4.11 (d, J = 17.1, 1 H, H-1'), 4.59 (s, 1 H, H-1), 6.96 (d, J = 6.58, 1 H, ArH), 7.1-7.3 (m, 6 H, ArH), 7.44 (d, J = 6.08, 1 H, ArH); IR (KBr) 1620, 3420 cm^{-1}; HRMS calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1459. The **minor epimer** was obtained as an oil (12 mg, 25%): ^1H NMR δ 2.38 (d, J = 16.9, 1 H), 2.53 (s, 3 H, NMe), 2.79 (d, J = 15.3, 1 H), 3.08 (d, J = 15.3, 1 H), 3.24 (d, J = 16.9, 1 H), 3.91 (d, J = 16.7, 1 H, H-1'), 4.11 (d, J = 16.7, 1 H, H-1'), 5.41 (s, 1 H, H-1), 6.9-7.4 (m, 8 H, ArH); IR (KBr) 1460, 3460 cm^{-1}; MS, m/z (rel intensity) 265 (M^+, 95), 264 (91), 247 (M^+ - 18, 5), 146 (100); HRMS calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1458.

Spiro[1-chloroindan-2,3'-(*N*-methyl-1',2',3',4'-tetrahydroisoquinoline)] (19b). A solution of the major epimer of amino alcohol **19a** (13 mg, 0.05 mmol) in concentrated HCl (3 mL) was maintained for 24 h at 95 °C. Addition of 10% aqueous KOH resulted in a white precipitate, which was extracted with CH_2Cl_2 (4 × 10 mL). The organic extracts were dried (Na_2SO_4) and concentrated to give an oil, which was chromatographed on neutral alumina (PTLC, CH_2Cl_2). Chloro derivative **19b** (6 mg, 43%) was obtained as a colorless oil together with some of the starting material and its C-1 epimer: ^1H NMR δ 2.56 (s, 3 H, NMe), 2.70 (s, 2 H), 2.85 (d, J = 15.0, 1 H), 3.37 (d, J = 15.0, 1 H), 4.13 (d, J = 17.9, 1 H, H-1'), 4.23 (d, J = 17.9, 1 H, H-1'), 5.03 (s, 1 H, H-1), 6.93 (d, 1 H, ArH), 7.1-7.5 (m, 7 H, ArH); MS, m/z (rel intensity) 285 (M^+, 31), 283 (93), 282 (100).

Spiro[1-phenylindan-2,3'-(*N*-methyl-1',2',3',4'-tetrahydroisoquinolines)] (19c). A solution of the major epimer of amino alcohol **19a** (36 mg, 0.14 mmol) and pTsOH (516 mg, 2.71 mmol) in benzene (15 mL) was refluxed for 80 h. The reaction mixture was washed with distilled water, dried (Na_2SO_4), and concentrated. The residue was chromatographed on neutral alumina (PTLC, CH_2Cl_2). The **lower R_f epimer** of **19c** was obtained as an oil (27%): ^1H NMR δ 2.34 (s, 3 H, NMe), 2.41 (d, J = 16.0, 1 H), 2.65 (d, J = 16.0, 1 H), 2.97 (d, J = 16.5, 1 H), 3.25 (d, J = 16.5, 1 H), 4.00 (s, 2 H), 4.62 (s, 1 H, H-1), 6.6-7.8 (m, 13 H, ArH); MS, m/z (rel intensity) 325 (M^+, 88), 324 (100); HRMS calcd for $C_{24}H_{23}N$ 325.1830, found 325.1811. The **higher R_f epimer** of **19c** was also obtained as an oil (20%): ^1H NMR δ 2.31 (s, 3 H, NMe), 2.83 (d, J = 16.9, 1 H), 2.89 (d, J = 16.9, 1 H), 2.96 (d, J = 15.4, 1 H), 3.60 (d, J = 15.4, 1 H), 3.86 (s, 2 H), 4.04 (s, 1 H, H-1), 6.9-7.3 (m, 13 H, ArH); MS, m/z (rel intensity) 325 (M^+, 100); HRMS calcd for $C_{24}H_{23}N$ 325.1830, found 325.1824.

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Synthesis and Characterization of Masked Aminopyrazolecarboxylic Acid Synthons

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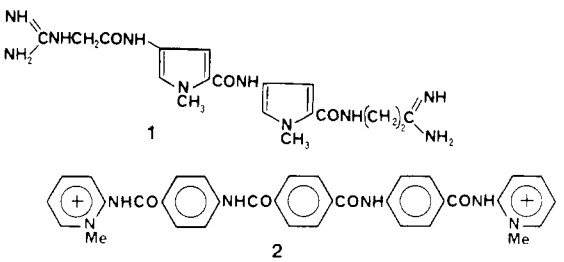
The synthesis of the masked aminopyrazolecarboxylic acid synthons (**11a,b** and **12a,b**) from pyrazole-3,5-dicarboxylic acid (**6**) and the determination of their structures by X-ray crystallography are detailed. The compounds are useful for the synthesis of polypyrazolecarboxamides analogous to the DNA minor groove binding antibiotics distamycin A and netropsin.

Compounds that bind to DNA by lodgement in the minor groove are of particular interest because of their high specificity for AT-rich base sequences.[1-3] The best studied compounds of this class are the polypyrrolecarboxamides, such as netropsin (**1**)[4] and the polybenzamides (e.g. **2**).[1] Apart from their interest as DNA-binding ligands, compounds such as **1** and **2** have potential therapeutic value as antitumor agents. Problems with the polybenzamides include insolubility and chronic toxicity,[5] while the polypyrrolecarboxamides are rather unstable.[4,6] For these reasons we have considered the synthesis of polypyrazolecarboxamides.

In the synthesis of all such oligomeric carboxamides, the key problem is the preparation of a synthon that contains both elements of the oligomer-linking amide moiety (amino and carboxylic acid) in such a form (or with such protection) that either can be selectively elaborated or demasked. In the case of the polybenzamides[7] the problem is a straightforward one, beginning with 4-nitrobenzoic acid (**3**), and an efficient synthesis of the corresponding nitropyrrolecarboxylic acid (**4**) has been the starting point for many polypyrrolecarboxamide syntheses.[8-10] Since the



oligomer unit of the polypyrazolecarboxamides is asymmetric, a completely general synthesis of these compounds

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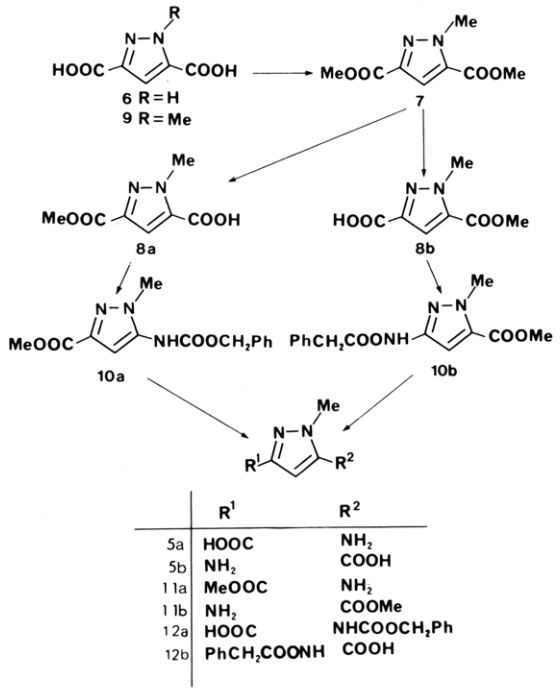
Scheme I



requires the availability of suitably protected precursors of the two basic units (the pyrazole amino acids **5a** and **5b**). This paper describes the synthesis (Scheme I) and crystallographic characterization of such compounds.

The nitropyrazolecarboxylic acids corresponding to **3** and **4** have not been reported, but it was expected that selective demasking of 3,5-bis(methoxycarbonyl)-1-methylpyrazole (**7**) would be possible, due to the differing environments of the two methoxycarbonyl groups. This proved to be the case, and hydrolysis of **7** with 1 equiv of KOH in MeOH gave a 90% yield of a single monoacid, mp 129–130.5 °C, tentatively designated as **8a** on the basis of previous work[11] on the selective hydrolysis of 1-methyl-3,4,5-tris(methoxycarbonyl)pyrazole. The preferential hydrolysis of the more hindered site is probably due to electronic effects, with attack on the 5-methoxycarbonyl group by base being assisted by the more electropositive adjacent N-CH_3 nitrogen. If this is the case, acid hydrolysis would be expected to preferentially hydrolyze the 3-methoxycarbonyl group, with the more electron-rich N-2 assisting proton approach. In agreement with this, treatment of **7** with a catalytic amount of sulfuric acid in aqueous dioxane gave a 68% isolated yield of a different monoacid, mp 172–172.5 °C, tentatively designated as **8b**. Curtius transformations on **8a** and **8b** then provided the key fully protected intermediates **10a** and **10b**, in which both the acid and amine functions are masked so that they could be deprotected separately, to give the free amines **11a** and **11b** by hydrogenolysis or the free acids **12a** and **12b** by hydrolysis. Hydrogenolysis of the latter compounds afforded the isomeric aminopyrazolecarboxylic acids **5a** and **5b**.

The NMR spectra of **5a** and **5b** were consistent with the tentative structural assignments. In the ^1H spectra, the

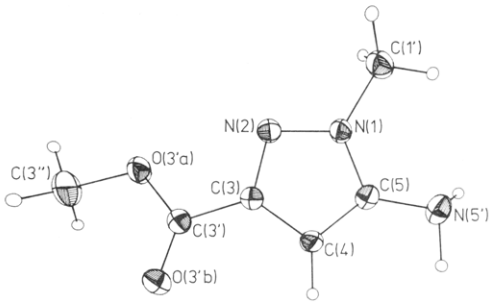


Figure 1. Molecular structure of **11a**. Anisotropic atoms are represented as 50% probability ellipsoids.

CH_3 proton singlet of **5b** was at lower field than that of **5a**, attributable to greater deshielding by an adjacent COOH group compared to an adjacent NH_2 group. In the ^{13}C NMR spectra of each pyrazole, the three ring carbons bearing the H, COOH, and NH_2 functions could be clearly distinguished from each other due to their increasing chemical shift. However, within each isomeric pair, the C-3 carbon was always at slightly lower field due to its C=N character (e.g. *C*NH_2, singlet at 147.8 for **5a**, 153.7 for **5b**; *C*COOH, singlet at 132.6 for **5b**, 141.1 for **5a**), and this was again in agreement with the assigned structures. Finally, the structure of the amino ester **11a** was determined by X-ray crystallography, confirming the tentative assignments made above. The molecular structure of **11a** is shown in Figure 1. The pyrazole ring is planar, but substituent atoms C(1′) and N(5′) are significantly displaced from the plane (by −0.085 and −0.057 Å, respectively). Bond lengths are normal, but some angles are unusually large, e.g. N(5′)–C(5)–C(4) 131.2(3)°, C(5)–N1)–C(1′) 127.1(4)°. It is noted that N(5′) is involved in hydrogen bonds with O(3′b) and N(2) in neighboring molecules (N(5′)···O(3′b) 3.14, N(5′)···N(2) 3.00 Å), and the angles quoted above may in part be a consequence of these interactions.

Experimental Section

Analyses were carried out in Microchemical Laboratory, University of Otago, Dunedin, under the direction of Professor A. D. Campbell. Melting points were determined on an Electrothermal apparatus with the supplied stem-corrected thermometer and are reported as read. NMR spectra were obtained on a Bruker AM-400 spectrometer (Me_4Si).

Pyrazole-3,5-dicarboxylic Acid (6). A solution of 3,5-dimethylpyrazole (480 g, 5 mol) and water (4 L) was heated to 70 °C in a 10-L beaker. The mixture was stirred vigorously, and finely ground $KMnO_4$ (3.185 kg, 20 mol) was added in 50-g aliquots every 5–10 min, while the temperature of the exothermic reaction was maintained between 90–95 °C. A slight excess of $KMnO_4$ was then added, until residual color remained after 1 h at reflux. The mixture was then filtered hot, the MnO_2 was washed with boiling water, and the combined filtrates were strongly acidified with concentrated HCl. After 20 h at 20 °C, the precipitated diacid **6** was filtered off (366 g, 47%), mp >360 °C (loss of water of hydration at 270–290 °C) (lit.[12] mp 287–290 °C).

3,5-Bis(methoxycarbonyl)-1-methylpyrazole (7). Thionyl chloride (464 mL, 6.5 equiv) was added dropwise to a stirred suspension of the above diacid (**6**) (155 g, 0.99 mol) in MeOH (1.5 L) at 0 °C. After the addition, the mixture was heated under reflux for 24 h, solvent was removed under vacuum, and the residue was suspended in Me_2CO (500 mL). K_2CO_3 (1.5 equiv) and Me_2SO_4 (1.1 equiv) were added, and the mixture was heated under reflux for 1 h and filtered. The filtrate was evaporated to dryness, and the residue was triturated with water to remove colored impurities. Crystallization from EtOAc/Et_2O gave the

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diester **7** (108 g, 55%): mp 72–73 °C (lit.[13] mp 71–72 °C); ^{1}H NMR ($CDCl_3$) δ 3.91 (br s, 6 H, OCH_3), 4.23 (s, 3 H, NCH_3), 7.25 (s, 1 H, CH). Direct treatment of the diacid **6** with Me_2SO_4 and K_2CO_3 in Me_2CO for 24 h gave the diester directly, but yields were lower on a large scale.

3-(Methoxycarbonyl)-1-methylpyrazole-5-carboxylic Acid (8a). The above diester (**7**) (107.5 g, 0.54 mol) was dissolved in MeOH (1 L), a solution of KOH in MeOH (249.6 mL of a 2.197 M standardized solution; 1.01 equiv) was added, and the mixture was stirred at 20 °C for 24 h. After removal of the solvent under vacuum at low temperature, the residue was dissolved in water (500 mL) and the solution was clarified and neutralized with aqueous HCl (542 mL of a standardized 1 N solution, 1.01 equiv). On being allowed to stand for 20 h at 0 °C, the monoacid **8a** crystallized (88.4 g, 89%). Recrystallization from aqueous MeOH gave needles: mp 129–130.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.96 (s, 3 H, NCH_3), 4.28 (s, 3 H, $COOCH_3$), 7.45 (s, 1 H, H4). Anal. Calcd for $C_7H_8N_2O_4H_2O{\cdot}H_2O$: C, 41.58; H, 5.00; N, 13.86. Found: C, 41.54; H, 5.06; N, 13.85. Concentration of the mother liquor gave traces of the corresponding diacid **9**: mp 266–268 °C (water); ^{1}H NMR (acetone-d_6) δ 4.21 (s, 3 H, NCH_3), 7.28 (s, 1 H, H4). Anal. Calcd for $C_6H_6N_2O_4$: C, 42.36; H, 3.56; N, 16.47. Found: C, 42.15; H, 3.46; N, 16.85.

5-(Methoxycarbonyl)-1-methylpyrazole-3-carboxylic Acid (8b). The diester **7** (56.4 g, 0.284 mol) was dissolved in a mixture of dioxane (200 mL) and water (500 mL), and a solution of concentrated H_2SO_4 (6 mL, 0.11 mol) in water (8 mL) was added. The mixture was heated under reflux for 18 h, cooled, and concentrated under reduced pressure until precipitation began. After the mixture was kept at 0 °C for 4 h, the precipitate was collected, washed several times with cold water, and dried to give pure **8b** (28.5 g). The combined filtrates were extracted with CH_2Cl_2 and recrystallized from EtOAc/MeOH to give a further 7 g, for a total yield of **8b** of 35.5 g (68%). A sample crystallized from EtOAc had mp 172–172.5 °C: ^{1}H NMR ($CDCl_3$) δ 3.93 (s, 3 H, NCH_3), 4.29 (s, 3 H, $COOCH_3$), 7.42 (s, 1 H, H4). Anal. Calcd for $C_7H_8H_2O_4$: C, 45.65; H, 4.38; N, 15.21. Found: C, 45.58; H, 4.29; N, 14.76. On standing, the diacid **9** (8.5 g, 18%) precipitated from the aqueous solution.

Methyl 5-[(Benzyloxycarbonyl)amino]-1-methylpyrazole-3-carboxylate (10a). The monoacid **8a** (3.68 g, 20 mmol) was heated under reflux in excess $SOCl_2$ for 30 min, the excess reagent was removed under vacuum, finally by azeotroping with dry benzene. The solid residue was dissolved in Me_2CO (20 mL), and a solution of NaN_3 (3.9 g, 60 mmol) in water (10 mL) was added rapidly. After being stirred for an additional minute, the orange-red solution was poured into excess water to precipitate the crude acyl azide, which was washed with water and dried under vacuum. A mixture of the crude acyl azide (2.0 g, 9.95 mmol) and benzyl alcohol (1.01 mL, 1.02 equiv) in dry toluene (25 mL) was heated under reflux for 30 min. The solvent was removed under vacuum, and the residue was crystallized from ethyl acetate to give the urethane ester **10a** (4.33 g, 75%): mp 89.5–90.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3 H, NCH_3), 3.90 (s, 3 H, $COOCH_3$), 5.21 (s, 2 H, CH_2), 6.63 (s, 1 H, exch with D_2O, NH), 6.72 (s, 1 H, H4), 7.38 (s, 5 H, phenyl). Anal. Calcd for $C_{14}H_{15}N_3O_4$: C, 58.12; H, 5.22; N, 14.53. Found: C, 58.05; H, 5.25; N, 14.51.

Methyl 3-[(Benzyloxycarbonyl)amino]-1-methylpyrazole-5-carboxylate (10b). Similar treatment of the isomeric monoacid **8b** (11.04 g, 60 mmol) gave the corresponding crude acyl azide. This was heated under reflux in dry benzyl alcohol (7 mL) and toluene (150 mL) for 30 min. Solvents were removed under reduced pressure, and the solid residue was triturated with MeOH (150 mL) to give pure **10b** as a colorless solid (10.3 g, 60% yield): mp 127–128 °C; ^{1}H NMR (acetone-d_6) δ 2.84 (s, 1 H, exch with D_2O, NH), 3.86 (s, 3 H, NCH_3), 4.01 (s, 3 H, $COOCH_3$), 5.20 (s, 2 H, CH_2), 6.98 (s, 1 H, H4), 7.30–7.48 (m, 5 H, phenyl). Anal. Calcd for $C_{14}H_{15}N_3O_4$: C, 58.12; H, 5.22; N, 14.53. Found: C, 57.81; H, 5.10; N, 14.57.

5-Amino-3-(methoxycarbonyl)-1-methylpyrazole (11a). A solution of the above urethane ester **10a** (4 g, 13.8 mmol) in MeOH (50 mL) was shaken with 5% Pd/C in H_2 (3.5 atm) for 30 min. Filtration and removal of the solvent gave the crude amine **11a** as a pink solid (1.5 g, 95%). After filtration through a column of SiO_2 in EtOAc, the compound was crystallized from EtOAc/Et_2O as needles: mp 101–102 °C; ^{1}H NMR ($CDCl_3$) δ 3.62 (s, 2 H, exch with D_2O, NH_2), 3.74 (s, 3 H, NCH_3), 3.89 (s, 3 H, $COOCH_3$), 6.09 (s, 1 H, H4). Anal. Calcd for $C_6H_9N_3O_2$: C, 46.44; H, 5.84; N, 27.09. Found: C, 46.37; H, 5.61; N, 27.19. Similar treatment of the isomeric urethane ester **10b** gave 3-amino-5-(methoxycarbonyl)-1-methylpyrazole **11b** in 100% yield as a colorless solid: mp 112–113 °C (from MeOH); ^{1}H NMR ($CDCl_3$) δ 2.95 (br s, 2 H, exch with D_2O, NH_2), 3.85 (s, 3 H, NCH_3), 4.01 (s, 3 H, $COOCH_3$), 6.15 (s, 1 H, H4). Anal. Calcd for $C_6H_9N_3O_2$: C, 46.44; H, 5.84; N, 27.09. Found: C, 46.34; H, 5.85; N, 26.72.

5-[(Benzyloxycarbonyl)amino]-1-methylpyrazole-3-carboxylic Acid (12a). The urethane ester **10a** (3.68 g, 12.7 mmol) was dissolved in dioxane (40 mL) and 2 N aqueous KOH (9.5 mL) and stirred at 20 °C for 1 h. The mixture was then diluted with water (40 mL), cooled to 0 °C, and acidified to pH ca. 1 with concentrated HCl. The resulting precipitate was collected, washed well with water, and dried to give pure **12a** (3.5 g, 100% yield). A sample crystallized from aqueous Me_2CO had mp 179–179.5 °C: ^{1}H NMR (acetone-d_6) δ 3.75 (s, 3 H, NCH_3), 5.16 (s, 2 H, $PhCH_2O$), 6.71 (s, 1 H, CH), 7.34 (s, 5 H, phenyl). Anal. Calcd for $C_{13}H_{13}N_3O_4$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.72; H, 4.82; N, 15.16. Similar treatment of the isomeric urethane ester **10b** gave 3-[(benzyloxycarbonyl)amino]-1-methylpyrazole-5-carboxylic acid (**12b**): mp 219–220 °C (aqueous Me_2CO); ^{1}H NMR (acetone-d_6) δ 3.05 (br s, exch with D_2O, NH and COOH), 4.01 (s, 3 H, NCH_3), 5.20 (s, 2 H, CH_2), 7.01 (s, 1 H, H4), 7.40 (m, 5 H, phenyl). Anal. Calcd for $C_{13}H_{13}N_3O_4$: C, 56.72; H, 4.82; N, 15.16. Found: C, 56.28; H, 4.82; N, 15.29.

Amino Acids 5a and 5b. Hydrogenolysis (Pd/C/H_2) of **12a** gave a quantitative yield of 1-methyl-5-aminopyrazole-3-carboxylic acid (**5a**): mp (AcOH/toluene) 162–164 °C; ^{1}H NMR (DMSO-d_6) δ 3.58 (s, 3 H, NCH_3) 5.35 (s, 2 H, exchangeable with D_2O, NH_2), 5.68 (s, 1 H, H-4); ^{13}C NMR (DMSO-d_6) δ 34.66 (CH_3), 90.11 (C-4), 141.10 (C-3), 147.79 (C-5), 163.59 (COOH). Anal. Calcd for $C_5H_7N_3O_2$: C, 42.54; H, 5.00; N, 29.78. Found: C, 42.69; H, 5.24; N, 29.65.

Similar treatment of **12b** gave 1-methyl-3-aminopyrazole-5-carboxylic acid (**5b**): mp (aqueous MeOH) 240.5–241.5 °C; ^{1}H NMR (DMSO-d_6) δ 3.82 (s, 3 H, NCH_3), 5.92 (s, 1 H, H-4); ^{13}C NMR (DMSO-d_6) δ 37.76 (CH_3), 96.24 (C-4), 132.61 (C-5), 153.74 (C-3), and 160.74 (COOH). Anal. Calcd for $C_5H_7N_3O_2$: C, 42.54; H, 5.00. Found: C, 42.55; H, 5.05.

X-ray Structure Determination of 11a. Crystal data: $C_6H_9N_3O_2$, M_r = 155.16, orthorhombic, space group *Pna*21, a = 14.348 (1) Å, b = 9.1987 (7) Å, c = 5.9048 (8) Å, V = 779.4 (1) Å^3, Z = 4, d_m = 1.32 g cm^{-3} (by flotation by aqueous KI/KCl), d_c = 1.322 g cm^{-3}, Mo Kα radiation of λ = 0.7107 Å, Zr filter, T = 293 ± 1 K, u = 0.74 cm^{-1}. Colorless equant crystals of quality suitable for the X-ray diffraction study were prepared by controlled diffusion of diethyl ether into an ethyl acetate solution of the compound. The crystal selected for intensity data collection measured 0.44 × 0.24 × 0.16mm. Accurate unit cell dimensions were derived from a least-squares fit to the setting angles of 25 widely dispersed reflections on a Nonius CAD-4 diffractometer. Intensity data were collected by variable width, variable speed $2\theta/x$ scans to the practical diffraction limit of θ = 25.5° for four octants of reciprocal space, and equivalent reflections were averaged together. Lorentz and polarization corrections were made; no absorption corrections were required. There were no nonstatistical variations in the intensities of three standard reflections monitored throughout the data collection, and no reflection was sufficiently intense to warrant the use of an attenuator. After averaging, the intensity data set consisted of 798 unique reflections of width 569 were classed as observed ($I > 2.5\sigma(I)$).[14]

Structure determination was achieved using direct methods with the MULTAN program,[15] and refinement of atom positions was by full-matrix least-squares fits. Hydrogen atoms were in-

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cluded either in calculated positions or else in positions obtained from a difference Fourier map, and non-hydrogen atoms were assigned anisotropic thermal parameters. Final residuals were $R = 0.040$ and $R_w = 0.045$.

Acknowledgment. This work was supported by the Auckland Division of the Cancer Society of New Zealand and by the Medical Research Council of New Zealand.

Registry No. **5a**, 117860-53-4; **5b**, 117860-54-5; **6**, 3112-31-0; **7**, 33146-99-5; **8a**, 117860-55-6; **8b**, 117860-56-7; **9**, 75092-39-6; **10a**, 117860-57-8; **10b**, 117860-58-9; **11a**, 92406-53-6; **11b**, 89088-56-2; **12a**, 117860-59-0; **12b**, 117860-60-3; 3,5-dimethylpyrazole, 67-51-6.

Supplementary Material Available: Atomic coordinates, bond lengths, and bond angles for **11a** (2 pages). Ordering information is given on any current masthead page.

A New Versatile Synthesis of Oxazoles by Intramolecular Aza-Wittig Reaction[1]

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A new synthesis of oxazoles by an intramolecular aza-Wittig reaction is described. Readily available α-azido ketones **2** were converted to (*Z*)-β-(acyloxy)vinyl azides **3** by selective enol acylation. These vinyl azides **3** reacted with triethyl phosphite to afford the corresponding oxazole derivatives **5** via the Staudinger reaction, followed by an intramolecular aza-Wittig reaction. In particular, this oxazole synthesis was useful for oxazoles having acid-labile substituents.

Azido functionality is very useful in the synthesis of various types of nitrogen compounds including nitrogen heterocycles.[2] For example, the ready and clean generation of iminophosphoranes, aza ylides, via the Staudinger reaction,[3] and their utility for synthesis of compounds containing carbon–nitrogen double bonds (or single bonds) via the aza-Wittig-type reaction are well recognized.[4,5] The intramolecular version of the aza-Wittig reaction should have a high potential for the synthesis of nitrogen heterocycles. However, synthetic applications of this methodology for nitrogen heterocyles have drawn increasing attention only recently.[6,7] Among these applications, there are reports in which 2-(acyloxy)phenyl azides reacts with triethyl phosphite to afford 2-substituted benzoxazoles (eq 1)[6a] but the reaction with hexamethylphosphorous triamide leads to the 1,3,2-benzoxazaphosphole derivative.[6c] These

Table I. α-Azido Ketones 2 from α-Bromo Ketones 1

2[a]	R_1	R_2	yield,[b] %	mp, °C
a	Ph	H	86	oil
b	*p*-ClC_6H_4	H	92	67–70
c	*p*-BrC_6H_4	H	90	79.5–81
d	*p*-MeC_6H_4	H	80	59–62
e	*p*-$MeOC_6H_4$	H	97	71–73
f	2-furyl	H	86	32–33
g	Ph	Me	80	oil
h	Ph	*i*-Pr	98	oil

[a] C, H, N analyses were within 0.3% of calculated values. [b] Isolated yields.

Table II. (Acyloxy)vinyl Azides 3 by Enol Acylation

entry	3[a]	R_1	R_2	R_3	yield,[b] %	mp, °C
1	**a**	Ph	H	Me	77	60[d]
2	**b**	*p*-ClC_6H_4	H	Me	55	87[d]
3	**c**	*p*-BrC_6H_4	H	Me	71	82[d]
4	**d**	*p*-MeC_6H_4	H	Me	60	46[d]
5	**e**	*p*-$MeOC_6H_4$	H	Me	79	74[d]
6	**f**	2-furyl	H	Me	67	34[d]
7	**g**	Ph	Me	Me	62	oil
8	**h**	Ph	*i*-Pr	Me	16	33–37
9	**i**	Ph	H	Et	84	oil
10	**j**	Ph	H	cyclopropyl	59	61[d]
11	**k**	Ph	H	Ph	trace	47[d]
12	**k**				43[c]	
13	**l**	Ph	H	2-furyl	72[c]	68[d]
14	**m**	Ph	H	3-pyridyl	14[c]	80[d]
15	**n**	2-furyl	H	2-furyl	67[c]	oil

[a] C, H, N analyses were within 0.3% of calculated values. [b] Isolated yields. [c] Addition of 1 equiv of HMPA. See Experimental Section. [d] Decomposition.

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