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Abnormal Diels–Alder Reaction of 5-Alkoxyoxazoles with Tetracyanoethylene and X-Ray Crystal Structure of an Adduct

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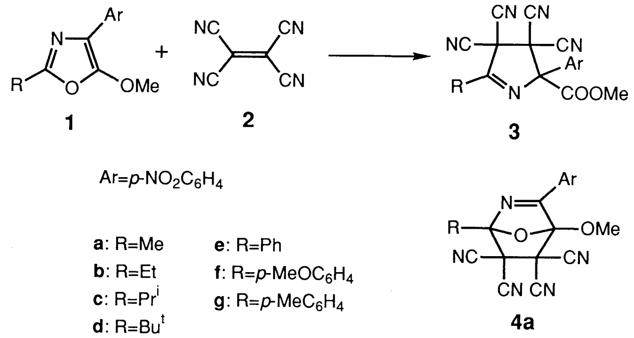
The reaction of 2-alkyl- or 2-aryl-substituted 5-methoxy-4-(*p*-nitrophenyl)oxazoles with tetracyanoethylene gave methyl esters of 5-substituted 3,3,4,4-tetracyano-2-(*p*-nitrophenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylic acids as formal [3+2] cycloadducts through oxazole ring opening. Zwitterionic mechanisms were proposed on the basis of the solvent effect on the reaction. The molecular structure of 2-isopropyl-substituted product was determined by means of X-ray crystallography. Crystals of the cycloadduct are orthorhombic with space group *Pcab* having unit-cell dimensions of a=17.998 (2), b=27.188 (6), c=15.833 (3) Å, and Z=16, which contains two crystallographically independent molecules. The final R value is 0.070 for 4629 observed reflections.

Oxazole is an aromatic heterocycle having a 2-azadiene structure and has been utilized widely in organic synthesis as a diene component in Diels–Alder reaction,[1] especially in connection with the synthesis of vitamin B_6.[2] For example, reactions of 5-alkoxyoxazoles with ethylenic dienophiles yielded 3-hydroxypyridine derivatives through the ring opening of the corresponding Diels–Alder adducts accompanying elimination of an alcohol. In continuation of our studies on stereochemistry and cycloreversion of the Diels–Alder reactions of oxazoles with ethylenic dienophiles,[3] we studied the reaction of 5-alkoxyoxazoles with tetracyanoethylene (TCNE) which has been used as a strong dienophile.[4]

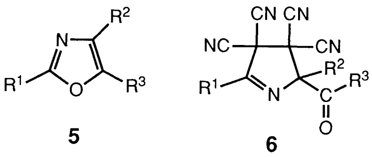
When we published a preliminary paper of this series,[5] only a few papers had been reported on the abnormal Diels–Alder reaction of oxazoles with ethylenic dienophiles by Kondrat'eva and his co-workers on the reaction of 5-(dialkylamino)oxazoles with maleimide to give 2-carbamoyl-3,4-dihydro-2*H*-pyrrole-3,4-dicarboximide derivatives together with the normal Diels–Alder adducts.[6] Later, similar type of cycloadditions of oxazoles were reported with 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (PTAD),[7] thioaldehydes,[8] diethyl azodicarboxylate,[9] diethyl oxomalonate,[9] nitrosobenzene,[10] and various aldehydes in the presence of Lewis acid catalyst.[11]



1 **2** **3** **4a**

Ar=p-$NO_2C_6H_4$

a: R=Me
b: R=Et
c: R=Pr^i
d: R=Bu^t
e: R=Ph
f: R=p-$MeOC_6H_4$
g: R=p-MeC_6H_4



5 **6**

a: R^1=Me, R^2=COOEt, R^3=OEt
b: R^1=p-$MeOC_6H_4$, R^2=H, R^3=OMe
c: R^1=Ph, R^2=H, R^3=OEt
d: R^1=R^3=Ph, R^2=H
e: R^1=R^2=R^3=Me

Reaction of 5-Alkoxyoxazoles with TCNE. A reaction mixture of 5-methoxy-2-methyl-4-(*p*-nitrophenyl)oxazole (**1a**) and TCNE in acetonitrile gave dark olive color which disappeared gradually under reflux. Column chromatography of the reaction mixture on silica gel isolated a colorless crystalline product **3a** in a 85% yield. A result of elemental analysis suggests that the product is a 1 : 1-adduct of **1a** and TCNE. The IR spectrum of the product shows an absorption band of an ester carbonyl group at 1758 cm^{-1} which is inconsistent with the normal Diels–Alder adduct **4a**. The low-field shift of ^1H NMR siganls of methoxyl group (at δ=3.91) and methyl proton (at δ=2.74) also can not be explained by the structure **4a**. Moreover, ^{13}C NMR spectrum of **3a** shows signals of ester-carbonyl and imino-carbon at δ=164.4 and 163.3. These results indicate that the product is not the normal Diels–Alder adduct **4a** but the abnormal adduct having 1-pyrroline structure, methyl 3,3,4,4-tetracyano-3,4-dihydro-5-methyl-2-(*p*-nitrophenyl)-2*H*-pyrrole-2-carboxylate (**3a**), formed by the formal [3+2] cycloaddition of TCNE toward C-2 and C-4 of the oxazole ring accompanying its ring opening.

Similar results were obtained when ethyl, isopropyl, *t*-butyl, and aryl groups were introduced at the C-2 position of the oxazole ring (Table 1). The carbonyl absorption band at near 1750 cm^{-1} and other spectroscopic data indicate that these products have also the 3,4-dihydro-2*H*-pyrrole-2-carboxylate structure.

Table 1. Yields, Melting Points, and Spectral Data of 1-Pyrroline Derivatives **3**

Compound	R	Yield	Mp	^{1}H NMR/δ			IR/cm^{-1}
		%	°C	OCH$_3$	R	p-NO$_2$C$_6$H$_4$ (ABq)	C=O
3a	CH$_3$	85	175—176	3.91	2.73 (s)	7.86 (J=9.2), 8.39	1758
3b	CH$_3$CH$_2$	73	145—146	3.90	1.56 (t), 3.00 (q)	7.83 (J=9.2), 8.34	1766
3c	(CH$_3$)$_2$CH	67	156—157	3.89	1.59 (d), 3.23 (sep)	7.85 (J=9.2), 8.34	1768
3d	(CH$_3$)$_3$C	66	134—135	3.89	1.64 (s)	7.88 (J=9.2), 8.35	1748
3e	C$_6$H$_5$	16	211—213	3.89	7.43 (m), 7.97 (m)	7.90 (J=9.0), 8.36	1739
3f	p-CH$_3$OC$_6$H$_4$	47	194—196	3.88	3.95 (s),[a] 7.10,[b] 8.18[b]	7.90 (J=9.1), 8.35	1744
3g	p-CH$_3$C$_6$H$_4$	58	215—216	3.89	2.52 (s),[c] 7.44,[b] 8.10[b]	7.90 (J=9.1), 8.36	1766

a) CH$_3$O. b) Arom-H (m). c) CH$_3$.

Table 2. Effect of Solvent Polarity and Temperature on the Reaction of **1a** with TCNE[a)]

Run	Solvent	Temp[b)]	Time	Yield of **3a**	Recovered **1a**	D
		°C	h	%	%	
1	Toluene	100	20	30	60	2.4
2	Toluene	110	20	60	—	
3	p-Xylene	120	20	74	24	2.3
4	CH$_3$CN	80	20	85	15	37.5
5	CH$_3$NO$_2$	40	120	17	65	38.6
6	CH$_3$NO$_2$	100	20	64	6	
7	THF	80	20	—	86	7.4
8	THF	100	20	8.8	75	
9	Diglyme	80	20	37	56	
10	Diglyme	100	20	43	22	
11	DMF	80	20	9	73	36.7
12	i-PrOH	100	20	—	18	18.3

a) Molar ratio; **1a**:TCNE=1:1.2. b) Oil bath temperature was recorded.

Yields of the adducts decreased by the increase of the bulkiness of the substituent R on C-2 of the oxazole. Low yields of **3e**—**3g** may be attributed to the low reactivity of the oxazoles due to the bulkiness of R(=Ar) and the resonance stabilization of oxazole ring system by aryl group substitution.

Ethyl 5-ethoxy-2-methyl-4-oxazolecarboxylate (**5a**) also reacts with TCNE in a similar manner, and the reaction mixture showed a singlet signal at δ=2.56 attributable to a methyl group of the corresponding 1-pyrroline derivative. However, an attempt to isolate the adduct by use of medium-pressure column chromatography was unsuccessful because of its unstability. Although 2-(p-methoxyphenyl)-5-methoxyoxazole (**5b**), also gave similar results, 5-ethoxy-2-phenyloxazole (**5c**) gave only an unidentified complex mixture. Other oxazoles such as 2,5-diphenyloxazole (**5d**), 5-(p-methoxyphenyl)-2-methyloxazole and 2,4,5-trimethyloxazole (**5e**) did not give a similar type of product and recovered the oxazoles. This indicates that an electron-releasing group such as alkoxyl group is necessary for the promotion of this abnormal Diels–Alder reaction, and that p-nitrophenyl group is necessary for the stabilization of the adduct.

Solvent effect on the yields of 1-pyrroline **3a** was studied in order to have informations about the reaction intermediates. Table 2 indicates that **3a** was obtained in high yield in polar solvents. Acetonitrile gave the highest yield in the solvents used. However, there is no linear relationship between the yield and dielectric constant of solvent. Low yield of the reaction in etheral solvents such as THF and diglyme is attributed to the formation of CT-complex between the solvent and TCNE which gave a mixture of unidentified products. Similarly, DMF and isopropyl alcohol are found not to be a good solvent for this reaction due to the CT-complex formation with TCNE. In nonpolar solvents such as toluene and xylene the reaction proceeds slowly and recovered the starting oxazole **1a**. However, the yield of **3a** increased at higher temperature decreasing the recovery of **1a**.

X-Ray Crystal Analysis of 3c. In order to ascertain the 1-pyrroline structure of the reaction product, single crystal X-ray crystallography was carried out on **3c** which gave good crystals for X-ray structure analysis from benzene–hexane solution. The crystal data and experimental details are listed in Table 3. The X-ray intensity data were collected on a Rigaku four-circle diffractometer AFC-5R with Ni-filtered Cu $K\alpha$ radiation. Corrections were made for Lorentz and polarization effects, but not for absorption. The 4623 reflections with $|F_o|>2\sigma|F_o|$ were used in the structural determination.

The crystals are orthorhombic, and the space group

Table 3. Crystal Data and Experimental Details of **3c**

Molecular formula	$C_{19}H_{14}N_6O_4$
Crystal system	Orthorhombic
Space group	P_{cab}
a/Å	17.998 (2)
b/Å	27.188(6)
c/Å	15.833(3)
V/Å^3	7747(3)
Z	16
D_m/Mg m^{-3}	1.34
D_x/Mg m^{-3}	1.34
μ(Cu $K\alpha$)/cm^{-1}	8.31
Scan method	2θ–ω
Scan speed in ω/deg min^{-1}	4
Scan width/degree	1.1+0.15 tanθ
Back ground	2×4s
No. of Reflections	6183
No. of Reflections ($\lvert F_o\rvert>2\sigma\lvert F_o\rvert$)	4623
R	0.070 (for 4629 observed reflections)
Crystal size/mm^3	0.2×0.3×0.4
$2\theta_{max}$ (Cu $K\alpha$)/degree	125

Pcab was confirmed by a statistical distribution of E values. The structure was solved by direct methods, and refined by block-diagonal least-squares techniques. The function minimized was $\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2$, with $w=(\sigma^2(F_o)+0.0933\lvert F_o\rvert+0.0002\lvert F_o\rvert^2)^{-1}$. The final R value is 0.070 for observed reflections. All the atomic scattering factors were taken from "International Tables for X-Ray Crystallography." The computations were carried out with The Universal Crystallographic Computing System-Osaka (1979), MULTAN 80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and ORTEP II (Johnson, 1976) on an ACOS-S850 computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University.

Lists of structure factors are deposited as Document No. 9009 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 4 lists the final atomic and thermal parameters along with their estimated standard deviations. There are two crystallographically independent molecules, **3c-A** and **3c-B**, in the asymmetric unit. The molecular structure with the atomic numbering scheme is shown in Fig. 1. It was confirmed from this structure that the assignment of the configuration to the title compound on the basis of the NMR data was correct. The bond distances and angles are given in Table 5. The corresponding values in the independent molecules agree fairly well with each other. The C(1A)–C(2A), C(2A)–C(3A), and C(3A)–C(4A) bond distances (1.565, 1.582, and 1.622 Å, respectively) in the 1-pyrroline ring of the **3c-A** molecule are appreciably longer than the normal C–C single bond distance (1.54 Å). A similar effect is also observed in the pyrroline ring of the **3c-B**. The lengthening of these bonds is caused by the electron-withdrawing ability of the cyano groups. Both 1-pyrroline rings of the **3c-A** and **3c-B** molecules adopt envelope conformations; the C(3A) atom deviates from the plane through the C(1A), C(2A), C(4A), and N(1A) atoms by 0.34 Å, and the C(3B) atom from the plane through the C(1B), C(2B), C(4B), and N(1B) atoms by 0.33 Å.

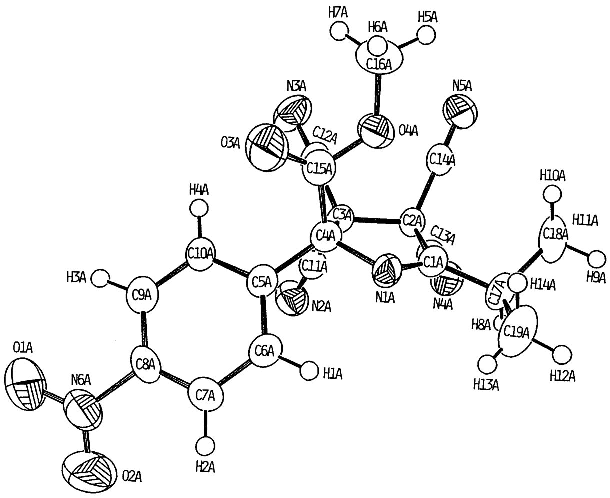


Fig. 1. Molecular structure of **3c-A** with atomic numbering scheme. The same atomic numbering scheme as **3c-A** was used for **3c-B**, and the distinction between the atoms in **3c-A** and those in **3c-B** was made by the letters A and B.

Each two cyano groups on C-3 and C-4 atoms of the 1-pyrroline ring are directing above and below the ring. The two pairs of cyano groups on the same side of the ring system are twisted by 17—19 degree from the eclipsed conformation avoiding van der Waals repulsion. Torsion angles, C(11)–C(3)–C(2)–C(13) and C(12)–C(3)–C(2)–C(14), are 17.2 and 18.2° for **3c-A** molecule and 19.1 and 18.0° for **3c-B** molecule.

Table 4a. Final Atomic Coordinates of Non-H Atoms and Equivalent Isotropic Thermal Parameters with Their esd's in Parentheses

$B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
3c-A					**3c-B**				
C(1A)	0.6909(2)	0.0313(1)	0.1066(3)	3.3(1)	C(1B)	0.6853(2)	−0.2263(1)	0.3666(2)	3.3(1)
C(2A)	0.7196(2)	−0.0161(1)	0.0606(2)	3.1(1)	C(2B)	0.7100(2)	−0.1787(1)	0.3180(2)	3.2(1)
C(3A)	0.7941(2)	0.0038(1)	0.0199(2)	3.0(1)	C(3B)	0.7854(2)	−0.1970(1)	0.2761(2)	2.8(1)
C(4A)	0.8091(2)	0.0538(1)	0.0730(2)	3.1(1)	C(4B)	0.8040(2)	−0.2459(1)	0.3306(2)	2.9(1)
C(5A)	0.8393(2)	0.0940(1)	0.0164(3)	3.4(1)	C(5B)	0.8339(2)	−0.2867(1)	0.2737(3)	3.0(1)
C(6A)	0.7975(2)	0.1349(1)	−0.0021(3)	3.4(1)	C(6B)	0.7926(2)	−0.3283(1)	0.2580(3)	3.5(1)
C(7A)	0.8234(2)	0.1693(1)	−0.0594(3)	3.8(1)	C(7B)	0.8174(2)	−0.3629(1)	0.2009(3)	4.1(1)
C(8A)	0.8915(2)	0.1621(1)	−0.0956(3)	3.9(1)	C(8B)	0.8843(2)	−0.3549(1)	0.1607(3)	3.5(1)
C(9A)	0.9359(2)	0.1224(1)	−0.0763(3)	4.2(1)	C(9B)	0.9281(2)	−0.3144(1)	0.1776(3)	3.7(1)
C(10A)	0.9091(2)	0.0883(1)	−0.0196(3)	3.7(1)	C(10B)	0.9027(2)	−0.2806(1)	0.2343(3)	3.8(1)
C(11A)	0.7829(2)	0.0149(1)	−0.0701(3)	3.2(1)	C(11B)	0.8464(2)	−0.1606(1)	0.2781(3)	3.5(1)
C(12A)	0.8574(2)	−0.0306(1)	0.0265(3)	3.7(1)	C(12B)	0.7726(2)	−0.2099(1)	0.1870(3)	3.4(1)
C(13A)	0.6636(2)	−0.0331(1)	0.0001(3)	3.5(1)	C(13B)	0.7219(2)	−0.1365(1)	0.3748(3)	3.8(1)
C(14A)	0.7344(2)	−0.0571(1)	0.1199(3)	3.5(1)	C(14B)	0.6523(2)	−0.1638(1)	0.2577(3)	3.4(1)
C(15A)	0.8622(2)	0.0429(1)	0.1469(3)	3.7(1)	C(15B)	0.8592(2)	−0.2332(1)	0.4015(3)	3.5(1)
C(16A)	0.8774(3)	−0.0128(2)	0.2605(3)	5.7(2)	C(16B)	0.8805(3)	−0.1750(1)	0.5096(3)	5.8(2)
C(17A)	0.6118(2)	0.0342(2)	0.1376(3)	4.0(1)	C(17B)	0.6080(2)	−0.2309(1)	0.4009(3)	3.7(1)
C(18A)	0.5927(3)	−0.0098(2)	0.1940(4)	5.4(2)	C(18B)	0.5851(3)	−0.1879(2)	0.4558(4)	6.4(2)
C(19A)	0.5986(3)	0.0826(2)	0.1836(4)	6.2(2)	C(19B)	0.6010(3)	−0.2794(2)	0.4489(4)	5.4(2)
N(1A)	0.7375(2)	0.0661(1)	0.1088(2)	3.2(1)	N(1B)	0.7345(2)	−0.2594(1)	0.3702(2)	3.1(1)
N(2A)	0.7753(2)	0.0243(1)	−0.1398(2)	5.0(1)	N(2B)	0.8962(2)	−0.1357(1)	0.2797(3)	5.4(1)
N(3A)	0.9091(2)	−0.0539(1)	0.0334(3)	5.5(1)	N(3B)	0.7648(2)	−0.2191(1)	0.1172(2)	5.0(1)
N(4A)	0.6163(2)	−0.0444(1)	−0.0436(2)	5.5(1)	N(4B)	0.7294(2)	−0.1033(1)	0.4179(3)	5.7(1)
N(5A)	0.7464(2)	−0.0897(1)	0.1632(3)	5.0(1)	N(5B)	0.6054(2)	−0.1532(1)	0.2130(2)	5.1(1)
N(6A)	0.9180(2)	0.1976(1)	−0.1577(3)	4.7(1)	N(6B)	0.9096(2)	−0.3901(1)	0.0959(2)	4.8(1)
O(1A)	0.9820(2)	0.1980(2)	−0.1748(4)	8.1(2)	O(1B)	0.8670(2)	−0.4219(1)	0.0727(3)	8.8(2)
O(2A)	0.8751(2)	0.2247(2)	−0.1912(3)	6.1(2)	O(2B)	0.9706(2)	−0.3848(1)	0.0659(3)	8.9(2)
O(3A)	0.9196(2)	0.0623(1)	0.1596(2)	7.5(1)	O(3B)	0.9156(2)	−0.2546(1)	0.4155(2)	6.6(1)
O(4A)	0.8333(2)	0.0073(1)	0.1932(2)	4.4(1)	O(4B)	0.8337(1)	−0.1954(1)	0.4443(2)	4.4(1)

Table 4b. Final Atomic Coordinates of H Atoms and Isotropic Thermal Parameters with Their esd's in Parentheses

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
3c-A					**3c-B**				
H(1A)	0.750(2)	0.139(1)	0.023(2)	1.5(8)	H(1B)	0.742(2)	−0.332(1)	0.286(2)	2.0(9)
H(2A)	0.795(2)	0.197(2)	−0.077(3)	3.4(10)	H(2B)	0.789(2)	−0.392(1)	0.188(2)	2.7(9)
H(3A)	0.983(2)	0.119(1)	−0.104(2)	2.9(10)	H(3B)	0.978(2)	−0.311(1)	0.148(2)	1.4(8)
H(4A)	0.939(2)	0.061(1)	−0.005(3)	2.5(9)	H(4B)	0.934(2)	−0.251(1)	0.251(2)	2.2(9)
H(5A)	0.849(3)	−0.039(2)	0.293(3)	5.8(14)	H(5B)	0.852(3)	−0.155(2)	0.550(3)	4.9(12)
H(6A)	0.925(3)	−0.025(2)	0.239(3)	4.8(12)	H(6B)	0.920(2)	−0.160(2)	0.481(3)	4.3(11)
H(7A)	0.889(3)	0.012(2)	0.304(3)	3.9(11)	H(7B)	0.895(3)	−0.204(2)	0.542(3)	5.0(13)
H(8A)	0.576(2)	0.032(2)	0.086(3)	4.2(12)	H(8B)	0.577(2)	−0.233(1)	0.348(2)	1.7(8)
H(9A)	0.543(2)	−0.006(2)	0.216(3)	3.8(11)	H(9B)	0.622(2)	−0.187(2)	0.501(3)	3.3(10)
H(10A)	0.634(3)	−0.014(2)	0.248(3)	5.2(13)	H(10B)	0.582(3)	−0.156(2)	0.417(3)	5.7(14)
H(11A)	0.577(3)	−0.041(2)	0.151(4)	7.3(16)	H(11B)	0.533(2)	−0.195(2)	0.473(3)	3.4(10)
H(12A)	0.549(3)	0.086(2)	0.199(3)	5.1(13)	H(12B)	0.554(3)	−0.283(2)	0.467(3)	4.7(12)
H(13A)	0.608(3)	0.108(2)	0.153(3)	4.6(12)	H(13B)	0.605(3)	−0.304(2)	0.400(3)	5.9(14)
H(14A)	0.640(4)	0.076(2)	0.239(5)	11.2(22)	H(14B)	0.637(2)	−0.281(2)	0.500(3)	4.1(11)

Mechanism of the Abnormal Diels–Alder Reaction. Reactions of TCNE with vinyl ethers are well-known to proceed through a stepwise mechanism involving CT-complex and a zwitterionic intermediate to give alkoxycyclobutane derivatives.[12] The present reaction of TCNE with 5-alkoxyoxazoles is also considered to proceed through a similar CT-complex, because oxazoles can be recognized as a sort of vinyl ether. In facts, the reaction mixture of the oxazoles and TCNE showed olive color having an absorption maximum at 550 nm which

Table 4c. Anisotropic Thermal Parameters with Their esd's in Parentheses
The Form is $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$

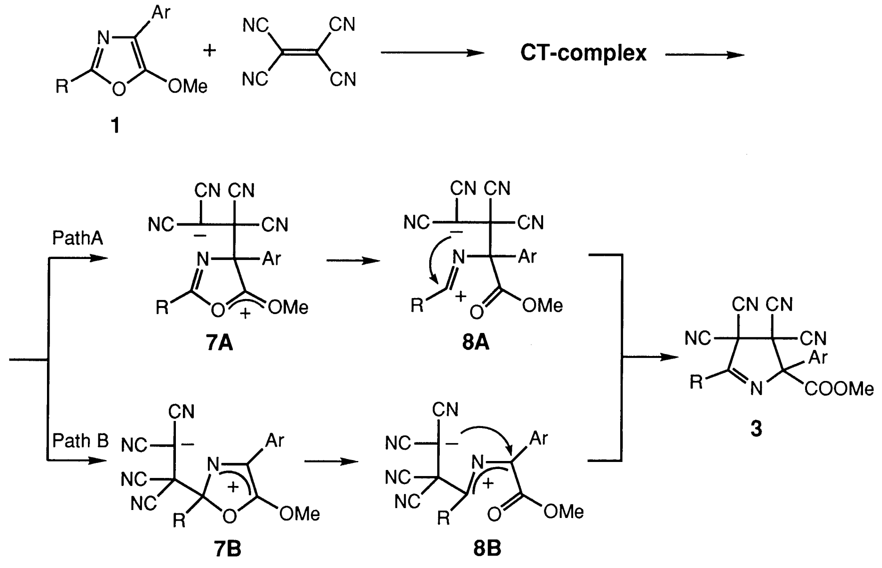
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
3c-A						
C(1A)	0.0023(1)	0.00115(6)	0.0044(2)	0.0002(1)	0.0006(3)	0.0004(2)
C(2A)	0.0020(1)	0.00098(5)	0.0040(2)	−0.0002(1)	0.0005(2)	0.0004(2)
C(3A)	0.0021(1)	0.00092(5)	0.0041(2)	0.0002(1)	0.0006(2)	0.0001(2)
C(4A)	0.0024(1)	0.00091(5)	0.0040(2)	0.0003(1)	0.0005(2)	−0.0002(2)
C(5A)	0.0022(1)	0.00093(5)	0.0045(2)	−0.0003(1)	0.0001(2)	−0.0001(2)
C(6A)	0.0024(1)	0.00103(6)	0.0052(2)	0.0005(1)	0.0013(3)	0.0001(2)
C(7A)	0.0033(2)	0.00100(6)	0.0052(2)	0.0000(2)	0.0009(3)	0.0008(2)
C(8A)	0.0032(1)	0.00082(5)	0.0051(2)	−0.0011(1)	0.0011(3)	0.0004(2)
C(9A)	0.0027(1)	0.00121(6)	0.0058(2)	−0.0004(2)	0.0010(3)	0.0002(2)
C(10A)	0.0023(1)	0.00107(6)	0.0065(2)	−0.0001(1)	0.0011(3)	0.0011(2)
C(11A)	0.0024(1)	0.00091(5)	0.0047(2)	0.0003(1)	0.0010(3)	0.0001(2)
C(12A)	0.0024(1)	0.00102(6)	0.0051(2)	−0.0000(1)	0.0009(3)	−0.0005(2)
C(13A)	0.0026(1)	0.00101(6)	0.0048(2)	0.0000(1)	0.0004(3)	0.0005(2)
C(14A)	0.0023(1)	0.00105(6)	0.0048(2)	−0.0005(1)	0.0009(3)	0.0006(2)
C(15A)	0.0026(1)	0.00124(6)	0.0044(2)	−0.0001(1)	0.0003(3)	0.0004(2)
C(16A)	0.0044(2)	0.00216(9)	0.0049(2)	0.0003(2)	−0.0028(4)	0.0016(2)
C(17A)	0.0022(1)	0.00168(7)	0.0056(2)	0.0006(2)	0.0020(3)	0.0000(2)
C(18A)	0.0032(2)	0.00220(9)	0.0084(3)	−0.0009(2)	0.0050(4)	0.0013(3)
C(19A)	0.0045(2)	0.00194(9)	0.0118(5)	0.0014(2)	0.0078(5)	−0.0003(3)
N(1A)	0.0024(1)	0.00095(4)	0.0047(2)	0.0003(1)	0.0016(2)	0.0001(1)
N(2A)	0.0042(2)	0.00186(7)	0.0044(2)	−0.0004(2)	0.0005(3)	0.0006(2)
N(3A)	0.0030(1)	0.00155(6)	0.0085(3)	0.0011(1)	0.0000(3)	−0.0006(2)
N(4A)	0.0035(2)	0.00180(7)	0.0058(2)	−0.0006(2)	−0.0005(3)	0.0001(2)
N(5A)	0.0036(1)	0.00142(6)	0.0070(2)	−0.0008(2)	−0.0000(3)	0.0023(2)
N(6A)	0.0044(2)	0.00132(6)	0.0072(2)	−0.0002(2)	0.0036(3)	0.0014(2)
O(1A)	0.0053(2)	0.00375(10)	0.0178(4)	−0.0004(2)	0.0081(5)	0.0099(4)
O(2A)	0.0071(2)	0.00286(8)	0.0108(3)	0.0025(2)	0.0054(4)	0.0068(3)
O(3A)	0.0040(1)	0.00241(7)	0.0075(2)	−0.0027(2)	−0.0034(3)	0.0020(2)
O(4A)	0.0033(1)	0.00155(5)	0.0043(1)	−0.0005(1)	−0.0012(2)	0.0013(1)
3c-B						
C(1B)	0.0022(2)	0.00095(5)	0.0035(2)	−0.0005(1)	−0.0002(2)	−0.0003(2)
C(2B)	0.0019(1)	0.00097(5)	0.0039(2)	−0.0001(1)	0.0000(2)	−0.0004(2)
C(3B)	0.0019(1)	0.00089(5)	0.0034(2)	0.0000(1)	0.0000(2)	−0.0001(2)
C(4B)	0.0018(1)	0.00087(5)	0.0040(2)	−0.0000(1)	0.0003(2)	0.0003(2)
C(5B)	0.0020(1)	0.00087(5)	0.0042(2)	0.0001(1)	−0.0001(2)	0.0005(2)
C(6B)	0.0024(1)	0.00096(6)	0.0050(2)	−0.0002(1)	0.0012(3)	0.0000(2)
C(7B)	0.0031(1)	0.00095(5)	0.0052(2)	−0.0005(1)	0.0008(3)	0.0001(2)
C(8B)	0.0027(1)	0.00104(6)	0.0048(2)	0.0006(1)	0.0005(3)	−0.0001(2)
C(9B)	0.0023(1)	0.00131(6)	0.0047(2)	0.0003(1)	0.0008(3)	−0.0003(2)
C(10B)	0.0021(1)	0.00111(6)	0.0051(2)	−0.0003(1)	0.0007(3)	−0.0003(2)
C(11B)	0.0020(1)	0.00110(6)	0.0047(2)	−0.0003(1)	0.0002(2)	0.0002(2)
C(12B)	0.0023(1)	0.00102(5)	0.0045(2)	0.0000(1)	0.0004(3)	0.0001(2)
C(13B)	0.0022(1)	0.00111(6)	0.0049(2)	−0.0000(1)	−0.0002(3)	−0.0003(2)
C(14B)	0.0022(1)	0.00118(6)	0.0038(2)	−0.0004(1)	0.0002(2)	0.0002(2)
C(15B)	0.0024(1)	0.00115(6)	0.0042(2)	−0.0002(1)	−0.0002(3)	0.0004(2)
C(16B)	0.0038(2)	0.00204(9)	0.0045(2)	0.0001(2)	−0.0015(3)	−0.0017(2)
C(17B)	0.0023(1)	0.00123(6)	0.0045(2)	−0.0003(1)	0.0013(3)	−0.0004(2)
C(18B)	0.0033(2)	0.00223(9)	0.0079(3)	−0.0006(2)	0.0036(4)	−0.0022(3)
C(19B)	0.0033(2)	0.00211(9)	0.0089(4)	−0.0006(2)	0.0038(4)	0.0023(3)
N(1B)	0.0020(1)	0.00092(4)	0.0044(2)	−0.0003(1)	0.0009(2)	0.0003(1)
N(2B)	0.0028(1)	0.00139(6)	0.0085(3)	−0.0009(1)	0.0008(3)	0.0006(2)
N(3B)	0.0042(2)	0.00162(6)	0.0048(2)	0.0005(2)	−0.0000(3)	−0.0004(2)
N(4B)	0.0034(1)	0.00146(6)	0.0066(2)	−0.0002(1)	0.0002(3)	−0.0020(2)
N(5B)	0.0028(1)	0.00207(7)	0.0058(2)	0.0002(2)	−0.0010(3)	0.0009(2)
N(6B)	0.0043(1)	0.00130(6)	0.0053(2)	0.0002(1)	0.0016(3)	−0.0008(2)
O(1B)	0.0062(2)	0.00196(6)	0.0099(3)	−0.0022(2)	0.0055(3)	−0.0045(2)
O(2B)	0.0049(2)	0.00296(8)	0.0105(3)	−0.0009(2)	0.0071(3)	−0.0049(3)
O(3B)	0.0034(1)	0.00190(6)	0.0077(2)	0.0016(1)	−0.0039(3)	−0.0017(2)
O(4B)	0.0030(1)	0.00153(4)	0.0040(1)	0.0007(1)	−0.0011(2)	−0.0011(1)

Table 5a. Bond Distances (Å) with esd's in Parentheses

C(1A)–C(2A)	1.565(6)	C(1B)–C(2B)	1.571(5)	C(7A)–C(8A)	1.365(6)	C(7B)–C(8B)	1.379(6)
C(1A)–C(17A)	1.507(6)	C(1B)–C(17B)	1.498(6)	C(8A)–C(9A)	1.378(6)	C(8B)–C(9B)	1.381(6)
C(1A)–N(1A)	1.265(5)	C(1B)–N(1B)	1.263(5)	C(8A)–N(6A)	1.459(6)	C(8B)–N(6B)	1.475(6)
C(2A)–C(3A)	1.582(5)	C(2B)–C(3B)	1.589(5)	C(9A)–C(10A)	1.377(7)	C(9B)–C(10B)	1.365(6)
C(2A)–C(13A)	1.466(6)	C(2B)–C(13B)	1.472(6)	C(11A)–N(2A)	1.141(6)	C(11B)–N(2B)	1.124(6)
C(2A)–C(14A)	1.483(6)	C(2B)–C(14B)	1.467(5)	C(12A)–N(3A)	1.131(6)	C(12B)–N(3B)	1.141(6)
C(3A)–C(4A)	1.622(5)	C(3B)–C(4B)	1.620(5)	C(13A)–N(4A)	1.138(6)	C(13B)–N(4B)	1.140(6)
C(3A)–C(11A)	1.471(6)	C(3B)–C(11B)	1.478(5)	C(14A)–N(5A)	1.140(6)	C(14B)–N(5B)	1.139(6)
C(3A)–C(12A)	1.475(6)	C(3B)–C(12B)	1.472(5)	C(15A)–O(3A)	1.178(6)	C(15B)–O(3B)	1.190(5)
C(4A)–C(5A)	1.513(6)	C(4B)–C(5B)	1.525(5)	C(15A)–O(4A)	1.319(5)	C(15B)–O(4B)	1.314(5)
C(4A)–C(15A)	1.539(6)	C(4B)–C(15B)	1.538(5)	C(16A)–O(4A)	1.437(6)	C(16B)–O(4B)	1.444(6)
C(4A)–N(1A)	1.446(5)	C(4B)–N(1B)	1.446(5)	C(17A)–C(18A)	1.532(7)	C(17B)–C(18B)	1.513(7)
C(5A)–C(6A)	1.376(6)	C(5B)–C(6B)	1.377(6)	C(17A)–C(19A)	1.523(9)	C(17B)–C(19B)	1.529(7)
C(5A)–C(10A)	1.386(6)	C(5B)–C(10B)	1.395(6)	N(6A)–O(1A)	1.183(7)	N(6B)–O(1B)	1.213(6)
C(6A)–C(7A)	1.384(6)	C(6B)–C(7B)	1.378(6)	N(6A)–O(2A)	1.192(6)	N(6B)–O(2B)	1.204(6)

Table 5b. Bond Angles (°) with esd's in Parentheses

C(2A)–C(1A)–C(17A)	120.4(4)	C(2B)–C(1B)–C(17B)	120.6(3)
C(2A)–C(1A)–N(1A)	114.2(4)	C(2B)–C(1B)–N(1B)	114.2(3)
C(17A)–C(1A)–N(1A)	125.2(4)	C(17B)–C(1B)–N(1B)	125.1(4)
C(1A)–C(2A)–C(3A)	100.9(3)	C(1B)–C(2B)–C(3B)	100.8(3)
C(1A)–C(2A)–C(13A)	109.7(3)	C(1B)–C(2B)–C(13B)	112.6(3)
C(1A)–C(2A)–C(14A)	112.6(3)	C(1B)–C(2B)–C(14B)	110.2(3)
C(3A)–C(2A)–C(13A)	115.1(3)	C(3B)–C(2B)–C(13B)	112.0(3)
C(3A)–C(2A)–C(14A)	111.3(3)	C(3B)–C(2B)–C(14B)	114.7(3)
C(13A)–C(2A)–C(14A)	107.4(3)	C(13B)–C(2B)–C(14B)	106.6(3)
C(2A)–C(3A)–C(4A)	102.5(3)	C(2B)–C(3B)–C(4B)	102.3(3)
C(2A)–C(3A)–C(11A)	110.4(3)	C(2B)–C(3B)–C(11B)	114.5(3)
C(2A)–C(3A)–C(12A)	114.2(3)	C(2B)–C(3B)–C(12B)	110.0(3)
C(4A)–C(3A)–C(11A)	110.7(3)	C(4B)–C(3B)–C(11B)	112.6(3)
C(4A)–C(3A)–C(12A)	111.5(3)	C(4B)–C(3B)–C(12B)	110.4(3)
C(11A)–C(3A)–C(12A)	107.7(3)	C(11B)–C(3B)–C(12B)	107.1(3)
C(3A)–C(4A)–C(5A)	111.0(3)	C(3B)–C(4B)–C(5B)	110.8(3)
C(3A)–C(4A)–C(15A)	109.6(3)	C(3B)–C(4B)–C(15B)	109.8(3)
C(3A)–C(4A)–N(1A)	104.4(3)	C(3B)–C(4B)–N(1B)	105.0(3)
C(5A)–C(4A)–C(15A)	111.5(3)	C(5B)–C(4B)–C(15B)	111.5(3)
C(5A)–C(4A)–N(1A)	112.7(3)	C(5B)–C(4B)–N(1B)	112.2(3)
C(15A)–C(4A)–N(1A)	107.4(3)	C(15B)–C(4B)–N(1B)	107.3(3)
C(4A)–C(5A)–C(6A)	120.9(4)	C(4B)–C(5B)–C(6B)	120.9(4)
C(4A)–C(5A)–C(10A)	119.2(4)	C(4B)–C(5B)–C(10B)	119.4(3)
C(6A)–C(5A)–C(10A)	119.8(4)	C(6B)–C(5B)–C(10B)	119.7(4)
C(5A)–C(6A)–C(7A)	120.1(4)	C(5B)–C(6B)–C(7B)	120.3(4)
C(6A)–C(7A)–C(8A)	118.7(4)	C(6B)–C(7B)–C(8B)	118.6(4)
C(7A)–C(8A)–C(9A)	122.7(4)	C(7B)–C(8B)–C(9B)	122.3(4)
C(7A)–C(8A)–N(6A)	118.8(4)	C(7B)–C(8B)–N(6B)	119.3(4)
C(9A)–C(8A)–N(6A)	118.6(4)	C(9B)–C(8B)–N(6B)	118.4(4)
C(8A)–C(9A)–C(10A)	117.9(4)	C(8B)–C(9B)–C(10B)	118.3(4)
C(5A)–C(10A)–C(9A)	120.7(4)	C(5B)–C(10B)–C(9B)	120.8(4)
C(3A)–C(11A)–N(2A)	178.5(4)	C(3B)–C(11B)–N(2B)	175.1(5)
C(3A)–C(12A)–N(3A)	174.7(5)	C(3B)–C(12B)–N(3B)	177.9(4)
C(2A)–C(13A)–N(4A)	174.9(5)	C(2B)–C(13B)–N(4B)	178.1(4)
C(2A)–C(14A)–N(5A)	177.7(5)	C(2B)–C(14B)–N(5B)	177.1(4)
C(4A)–C(15A)–O(3A)	126.0(4)	C(4B)–C(15B)–O(3B)	125.2(4)
C(4A)–C(15A)–O(4A)	108.6(3)	C(4B)–C(15B)–O(4B)	109.1(3)
O(3A)–C(15A)–O(4A)	125.4(4)	O(3B)–C(15B)–O(4B)	125.7(4)
C(1A)–C(17A)–C(18A)	111.1(4)	C(1B)–C(17B)–C(18B)	113.3(4)
C(1A)–C(17A)–C(19A)	110.5(4)	C(1B)–C(17B)–C(19B)	109.2(4)
C(18A)–C(17A)–C(19A)	111.1(5)	C(18B)–C(17B)–C(19B)	111.0(4)
C(1A)–N(1A)–C(4A)	114.0(3)	C(1B)–N(1B)–C(4B)	114.0(3)
C(8A)–N(6A)–O(1A)	118.6(5)	C(8B)–N(6B)–O(1B)	118.5(4)
C(8A)–N(6A)–O(2A)	119.8(4)	C(8B)–N(6B)–O(2B)	118.6(4)
O(1A)–N(6A)–O(2A)	121.6(5)	O(1B)–N(6B)–O(2B)	122.8(4)
C(15A)–O(4A)–C(16A)	118.3(3)	C(15B)–O(4B)–C(16B)	117.8(3)



Scheme 1.

Table 6. Results of the Elemental Analysis of 3

Compound	Found/%			Calcd/%			Molecular formula
	C	H	N	C	H	N	
3a	56.53	2.78	23.19	56.36	2.78	23.20	$C_{17}H_{10}N_6O_4$
3b	57.45	3.21	22.31	57.45	3.21	22.33	$C_{18}H_{12}N_6O_4$
3c	58.65	3.59	21.49	58.46	3.62	21.53	$C_{19}H_{14}N_6O_4$
3d	59.68	4.18	20.46	59.40	3.99	20.79	$C_{20}H_{16}N_6O_4$
3e	62.43	3.10	19.59	62.26	2.85	19.81	$C_{22}H_{12}N_6O_4$
3f	60.80	3.11	18.50	60.79	3.11	18.49	$C_{23}H_{14}N_6O_5$
3g	63.36	3.28	18.92	63.01	3.22	19.17	$C_{23}H_{14}N_6O_4$

can be attributed to the CT-complex. The absorption disappeared after refluxing the reaction mixture for 20 h.

The mechanism of the reaction can tentatively be explained as follows. An electrophilic attack of an ethylenic carbon of TCNE on C-4 or C-2 of the oxazole initiates the reaction to give a zwitterionic intermediate **7A** (path A) or **7B** (path B) which give another zwitterionic intermediate **8A** or **8B** respectively, through ring opening of the oxazole. The alternative mechanism which proceeds by the attack of TCNE anion radical formed by the electron-transfer reaction on oxazole cation radical is also possible. Cyclization of these intermediates **8A** or **8B** gives the corresponding 1-pyrroline derivatives **3** (Scheme 1.). Several attempts to distinguish the path A from path B by trapping the expected intermediates were unsuccessful. For example, trapping experiment of the intermediates **7** or **8** by adding methanol or acetic acid to the reaction system did not give successful result.

Alternative mechanisms through normal Diels–Alder adduct[8)] are not completely excluded in this stage of experiment, despite the thermolysis of Diels–Alder adducts of **1** with maleimide leads only retro-Diels–Alder reaction without affording a rearranged product of type **3**.[3a)] However, the mechanism through nitrile ylide intermediate which was expected by the ring opening of oxazole[13)] prior to the attack of TCNE can be eliminated, because **1a** gave usual Diels–Alder adducts in the reaction with *N*-alkyl- and *N*-phenylmaleimides in similar reaction conditions.[3a,b)]

Experimental

Melting points were measured with a Yanagimoto Melting Point Apparatus and were not corrected. IR spectra were recorded on a Perkin-Elmer model 983. NMR spectra were recorded on a Varian EM-390 for proton and on a Bruker AM 360 for ^{13}C NMR in $CDCl_3$ using TMS as an internal standard.

Materials. All 2-alkyl-5-methoxy-4-(*p*-nitrophenyl)oxazoles (**1**) were prepared by the BF_3-catalyzed reaction of methyl *p*-nitrophenyldiazoacetate with the corresponding nitriles.[14)] Ethyl 5-ethoxy-2-methyl-4-oxazolecarboxylate (**5a**) was synthesized by the dehydrocyclization of diethyl 2-(acetylamino)malonate using P_2O_5 in chloroform solution.[15)]

TCNE was purified by sublimation under reduced pressure and kept under the atmosphere of nitrogen.

Acetonitrile was purified by distillation first from P_2O_5 and then from CaH_2, and kept over molecular sieves type 4A.

General Procedure of the Reaction of Oxazole 1 with TCNE. A solution of **1** (1.0 mmol) and TCNE (1.2 mmol) dissolved in 20 ml of acetonitrile was refluxed until the olive color of the reaction mixture disappeared. After 20 h, solvent was removed under reduced pressure. The residue was separated by the medium-pressure column chromatography on silica gel using benzene as an eluent. Products were characterized by elemental analysis (Table 6) and IR, ^{1}H NMR, and ^{13}C NMR spectra.

The ^{13}C NMR (CDCl$_3$) spectra of adducts are shown below.

3a: δ=17.53 (N=C$\underline{\text{Me}}$), 53.53 (4-C), 55.26 (COO$\underline{\text{Me}}$), 56.40 (3-C), 91.27 (5-C), 106.26 (CN), 107.40 (CN), 107.99 (CN), 108.44 (CN), 124.51 (2′-C), 128.26 (3′-C), 138.73 (1′-C), 149.55 (4′-C), 163.21 (C=O), 164.36 (C=N).

3b: δ=10.10 (CH$_2\underline{\text{C}}$H$_3$), 25.39 (CH$_2$), 53.55 (4-C), 55.30 (COO$\underline{\text{Me}}$), 55.70 (3-C), 90.95 (5-C), 106.47 (CN), 107.52 (CN), 107.99 (CN), 108.41 (CN), 124.49 (2′-C), 128.20 (3′-C), 138.84 (1′-C), 149.39 (4′-C), 164.40 (C=O), 167.64 (C=N).

3c: δ=20.43 (q, $J_{\text{C-H}}$=129.5 Hz, C$\underline{\text{Me}}$), 20.59 (q, $J_{\text{C-H}}$=129.5 Hz, C$\underline{\text{Me}}$), 32.78 (d, $J_{\text{C-H}}$=129.9 Hz, $\underline{\text{C}}$Me), 53.96 (s, 4-C), 54.59 (d, $^{3}J_{\text{C-H}}$=1.8 Hz, 3-C), 55.25 (q, $J_{\text{C-H}}$=150.1 Hz, O$\underline{\text{Me}}$), 89.84 (s, 5-C), 106.60 (s, CN), 107.48 (s, CN), 107.93 (s, CN), 108.29 (s, CN), 124.47 (d, $J_{\text{C-H}}$=170.9 Hz, 2′-C), 128.12 (d, $J_{\text{C-H}}$=166.0 Hz, 3′-C), 138.70 (s, 1′-C), 149.37 (s, 4′-C), 164.33 (q, $^{3}J_{\text{C-H}}$=3.7 Hz, CO), 171.09 (s, C=N).

3d: δ=28.47 (q, $J_{\text{C-H}}$=128.8 Hz, C$\underline{\text{Me}}$), 40.10 (s, $\underline{\text{C}}$Me), 52.30 (s, 4-C), 54.99 (s, 3-C), 55.35 (q, $J_{\text{C-H}}$=150.1 Hz, O$\underline{\text{Me}}$), 87.77 (s, 5-C), 106.93 (s, CN), 107.96 (s, CN), 108.08 (s, CN), 108.21 (s, CN), 124.56 (d, $J_{\text{C-H}}$=170.9 Hz, 2′-C), 128.09 (d, $J_{\text{C-H}}$=166.0 Hz, 3′-C), 138.70 (s, 1′-C), 149.37 (s, 4′-C), 164.53 (q, $^{3}J_{\text{C-H}}$=3.9 Hz, CO), 172.62 (s, C=N).

3e: δ=53.59 (4-C), 54.79 (3-C), 55.22 (COO$\underline{\text{Me}}$), 90.21 (5-C), 107.23 (CN), 108.20 (2×CN), 108.52 (CN), 124.54 (2″-C), 126.55 (1″-C), 128.36 (2′-C), 129.63 (3′-C), 130.02 (3″-C), 135.54 (4″-C), 139.23 (1′-C), 149.57 (4′-C), 161.08 (C=O), 164.55 (C=N).

3f: δ=53.38 (s, 4-C), 54.72 (s, 3-C), 55.16 (q, $J_{\text{C-H}}$=150.1 Hz, arom-O$\underline{\text{Me}}$), 56.04 (q, $J_{\text{C-H}}$=145.3 Hz, COO$\underline{\text{Me}}$), 90.20 (s, 5-C), 107.50 (s, CN), 108.39 (s, CN), 108.56 (s, CN), 108.73 (s, CN), 115.53 (d, $J_{\text{C-H}}$=163.9 Hz, 2″-C), 118.76 (s, 1″-C), 124.50 (d, $J_{\text{C-H}}$=170.9 Hz, 2′-C), 128.40 (d, $J_{\text{C-H}}$=165.7 Hz, 3′-C), 132.01 (d, $J_{\text{C-H}}$=161.4 Hz, 3″-C), 139.63 (s, 1′-C), 149.42 (s, 4′-C), 159.97 (t, 4″-C), 164.94 (q, $^{3}J_{\text{C-H}}$=4.3 Hz, CO), 165.55 (s, C=N).

3g: δ=22.00 (Ar$\underline{\text{Me}}$), 53.53 (4-C), 54.76 (3-C), 55.13 (COO$\underline{\text{Me}}$), 90.17 (5-C), 107.37 (CN), 108.30 (CN), 108.35 (CN), 108.62 (CN), 123.84 (1″-C), 124.48 (2″-C), 128.39 (2′-C), 129.67 (3′-C), 130.72 (3″-C), 139.40 (1′-C), 147.28 (4″-C), 149.53 (4′-C), 160.89 (C=O), 164.71 (C=N).

Reaction of Ethyl 5-Ethoxy-2-methyl-4-oxazolecarboxylate (5a) with TCNE. The reaction was carried out in a similar manner described above. Although the isolation of the product was unsuccessful, NMR spectra of the reaction mixture indicated the presence of the corresponding adduct, diethyl 3,3,4,4-tetracyano-3,4-dihydro-5-methyl-2*H*-pyrrole-2,2-dicarboxylate (**6a**) as shown below: ^{1}H NMR (CDCl$_3$) δ=1.34 (t, J=7.1 Hz, CH$_2\underline{\text{CH}_3}$), 2.59 (s, Me), ca. 4.48 (overlapped with impurity peaks); ^{13}C NMR (CDCl$_3$) δ=13.73 (q, $J_{\text{C-H}}$=125.5 Hz, CH$_2\underline{\text{CH}_3}$), 17.39 (q, $J_{\text{C-H}}$=132.2 Hz, Me), 49.31 (s, 4-C), 56.46 (q, $^{3}J_{\text{C-H}}$=3.1 Hz, 3-C), 65.70 (t, $J_{\text{C-H}}$=150.8 Hz, $\underline{\text{C}}$H$_2$), 92.69 (s, 5-C), 106.74 (s, CN), 108.25 (s, CN), 164.26 (q, $^{2}J_{\text{C-H}}$=7.5 Hz, 2-C), and 166.39 (s, CO). An attempt to isolate the product by use of medium pressure silica-gel column chromatography was unsuccessful.

Reaction of 5-Methoxy-2-(*p*-methoxyphenyl)oxazole (5b) with TCNE. The ^{1}H NMR and ^{13}C NMR spectra of the ether-soluble part of the reaction mixture also suggest the presence of the corresponding 1-pyrroline derivative: ^{1}H NMR (CDCl$_3$) δ=3.93 (s, arom-OMe), 4.02 (s, COOMe), 5.66 (s, 5-H), 7.03—7.10 (m, 3′-H), and 8.03—8.10 (m, 2′-H); ^{13}C NMR (CDCl$_3$) δ=48.48 (d, $^{2}J_{\text{C-H}}$=1.2 Hz, 4-C), 52.40 (s, 3-C), 54.47 (q, $J_{\text{C-H}}$=149.7 Hz, arom-OMe), 55.87 (q, $J_{\text{C-H}}$=145.3 Hz, COOMe), 79.91 (d, $J_{\text{C-H}}$=153.8 Hz, 5-C), 107.38 (s, CN), 107.86 (s, CN), 108.19 (d, $^{3}J_{\text{C-H}}$=4.9 Hz, HCC$\underline{\text{C}}$N), 108.96 (d, $^{3}J_{\text{C-H}}$=4.3 Hz, HCC$\underline{\text{C}}$N), 115.24 (d, $J_{\text{C-H}}$=163.6 Hz, 2′-C), 118.72 (s, 1′-C), 131.44 (d, $J_{\text{C-H}}$=161.4 Hz, 3′-C), 159.76 Hz (q, $^{3}J_{\text{C-H}}$=4.9 Hz, 2-C), 163.90 (quint, J=3.9 Hz, CO), and 164.98 (s, 4′-C).

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