

Short Note

3,4,5,6,7,8,9-Heptachlorophenaleno[1,9-*bc*]pyrazole

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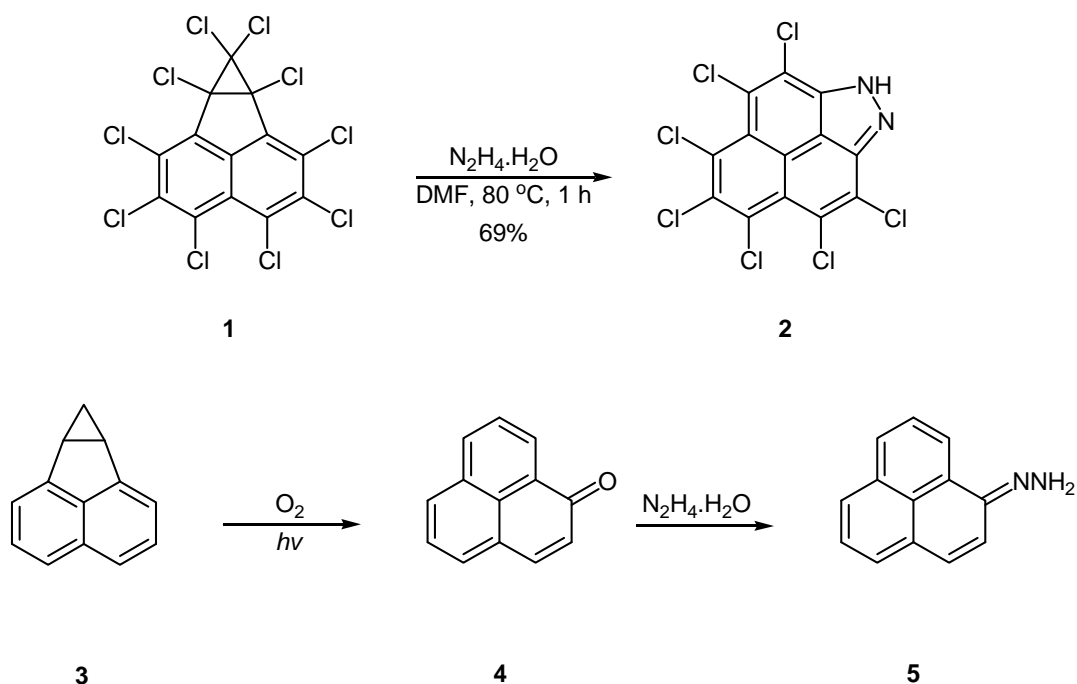
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Abstract: Treatment of perchloro-7*H*-cyclopropano[*a*]acenaphthylene **1** with hydrazine hydrate in DMF at *ca.* 80 °C gives the new 3,4,5,6,7,8,9-heptachlorophenaleno[1,9-*bc*]pyrazole **2** in 69% yield. This compound is the first example of a phenalene fused pyrazole.

Keywords: phenalene; pyrazole; cyclopropane

Phenalene fused heteroles are rare. To date only phenaleno[1,9-*bc*]furan [1] and phenaleno[1,9-*bc*]thiophenes [2–4] have been reported. During a study on the chemistry of perchloro-7*H*-cyclopropano[*a*]acenaphthylene **1** a new phenalene fused heterole **2** was formed. Perchloro-7*H*-cyclopropano[*a*]acenaphthylene **1**, which can be prepared from perchloroacenaphthylene and dichlorocarbene [5], was a valuable intermediate for the preparation of the stable perchlorophenalenyl radical [6].

The chemistry of cyclopropano[*a*]acenaphthylene **1** has been little explored; on treatment with mild Lewis acids halogen abstraction led to the formation of perchlorophenalenium cation [5,6]. During these studies traces of the perchlorophenalenone were observed. Interestingly, non substituted cyclopropano[*a*]acenaphthylene **3** irradiated with oxygen led to the formation of phenalenone **4** [7], which on treatment with hydrazine hydrate in ethylene glycol afforded the phenalenehydrazone **5** [8]. In light of this, we investigated the reaction of perchloro-7*H*-cyclopropano[*a*]acenaphthylene **1** with hydrazine hydrate, since in the presence of a *peri* halogen hydrazone formation should lead to rapid *peri* cyclisation to afford the fused pyrazole **2**.



Treatment of perchloro-7H-cyclopropano[a]acenaphthylene **1** with excess hydrazine hydrate (30 equiv) in DMF at *ca.* 80 °C, led to the formation of a yellow precipitate identified as 3,4,5,6,7,8,9-heptachlorophenaleno[1,9-*bc*]pyrazole **2**. The product gave a correct elemental analysis for a formula C₁₃HCl₇N₂ and LREI mass spectroscopy afforded a parent ion of *m/z* 432 Da (100%) supporting the 7 × Cl isotope pattern [*m/z* 438 Da (16.5%), 436 (53), 434 (95), 432 (100), 430 (45)]. It was not possible to obtain a ¹H NMR spectrum owing to the compounds poor solubility, however, a D₂SO₄ solution gave the ¹³C NMR spectrum which indicated a symmetrical system with only 8 sp² carbon resonances between the range of δ_C 139.5 to 110.8 ppm in agreement with the proposed structure.

Experimental Section

Melting point was determined using a PolyTherm-A, Wagner & Munz, Kofler-Hotstage Microscope apparatus. IR spectrum was recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with Pike Miracle Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w respectively. ¹³C NMR spectrum was recorded on a Bruker Avance 300 NMR spectrometer (at 75 MHz). Deuterated chloroform was used for homonuclear lock and the signals are referenced to the deuterated solvent peak. Low resolution (EI) mass spectrum was recorded on a Shimadzu Q2010 GCMS with direct inlet probe. Microanalysis was performed at London Metropolitan University on a Perkin Elmer 2400 Series II CHN Analyzer.

3,4,5,6,7,8,9-Heptachlorophenaleno[1,9-*bc*]pyrazole (**2**)

To a stirred mixture of perchloro-7H-cyclopropano[a]acenaphthylene **1** (0.58 g, 1.14 mmol) in DMF (30 mL) at *ca.* 30 °C, was added hydrazine hydrate (1.65 mL, 34.2 mmol). The mixture was then warmed to *ca.* 80 °C for 1 h and then allowed to cool to *ca.* 20 °C. On cooling a yellow precipitate

formed which was isolated by filtration, washed first with EtOH and then with DCM, and finally recrystallised to afford the *title compound 2* (342 mg, 69%) as colourless cotton fibers, mp > 295 °C (from PhMe); (Found: C, 36.16; H, 0.20; N, 6.38. C₁₃HCl₇N₂ requires: C, 36.03; H, 0.23; N, 6.46%); $\nu_{\max}/\text{cm}^{-1}$ 3200w (NH), 1532m, 1506m, 1482m, 1477m, 1331w, 1244s, 1198w, 1111s, 1090s, 1063s, 1010m, 930s, 862m, 845m, 755m, 746s; δ_{C} (75 MHz, D₂SO₄/CDCl₃) 139.5, 139.2, 136.4, 134.9, 122.8, 120.3, 118.1, 110.8; *m/z* (EI) 438 (16.5%), 436 (53), 434 (95), 432 (M⁺, 100), 430 (45), 400 (12), 398 (15), 396 (8), 373 (10), 372 (12), 371 (23), 370 (16), 369 (28), 367 (15), 362 (9), 335 (12), 333 (11), 327 (9), 301 (8), 300 (13), 299 (13), 298 (12), 297 (9), 255 (9), 228 (9), 217 (16), 216 (17), 185 (11), 184 (11), 181 (9), 167.4 (12), 166.35 (16), 156 (9), 149 (9).

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Sample Availability: Samples of the compounds are available from the corresponding author.