 207 (3.11), 272 (3.21), 281 (3.14), 288 (3.10). IR (KBr): 3151, 3061, 1716, 1381, 1219, 1156, 779 cm^{-1}. ^{1}H-NMR δ: 1.43 (3H, t, *J*=7.0 Hz, $MeCH_2O$), 3.90 (2H, br s, H-4), 4.45 (2H, q, *J*=7.0 Hz, $MeCH_2O$), 6.84 (1H, br s, H-3), 7.25 (1H, t, *J*=7.4 Hz, H-6), 7.42 (1H, t, *J*=7.5 Hz, H-7), 7.47 (1H, d, *J*=7.5 Hz, H-5), 7.80 (1H, d, *J*=7.8 Hz, H-8). ^{13}C-NMR δ: 14.4 ($MeCH_2O$), 28.2 (C-4), 61.0 ($MeCH_2O$), 103.8 (C-3), 111.7 (C-8), 125.7 (C-6), 125.9 (C-5), 128.2 (C-7), 133.9 (C-3a), 139.9 (C-4a), 145.2 (C-8a), 147.5 (C-2), 162.6 (CO). *Anal.* Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.33; H, 5.30; N, 12.26.

2-Carboxy-4*H*-pyrazolo[1,5-*a*]indole (5b) A solution of **5a** (250 mg) and 3 M potassium hydroxide in 80% ethanol was refluxed for 2 h. After adjustment of the pH to 5.5 with 3 M hydrochloric acid, the reaction mixture was extracted with ethyl acetate. The extract was washed with saturated brine, dried over magnesium sulfate, then evaporated. The crude product was recrystallized from dichloromethane and the crystal (162 mg, 74%) were sublimed at 150—170 °C (3 mmHg) to give **5b**, mp 264.0—264.5 °C (dec.). MS *m/z*: 200 (M^+, 100), 182 (20.7), 155 (53.6), 129 (33.5). IR (KBr): 3500—2600, 1695, 1470, 1250, 1229, 746 cm^{-1}. ^{1}H-NMR ($CD_3OD+CDCl_3$) δ: 3.96 (2H, s, H-4), 6.88 (1H, br s, H-3), 7.30 (1H, dt, *J*=0.7, 7.6 Hz, H-6), 7.45 (1H, t, *J*=7.6 Hz, H-7), 7.53 (1H, d, *J*=7.6 Hz, H-5), 7.77 (1H, d, *J*=7.6 Hz, H-8). ^{13}C-NMR ($CD_3OD+CDCl_3$) δ: 28.0 (C-4), 103.7 (C-3), 111.3 (C-8), 125.7 (C-6), 125.9 (C-5), 128.1 (C-7), 133.8 (C-4a), 139.4 (C-2), 145.4 (C-3a), 147.3 (C-8a), 164.2 (CO). *Anal.* Calcd for $C_{11}H_8N_2O_2$: C, 66.00; H, 4.03; N, 13.99. Found: C, 65.85; H, 4.02; N, 13.84.

2-Hydroxymethyl-4*H*-pyrazolo[1,5-*a*]indole (5c) A solution of **5a** (1.153 g) in dry ether (50 ml) was dropped into a solution of lithium aluminum hydride (0.64 g) in dry ether (250 ml). The mixture was refluxed for 2 h, the excess reagent was decomposed by the addition of 10% potassium hydroxide (2.2 ml) and sodium fluoride (1 g), followed by warming of the mixture. Inoganic materials were removed by filtration, and evaporation of the filtrates gave the crude product, which was recrystallized from benzene to yield **5c** (0.84 g, 90%), mp 121.0—122.0 °C. MS *m/z*: 186 (M^+, 100), 185 (33.0), 169 (71.3), 157 (64.9), 156 (60.1), 155 (85.6), 130 (86.7), 129 (51.6), 128 (29.8). IR (KBr): 3294, 3056, 1623, 1542, 1477, 1407, 1348, 1033, 994, 785, 746 cm^{-1}. ^{1}H-NMR δ: 3.78 (2H, s, H-4), 4.78 (2H, s, CH_2OH), 6.27 (1H, s, H-3), 7.15 (1H, dt, *J*=0.9, 7.5 Hz, H-6), 7.35 (1H, t, *J*=7.5 Hz, H-7), 7.40 (1H, d, *J*=7.5 Hz, H-5), 7.58 (1H, d, *J*=7.5 Hz, H-8). ^{13}C-NMR δ: 28.2 (C-4), 59.3 (CH_2OH), 99.5 (C-3), 110.4 (C-8), 124.3 (C-6), 125.8 (C-5), 128.0 (C-7), 133.2 (C-2), 140.3 (C-4a), 145.5 (C-3a), 157.2 (C-8a). *Anal.* Calcd for $C_{11}H_{10}N_2O_2$: C, 70.95; H, 5.41; N, 15.04. Found: C, 71.04; H, 5.38; N, 15.06.

2-Formyl-4*H*-pyrazolo[1,5-*a*]indole (5d) A solution of oxalyl chloride (0.10 ml, 1.1 mmol) and dry dimethyl sulfoxide (DMSO) (0.18 ml, 1 mmol) in dry dichloromethane (5 ml) was stirred at −60 °C for 15 min in an atmosphere of dry nitrogen. Then a solution of **5c** (184 mg, 1 mmol) in dry dichloromethane (5 ml) was slowly introduced into this reagent over a period of 10 min and the resulting mixture was allowed to react for 15 min. Triethylamine (0.7 ml) was then added and the mixture was slowly warmed to −15 °C and kept at this temperature for 20 min. Dichloromethane (5 ml) and saturated brine were added and the mixture was stirred for 1 h at room temperature. The extraction with dichloromethane gave the crude product (241 mg), which was chromatographed (silica gel 5 g, dichloromethane containing 5% ethyl acetate) to afford **5d** (133 mg, 72%), mp 144.0—145.5 °C (benzene). MS *m/z*: 184 (M^+, 100), 155 (54), 129 (24). IR (KBr): 2867, 2784, 1688, 1456, 1305, 1111, 819, 808, 755 cm^{-1}. ^{1}H-NMR δ: 3.94 (2H, s, H-4), 6.84 (1H, s with small splittings, H-3), 7.31 (1H, dt, *J*=1.2, 7.6 Hz, H-6), 7.46 (1H, br t, *J*=7.6 Hz, H-7), 7.52 (1H, d, *J*=7.6 Hz, H-5), 7.75 (1H, d, *J*=7.6 Hz, H-8), 10.06 (1H, s, CHO). ^{13}C-NMR δ: 28.2 (C-4), 100.7 (C-3), 111.5 (C-8), 126.2 (C-5+C-6), 128.4 (C-7), 134.2 (C-4a), 139.5 (C-2), 145.9 (C-3a), 155.3 (C-8a), 186.8 (C-9). *Anal.* Calcd for $C_{11}H_8N_2O$: C, 71.73; H, 4.37; N, 15.21. Found: C, 71.99; H, 4.35; N, 15.23.

4*H*-Pyrazolo[1,5-*a*]indole (3) A mixture of the aldehyde **5d** (184 mg, 1 mmol) and Wilkinson's catalyst (987 mg, 1 mmol) in dry toluene (10 ml) was refluxed for 5 h. The reaction mixture was evaporated and the residue was dissolved in ethanol (5 ml). This solution was filtered to remove yellow precipitates. The oil (511 mg) obtained by evaporation of the filtrate was chromatographed on silica gel (15 g, petroleum ether–dichloromethane, 1 : 1) to separate triphenylphosphine and crude **3** (144 mg, 92%). Further purification was carried out by recrystallization from pentane under cooling to give pure **3** (50%). Reduction of the impure product with sodium borohydride, followed by chromatography, was also effective for the removal of contaminating starting material. **3**: mp 41.0—42.5 °C. MS *m/z*: 156 (M^+, 100), 155 (35.5), 129 (71.8), 128 (17.5), 102 (27.5), 101 (7.9). UV λ_{max}^{MeCN} (log ε): 254 (sh 3.71), 259 (3.75), 263 (sh, 3.72). IR (KBr): 1622, 1542, 1472, 1397, 755 cm^{-1}. ^{1}H-NMR δ: 3.81 (2H, s, H-4), 6.25 (1H, m with long-range couplings, H-3), 7.15 (1H, dt, *J*=0.9, 7.5 Hz, H-6), 7.30 (1H, t, *J*=7.5 Hz, H-7), 7.41 (1H, d, *J*=7.5 Hz, H-5), 7.62 (1H, d, *J*=7.5 Hz, H-8), 7.70 (1H, d, *J*=1.9 Hz, H-2). ^{13}C-NMR δ: 28.0 (C-4), 100.5 (C-3), 110.4 (C-8), 124.3 (C-6), 125.8 (C-5), 127.9 (C-7), 133.6 (C-4a), 140.5 (C-3a), 143.7 (C-2), 144.4 (C-8a). *Anal.* Calcd for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.93. Found: C, 77.10; H, 5.13; N, 17.96.

2-Carboxy-3a,4-dihydro-3*H*-pyrazolo[1,5-*a*]indole (4b) A solution of **4a** (2.310 g) and 3 M potassium hydroxide in 80% ethanol (30 ml) was refluxed for 2 h. The solution was neutralized to pH *ca.* 6 and extracted with ethyl acetate. The crude product (2.19 g) was recrystallized from methanol to give **4b** (1.587 g, 78%), mp 127.0—128.5 °C (dec.). MS *m/z*: 202 (M^+, 14.3), 158 (14.9), 130 (14.4), 118 (100), 91 (27.6). IR (KBr): 3200—2600, 1681, 1257, 753 cm^{-1}. ^{1}H-NMR δ: 3.01 (1H, dd, *J*=6.3, 18.3 Hz, H-3), 3.02 (1H, dd, *J*=9.2 Hz, 15.6 Hz, H-4), 3.27 (1H, dd, *J*=9.2, 15.6 Hz, H-4), 3.35 (1H, dd, *J*=11.7, 18.3 Hz, H-3), 4.78 (1H, dtd, *J*=6.3, 9.2, 11.7 Hz, H-3a), 7.09 (1H, t, *J*=7.5 Hz, H-6), 7.20 (1H, d, *J*=7.5 Hz, H-5), 7.24 (1H, t, *J*=7.5 Hz, H-7), 7.39 (1H, d, *J*=7.5 Hz, H-8). ^{13}C-NMR δ: 38.0 (C-3), 39.3 (C-4), 65.0 (C-3a), 118.3 (C-8), 126.3 (C-6), 126.4 (C-5), 128.8 (C-7), 132.5 (C-4a), 148.5 (C-2), 150.1 (C-8a), 165.0 (CO). *Anal.* Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.30; H, 4.96; N, 13.82.

Pyrolysis of 2-Carboxy-3a,4-dihydro-3*H*-pyrazolo[1,5-*a*]indole (4b) The acid **4b** (102 mg) was placed in a sublimation apparatus and heated to 160 °C. When gas evolution was complete, the residue was sublimed at the same temperature under vacuum (2 mmHg) to give fine needles (72 mg, 91%); this product was identical with authentic 2-cyanomethylindoline (**7**) prepared by reduction of 2-cyanomethylindole[9] with sodium cyanoborohydride in acetic acid.[10]

Reduction of 2-Ethoxycarbonyl-3a,4-dihydro-3*H*-pyrazolo[1,5-*a*]indole (4a) with Lithium Aluminum Hydride A solution of ester **4a** (2.436 g) dissolved in dry ether (100 ml) was added to a suspension of lithium aluminum hydride (2.0 g) in dry ether (900 ml) during 10 min. The resulting mixture was refluxed for 2 h. Excess reagent was decomposed by the successive addition of 10% potassium hydroxide (9.5 ml) and sodium fluoride (1.50 g) and the mixture was refluxed for 0.5 h. The precipitates

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were removed by filtration and washed with ether twice. The combined filtrate and washings were evaporated and the crude product (3.809 g) was chromatographed on silica gel (100 g) with dichloromethane containing 5% methanol. The first eluate contained **9a** (1.180 g, 31%) and the second, **9b** (1.174 g, 31%). Between these two fractions a mixture of the two isomers (1.13 g) was obtained.

2*RS*,3a*SR*-2-Hydroxymethyl-1,2,3a,4-tetrahydro-3*H*-pyrazolo[1,5-*a*]-indole (**9a**): mp 83.5—84.0 °C (benzene). MS *m/z*: 190 (M^+, 37.5), 159 (14.3), 132 (100), 131 (32.7), 130 (24.5), 117 (24.5). IR (KBr): 3362, 3261, 1606, 1484, 1471, 1071, 1060, 764, 724 cm^{-1}. ^{1}H-NMR δ: 1.35 (1H, ddd, J=6.8, 9.0, 12.7 Hz, H-3), 2.26 (1H, td, J=8.0, 12.6 Hz, H-3), 2.42 (1H, br, NH), 2.80 (1H, dd, J=8.3, 10.7 Hz, CHHOH), 2.97 (1H, d, J=15.4 Hz, H-4), 3.15 (1H, dd, J=7.6, 15.4 Hz, H-4), 3.31 (1H, dd, J=4.4, 10.7 Hz, CHHOH), 3.57 (1H, m, H-2), 3.97 (1H, m, H-3a), 4.38 (1H, br, OH), 6.85 (1H, dt, J=0.9, 7.5 Hz, H-6), 6.96 (1H, d, J=7.5 Hz, H-8), 7.08 (1H, d, J=7.5 Hz, H-5), 7.13 (1H, t, J=7.5 Hz, H-7). ^{13}C-NMR δ: 33.3 (C-4), 35.1 (C-3), 61.7 (C-2), 65.0 (C-9), 66.6 (C-3a), 113.3 (C-8), 121.7 (C-6), 125.3 (C-5), 127.1 (C-4a), 127.8 (C-7), 154.0 (C-8a). *Anal.* Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.72. Found: C, 69.46; H, 7.29; N, 14.70.

2*SR*,3a*SR*-2-Hydroxymethyl-1,2,3a,4-tetrahydro-3*H*-pyrazolo[1,5-*a*]-indole (**9b**): mp 90.0—91.0 °C (benzene). MS *m/z*: 190 (M^+, 46.8), 159 (19.4), 132 (100), 131 (90.3), 130 (28.0), 117 (25.1). IR (KBr): 3253, 3181, 1606, 1593, 1474, 1464, 1065, 1052, 752, 714 cm^{-1}. ^{1}H-NMR δ: 1.72 (1H, ddd, J=6.5, 8.7, 12.7 Hz, H-3), 2.64 (1H, ddd, J=6.8, 8.7, 12.7 Hz, H-3), 2.96 (1H, dd, J=1.7, 15.8 Hz, H-4), 3.19 (1H, dd, J=8.0, 15.8 Hz, H-4), 3.15 (1H, m, H-2), 3.63 (1H, dd, J=3.8, 11.2 Hz, CHHOH), 3.81 (1H, dd, J=3.4, 11.2 Hz, CHHOH), 3.98 (1H, m, H-3a), 6.88 (1H, dt, J=1.2, 7.3 Hz, H-6), 7.02 (1H, d, J=7.3 Hz, H-8), 7.09 (1H, d, J=8.0 Hz, H-5), 7.15 (1H, t, J=7.3 Hz, H-7). ^{13}C-NMR δ: 34.7 (C-4), 36.4 (C-3), 59.8 (C-2), 62.0 (CH_2OH), 65.7 (C-3a), 114.8 (C-8), 122.1 (C-6), 124.8 (C-5), 127.7 (C-7), 128.8 (C-4a), 152.5 (C-8a). *Anal.* Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.72. Found: C, 69.55: H, 7.39; N, 14.72.

Periodate Oxidation of a Mixture of 2-Hydroxymethyl-2,3,3a,4-tetrahydro-1*H*-pyrazolo[1,5-*a*]indole (9a and 9b) A solution of periodic acid dihydrate (1.157 g, 50 mmol) in water (10 ml) was slowly dropped into a solution of a mixture of the two isomers (0.955 g, 5 mmol) dissolved in methanol (40 ml) at 5 °C under vigorous stirring. Then the mixture was allowed to react at the same temperature until the starting material was no longer detectable (0.5 h). The reaction mixture was basified with sodium carbonate and extracted with dichloromethane. The black crude product was chromatographed (silica gel 15 g, dichloromethane containing 5% methanol) to afford an oil (0.351 g, 37%), which was found to be identical with **5c** after recrystallization from benzene (0.146 g).

Reaction of 1-(2′-Ethoxycarbonylphenyl)pyrazole (10b) with LDA Under dry nitrogen at −15 °C, 1.4 M *n*-butyl lithium in hexane (4 M, 15.5 ml, 21.7 mmol) was slowly introduced into a solution of the diisopropylamino (3.1 ml, 22.1 mmol) in dry tetrahydrofuran (THF) (200 ml) over 5 min. The resulting solution was slowly warmed to 0 °C then recooled to −78 °C. A solution of **10b** (4.325 g, 20 mmol; bp 165 °C/30 mmHg, Kugelrohr) in dry THF (10 ml) was added dropwise into this solution for 10 min and the mixture was stirred vigorously at −78 °C for 45 min. The red solution was quenched with saturated ammonium chloride and extracted with dichloromethane. The solid product (3.774 g) was separated by column chromatography (silica gel 120 g, ethyl acetate–petroleum ether) to give **11a** (1.973 g, 65% corrected yield based on the consumed starting material), the starting material **10b** (0.511 g, 12%), and **11c** (0.515 g, 15%).

4-Oxo-4*H*-pyrazolo[1,5-*a*]indole (**11a**): mp 107—109 °C (sublimed) (lit.[11] 107—109 °C). MS *m/z*: 170 (M^+, 100), 144 (17.4), 143 (25.8), 115 (32.1). UV λ_{max}^{MeOH} (log ε): 215 (4.05), 243 (sh), 250 (4.56), 267 (4.11), 287 (4.08), 302 (3.62), 314 (3.68). IR (KBr): 3140, 1724, 1626, 1599, 1462, 1372, 1310, 1296, 1184, 1145, 1124, 931, 885, 831, 752 cm^{-1}. ^{1}H-NMR δ: 6.67 (1H, d, J=1.9 Hz, H-3), 7.20 (1H, dt, J=0.9, 7.5 Hz, H-6), 7.43 (1H, d, J=7.5 Hz, H-8), 7.54 (1H, dt, J=1.2, 7.5 Hz, H-7), 7.61 (1H, d, J=7.5 Hz, H-5), 7.67 (1H, d, J=1.9 Hz, H-2); ^{13}C-NMR δ: 106.4 (C-3), 110.8 (C-8), 125.0 (C-5), 126.4 (C-6), 128.3 (C-4a), 135.5 (C-7), 138.7 (C-3a), 143.8 (C-8a), 145.4 (C-2), 179.2 (C-4).

4-Hydroxy-4*H*-pyrazolo[1,5-*a*]indole (**11c**): mp 155—158 °C (dichloromethane–methanol). MS *m/z*: 172 (M^+, 100), 155 (14), 145 (38), 144 (57), 128 (12), 117 (34), 105 (19), 101 (10). UV λ_{max}^{MeOH} (log ε): 270 (4.11), 219 (4.31); IR (KBr): 3225, 1620, 1478, 1374, 1050, 755 cm^{-1}. ^{1}H-NMR δ: 3.20 (1H, d, J=10 Hz, OH), 5.65 (1H, d, J=10 Hz, H-4), 6.35 (1H, s, with small splittings, H-3), 7.18 (1H, dt, J=1.9, 7.6 Hz, H-6), 7.36 (1H, t, J=7.6 Hz, H-7), 7.42 (1H, d, J=7.6 Hz, H-5), 7.46 (1H, d, J=1.9 Hz, H-2), 7.55 (1H, d, J=7.3 Hz, H-8). ^{13}C-NMR δ: 66.9 (C-4), 102.8 (C-3), 110.5 (C-8), 125.2 (C-6), 125.9 (C-5), 129.9 (C-7), 137.2 (C-4a), 139.3 (C-3a), 144.3 (C-2), 147.2 (C-8a). *Anal.* Calcd for $C_{10}H_8N_2O$: C, 69.75; 4.68; N, 16.27. Found: C, 69.65; H, 4.72; N, 16.21. The alcohol **11c** was identical with the specimen prepared by the usual reduction of the ketone **11a** with sodium borohydride in 99% yield, and was oxidized to **11a** by PCC[16] in 97% yield.

4-Oxo-4*H*-pyrazolo[1,5-*a*]indole Semicarbazone (11b) A mixture of **11a** (0.645 g) and semicarbazide hydrochloride (2 g) in ethanol (20 ml) was refluxed until the ketone was completely consumed. The reaction mixture was diluted with water and left in a refrigerator overnight. The precipitates were collected to give the semicarbazone **11b** (0.775 g), mp > 300 °C (dichloromethane–methanol). MS *m/z*: 227 (M^+, 47), 216 (14), 210 (4), 184 (80), 171 (46), 155 (10), 149 (29), 144 (34), 129 (24), 43 (100). IR (KBr): 3477, 3323, 3225, 3130, 1739, 1635, 1577, 807, 747 cm^{-1}. ^{1}H-NMR δ (d_6-DMSO): 7.04 (2H, br, NH_2), 7.31 (1H, br t, J=7.5 Hz, H-6), 7.44 (1H, d, J=1.9 Hz, H-3), 7.50 (1H, t, J=7.5 Hz, H-7), 7.58 (1H, d, J=7.5 Hz, H-8), 7.87 (1H, d, J=1.9 Hz, H-2), 8.02 (1H, d, J=7.5 Hz, H-5). ^{13}C-NMR δ (d_6-DMSO): 105.0 (C-3), 109.6 (C-8), 122.0 (C-5), 124.8 (C-6), 128.8 (C-4a), 129.7 (C-7), 132.8 (C-3a), 137.8 (C-8a), 144.1 (C-2), 155.9 (C-4+CO).

Hydrogenolysis of 4-Hydroxy-4*H*-pyrazolo[1,5-*a*]indole (11c) A solution of **11c** (2.0 g) in ethyl acetate (100 ml) was stirred vigorously with 10% palladium on charcoal (2 g) in an atmosphere of hydrogen for 2 d (50% completion). The catalyst was removed and replaced with fresh catalyst (1 g). The reaction was resumed for 2 d. Filtration of the reaction mixture and evaporation of the filtrate give an oil (1.5 g), which was dissolved in hexane–dichloromethane (3:2) and left in refrigerator overnight. Removal of the precipitated starting material (0.05 g) and evaporation of the filtrate yielded **3** (1.4 g, 77%), which was identical with the specimen prepared by the decarbonylation of **5d**.

References and Notes

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