

2,3:5,6-DICYCLOBUTAPYRIDINE

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2,3:5,6-Dicyclobutapyridine^[**]

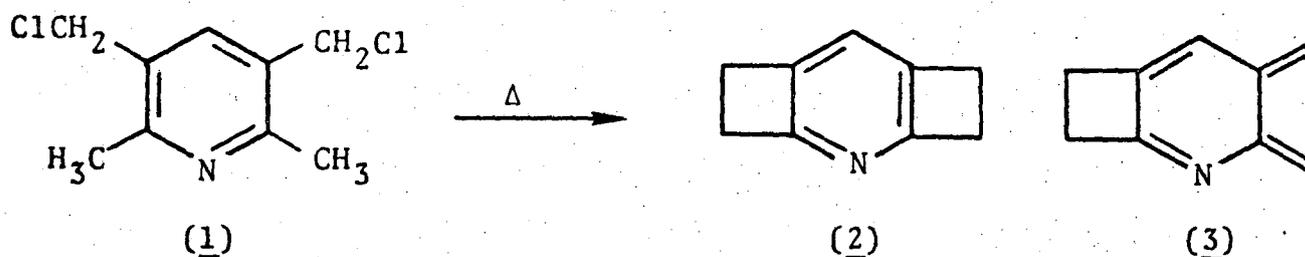
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Benzenoid hydrocarbons fused to strained rings have been the target of recent synthetic efforts aimed at the preparation of aromatic rings in which bond fixation or other perturbations of aromaticity might be observed. So far evidence for the former has been tenuous^[1]. The decreased aromaticity of pyridine [estimated 21 kcal/mol]^[2] when compared with benzene suggests that it might be more easily subjected to bond localization. Some support for this is found in the physical and chemical properties of cyclobuta[b]- and cyclobuta[c]pyridine^[3]. We report the synthesis of (2), presently the most strained annelated pyridine.

Flash vacuum pyrolysis (800°C, 10⁻⁴ torr) of dichloride (1)^[4] proceeds through double HCl-elimination^[5], providing on basic work-up the pyridine (2) in ca. 30% yield. Fractional sublimation (40°C, 10⁻³ torr) to separate (2) from (1) furnished colorless crystals



(m.p. 117.5-118.5°C). The structural assignment rests on the physical and chemical properties [MS: m/e 131.0732 (calc. 131.0735, M⁺ 84%. 130 (100%), 91 (25%), 65 (42%), 51 (21%), 39 (25%); ¹H-NMR (CDCl₃) δ 7.01 (b.s., 1H), 3.28 (m, 4H), 2.78 (m, 4H); ¹³C-NMR (CDCl₃) δ 26.8

(t, $J_{C-H} = 139.9$ Hz), 34.2 (t, 138.6 Hz), 124.4 (d, 163.5 Hz), 138.6, 161.7; UV (95% ethanol): $\lambda_{max} = 286$ sh ($\lg \epsilon = 3.97$), 289 (4.00), 292 sh (3.98), 299 sh (3.78); IR ($CHCl_3$): ν_{max} 2980, 2937, 1599, 1369, 1230, 905 cm^{-1}].

Reaction with neat bis(trimethylsilyl)acetylene (200°C, 12 hr) followed by oxidation with DDQ (C_6H_6 , 80°C, 2 hr) and protodesilylation ($C_6H_5CH_2\overset{+}{N}(CH_3)_3F^-$, DMSO, RT, 2 hr) gave acridine.

The isolation of (2) under conditions conducive to equilibration with the ring-opened o-quinodimethane ("o-lutidylene") (3) suggests appreciable residual aromaticity in (2). This is also indicated by the nuclear magnetic resonance data and the electronic spectrum. As might be expected, the latter shows bathochromic shifts and larger extinction coefficients in comparison with suitable bisannelated models.^[6] The significant ring strain experienced by (2) is likewise reflected in the ^{13}C -NMR chemical shifts and ^{13}C -H coupling constants. A detailed investigation of the chemistry of (2) and other physical properties of interest will be described in a full account.

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