Notes

New Perspectives in Oxazole Chemistry: Synthesis and Cycloaddition Reactions of a 4-Nitro-2-phenyl Derivative[1]

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Introduction

Whereas 4-nitroisoxazoles have been extensively investigated over the past century,[2] the corresponding oxazole derivatives remained practically unexplored in the same period,[3] probably due to the discouraging results achieved by different synthetic approaches. Since the 4-position of this heterocycle is quite resistant to direct electrophilic nitration,[4] a mercuration−iodination sequence followed by treatment of the resulting 4-halo derivative with nitrogen tetraoxide was examined with 2-methyl-5-phenyl- and 2-methyl-5-(*p*-chlorophenyl)oxazole, but the desired nitro compounds were obtained in 4−5% yields.[5] On the other hand, although thermal isoxazole isomerization represents a well established and attractive entry into the oxazole system,[6] flash vacuum pyrolysis (FVP) of some 5-alkyl-3-methyl-4-nitro derivatives afforded only 1-cyano-1-nitroacetone in quantitative yields.[7]

In order to probe if this latter disappointing finding can be ascribed to the peculiar acidic properties of the substituents at position 5 rather than to a retarding effect of the NO_2 group on the ring closure of the intermediate nitrile ylide,[7] we decided to explore the FVP chemistry of 4-nitro-3-phenylisoxazole **1**.

Results and Discussion

Attempts to obtain the 4-nitrooxazole **5** by FVP of **1** under different conditions were completely unsuccessful. Isoxazole **1** was recovered unchanged at 425 °C (1 Torr), and its progressive decomposition was observed at 550−700 °C (10^{-2} Torr) without any appearance of the desired product. In contrast, prolonged heating of the same compound in boiling anisole (170 °C) afforded **5** in 35−40% yields.[1] Interestingly, this isomerization vanished for repeated experiments on more and more purified samples of **1**, that were substantially stable under these conditions. Bearing in mind that the starting material was prepared by treatment of the corresponding 5-methoxycarbonyl derivative with concentrated HCl,[8] it appeared reasonable to account for the original results by adventitious acid catalysis. Indeed, when **1** was heated in xylene at 155 °C with a trace amount of the same acid, 4-nitro-2-phenyloxazole **5** was isolated in 29% absolute yield.[9]

Nitrogen protonation probably favors the cleavage of both N−O and C−C bonds in the intermediates **2** and **3**, respectively, and the resulting nitrile ylide **4** is now able to convert into **5** despite the presence of the NO_2 group (Scheme 1).

The same electron-withdrawing substituent enabled the oxazole system to participate as a dienophile in normal [2 + 4] cycloaddition processes. Treatment of **5** with an excess of 2,3-dimethylbuta-1,3-diene (DMB) (**6**) in chloroform at 110 °C afforded predominantly the dihydrobenzoxazole **8** through the labile adduct **7**, together with a minor amount of compound **9** that could be easily obtained from **8** and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Scheme 2).

The nitro derivative **5** was found to react even at 40 °C both with cyclopentadiene (**10**) and 6,6-dimethylfulvene (**13**), leading in good yields to mixtures of the diastereomeric tricyclic systems **11** and **12**, and **14** and **15**, respectively (Scheme 3). The former compounds were smoothly separated in chromatography, but efforts to isolate the more strained species **14** and **15** as pure products failed, due to their tendency to undergo retro Diels−Alder reactions.

Increasingly forcing conditions were required with cyclohexa-1,3-diene (**16**) and 2-pyrone (**19**), giving comparable amounts of **17** and **18** (overall yield 63%) and 2-phenylbenzoxazole (**21**) in 25% yield, respectively. The formation of the latter compound can be explained by a concomitant loss of carbon dioxide and nitrous acid from unstable primary adducts of type **20** (Scheme 4).[10]

In order to test the possibility of exploiting **5** for a new synthetic approach to oxazolopyridines, this species was allowed to react with 1-(dimethylamino)-3-methyl-1-azabuta-1,3-diene (**22**). As a result of a [2 + 4] cycloaddition process followed by elimination of nitrous acid and dimethylamine from the labile intermediate **23**, 6-methyl-2-phenyloxazolo[4,5-*b*]pyridine (**24**) was obtained in 30% yield (Scheme 5).

A quite different reaction course was observed on going from **22** to the uracil **25**, previously employed as a 2-azadiene partner with electrophilic alkenes,[11] and we isolated the pyridopyrimidine system **28** in 67% yield. Ring-opening of the oxazoline moiety of the Michael adduct **26** now gives rise to the polyfunctionalized derivative **27** that leads to **28** by a 6π-electron cyclization, followed by elimination of nitrous acid (Scheme 6).

(1) For a preliminary communication on a part of this work, see: Nesi, R.; Turchi, S.; Giomi, D.; Papaleo, S. *J. Chem. Soc., Chem. Commun.* **1993**, 978.

(2) (a) Boyer, J. H. *Nitroazoles. The C-Nitro Derivatives of Five-membered N- and N,O-Heterocycles*; Feuer, H., Ed.; VHC Publishers: New York, 1986; Chapter 5. (b) Grünanger, P.; Vita-Finzi, P. *Isoxazoles, The Chemistry of Heterocyclic Compounds*; Taylor, E. C., Ed.; Wiley-Interscience: New York, 1991; Vol. 49, Part 1, Chapter 1.

(3) Reference 2a, p 340.

(4) Turchi, I. J. *Oxazoles, The Chemistry of Heterocyclic Compounds*; Turchi, I. J., Ed.; Wiley-Interscience: New York, 1986; Vol. 45, p 103.

(5) Hammar, W. J.; Rustad, M. A. *J. Heterocycl. Chem.* **1981**, *18*, 885.

(6) Reference 2b, p 285.

(7) Perez, J. D.; Wunderlin, D. A. *J. Org. Chem.* **1987**, *52*, 3636.

(8) Nesi, R.; Giomi, D.; Turchi, S.; Tedeschi, P.; Ponticelli, F. *Gazz. Chim. Ital.* **1993**, *123*, 633.

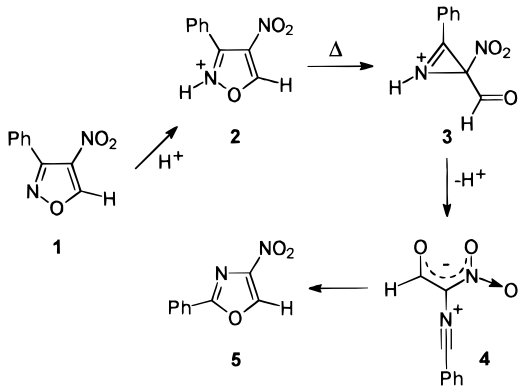
(9) Attemps to improve this value at the expense of the recovered nitroisoxazole **1** (Experimental Section) by longer reaction times failed, due to increased decomposition processes.

(10) The regiochemistry of these intermediates is arbitrarily portrayed.

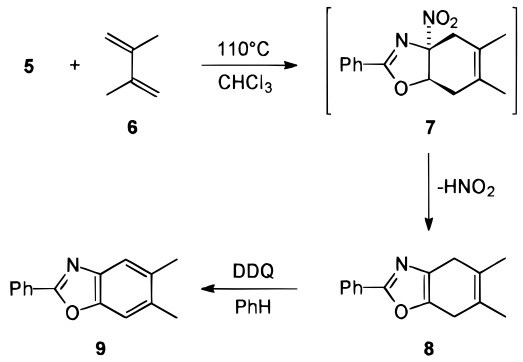
(11) Walsh, E. B.; Nai-Jue, Z.; Fang, G.; Wamhoff, H. *Tetrahedron Lett.* **1988**, *29*, 4401.

S0022-3263(96)00858-4 CCC: $12.00

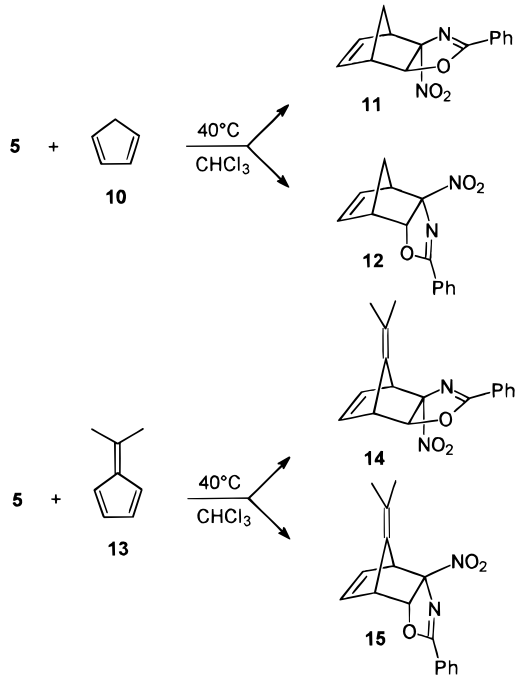
Scheme 1



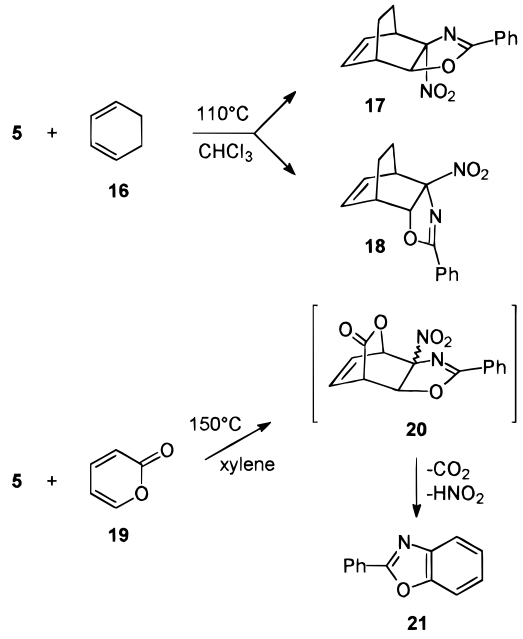
Scheme 2



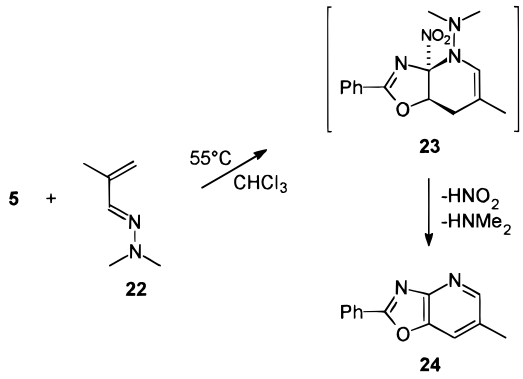
Scheme 3



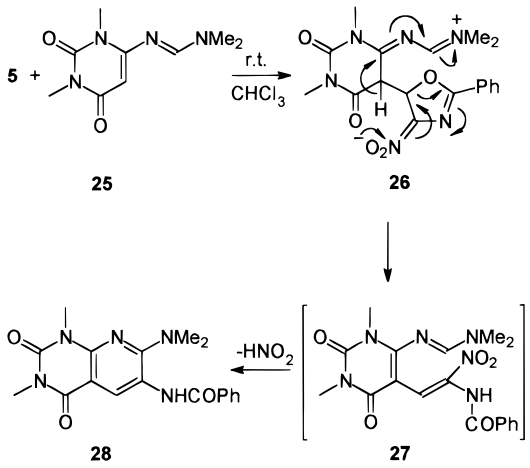
Scheme 4



Scheme 5



Scheme 6



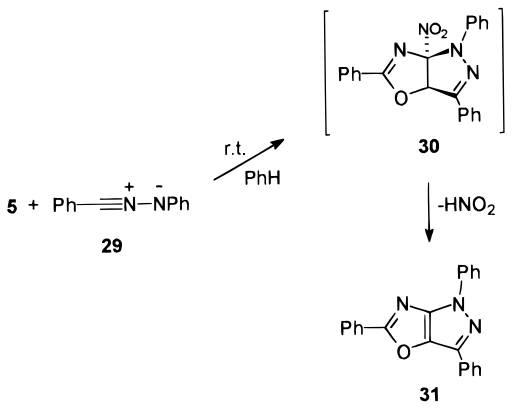
Finally, treatment of **5** with diphenylnitrilimine (**29**) at room temperature afforded compound **31** in 49% yield through a regioselective 1,3-dipolar cycloaddition involving a primary adduct **30** that suffers from extrusion of nitrous acid (Scheme 7).

Whereas the regiochemistry of the bicyclic compound **24** was firmly established on the basis of the available ^{13}C NMR data for the different oxazolopyridine systems,[12] the stucture of **31** was suggested by comparison of the ^{13}C NMR spectrum with that of the corresponding unequivocal *N*-methyl derivative.[13] The relative stereochemistry of the *endo* adducts **11**, **14**, and **17** and the *exo* isomers **12**, **15**, and **18** was inferred by a careful analysis of the shape of the H-2 resonance in the range δ 5.15−5.65 (Experimental Section). In particular, as a

(12) Chimichi, S.; Tedeschi, P.; Nesi, R.; Ponticelli, F. *Magn. Reson. Chem.* **1985**, *23*, 86.

(13) Cecchi, L.; Melani, F.; De Sio, F. *J. Heterocycl. Chem.* **1985**, *22*, 951.

Scheme 7



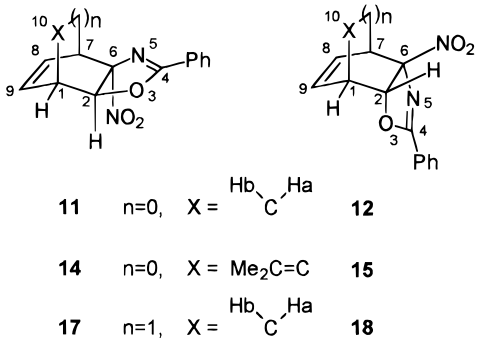


Figure 1.

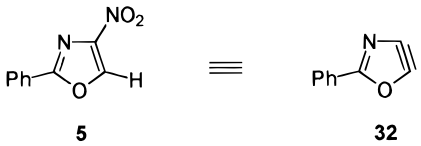


Figure 2.

consequence of different dihedral angles between the H-1 and H-2 protons, the corresponding $J_{1,2}$ values increased (1.0 Hz vs 4.5 Hz) on going from the nitro derivatives **11** and **14** to **12** and **15**, respectively. On the other hand, COSY experiments on **11** and **17** clearly showed, although to a different extent, a diagnostic interaction of the *endo* H-2 with the bridge methylene H-b10 proton.

In conclusion, a practical route to a 4-nitrooxazole system **5** was devised for the first time, based on the acid-catalyzed thermal isomerization of the corresponding isoxazole derivative **1**. The former compound behaves both as a dienophile and a dipolarophile toward different 4π counterparts and, in some instances, it can be formally regarded as a synthetic equivalent of the hetaryne **32** for direct carbo- and heteroannulations of the oxazole ring through tandem cycloaddition−elimination processes.

Experimental Section

General. Melting points are uncorrected. Unless otherwise stated, IR spectra were taken as dispersions in KBr, while ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 200 MHz and 50 MHz, respectively. Silica gel plates (Merck F_{254}) and silica gel 60 (Merck, 230−400 mesh) were used for TLC and flash chromatographies, respectively; petroleum ether and ligroin employed for chromatographic workup refer to the fractions of bp 40−70 °C and 75−120 °C, respectively. The raw products, obtained by evaporation to dryness under reduced pressure of the reaction mixtures, were dried over phosphorus pentoxide. The R_f values of the isolated compounds refer to the different solvent systems employed as eluents. Unless otherwise indicated, the reactions of the nitrooxazole **5** were carried out in a screw-capped tube (Pyrex No. 13) on 1 mmol scale in the specified solvent (1 mL); magnetic stirring was adopted for those experiments performed at room temperature.

4-Nitro-2-phenyloxazole (5). A solution of the nitroisoxazole **1** (0.190 g, 1 mmol) in xylene (3 mL) containing a catalytic amount of concentrated aqueous HCl (37%, 2−3 μL) was heated in a screw-capped tube (Pyrex No. 18) at 155 °C for 72 h. The brown residue was subjected to flash chromatography with toluene/ligroin (3:1 v/v) as eluent. After the unreacted **1** was recovered from the faster moving band (R_f = 0.48, 0.057 g), the slower one afforded compound **5** (R_f = 0.28, 0.056 g, 29%) that was crystallized from *n*-pentane as ivory-colored needles: mp 153−154 °C; IR 3163, 1608, 1561, 1513, and 1377 cm^{-1}; ^{1}H NMR δ 7.45−7.60 (m, 3H), 8.06−8.12 (m, 2H), 8.50 (s, 1H); ^{13}C NMR δ 125.15 (s), 127.0 (d), 129.1 (d), 132.2 (d), 137.7 (d), 149.4 (s), 161.5 (s). Anal. Calcd for $C_9H_6N_2O_3$: C, 56.85; H, 3.18; N, 14.73. Found: C, 57.04; H, 3.22; N, 14.55.

Cycloaddition Reactions of 5 with the Dienes 6, 10, and 16: Synthesis of Compounds 8, 9, 11, 12, 17, and 18. General Procedure. A mixture of **5** and the reagent (5 mmol) in $CHCl_3$ was heated at the temperature indicated in the schemes until the starting material was completely consumed (TLC, ^{1}H NMR). The residue was resolved into two components by flash chromatography with toluene as eluent.

A. The first band gave 5,6-dimethyl-2-phenylbenzoxazole (**9**) as a white solid (R_f = 0.34, 0.030 g, 13%): mp 161−162 °C [after sublimation at 65−70 °C (10^{-2} Torr)]; IR 3059, 3030, 1620, 1585, and 1549 cm^{-1}; ^{1}H NMR δ 2.37 (s, 3H), 2.39 (s, 3H), 7.36 (s, 1H), 7.48−7.55 (m, 4H), 8.20−8.27 (m, 2H); ^{13}C NMR δ 20.2 (q), 20.6 (q), 110.85 (d), 120.0 (d), 127.0 (s), 127.4 (d), 128.8 (d), 131.1 (d), 133.3 (s), 134.3 (s), 140.2 (s), 149.4 (s), 162.3 (s). Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.97; N, 6.27. Found: C, 80.46; H, 6.04; N, 5.97.

The slower moving fractions yielded 4,7-dihydro-5,6-dimethyl-2-phenylbenzoxazole (**8**) (R_f = 0.17, 0.160 g, 71%) that was crystallized from 30−50 °C petroleum ether as colorless needles: mp 148−148.5 °C; IR 3059, 3036, 1686, 1646, and 1546 cm^{-1}; ^{1}H NMR δ 1.79 (s, 6H), 3.25 (m, 4H), 7.39−7.48 (m, 3H), 7.98−8.05 (m, 2H); ^{13}C NMR δ 19.15 (q), 19.25 (q), 29.9 (t), 31.9 (t), 121.9 (s), 124.3 (s), 125.9 (d), 127.9 (s), 128.6 (d), 129.7 (d), 132.8 (s), 144.5 (s), 159.95 (s). Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.00; H, 6.82; N, 6.06.

B. The faster running band afforded (2*SR*,6*SR*)-6-nitro-4-phenyl-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]deca-4,8-diene (**11**) as ivory-colored crystals (R_f = 0.25, 0.049 g, 19%): mp 70−71 °C (from 30−50 °C petroleum ether); IR 3080, 2998, 1631, 1578, 1534, and 1350 cm^{-1}; ^{1}H NMR δ 1.73 (br, d, J = 10.2 Hz, 1H), 1.90 (dq, J = 10.2 and 2.0 Hz, 1H), 3.34−3.40 (m, 1H), 3.51−3.56 (m, 1H), 5.20 (dd, J = 2.0 and 1.0 Hz, 1H), 6.22 (dd, J = 5.7 and 3.0 Hz, 1H), 6.30 (dd, J = 5.7 and 2.8 Hz, 1H), 7.40−7.60 (m, 3H), 7.98−8.03 (m, 2H); ^{13}C NMR δ 43.7 (t), 47.9 (d), 49.5 (d), 87.2 (d), 119.0 (s), 125.9 (s), 128.6 (d), 129.1 (d), 132.95 (d), 135.5 (d), 137.2 (d), 171.0 (s). Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.34; H, 4.79; N, 10.66.

The second one gave (2*RS*,6*RS*)-6-nitro-4-phenyl-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]deca-4,8-diene (**12**) as a colorless oil (R_f = 0.20, 0.169 g, 66%): an analytical sample was obtained by dissolution in 30−50 °C petroleum ether, filtration, evaporation to dryness, and prolonged evacuation at room temperature (10^{-2} Torr); IR (liquid film) 3072, 1630, 1600, 1577, 1544, and 1350 cm^{-1}; ^{1}H NMR δ 1.78 (br d, J = 10.2 Hz, 1H), 1.90 (dt, J = 10.2 and 1.7 Hz, 1H), 3.41−3.48 (m, 1H), 3.82−3.88 (m, 1H), 5.65 (d, J = 4.5 Hz, 1H), 6.08−6.18 (m, 2H), 7.35−7.58 (m, 3H), 7.85−7.95 (m, 2H); ^{13}C NMR δ 44.3 (t), 45.9 (d), 51.6 (d), 87.6 (d), 121.5 (s), 125.9 (s), 128.5 (d), 128.9 (d), 132.7 (d), 134.2 (d), 136.0 (d), 169.0 (s). Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.40; H, 4.94; N, 10.82.

C. (2*SR*,6*SR*)-6-Nitro-2-phenyl-3-oxa-5-azatricyclo[5.2.2.0^{2,6}]-undeca-4,8-diene (**17**) was obtained from the first fraction as a white solid (R_f = 0.22, 0.080 g, 30%): mp 89 °C (from 30−50 °C petroleum ether); IR 3070, 3057, 1628, 1579, 1546, and 1352 cm^{-1}; ^{1}H NMR δ 1.08−1.39 (m, 2H), 1.54−1.86 (m, 2H), 3.18−3.27 (m, 1H), 3.61−3.68 (m, 1H), 5.15 (br d, J = 4.0 Hz, 1H), 6.26 (ddd, J = 8.1, 6.8, and 1.1 Hz, 1H), 6.46 (ddd, J = 8.1, 6.2, and 1.1 Hz, 1H), 7.42−7.62 (m, 3H), 8.01−8.08 (m, 2H); ^{13}C NMR δ 15.5 (t), 21.0 (t), 34.3 (d), 35.9 (d), 83.8 (d), 116.9 (s), 126.0 (s), 128.6 (d), 129.0 (d), 130.9 (d), 132.95 (d), 134.1 (d), 169.8 (s).

Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.75; H, 5.33, N, 10.35.

The following band yielded (2*RS*,6*RS*)-6-nitro-4-phenyl-3-oxa-5-azatricyclo[5.2.2.0^{2,6}]undeca-4,8-diene (**18**) (R_f = 0.15, 0.089 g, 33%) that was crystallized from *n*-pentane as colorless crystals: mp 114−115 °C; IR 3090, 3070, 3052, 1631, 1578, 1547, and 1351 cm^{-1}; ^{1}H NMR δ 1.23−1.79 (m, 4H), 3.18−3.27 (m, 1H), 3.60−3.69 (m, 1H), 5.58 (d, J = 3.7 Hz, 1H), 6.11−6.26 (m, 2H), 7.35−7.57 (m, 3H), 7.89−7.98 (m, 2H); ^{13}C NMR δ 19.2 (t), 19.35 (t), 33.7 (d), 37.7 (d), 83.3 (d), 117.3 (s), 125.7 (s), 128.4 (d), 128.9 (d), 130.6 (d), 131.8 (d), 132.7 (d), 169.2 (s). Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.38; H, 5.20; N, 10.34.

Conversion of the Dihydro Derivative 8 into 9. A mixture of **8** (0.060 g, 0.27 mmol) and DDQ (0.067 g, 0.3 mmol) in anhydrous benzene (1 mL) was refluxed with stirring for 1 h. Chromatographic workup [petroleum ether/ethyl acetate (6:1 v/v)] of the brown solid left by evaporation to dryness gave **9** (R_f = 0.6, 0.057 g, 95%).

Reaction of 5 with 6,6-Dimethylfulvene (13). The raw product coming from the reaction of **5** with **13** (0.53 g, 0.60 mL, 5 mmol) in $CHCl_3$ at 40 °C for 7 days was subjected to flash chromatography [petroleum ether/ethyl acetate (10:1 v/v)] to give a 12:1 mixture of (2*SR*,6*SR*)- and (2*RS*,6*RS*)-10-isopropylidene-6-nitro-4-phenyl-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]deca-4,8-diene (**14** and **15**) as a white solid (R_f = 0.44, 0.156 g, 53%): ^{1}H NMR δ 1.49 (s, 3H), 1.51 (s, 3H), [1.63 (s, 3H)], [1.64 (s, 3H)], 3.82−3.87 (m, 1H), [3.88−3.92 (m, 1H)], 4.01−4.06 (m, 1H), [4.34−4.37 (m, 1H)], 5.22 (d, J = 1.0 Hz, 1H), [5.52 (d, J = 4.5 Hz, 1H)], [6.24−6.27 (m, 2H)], 6.29−6.40 (m, 2H), 7.35−7.58 (m, 3H), 7.88-7.94 (m, 2H); ^{13}C NMR δ 19.5 (q), [19.7 (q)], 20.0 (q), [29.6 (q)], [46.6 (d)], 49.35 (d), [50.9 (d)], 51.5 (d), [86.5 (d)], 86.7 (d), 119.8 (s), 120.3 (s), 126.1 (s), 128.5 (d), 128.7 (d), 132.6 (d), 135.0 (d), 136.25 (d), 160.7 (s), 169.55 (s).[14]

Some unreacted **5** was recovered from the slower running fractions (R_f = 0.30, 0.030 g).

Cycloaddition of 5 with 2-Pyrone (19). Compound **5** was heated with **19** (0.49 g, 0.4 mL, 5 mmol) in xylene at 150 °C for 48 h; the brown residue was purified by flash chromatography [petroleum ether/ethyl acetate (10:1 v/v)] to give 2-phenylbenzoxazole (**21**) as a white solid (R_f = 0.53, 0.040 g, 21%): mp 101−102 °C [after sublimation at 50 °C (10^{-2} Torr)] (lit.[15] mp 102 °C).

6-Methyl-2-phenyloxazolo[4,5-*b*]pyridine (24). A mixture of **5** and **22**[16] (0.34 g, 3 mmol) in $CHCl_3$ was heated at 55 °C for 48 h; chromatographic workup [petroleum ether/ethyl acetate (3:1 v/v)] of the residue afforded compound **24** (R_f = 0.22, 0.060 g, 29%) that was crystallized from ether as colorless flakes: mp 157−158 °C; IR 3059, 3035, 1611, and 1546 cm^{-1}; ^{1}H NMR δ 2.51 (t, J = 0.7 Hz, 3H), 7.51−7.58 (m, 3H), 7.68 (m, 1H), 8.28−8.33 (m, 2H), 8.42 (m, 1H); ^{13}C NMR δ 18.8 (q), 118.4 (d), 126.6 (s), 127.9 (d), 128.9 (d), 130.4 (s), 132.1 (d), 143.1 (s), 147.3 (d), 154.3 (s), 164.95 (s). Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.32. Found: C, 73.98; H, 4.74; N, 13.32.

6-(Benzoylamino)-1,3-dimethyl-7-(dimethylamino)pyrido-[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (28). A mixture of **5** and the uracil **25**[17] (0.63 g, 3 mmol) in $CHCl_3$ was stirred at room temperature for 96 h; the raw product was subjected to flash chromatography with ethyl acetate/petroleum ether (3:1 v/v) as eluent to give compound **28** (R_f = 0.5, 0.236 g, 67%) that was crystallized from $CHCl_3$ as white needles: mp 224−225 °C; IR 3487, 3420, 3212, 1694, 1650, and 1639 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.14 (s, 6H), 3.25 (s, 3H), 3.50 (s, 3H), 7.48−7.62 (m, 3H), 7.83 (s, 1H), 7.96-8.05 (m, 2H), 10.11(br s, 1H); ^{13}C NMR (DMSO-d_6) δ 28.0 (q), 29.1 (q), 40.1 (q), 99.6 (s), 115.4 (s), 127.9 (d), 128.8 (d), 132.0 (d), 133.9 (s), 137.6 (d), 148.3 (s), 151.6 (s), 158.3 (s), 160.3 (s), 166.1 (s). Anal. Calcd for $C_{18}H_{19}N_5O_3$: C, 61.18; H, 5.42; N, 19.82. Found: C, 60.97; H, 5.73; N, 19.76.

1,3,5-Triphenyl-1*H*-pyrazolo[3,4-*d*]oxazole (31). Triethylamine (0.304 g, 0.42 mL, 3 mmol) was added dropwise to a solution of **5** and *N*-phenylbenzoylhydrazonoyl chloride[18] (0.69 g, 3 mmol) in anhydrous benzene (4 mL), and the mixture was stirred at room temperature for 24 h. After removal of the solid by filtration, the organic solution was evaporated to dryness; chromatographic workup of the residue with ligroin/toluene (5:4 v/v) as eluent afforded the tricyclic derivative **31** (R_f = 0.40, 0.165 g, 49%) that was crystallized from acetone as white needles: mp 234 °C; IR 3060, 3040, 1599, 1570, and 1538 cm^{-1}; ^{1}H NMR δ 7.20−7.57 (m, 9H), 8.08−8.32 (m, 6H); ^{13}C NMR (75 MHz) δ 117.7 (d), 125.55 (d), 126.2 (d), 127.2 (d), 127.65 (s), 128.5 (d), 128.8 (d), 128.9 (d), 129.3 (d), 130.6 (s), 131.5 (d), 132.05 (s), 139.1 (s), 139.5 (s), 150.1 (s), 167.8 (s). Anal. Calcd for $C_{22}H_{15}N_3O$: C, 78.32; H, 4.48; N, 12.45. Found: C, 78.26; H, 4.53; N, 12.67.

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(14) The values in square brackets refer to the most evident resonances of the minor diastereoisomer.

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