View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1986. Downloaded by State University of New York at Stony Brook on 26/10/2014 07:31:47.

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

Toshikazu Ibata,* Yasushi Isogami, Shuji Nakano, Hiroyuki Nakawa, and Hatsue Tamura

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka, Japan

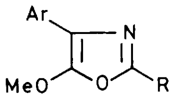
The reaction of 2-alkyl or -aryl substituted 5-methoxy-4-(*p*-nitrophenyl)oxazoles (**1**) with tetracyanoethylene gave 2-substituted methyl 3,3,4,4-tetracyano-5-(*p*-nitrophenyl)-4,5-dihydro-3*H*-pyrrole-5-carboxylates (**2**) as formal [3 + 2] cycloadducts; these were produced *via* a zwitterionic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

Since its discovery in 1958,[1] tetracyanoethylene (TCNE) has attracted the interest of organic chemists because of its high dienophilicity[2] and strong electron-acceptor properties.[3] The Diels–Alder reaction of oxazoles has extensively been studied in connection with the synthesis of vitamin B_6.[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.

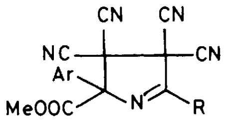
The reaction of the oxazole (**1a**) with TCNE (1.5 mol. equiv.) in refluxing acetonitrile for 20 h gave the dihydropyrrole derivative (**2a**; R = Me) in 85% yield (colourless crystals, m.p. 175—176 °C). Although elemental analysis of the product was consistent with an adduct between (**1a**) and TCNE,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

View Article Online

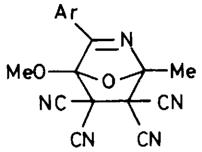
Published on 01 January 1986. Downloaded by State University of New York at Stony Brook on 26/10/2014 07:31:47.



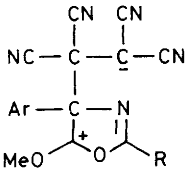
(1)



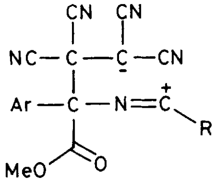
(2)



(3)



(4)



(5)

Ar = p-$NO_2C_6H_4$

a; R = Me **b**; R = Et
c; R = Pr^i **d**; R = Bu^t
e; R = Ph

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)-3H-pyrrole-5-carboxylate. The ^{13}C 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 ($\lambda_{max.}$ 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 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.

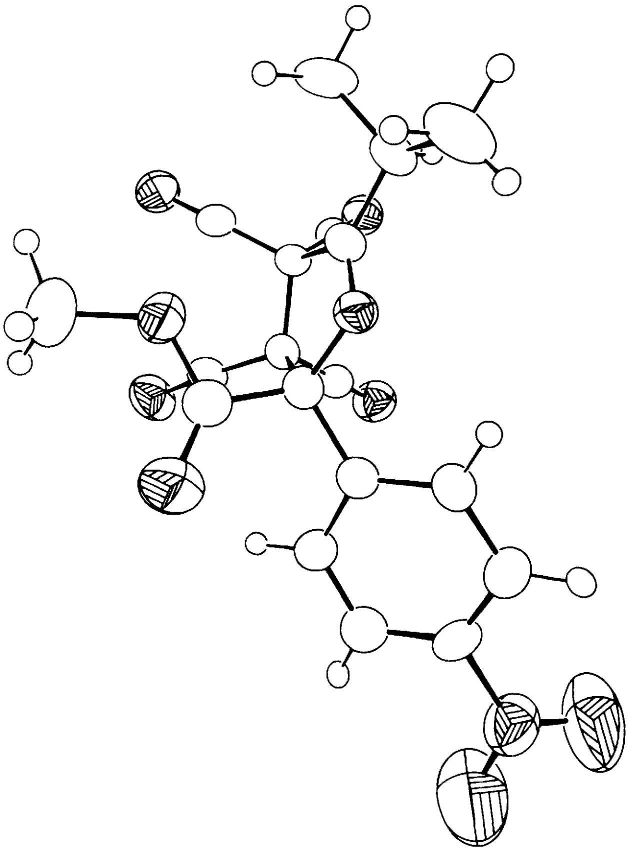


Figure 1. ORTEP view of (**2c**).

Received, 8th July 1986; Com. 942

References

1 T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, 1958, **80**, 2775.
2 W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, 1958, **80**, 2783.
3 R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, 1958, **80**, 2778; A. J. Fatiadi, *Synthesis*, 1986, 249.
4 E. E. Harris, R. A. Firestone, K. Pfister, III, R. R. Boettcher, F. J. Cross, R. B. Currie, M. Monaco, E. R. Peterson, and W. Reuter, *J. Org. Chem.*, 1962, **27**, 2705.
5 R. Lakhan and B. Ternai, *Adv. Heterocycl. Chem.*, 1975, **17**, 182.
6 T. Ibata, S. Nakano, H. Nakawa, J. Toyoda, and Y. Isogami, *Bull. Chem. Soc., Jpn.*, 1986, **59**, 433.
7 R. Huisgen, *Acc. Chem. Res.*, 1977, **10**, 117, and references cited therein.
8 R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, 1973, **95**, 5054, 5055, 5056.

---

† *Crystal data* for (**2c**): $C_{19}H_{14}N_6O_4$, 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^{-1}. 4629 Independent observed reflections [$F_o > 2\sigma(F_o)$] 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.