

Reaction of Oxazoles. Formation of Abnormal Diels–Alder Adducts of 5-Methoxy-4-(*p*-nitrophenyl)oxazoles with Tetracyanoethylene, and X-Ray Crystal Structure of One of the Products

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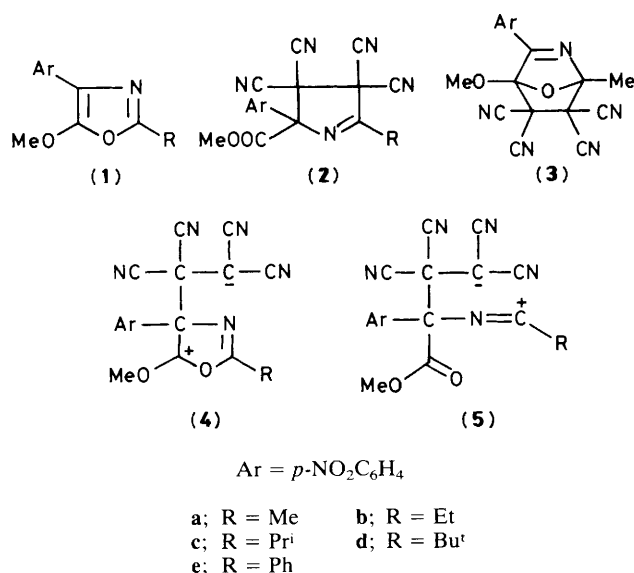
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The reaction of 2-alkyl or -aryl substituted 5-methoxy-4-(*p*-nitrophenyl)oxazoles (**1**) with tetracyanoethylene gave 2-substituted methyl 3,3,4,4-tetracyano-5-(*p*-nitrophenyl)-4,5-dihydro-3*H*-pyrrole-5-carboxylates (**2**) as formal [3 + 2] cycloadducts; these were produced *via* a zwitterionic mechanism involving oxazole ring opening.

Since its discovery in 1958,¹ tetracyanoethylene (TCNE) has attracted the interest of organic chemists because of its high dienophilicity² and strong electron-acceptor properties.³ The Diels–Alder reaction of oxazoles has extensively been studied in connection with the synthesis of vitamin B₆.⁴ Reactions with electron-deficient ethylenic and acetylenic compounds have been reported to give Diels–Alder adducts in high yields.⁵ However, as previously reported TCNE was found not to give the usual Diels–Alder adduct with 2-methyl-5-methoxy-4-(*p*-

nitrophenyl)oxazole despite its high reactivity as a dienophile.⁶ We now describe the formation of non-Diels–Alder cycloadducts of TCNE with oxazoles.

The reaction of the oxazole (**1a**) with TCNE (1.5 mol. equiv.) in refluxing acetonitrile for 20 h gave the dihydropyrrole derivative (**2a**; R = Me) in 85% yield (colourless crystals, m.p. 175–176 °C). Although elemental analysis of the product was consistent with an adduct between (**1a**) and TCNE, its i.r. absorption at 1758 cm⁻¹ (ester C=O) suggested



that the product was not the usual Diels–Alder adduct (3) but was methyl 3,3,4,4-tetracyano-4,5-dihydro-2-methyl-5-(*p*-nitrophenyl)-3*H*-pyrrole-5-carboxylate. The ¹³C n.m.r. spectrum of the product agreed with the structure (2a) (δ 164.4 and 163.3, carbonyl and/or imido carbon).

The oxazole (1a) has a ketene acetal-type structure which would be highly reactive towards TCNE to give a [2 + 2] cycloadduct *via* a charge-transfer (C.T.) complex and zwitterionic intermediate.⁷ When (1a) and TCNE were dissolved in acetonitrile at room temperature, the solution became dark olive in colour (λ_{max} , 550 nm), the colour disappearing upon heating of the reaction mixture at 80 °C. This indicates that the reaction proceeds through a C.T. complex as expected. Heating of the C.T. complex may cause attack of the olefinic carbon atom of TCNE on C-4 of the oxazole ring to give the zwitterionic intermediate (4a), which is the usual pathway of the reaction of TCNE with vinyl ethers.^{7,8} Ring opening of (4a) would generate another zwitterionic intermediate (5a) which would give the dihydro-pyrrole (2a) *via* intramolecular cyclization. The acceleration of the reaction of (1a) with TCNE in aprotic polar solvents such as acetonitrile, nitromethane, and dimethylformamide also supports the zwitterionic mechanism.

Other 2-alkyl-5-methoxy-4-(*p*-nitrophenyl)oxazoles also gave the corresponding dihydro-pyrroles: (2b), 73%; (2c), 67%; (2d), 64%. However, the 2-phenyloxazole (1e) gave only a low yield (15%) of (2e), and other 2-aryl oxazoles behaved similarly.

The structure of (2c) was confirmed by X-ray crystallography (Figure 1).[†] The unusually long bond lengths of

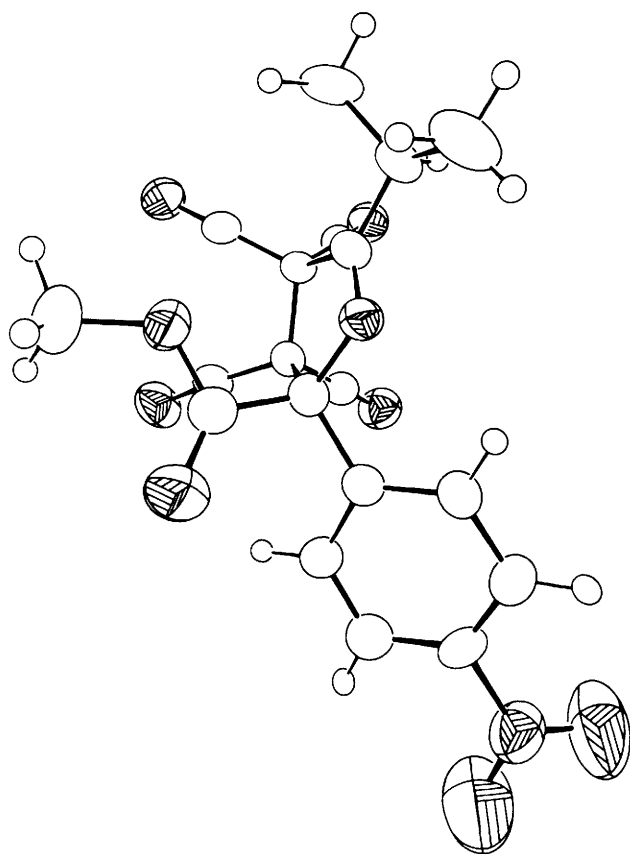


Figure 1. ORTEP view of (2c).

C-3–C-4 (1.585 Å) and C-4–C-5 (1.621 Å) are attributed to crowding by the substituents on the dihydropyrrole ring. Experiments to determine the scope of the reaction are in progress.

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[†] Crystal data for (2c): C₁₉H₁₄N₆O₄, *M* = 390.36, orthorhombic, *a* = 17.998(2), *b* = 27.188(6), *c* = 15.833(4) Å, space group *Pcab*, *Z* = 16, *D*_m = 1.34, *D*_c = 1.34 g cm⁻³. 4629 Independent observed reflections [*F*_o > 2 σ(*F*_o)] were measured on a Rigaku four-circle diffractometer with Cu-K_α radiation using the 2θ-ω method. The structure was solved by direct methods (RANTAN 81); anisotropic refinement for the non-hydrogen atoms and isotropic for the hydrogen atoms led to *R* = 0.070. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.