

Indazolo[2,3-*a*]quinazoline

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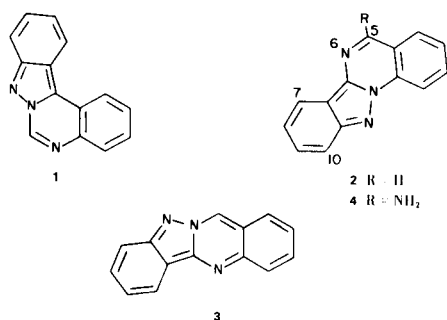
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Received July 15, 1976

Zinc-acetic acid reduction of 2,2'-dicyanoazobenzene affords, beside the expected 5-aminoindazolo[2,3-*a*]quinazoline, the previously unreported parent compound: indazolo[2,3-*a*]quinazoline.

J. Heterocyclic Chem., 13, 1325 (1976).

Although substituted derivatives of the structural isomers of the indazoloquinazolines **1**, **2**, and **3** have been known for some time (**1**), the only reported parent compound is the recently synthesized (**2**) indazolo[2,3-*c*]-



quinazoline (**1**). We now report the preparation of the second member in this series, indazolo[2,3-*a*]quinazoline (**2**), encountered unexpectedly in the course of repeating Stevens' preparation (**3**) of 5-aminoindazolo[2,3-*a*]quinazoline (**4**) by the zinc-acetic acid reduction of 2,2'-dicyanoazobenzene (**5**). This new material was isolated (16%) as greenish-yellow needles, m.p. 170-171°.

The elemental and spectroscopic data support the assigned structure. No bands were observed in the ir spectrum below 6.1 microns (lack of NH). The elemental analysis together with its mass spectrum, which showed a molecular ion at 219 (100%) with little further fragmentation, indicated a molecular formula of C₁₄H₉N₃. The nmr spectrum (deuteriochloroform) showed only aromatic protons including a one proton singlet at δ 9.0 assigned to H₅ and two finely split one proton doublets ($J = 6.0$ Hz, $J < 1.0$ Hz) at δ 8.80 and δ 8.30 assigned to H₇ and H₁₀, respectively. In accordance with their assignment, irradiation experiments demonstrated that these finely split doublets were not mutually coupled. The uv spectrum (ethanol) of **2** was virtually superposable over that of **4** showing

bands at 242 nm, 298 nm, and 370 nm.

Finally, subsection of **4** to the conditions of its formation gave **2** in low yield (3%) (**6**). These data are consistent only with structure **2**. Formation of **2** may best be explained by the reduction of the 5,6 carbon-nitrogen double bond of **4** followed by the elimination of ammonia.

EXPERIMENTAL (7)

Melting points (uncorrected) were determined in a Thomas-Hoover Uni-Melt capillary m.p. apparatus. Ir spectra were recorded on a Perkin-Elmer model 137B spectrophotometer; nmr spectra were obtained on a Perkin-Elmer R32 90 MHz spectrometer; mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E mass spectrometer and uv spectra were obtained on a Carey 14 uv spectrometer.

5-Aminoindazolo[2,3-*a*]quinazoline (**4**) and indazolo[2,3-*a*]quinazoline (**2**).

A mixture of 48 g. (0.72 g.-atom) of powdered zinc, 18.5 g. (0.08 mole) of 2,2'-dicyanoazobenzene (**5**) (**3**) and glacial acetic acid (1.95 l.) was refluxed for 1 hour. The hot mixture was filtered and the filter cake washed with ethanol. The combined filtrates on cooling to room temperature gave a yellow precipitate (**4**). After filtration, the solvent was removed *in vacuo* to give a yellow solid residue. "Dry-column" chromatography (**8**) (alumina, chloroform) of the residue gave two yellow bands. The second yellow band eluted (**4**) was combined with the first precipitate and recrystallized to give 12.8 g. (68%) of **4**, m.p. 221-223° (ethanol) (lit. (**3**) m.p. 223-224°); nmr (dimethylsulfoxide-*d*₆): δ TMS 8.5-6.7; uv λ max (ethanol): $m\mu$ (log ϵ) 239 (4.69), 295 (4.33), 372 (3.94); mass spectrum (70 e/v): m/e (relative intensity) 234 (100), 208, 127, 103, 102, 90, 76.

The first band eluted gave a yellow solid which was recrystallized to give 2.8 g. (16%) of **2**, m.p. 170-171° (greenish-yellow needles from ethanol), nmr (deuteriochloroform): δ TMS 9.0 (1H, s, H₅), 8.8 (1H, d, $J = 6.0$ Hz, H₇), 8.3 (1H, d, $J = 6.0$ Hz, H₁₀), 8.1-7.2 (6H, m); uv λ max (ethanol): $m\mu$ (log ϵ) 242 (4.64), 298 (4.09), 370 (3.97); mass spectrum (70 e/v): m/e (relative intensity) 219 (100), 189 (8), 163 (4), 109 (6) 102 (4).

Anal. Calcd. for $C_{14}H_9N_3$: C, 76.70; H, 4.14; N, 19.17.
Found: C, 76.48; H, 4.23; N, 19.01.

Compound **2** formed an unstable hydrochloride (reverted to the free base at room temperature) and a stable orange picrate, m.p. 120-122° (ethanol).

Anal. Calcd. for $C_{20}H_{11}N_6O_7$: C, 53.70; H, 2.48; N, 18.79.
Found: C, 53.69; H, 2.78; N, 18.89.

Zinc Dust Deamination of **4**.

A mixture of 0.6 g. (0.1 mg.-atom) of powdered zinc, 0.23 g. (0.1 mmole) of **4** and glacial acetic acid (25 ml.) was refluxed for 2.5 days. The mixture was filtered and the filter cake was washed with ethanol. The solvent from the combined filtrates was removed *in vacuo* and the residue subjected to "dry-column" chromatography (8) (alumina, chloroform). The first yellow band eluted (28 mg., m.p. 158-163°) was recrystallized (ethanol) to give 6 mg. (3%) of **2**, m.p. 169-170°, identical in all respects (mixed m.p., ir, mass spectrum, tlc) with pure **2**.

REFERENCES AND NOTES

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- (6) Recrystallized; no attempts were made to optimize the yield.
- (7) We wish to thank Ms. E. A. Reich, Dr. E. White, V, and Mr. R. J. Warren and coworkers for the elemental analyses, mass spectra and nmr spectra.
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