

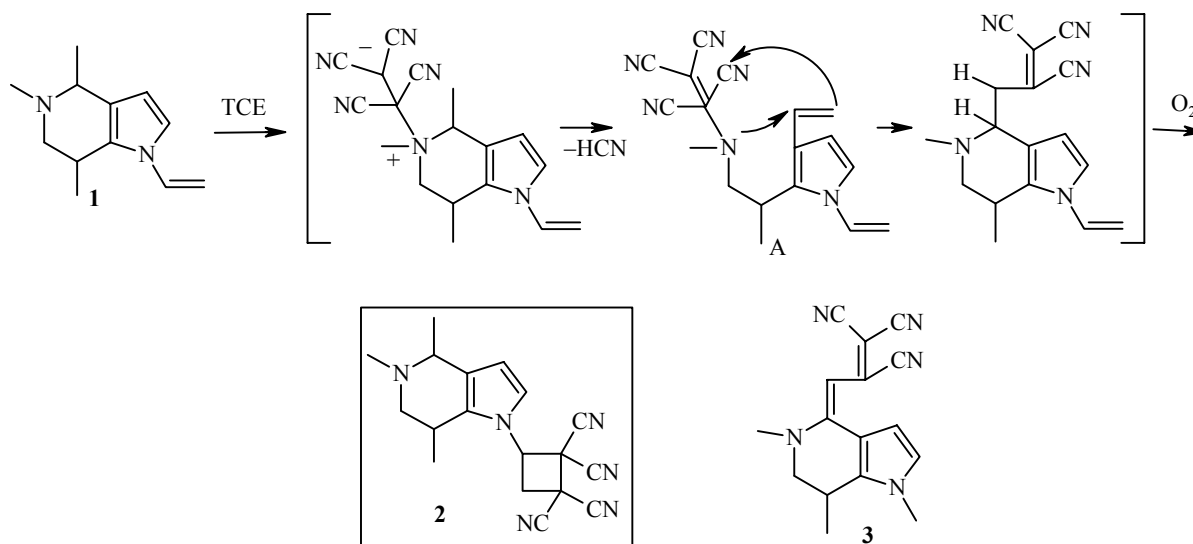
UNUSUAL REACTION OF 4,5,7-TRIMETHYL-1-VINYL- 4,5,6,7-TETRAHYDROPYRROLO- [3,2-*c*]PYRIDINE WITH TETRACYANOETHYLENE

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Gorshkov et al. [1] have reported that 1-vinylpyrroles react with tetracyanoethylene to give 1-tetracyanocyclobutylpyrroles. We have found that the reaction of 4,5,7-trimethyl-1-vinyl-4,5,6,7-tetrahydropyrrolo[3,2-*c*]pyridine (**1**) with tetracyanoethylene does not give the expected 1-tetracyanocyclobutyl derivative **2**. The major product of this reaction was 5,7-dimethyl-(2,3,3-tricyano-1-propenylidene)-1-vinyl-4,5,6,7-tetrahydropyrrolo[3,2-*c*]pyridine (**3**) isolated in 26% yield.

By analogy to the ethyl ester of acetylenedicarboxylic acid [2], cleavage of the tetrahydropyridine ring in **1** likely occurs in the first step of this reaction.



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The resultant 3-vinylpyrrole A undergoes cyclization and oxidation to convert to **3**. The structure of **3** was established by X-ray diffraction analysis. The ¹H NMR spectrum of **3** correlates well with the proposed structure.

5,7-Dimethyl-4-(2',3',3'-tricyano-1-propylidene)-1-vinyl-4,5,6,7-tetrahydropyrrolo[3,2-c]pyridine (3). A solution of tetracyanoethylene (0.08 g, 0.6 mmol) in THF (5 ml) was added dropwise to a solution of **1** (0.1 g, 0.6 mmol) in THF (3 ml) cooled to -10°C. The mixture was warmed to 20°C and maintained for 24 h with monitoring by thin-layer chromatography. The residue after evaporation of THF was subjected to chromatography on a alumina column (10 × 3 cm) using ether as the eluent to give 0.046 g (26%) of orange crystalline **3**; mp 218-220°C (ethyl acetate), *R_f* 0.6 (Alufol, ethyl acetate). ¹H NMR spectrum (CDCl₃), δ, ppm, *J* (Hz): 1.29 (3H, d, *J* = 7.0, 7-Me); 3.10 (1H, m, 7-H); 3.37 (1H, dd, *J* = 13.4 and 1.5, 6-He); 3.38 (3H, s, N-Me); 4.03 (1H, dd, *J* = 13.4 and 4.5, 6-Ha); 5.04 (1H, dd, *J* = 8.9 and 1.8, C=CH₂); 5.36 (1H, dd, *J* = 15.7 and 1.8, C=CH₂); 5.72 (1H, s, =CH-C(CN)=); 6.55 (1H, d, *J* = 3.4, 3-H); 6.78 (1H, dd, *J* = 15.7 and 8.9, N-CH=C); 6.97 (1H, d, *J* = 3.4, 2-H). Found, %: C 70.43; H 5.41; N 24.60; *M*⁺ 289. C₁₇H₁₅N₅. Calculated, %: C 70.59; H 5.19; N 24.22; *M* 289.

REFERENCES

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