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Oxazoles in Diels-Alder Reactions. Transformation of The Adducts to Either Pyridines or Pyrroles

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The cycloadducts between acrylic acid or acrylonitrile and 5-ethoxyoxazoles are converted as formed to 3-hydroxypyridines. The Diels-Alder adducts from ethyl acrylate, or methyl or phenyl vinyl ketone can be isolated. In ethanolic HCl the adducts are transformed into 3-hydroxypyridines; in aqueous HCl the products are acylpyrrole analogues. A 4-substituent in the oxazole affects the reaction. 4-Methyl-5-ethoxyoxazole reacts much faster than its 5-ethylthio analoque.

Adduct formation between 5-ethoxyoxazoles and dienophiles is a key step in an important synthetic route to substituted 3-hydroxypyridines.[1,2] The Diels-Alder adducts initially formed are unstable and are transformed further to pyridines. The positions of the substituents in the pyridine are consistent with strict regioselectivity in the adduct formation whereby C−2 of the oxazole forms the new C−C bond with the most electron deficient carbon atom. Hence the more electron attracting group from the ethene will be located in the 4- rather than in the 5-position in the pyridine.[3] In this report we describe work aimed at elucidating the effect of 4-substituents in 5-ethoxyoxazoles and 5-ethylthioxazoles on the course of the cycloaddition with electron deficient unsymmetrically substituted ethenes as well as ring-opening studies of the adducts.

5-Alkoxyoxazoles are commonly formed by cyclization of *N*-acylated amino acid esters.[1] The oxazoles are acid labile and the best yields are obtained using an acid anhydride as dehydrating agent in the presence of a base to neutralize the acid generated.[4,5] The time of heating may also be important for the outcome of the reaction. Thus in the cyclization of ethyl *N*-formylaminomalonate the yield of the *4*-ethoxycarbonyl derivate *4* was almost doubled (55 %) when the reaction time was reduced from the 6 h recommended[6] to 3 h. The 5-ethylthioxazole *5* is similarly prepared by cyclization of the corresponding thiol ester.[7]

The bicyclic Diels-Alder adducts are very sensitive to acid. In an acidic organic solvent the adduct will be transformed to pyridines. The acid instability also precludes isolation of Diels-Alder adducts in those cases where the dienophile carries an acid function (*e.g. 6a*). In the absence of an acidic function such as in ethyl acrylate, methyl vinyl ketone and phenyl vinyl ketone, the reaction with the 4-methyloxazole *2* does not proceed beyond the Diels-Alder adduct under mild conditions. With acrylonitrile, however, the reaction went all the way to the corresponding pyridine. The reaction times varied. The reaction with the acrylate *6b* was complete after 5 days, with the methyl ketone *6c* after *ca.* 20 h whereas the more polarizable phenyl ketone *6d* gave a rapid and highly exothermic reaction. The order of stability of the adducts was the reverse of their rate of formation. Both the ester *7b* and the methyl ketone *7c* could be distilled but the latter decomposed slowly on storage. Attempted distillation of the phenyl ketone adduct *7d* led to retro-Diels-Alder reaction. The *endo:exo* ratios of the adducts were *ca.* 3:1 (^{1}H NMR). The isomer assignments are based on the chemical shifts for H−5 which is found at lower field in the *endo* isomer than in the *exo* isomer (Scheme 2);[8,9] H−5 resonates as a quartet partially or fully resolved. H−1 appears as a doublet (*J* 4 Hz) by coupling with the *exo*-proton on C−6 in agreement with findings in related series.[8] Normal

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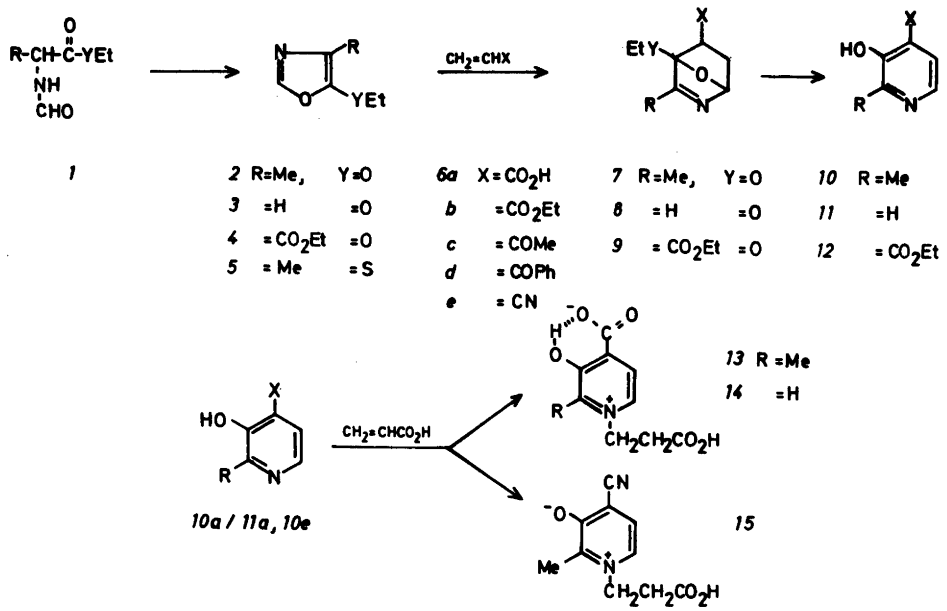


Scheme 1.

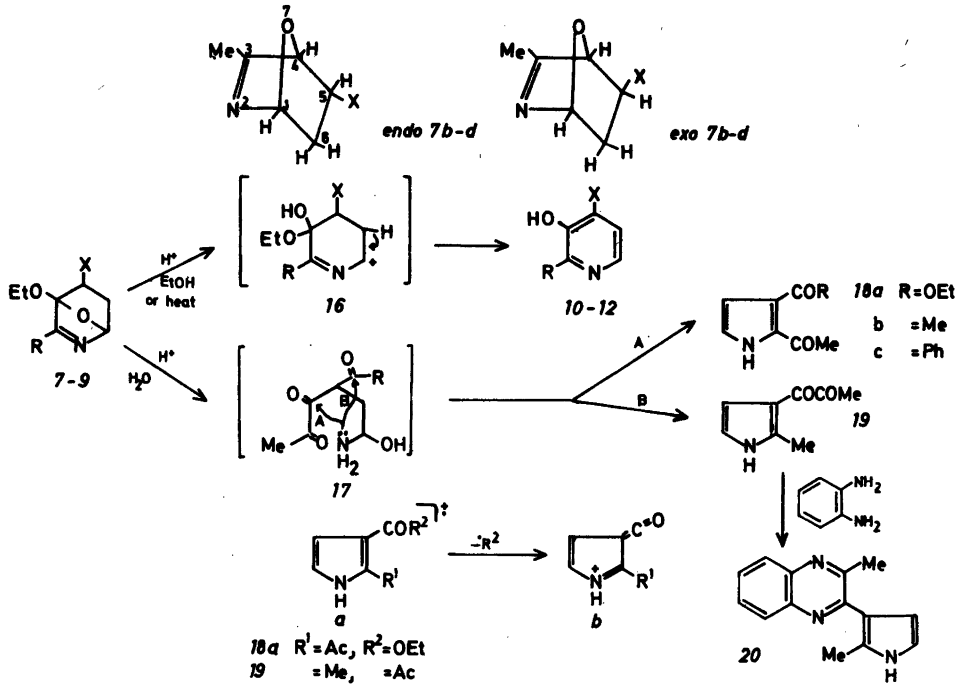
carbonyl absorptions in IR are found at 1735 (*7b*), 1710 (*7c*) and 1680 cm^{-1} (*7d*) with the C=N band at *ca.* 1630 cm^{-1}. The mass spectra are characterized by a weak molecular ion and dominated by ions corresponding to retro-Diels-Alder reactions which may occur either before electron impact as a thermal process, or after electron impact.

Treatment of the adducts with ethanolic HCl rapidly gave the corresponding 3-hydroxypyridines. In aqueous acids, however, the reaction takes another way as discussed below. In the case of the phenyl ketone *7d* its high reactivity demanded slow addition of the ethanolic acid. ^1H NMR confirms the structures assigned to the pyridines. Thus the vicinal protons on C–5 and C–6 are confirmed by the magnitude of their coupling, *J ca.* 5 Hz, and hence the carbonyl substituent is on C–4. The two 3-hydroxypyridines *10b* and *10c* have previously been prepared directly from the Diels-Alder reactants using acetic acid as solvent;[10,11] the overall yield in the two-step process described above is superior.

In the reaction between acrylonitrile and the 4-methyloxazole *2* the intermediate adduct *7e* was at once transformed to the pyridine *10e*; the overall rate of the reaction is therefore controlled by the time (4 h) required for adduct formation. Acrylic acid gives *10a* rapidly and exothermally. The 4-desmethyl oxazole *3* is much less reactive in the cycloaddition than is the 4-methyl analogue *2*, the reaction time being increased to 48 h; the yields of the pyridines were lower and in no case was the Diels-Alder adduct isolated. The relative reactivities of the dienophiles were the same as before. A further decrease in the reactivity of the oxazole was observed for the 4-ethoxycarbonyl derivative *4*; the latter reacts slowly with acrylic acid to form the pyridine *12a* and hardly at all with phenyl vinyl ketone.

It is notable that there is a very marked difference in the effects of the 5-ethoxy and 5-ethylthio substituents in *2* and *5*, respectively, on the reactivity of the oxazole. The former gives an immediate and exotherm reaction with acrylic acid to form the pyridine *10a* whereas the latter gave 20 % conversion to *10a* after 4 days; with phenyl vinyl ketone 10 % yield of the pyridine *10d* was obtained after 12 days whereas methyl vinyl ketone did not react with *5* under the usual conditions.

In the absence of a solvent the main product is a 2:1 adduct between acrylic acid and the oxazole *2* or *3*. The products have been identified as the



Scheme 2.

Michael adducts between the initially formed pyridine and a second molecule of acrylic acid, *viz.* *13* and *14*. These betaines are volatile in the mass spectrometer without decarboxylation. The chemical shifts in the ^1H and ^{13}C NMR spectra are consistent with pyridinium structures formulated. The size of the C–H couplings on C–2 and C–6 in *14*, $^1J_{CH}$ 189 and 193 Hz, respectively, are in good agreement with the value 193 Hz reported for *N*-methylpyridinium-3-olate.[12,13] The structures assigned were also proved chemically by heating the pyridines *10a* and *11a* with acrylic acid, which gave the adducts *13* and *14*. In the same way the 4-cyanopyridine *10e* gave the 3-pyridiniopropanoic acid *15*.

The pathway to pyridines *10–12* from the Diels-Alder adducts *7–9* can be rationalized in terms of an initial cleavage of the Cl–O bond (*16*; Scheme 2) which is succeeded by elimination of ethanol. In aqueous acids, however, the reaction takes another course; the products isolated have been identified as pyrroles. Thus the product from the 5-ethoxycarbonyl adduct *7b* has been assigned the structure 2-acetyl-3-ethoxycarbonylpyrrole *18a*. In IR the product showed absorption bands for NH at 3310, for ester carbonyl at 1710 and for keto carbonyl at 1640 cm^{-1}; the latter agrees well with the value 1626 cm^{-1} reported for 2-acetylpyrrole.[14] The ^1H NMR shifts at δ 6.77 and 6.94 are at higher fields than in pyridines but agree well with the values δ 6.62 (H–4) and 7.18 (H–5) reported for 2-formyl-3-ethoxycarbonylpyrrole.[15] In the mass spectrum the base peak is due to [M–OEt] which is rationalized as a favourable process *a*→*b* shown in Scheme 2.

For the 5-acetyl derivative *7c* in conc. HCl the transformation took another course. The base peak in the mass spectrum is due to [M–Ac] which again is rationalized as a favourable process *a*→*b* for the structure *19* assigned (pathway B; Scheme 2). In IR the CO bands are at 1620 and 1700 cm^{-1}; the former corresponds well to the absorption at *ca.* 1630 cm^{-1} for both 2- and 3-acetylpyrrole,[15,16] whereas the latter corresponds to the normal carbonyl band in 1,2-diketones. In ^1H NMR the two methyl groups appear as singlets at δ 2.42 and 2.55 whereas the

two protons of the pyrrole ring overlap at *ca.* δ 6.6. Finally the structure assigned was confirmed in a condensation reaction with *o*-phenylenediamine in which case the guinoxaline *20* was formed. In 1 M HCl the course of the transformation of *7c* is different, and the new product has been assigned structure *18b* corresponding to pathway A. Its mass spectrum is characterized by [M−Me] and [M−Me−CO] and the remainder of the spectroscopic evidence is in agreement with structure *18b*. In the concentration region between the dilute HCl and conc. HCl, mixtures of the two isomeric structures *18b* and *19* were formed. No such dependency on the acid strength for the ethoxycarbonyl derivative *7b* was observed and *18a* was the only pyrrole isolated irrespective of the strength of the acid solution. Similarly the 5-benzoyl adduct *7d* gave only one pyrrole irrespective of the acid strength. The assignment of structure *18c* follows from spectroscopy; CO bands in IR at 1640 and 1650 cm^{-1}, ^1H NMR signals at δ 6.35 (H−4) and 7.00 (H−5) and a mass spectrum characterized by [M−Ph] and [M−Ph−CO].

The formation of pyrroles from the Diels-Alder adducts in aqueous acid solution may be rationalized by a reaction involving hydrolytic cleavage of the N2−C3 bond in *7*. In the postulated acyclic intermediate *17* cyclization to a five-membered ring may take two courses; pathway A gives the 2,3-diacylpyrroles *18* whereas pathway B gives a 3-(1,2-dioxoalkyl)pyrrole *19*.

EXPERIMENTAL

Formation of cycloadducts. The dienophile *6* (0.01 mol) and one of the oxazoles *2*−*5* (0.01 mol) were mixed and the mixture stirred at room temperature or at the temperature given below for the individual compounds; the progress of the reaction was monitored by TLC.

5-Ethoxy-4-ethoxycarbonyloxazole 4.[6] Diethyl *N*-formylaminomalonate (12.0 g, 0.06 mol) was added dropwise to a vigorously stirred suspension of phosphorus pentoxide (4.0 g, 0.33 mol) in chloroform (200 ml) at room temperature. The mixture was stirred at this temperature for 30 min after the addition was completed, and was then heated under reflux for 3 h. The cold reaction mixture was hydrolyzed by slow addition of 10 % NaOH and ice, the chloroform solution collected from the two-phase system, the water solution extracted twice with chloroform, the combined chloroform solutions washed with a little water, the dried ($MgSO_4$) solution evaporated and the residue distilled; yield 55 %, b.p. 104 °C/0.6 mmHg.

3-Methyl-4-ethoxy-5-ethoxycarbonyl-7-oxa-2-azabicyclo[2,2,1]-2-heptene 7b from 4-methyl-5-ethoxyoxazole and ethyl acrylate (4 h, 40 °C); yield 93 %, b.p. 78−80 °C/0.35 mmHg. Anal. $C_{11}H_{17}NO_3$: C, H. Isomer ratio *endo*−*exo* 3:1. ^1H NMR (CCl_4) for *endo* isomer: δ 1.27, 1.34 and 3.76 (OEt and the Me from OEt), 1.96 (3−Me), 2.89 (H−5, d), 5.47 (H−1, d, *J* 4 Hz), the rest unresolved. *exo* isomer: δ 1.24, 1.34 and 3.80, 4.04 (2 OEt), 2.01 (3−Me), 2.3 (m, 3H), 5.61 (H−1), d, *J* 4 Hz). IR (CCl_4): 1735 (CO) and 1630 cm^{-1} (C=N). MS[70 eV; *m/z* (% rel. int.)]: 227 (3, M), 181 (12), 135 (22), 127 (44), 107 (13), 99 (71), 71 (52), 55 (100).

3-Methyl-4-ethoxy-5-acetyl-7-oxa-2-azabicyclo-[2,2,1]-2-heptene 7c [8] from *5* and buten-2-one (20 h); yield 91 %, b.p. 62−64 °C/0.1 mmHg. Isomer ratio *endo*—*exo* 3:1. ^1H NMR (CCl_4) for *endo* isomer: δ 1.30 and 3.73 (OEt), 1.72 (H−6, 2 d), 1.85 (Me), 2.17 (Me), 2.1 (H−6, m), 3.06 (H−5, 2 d), 5.45 (H−1, d, *J* 3.5). *exo*-isomer: δ 1.10 and 3.78 (OEt), 2.03 (Me), 1.6−2.3 (3H), 2.13 (Me), 5.60 (H−1, d, *J* 3.5 Hz). IR (film): 1710 (CO), 1625 cm^{-1} (C=N). MS[70 eV; *m/z* (% rel. int.)]: 197 (1, M), 151 (9), 127 (45), 99 (66), 82 (11), 71 (48), 70 (47), 55 (100).

3-Methyl-4-ethoxy-5-benzoyl-7-oxa-2-azabicyclo[2,2,1]-2-heptene 7d from *5* and 1-phenyl-2-propen-1-one (5 min) in an exothermic reaction; yield almost quantitative. Unstable liquid which largely underwent retro-Diels-Alder reaction on attempted distillation. Isomer ratio *endo*−*exo* 3:1. ^1H NMR (CCl_4) for *endo* isomer: δ 1.23 and 3.80 (OEt), 1.81 (H−6, 2 d), 2.02 (3−Me), 2.3 (H−6, m), 3.45 (H−5, 2 d), 5.68 (H−1, d, *J* 4 Hz), 7.5−8.0 (Ph). *Exo* isomer: δ 1.02 and 3.88 (OEt), 1.58, (H−6, 2 d), 2.22 (3−Me), 2.23 (H−6, H−5, m). 5.83 (H−1, d, *J* 4 Hz), 7.5−8 (Ph). IR (film): 1680 (CO), 1635 cm^{-1} (C=N). MS[70 eV; *m/z* (% rel. int.)]: 259 (1, M), 213 (6), 132 (52), 127 (50), 105 (100), 99 (51), 77 (43), 71 (36), 55 (86).

3-Hydroxypyridines 10 *from Diels-Alder adducts* 7. *2-Methyl-3-hydroxy-4-ethoxycarbonylpyridine 10b* [10] was obtained in 90 % yield when *6b* was treated with ethanolic HCl as described below; aromatization in acetic acid gave 67 % yield.

2-Methyl-3-hydroxy-4-acetylpyridine 10c [6] was obtained in 72 % yield when *6c* was treated with ethanolic HCl as described below; aromatization in acetic acid gave 25 % yield.

2-Methyl-3-hydroxy-4-benzoylpyridine 10d. Ethanolic HCl (saturated, 5 ml) was added

dropwise to a solution of 3-methyl-4-ethoxy-5-benzoyl-7-oxa-2-azabicyclo[2,2,1]-2-heptene (2.59 g, 0.01 mol) in abs. ethanol (50 ml). After 10 min the solution was evaporated to dryness, the residual hydrochloride triturated with acetone, the insoluble material dissolved in water, the solution neutralized with sodium carbonate and the pyridine extracted into dichloromethane. Evaporation and distillation of the residue gave the title compound in 74 % yield, b.p. 130 °C/0.1 mmHg. Anal. $C_{13}H_{11}NO_2$: C, H. ^{1}H NMR (CCl_4): δ 2.47 (2−Me), 7.12 (H−5, J 5 Hz), 7.5 (Ph), 8.00 (H−6). IR (film): 1650 cm^{-1} (CO). MS[70 eV; *m/z* (% rel. int.)]: 213 (100, M), 212 (74), 136 (10), 135 (19), 115 (13), 108 (12), 107 (23), 105 (88).

Direct isolation of 3-hydroxypyridines from oxazoles. The oxazole and the dienophile were mixed directly together without solvent and the mixture was stirred at room temperature; the reaction time is given separately for each compound. The progress of the reactions was monitored by TLC.

2-Methyl-3-hydroxy-4-carboxypyridine[18] 10a. *Method A.* The reaction between 4-methyl-5-ethoxyoxazole *3* and acrylic acid was exothermic and was over as soon as the mixing was completed. The product was purified by recrystallization from water; yield 85 %.

Method B: When 4-methyl-5-ethylthioxazole and acrylic acid were mixed there was no heat evolution. The reaction mixture was worked up after 4 days; yield 20 %.

2-Methyl-3-hydroxy-4-cyanopyridine[10] *10e* was obtained in 85 % yield from *2* and acrylonitrile (4 h); purified by recrystallization from methanol.

3-Hydroxy-4-carboxypyridine[19] 11a. Equimolar amounts of 5-ethoxyoxazole *3* and acrylic acid were left in ethanolic solution for 48 h. Evaporation and recrystallization of the residue from water gave the title compound in 30 % yield.

3-Hydroxy-4-acetylpyridine 11c was formed from *3* and 3-buten-2-one (48 h) in 8 % after preparative GLC on a 15 % Apiezon L-column; MS molecular ion 137.0478; calc. for $C_7H_7NO_2$: 137.0477. ^{1}H NMR ($CDCl_3$): δ 2.71 (Me), 7.60 (H−5, J 5 Hz), 8.27 (H−6), J 5 Hz), 8.49 (H−2, J<1). IR (film):1660 cm^{-1} (CO). MS[70 eV; *m/z* (% rel. int.)]: 137 (69, M), 43 (100).

3-Hydroxy-4-benzoylpyridine[20] *11d* was formed from *3* and 1-phenyl-2-propen-1-one (48 h) and was isolated by thick-layer chromatography on silica gel (Merck PF 254; plates 20×40 cm^2, thickness 2 mm) using $CHCl_3$ for development. The desired product was extracted from the silica gel by dichloromethane, the solution evaporated and the residue crystallized from MeOH/Et_2O; yield 23 %, m.p. 105−106 °C. Anal. $C_{12}H_9NO_2$:C, H.

3-Hydroxy-4-cyanopyridine 11e from *3* and acrylonitrile (48 h). The reaction mixture was dissolved in ether; the title compound crystallized from this solution on slow concentration; yield 55 %, m.p. 166−167 °C. Anal. $C_6H_4N_2O$: C, H. ^{1}H NMR (acetone-d_6): δ 7.60 (H−5, J 5 Hz), 8.28 (H−6, J 5 Hz), 8.53 (H−2, J<1). IR (KBr) 2210 cm^{-1} (CN): MS[70 eV; *m/z* (% rel. int.)]: 120 (100, M), 93 (22), 92 (39), 65 (44), 64 (44), 52 (11).

2-Ethoxycarbonyl-3-hydroxy-4-carboxypyridine 12a from 4-ethoxycarbonyl-5-ethoxyoxazole and acrylic acid (48 h). The solid precipitate was recrystallized from ethanol; yield 34 %, m.p. 194 °C. Anal. $C_9H_9NO_5$: C, H. ^{1}H NMR (NaOD/D_2O):δ 1.14 and 3.62 (OEt), 7.05 (H−5, J 5 Hz), 7.43 (H−6, J 5 Hz). IR (KBr): 2550 (OH-acid), 1705 (CO-ester), 1665 cm^{-1} (CO-acid). MS[70 eV; *m/z* (% rel. int.)]: 211 (7, M), 167 (40), 166 (8), 148 (8), 139 (100), 121 (46), 120 (12), 93 (30).

1-(3-Propionic acid)-2-methyl-3-hydroxypyridinium-4-carboxylate 13. 2-Methyl-3-hydroxy-4-carboxypyridine (1.53 g, 0.01 mol) and acrylic acid (0.70 g, 0.01 mol) were heated together at 100 °C for 4 h. The solid was then filtered off and washed well with acetone; yield 63 %, m.p. 220 °C (decomp., water). Anal. $C_{10}H_{11}NO_5$:C, H. ^{1}H NMR (TFA): δ 2.92 (2−Me), 3.25 (2′−CH_2), 5.02 (3′−CH_2), 8.3 (H−5, H−6). IR (KBr):1700 (CO_2H), 1620 cm^{-1} (CO_2^-). MS[70 eV; *m/z* (% rel. int.)]: 225 (22, M), 153 (22), 136 (19), 135 (100), 108 (11), 107 (85), 79 (38), 55 (73).

1-(3-Propionic acid)-3-hydroxypyridinium-4-carboxylate 14. 5-Ethoxyoxazole (1.13 g, 0.01 mol) and acrylic acid (1.40 g, 0.02 mol) were stirred together at room temperature for 24 h. The reaction mixture was then triturated with acetone and the solid filtered off; yield 78 %, m.p. 230 °C (decomp., water). Anal. $C_9H_9NO_5$: C, H. ^{1}H NMR (TFA): δ 3.38 and 5.02 (prop.), 8.5 and 8.8 (3H, pyr.). IR (KBr):1685 and 1575 cm^{-1} (CO). MS [70 eV; *m/z* (% rel. int.)]: 211 (18, M), 139 (89), 122 (10), 121 (100), 94 (9), 93 (70), 72 (84), 66 (22), 65 (28), 55 (58).

1-(3-Propionic acid)-2-methyl-4-cyanopyridinium-3-olate 15. 2-Methyl-3-hydroxy-4-cyanopyridine (1.34 g, 0.01 mol) and acrylic acid (0.70 g, 0.01 mol) were heated together at 100 °C for 20 h. The cold reaction mixture was triturated with acetone and the solid filtered off; yield 47 %, m.p. 250 °C (decomp., water). Anal. $C_{10}H_{10}N_2O_3$: C, H. ^{1}H NMR (TFA): δ 2.98 (2-Me), 3.32 and 5.07 (prop.), 7.88 (H−5, J 5 Hz), 8.50 (H−6). IR (KBr) 2220 (CN), 1685 cm^{-1} (CO). MS[70 eV; *m/z* (% rel. int.)]: 206 (4,

M), 135 (8), 134 (100), 106 (23), 105 (90), 79 (30), 65 (13), 64 (22).

Formation of pyrroles 18, 19 *from the Diels-Alder adducts.* 18. The adducts 7 (0.01 mol) were added to 1 M HCl (20 ml), the mixture stirred for 15 min before extraction with ether. The ether solutions were evaporated and the residue subjected to thick-layer chromatography as above. The plates were developed with CH_2Cl_2–pentane (4:1) and thereafter with acetone. The compounds were extracted from the isolated silica gel bands by dichloromethane. *19*: Conc. HCl was used instead of 1 M HCl; the product was isolated as above.

2-Acetyl-3-ethoxycarbonylpyrrole 18a from 3-methyl-4-ethoxy-5-ethoxycarbonyl-7-oxa-2-azabicyclo[2,2,1]-2-heptene in 63 % yield, m.p. 75–77 °C (benzene–hexane). Anal. $C_9H_{11}NO_3$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.43 and 4.38 (OEt), 2.78 (Me), 6.77 (H–4), 6.94 (H–5). IR ($CHCl_3$): 3400 (NH), 1710 and 1640 cm^{-1} (CO). MS[70 eV; *m/z* (% rel. int.)]: 181 (71, M), 138 (35), 137 (10), 136 (100), 135 (64), 120 (51), 107 (11), 94 (49).

2,3-Diacetylpyrrole 18b from 3-methyl-4-ethoxy-5-acetyl-7-oxa-2-azabicyclo[2,2,1]-2-heptene in 56 % yield, m.p. 117–118 °C (benzene–hexane). Anal. $C_8H_9NO_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 2.59 (Me), 2.71 (Me), 6.69 (H–4), 6.96 (H–5). IR ($CHCl_3$): 3420 (NH), 1670 and 1630 cm^{-1} (CO). MS[70 eV; *m/z* (% rel. int.)]: 151 (88, M), 136 (100), 94 (61), 79 (5), 67 (6), 52 (7).

2-Acetyl-3-benzoylpyrrole 18c from 3-methyl-4-ethoxy-5-benzoyl-7-oxa-2-azabicyclo[2,2,1]-2-heptene in 42 % yield, m.p. 78–80 °C (benzene–hexane). Anal. $C_{13}H_{11}NO_2$: C, H. ^{1}H NMR (CCl_4): δ 2.43 (Me), 6.35 (H–4), 7.00 (H–5), 7.5–7.9 (Ph). IR ($CHCl_3$): 3400 (NH), 1650 and 1640 cm^{-1} (CO). MS[70 eV; *m/z* (% rel. int.)]: 214 (100, M), 198 (24), 184 (19), 136 (93), 122 (22), 105 (25), 94 (42), 77 (33).

2-Methyl-3-(1,2-dioxopropan-1-yl)pyrrole 19 from 3-methyl-4-ethoxy-5-acetyl-7-oxa-2-azabicyclo[2,2,1]-2-heptene in 46 % yield, m.p. 85–86 °C (benzene–hexane). Anal. $C_8H_{11}NO_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 2.42 (Me), 2.55 (Me), 6.55 (H–4), 6.60 (H–5). IR ($CHCl_3$): 3420 (NH), 1700 and 1620 cm^{-1} (CO) MS[70 eV; *m/z* (% rel. int.)]: 151 (10, M), 136 (5), 109 (9), 108 (100), 94 (6), 80 (16), 54 (25).

2-(2-Methylpyrrol-3-yl)-3-methylquinoxaline 20. A mixture of 2-methyl-3-(1,2-dioxopropan-1-yl)pyrrole (0.30 g, 0.002 mol) and *o*-phenylenediamine (0.22 g, 0.002 mol) in ethanol (20 ml) was heated under reflux for 2 h. The solvent was then evaporated and the residue triturated with ether; the title compound remained in 92 % yield, m.p. 159–160 °C (EtOH). Anal. $C_{14}H_{13}N_3$: C, H. ^{1}H NMR ($CDCl_3$): δ 2.40 (Me), 2.83 (Me), 6.45 (H–4), 6.70 (H–5), 7.6 (2H-quin), 8.0 (2H-quin.), IR (KBr): 3220 (NH). MS[70 eV; *m/z* (% rel. int.)]: 223 (56, M), 222 (14), 209 (15), 208 (100), 182 (5), 181 (6), 105 (28).

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