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Intramolecular and Intermolecular Diels-Alder Reactions of Acylhydrazones Derived From Methacrolein and Ethylacrolein [1]

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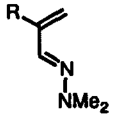
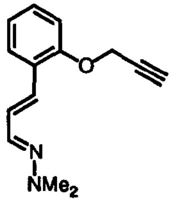
Abstract: *The intramolecular Diels-Alder reactions of hydrazones derived from methacrolein or ethylacrolein and terminally unsaturated* N-*acyl*-N-*methylhydrazines have been investigated. The hydrazones* ***7b*** *and* ***7c*** *derived from* N-*methyl*-N-*pent-4-enoylhydrazine* ***3b*** *were found to undergo intramolecular [4 + 2] cycloaddition above 140 °C and the pyridopyridazines* ***12*** *were isolated. The corresponding hydrazones* ***8b*** *and* ***8c*** *from* N-*methyl* N-*pent-4-ynoylhydrazone* ***4a*** *reacted similarly and gave as the final products the pyridines* ***13****. The scope of the reaction is limited, as was shown by the failure of several other terminally unsaturated hydrazones of αβ-unsaturated aldehydes to undergo intramolecular cycloaddition. These hydrazones did, however, undergo intermolecular [4 + 2] cycloaddition to* N-*phenylmaleimide. Other hydrazones* ***15*** *of methacrolein, including the benzoylhydrazone and the phenylhydrazone, also reacted with* N-*phenylmaleimide to give the pyridine* ***14b*** *by way of an isolable dihydropyridine* ***16****.*

Ghosez and his co-workers discovered that the *NN*-dimethylhydrazones **1** of methacrolein and other αβ-unsaturated aldehydes could participate in the Diels-Alder reaction as 1-azadienes.[2] At the time of the discovery there were few examples of isolable 1-azadienes which would undergo [4 + 2] cycloaddition, and the reaction has since proved to be a useful method of synthesis of pyridines and dihydropyridines.[3] An intramolecular variant, in which the dienophiles are attached through C-4 of the azadiene, has also been reported:[4] an example of a compound of this type is the hydrazone **2**.



1

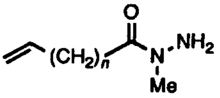


2

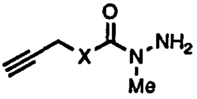
The scope of the Diels-Alder reaction of isolable 1-azadienes has subsequently been greatly extended by the use of imines substituted on nitrogen by acyl or sulphonyl groups, and with an additional electron withdrawing substituent on the α-carbon atom.[5] The cycloaddition reactions of these imines are typical inverse electron demand Diels-Alder reactions. Those of the hydrazones **1**, on the other hand, are Diels-Alder reactions with normal electron demand: the dimethylamino function is postulated to act as an electron releasing group.[2]

This paper summarises the results of our attempts to extend this type of cycloaddition to other hydrazones. We have carried out both intramolecular and intermolecular cycloaddition reactions of hydrazones derived from αβ-unsaturated aldehydes. The results are, in general, consistent with the postulate that an electron releasing substituent on nitrogen facilitates the cycloaddition. Even acylhydrazones can, however, be induced to undergo Diels-Alder reactions, albeit at higher temperatures than the dimethylhydrazones.

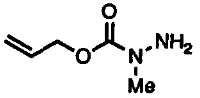
Intramolecular cycloaddition. A series of terminally unsaturated 1-acyl-1-methylhydrazines, **3**, **4** and **5**, was prepared by reaction of the corresponding carboxylic acid chlorides with methylhydrazine. The *N*-methyl group was incorporated into these structures as an electron donating sustituent. One acylhydrazine without such a group, the known[6] hydrazide of pent-4-enoic acid, was also prepared for comparison. These acylhydrazines were condensed with methacrolein and with other αβ-unsaturated aldehydes to give the acylhydrazones **6** to **11**. In compound **6**, the potential dienophile (the terminal double bond) is separated from the azadiene by a three atom chain, so that cycloaddition would result in the formation of a 6-5 fused ring system. In all the other hydrazones investigated, the diene and dienophile are separated by a four-atom chain.



3
a; $n = 1$
b; $n = 2$



4
a; X = CH_2
b; X = O



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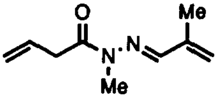
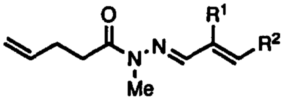
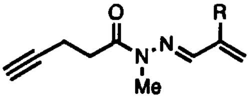


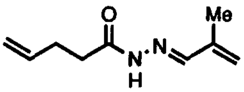
6



7
a; $R^1 = R^2 = H$
b; $R^1 = Me, R^2 = H$
c; $R^1 = Et, R^2 = H$
d; $R^1 = H, R^2 = Me$



8
a; R = H
b; R = Me
c; R = Et



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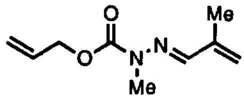
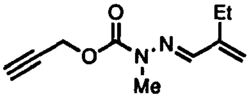
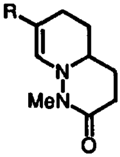


10



11

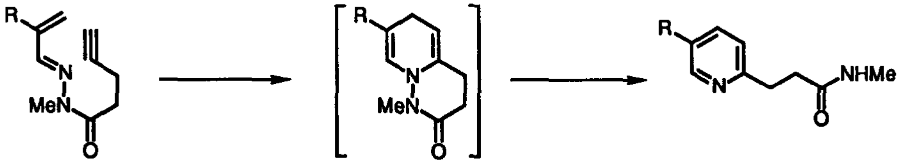
These hydrazones were heated in solution in an inert atmosphere at temperatures ranging from 140 °C to 200 °C. The hydrazone **6** was unchanged after being heated in xylene at 140 °C for 20 h but decomposed at a higher temperature (180 °C); no evidence could be found for the formation of a cycloadduct. The corresponding hydrazone **7b** derived from pent-4-enoic acid, did, however, show evidence of cyloaddition in xylene. After being heated for 120 h at 140 °C the solution contained a mixture of the hydrazone **7b** and a new compound, which was isolated by column chromatography. The product was assigned structure **12a** on the basis of analytical and spectroscopic data. Signals in the ^{1}H nmr spectrum for a single vinylic hydrogen (δ 5.74) and for the hydrogen at the ring junction (δ 3.45-3.56) supported this structural assgnment. The same compound was isolated in good yield when the hydrazone **7b** was heated in 1,2-dichlorobenzene (180 °C) for 48 h. An analogous cycloadduct **12b** was isolated from the hydrazone **7c** of ethylacrolein.



12 a ; R = Me
b ; R = Et

The scope of this intramolecular cycloaddition proved to be limited. The analogous hydrazones **7a** and **7d** derived from acrolein and from crotonaldehyde failed to undergo cycloaddition at temperatures up to 160 °C and decomposed at higher temperatures, as did the hydrazone **9** which lacks the *N*-methyl substituent. The allyloxycarbonylhydrazone **10** derived from methacrolein was unchanged after being heated in dichlorobenzene for 4 days but decomposed when heated above 180 °C. There thus appears to be a very limited temperature range within which the hydrazones can be induced to cyclise before decomposition occurs, and this range is sensitive to substituent effects. Ghosez and his colleagues showed that the dimethylhydrazones of 2-alkyl substituted aldehydes such as methacrolein were the most successful in cycloadditions[2] and the same pattern is apparent with the hydrazones **7**. The successful cycloaddition of the hydrazone **7b** but not of the hydrazones **6** and **10** may be due to a slightly more flexible linking chain between diene and dienophile in **7b**.

Further examples of intramolecular cycloaddition were, however, provided by the hydrazones **8b** and **8c** with a terminal ethynyl group. Both these hydrazones cyclised slowly when heated in 1,2-dichlorobenzene. After 48 h at 180 °C some starting hydrazone remained but a major product was isolated in each case. These products were identified as the 2,5-disubstituted pyridines **13**, which are probably formed by the route shown in Scheme 1. As before, this reaction failed with the hydrazone **8a** derived from acrolein and with the hydrazone **11** containing oxygen in the linking chain.



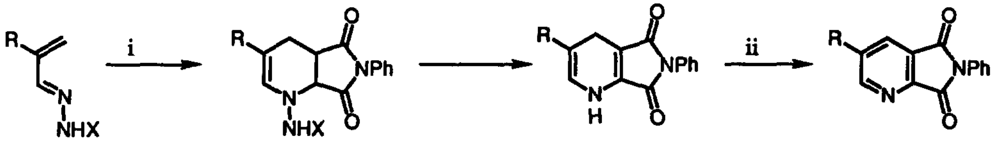
8 b ; R = Me
c ; R = Et

13 a; R = Me
b ; R = Et

Scheme 1

Intermolecular cycloaddition to N-*phenylmaleimide.* The experiments described above demonstrate that it is possible to carry out intramolecular cycloadditions with hydrazones which are less nucleophilic than those used previously, and to unactivated double and triple bonds. We wished to know whether these hydrazones would also undergo intermolecular cycloaddition, and if so, how effectively the intramolecular reaction could compete. *N*-Phenylmaleimide was chosen as the external dienophile since it has been shown by Waldner to be a very effective reagent for intercepting dimethylhydrazones of αβ-unsaturated aldehydes.[3f]

Accordingly, equimolar amounts of the hydrazone **7c** and *N*-phenylmaleimide were heated in mesitylene (b.p. 162 °C) for 36 h. The only product, which was isolated in good yield by flash column chromatography, was the pyridine **14c**. From this experiment it is clear that the intermolecular cycloaddition occurs in preference to the intramolecular reaction. A route by which the pyridine can be formed (following the suggestion of Waldner[3f]) is shown in Scheme 2. An oxidation step is required; despite the reaction having been carried out in degassed solvent under argon, it seems probable that the dehydrogenation is brought about either by traces of oxygen at the elevated temperature or by oxidation during chromatography.



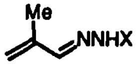
16

14 **a**; R = H
b; R = Me
c; R = Et

Scheme 2 *Reagents:* i, *N*-phenylmaleimide; ii, air.

This intermolecular reaction proved to be quite a general one, and analogous reactions were carried out with several of the hydrazones, including those which failed to undergo intramolecular reaction. Thus, pyridine **14a** was isolated from reactions of the hydrazones **7a** and **8a** with *N*-phenylmaleimide; pyridine **14b** was formed from hydrazones **8b** and **10**. From these experiments it became clear that intermolecular cycloaddition was feasible not only with dimethylhydrazones but also with acylhydrazones of αβ-unsaturated aldehydes.

We then undertook a brief study of the reactions of simpler hydrazones of methacrolein with *N*-phenylmaleimide. Four hydrazones (**15, a-d**) of methacrolein were prepared. These were then heated with *N*-phenylmaleimide in xylene..



15
a; X = COPh
b; X = $SO_2C_6H_4Me$-4
c; X = $C_6H_3(NO_2)_2$-2,4
d; X = Ph

The first three hydrazones all gave the pyridine **14b** which was isolated in moderate to good yield. Reaction of the phenylhydrazone **15d** with *N*-phenylmaleimide was appreciably faster than that of the other hydrazones (reaction also occurred in boiling toluene). The product isolated from this reaction was an orange crystalline solid which has been assigned the dihydropyridine structure **16** (R = Me) on the basis of spectroscopic data. This solid partly decomposed on attempted recrystallisation from ether in air and the aromatic pyridine **14b** was detected in the product mixture. Waldner was able to isolate analogous dihydropyridines from reactions of dimethylhydrazones with maleimides carried out at moderate temperatures.[3f]

EXPERIMENTAL

General. ^{1}H N.m.r. spectra were recorded on a Bruker ACE200 spectrometer operating at 200 MHz or, where indicated below, on a Bruker AMX400 instrument operating at 400 MHz. Signals are singlets where no multiplicity is shown. Deuteriochloroform was used as the solvent except where indicated otherwise. I.r. spectra, except where indicated, are for KBr disks. Mass spectra were recorded under electron impact at 70 meV on a VG Micromass 7070E instrument. Microanalyses were performed in the microanalytical laboratory at Liverpool University. M.p.'s were recorded on a Reichert hot stage apparatus and are uncorrected. Flash column chromatography was performed using Merck 9385 silica as the stationary phase.

1-Acyl-1-methylhydrazines

1-(But-3-enoyl)-1-methylhydrazine **3a**. But-3-enoic acid (5.00 g, 0.058 mol) was heated under reflux with freshly distilled thionyl chloride (7.60 g, 0.064 mol) for 0.5 h to give but-3-enoyl chloride.[7] The crude acid chloride was dissolved in dry dichloromethane (14 ml) and the solution added dropwise to a stirred solution of methylhydrazine (9.30 ml, 0.175 mol) in dry dichloromethane (50 ml) at 0°C. After 0.5 h the white solid was removed by filtration and washed with dichloromethane. The filtrate was evaporated and the yellow residue was distilled. After a small forerun *1-(but-3-enoyl)-1-methylhydrazine* **3a** was obtained as an orange oil (5.84 g, 88%), b.p.145-147 °C at 2 mmHg; $\nu_{max.}$ (film) 3330, 3230, 1655, 1400 and 930 cm^{-1}; δ (shows presence of two rotamers) 3.54-3.74 (5 H, m, NMe and CH_2CO), 5.14 (2 H, br, NH_2), 5.47-5.70 (2 H, m, CH_2=CH) and 6.20-6.56 (1 H, m, CH_2=CH). This compound was characterised as its *4-nitrobenzylidene derivative*, m.p. 156-157 °C (from methanol) (Found: C, 58.2; H, 5.3; N, 17.0. $C_{12}H_{13}N_3O_3$ requires C, 58.3; H, 5.3; N, 17.0%); $\nu_{max.}$ (nujol) 1680, 1515, 1347, 930 and 853 cm^{-1}; δ 3.41 (3 H), 3.69 (2 H, dt, J 1.4 and 4.1 Hz), 5.18-5.30 (2 H, m), 5.97-6.14 (1 H, m), 7.72 (1H), 7.85 (2 H, d, J 8.9 Hz) and 8.29 (2 H, d, J 8.9 Hz); m/z 247.0955 (M$^+$) (18%) ($C_{12}H_{13}N_3O_3$ requires 247.0957), 179 (46), 149 (8), 69 (42) and 41 (100).

1-Methyl-1-(pent-4-enoyl)hydrazine **3b**. Following the procedure for **3a**, pent-4-enoic acid (10.00 g, 0.10 mol) was treated with thionyl chloride (11.88 g, 0.10 mol) followed by methylhydrazine (20.8 ml, 0.39 mol). Distillation of the crude material gave a small forerun followed by *1-methyl-1-(pent-4-enoyl)hydrazine* **3b** as a pale yellow oil (11.40 g, 89%), b.p. 150 °C at 2 mmHg; $\nu_{max.}$ (film) 3260, 2990, 1640, 1435 and 910 cm^{-1}; δ (shows presence of two rotamers) 2.35-2.45 (2 H, m), 2.65-2.75 (2 H, m), 3.20 and 3.25 (together 3 H, NMe), 3.92 (2 H, br s, NH_2), 4.93-5.12 (2 H, m) and 5.76-5.97 (1 H, m). This compound was characterised as its *4-nitrobenzylidene derivative* m.p. 96-97 °C (from methanol) (Found: C, 59.8; H, 5.8; N, 16.1. $C_{13}H_{15}N_3O_3$ requires C, 59.8; H, 5.8; N, 16.1%); $\nu_{max.}$ (nujol) 1680, 1515, 1347 and 850 cm^{-1}; δ 2.50 (2 H, q, J 6.2 Hz), 3.00 (2 H, t, J 6.2 Hz), 3.40 (3 H), 5.00-5.16 (2 H, m), 5.74-6.02 (1 H, m), 7.70 (1 H), 7.85 (2 H, d, J 9.6 Hz) and 8.24 (2 H, d, J 9.6 Hz); m/z 261.1114 (M$^+$) (26%) ($C_{13}H_{15}N_3O_3$ requires 261.1113), 179 (94), 149 (10), 83 (82) and 55 (100).

1-Methyl-1-(pent-4-ynoyl)hydrazine **4a**. Following the procedure for **3a**, pent-4-ynoic acid (5.00 g, 0.05 mol) was treated with thionyl chloride (6.05 g, 0.05 mol) followed by methylhydrazine (10.60 ml, 0.20 mol). Distillation of the crude material gave *1-methyl-1-(pent-4-ynoyl)hydrazine* **4a** (4.63 g, 73%) b.p. 175 °C at 1 mmHg, which solidified to a colourless solid, m.p. 52-54 °C; $\nu_{max.}$ (nujol) 3320, 3230, 1625 and 1400 cm^{-1};

δ (shows presence of two rotamers) 1.97 (1 H, t, J 2.6 Hz), 2.44-2.60 (2 H, m), 2.87 (2 H, t, J 7.1 Hz), 3.21 and 3.26 (together 3 H, NMe) and 3.90 (2 H, br, NH_2); m/z 126.0793 (M$^+$) (8%) ($C_6H_{10}N_2O$ requires 126.0793), 81 (7), 53 (48) and 46 (100). This compound was characterised as its *4-nitrobenzylidene derivative* m.p.130-132°C (from methanol) (Found: C, 60.2; H, 5.0; N, 16.3. $C_{13}H_{13}N_3O_3$ requires C, 60.2; H, 5.05; N, 16.2%); $\nu_{max.}$ (nujol) 1685, 1585, 1345 and 850; δ 2.02 (1 H, t, J 2.7 Hz), 2.63 (2 H, dt, J 2.7 and 7.9 Hz), 3.17 (2 H, t, J 7.9 Hz), 3.42 (3 H), 7.74 (1 H), 7.86 (2 H, d, J 8.9 Hz) and 8.29 (2 H, d, J 8.9 Hz); m/z 259.0952 (M$^+$) (14%) ($C_{13}H_{13}N_3O_3$ requires 259.0957), 179 (60), 133 (5), 110 (9), 81 (53) and 53 (100).

1-Methyl-1-(prop-2-ynyloxycarbonyl)hydrazine **4b**. Methyl prop-2-ynyl carbonate was prepared (74%) from prop-2-yn-1-ol and methyl chloroformate; b.p. 40 °C at 1 mmHg (lit.,[8] b.p. 56 °C at 18 mmHg); δ 2.40 (1 H, t, J 2.2 Hz), 3.71 (3 H) and 4.60 (2 H, d, J 2.2 Hz). Methyl prop-2-ynyl carbonate (1.50 g, 0.013 mol) was treated with methylhydrazine (2.75 ml, 0.051 mol). Distillation of the crude material gave *1-methyl-1-(prop-2-ynyloxycarbonyl)hydrazine* **4b** (1.51 g, 91%) as a yellow oil, b.p. 45 °C at 0.5 mmHg; $\nu_{max.}$ (film) 3290, 2940, 1680 and 930; δ 1.45 (1 H, d, J 2.5 Hz), 3.04 (2 H, br, NH_2), 3.74 (3 H, s) and 4.26 (2 H, d, J 2.5 Hz). This compound was charactered as its *4-nitrobenzylidene derivative*, m.p. 142-145 °C (from ethanol) (Found: C, 54.9; H, 4.3; N, 16.2. $C_{12}H_{11}N_3O_4$ requires C, 55.2; H, 4.2; N, 16.1%) $\nu_{max.}$ (nujol) 1700, 1580, 1510, 1170 and 850 cm^{-1}; δ 1.57 (1 H), 3.46 (3 H), 3.94 (2 H), 7.72 (1 H), 7.88 (2 H, d, J 8.8 Hz) and 8.26 (2 H, d, J 8.8 Hz).

1-Allyloxycarbonyl-1-methylhydrazine **5**. Allyl chloroformate (5.00 g, 0.041 mol) and methylhydrazine (6.62 ml, 0.12 mol) gave *1-allyloxycarbonyl-1-methylhydrazine* **5** (5.11 g, 96%) directly as a yellow oil; $\nu_{max.}$ (film) 3285, 2940, 1690 and 925 cm^{-1}; δ 3.14 (3 H), 4.16 (2 H, br, NH_2), 4.61 (2 H, dt), 5.25 (1 H, dd, J 12 and 1 Hz), 5.35 (1 H, dd, J 17.5 and 1 Hz) and 5.86-6.05 (1 H, m). This compound was characterised as its *4-nitrobenzylidene derivative* m.p. 112-113 °C (from methanol) (Found: C, 54.9; H, 5.0; N, 16.0. $C_{12}H_{13}N_3O_4$ requires C, 54.75; H, 5.0; N, 16.0%); $\nu_{max.}$ (nujol) 1695, 1580, 1510, 1180 and 855 cm^{-1}; δ 3.45 (3 H), 4.80 (2 H, dt), 5.30 (1 H, dd, J 12 and 1 Hz), 5.43 (1 H, dd, J 17.5 and 1 Hz), 5.94-6.12 (1 H, m), 7.78 (1 H), 7.87 (2 H, d, J 8.5 Hz) and 8.24 (2 H, d, J 8.5 Hz); m/z 263.0908 (M$^+$) (12%) ($C_{12}H_{13}N_3O_4$ requires 263.0900), 178 (22), 132 (33), 89 (18) and 41(100).

Hydrazones of αβ-Unsaturated Aldehydes

Methacrolein N-*(but-3-enoyl)*-N-*methylhydrazone* **6**. 1-(But-3-enoyl)-1-methylhydrazine **3a** (2.00 g, 17.52 mmol) was dissolved in ethanol (40 ml). Methacrolein (1.24 g, 17.52 mmol) was added followed by 37% HCl (1.40 ml) as catalyst, and the solution was stirred under argon at room temperature for 45 min. The solution was neutralised with 20% aqueous sodium hydroxide and the ethanol removed under vacuum. The residue was partitioned between dichloromethane and water. The organic layer was dried ($MgSO_4$) and the solvent evaporated to give a yellow oil. Flash silica column chromatography (ethanol-dichloromethane, 1:199) gave *methacrolein* N-*(but-3-enoyl)*-N-*methylhydrazone* **6** (2.36 g, 81%) as a colourless oil, b.p. 75 °C at 0.1 mmHg (Found: C, 64.8; H, 8.8; N, 17.0. $C_9H_{14}N_2O$ requires C, 65.0; H, 8.5; N, 16.85%); $\nu_{max.}$ (film) 3080, 2980, 1690, 1475, 1072 and 925 cm^{-1}; δ 2.08 (3 H), 3.39 (3 H), 3.69 (2 H, d, J 6.9 Hz), 5.17-5.33 (2 H, m), 5.44 (1 H), 5.55 (1 H), 6.00-6.25 (1 H, m) and 7.57 (1 H); m/z 166.1106 (M$^+$) (98%) ($C_9H_{14}N_2O$ requires 166.1106), 151 (36), 125 (22), 98 (32), 97 (30) and 83 (24).

Acrolein N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7a** . 1-Methyl-1-(pent-4-enoyl)hydrazine **3b** (0.70 g, 5.47 mmol) was treated with acrolein (0.33 g, 5.89 mmol) as described for the preparation of hydrazone **6**. Flash silica chromatography (ethanol-dichloromethane, 1:199) of the crude material gave *acrolein* N-*methyl-*

N-*(pent-4-enoyl)hydrazone* **7a** (0.42 g, 46%) as a pale yellow oil which decomposed on standing; b.p. 114 °C at 0.6 mmHg; $\nu_{max.}$ (film) 2950, 1675, 1470, 1070 and 915 cm^{-1}; δ 2.33 (2 H, dt, J 7.55 and 6.9 Hz, $\underline{CH_2}CH_2CO$), 2.79 (2 H, t, J 6.9 Hz, $\underline{CH_2}CO$), 3.18 (3 H), 4.88-5.05 (2 H, m), 5.45-5.58 (2 H, m), 5.71-5.91 (1 H, m), 6.37-6.56 (1 H, m) and 7.31 (1 H, d, J 8.3 Hz, $N{=}C\underline{H}$); m/z 166.1109 (M^+) (23%) ($C_9H_{14}N_2O$ requires 166.1106), 84 (43), 83 (31), 55 (100) and 41 (32).

Methacrolein N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7b**. In a procedure analogous to that for the preparation of **6**, 1-methyl-1-(pent-4-enoyl)hydrazine **3b** (1.00 g, 7.81 mmol) was condensed with methacrolein (0.55 g, 7.86 mmol). Purification of the crude material by flash silica chromatography (ethanol-dichloromethane, 1:199) afforded *methacrolein* N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7b** (1.20 g, 85%) as colourless crystals, m.p. 22-23°C, b.p. 105 °C at 0.5 mmHg (Found: C, 66.5; H, 8.9; N, 15.6. $C_{10}H_{16}N_2O$ requires C, 66.6; H, 8.9; N, 15.5%); $\nu_{max.}$ (nujol) 1700, 1410, 1075 and 825 cm^{-1}; δ 1.96 (3 H), 2.36-2.49 (2 H, m), 2.95 (2 H, t, J 7.5 Hz), 3.27 (3 H), 4.95-5.12 (2 H, m), 5.33 (1 H), 5.45 (1 H), 5.79-6.00 (1 H, m) and 7.25 (1 H); m/z 180.1260 (M^+) (12%) ($C_{10}H_{16}N_2O$ requires 180.1263), 97 (11), 83 (27), 55 (100) and 41 (16).

Ethylacrolein N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7c**. By the method describe for **6**, 1-methyl-1-(pent-4-enoyl)hydrazine **3b** (1.00 g, 7.81 mmol) was condensed with ethylacrolein (0.66 g, 7.86 mmol). Flash silica chromatography (ethanol-dichloromethane, 1:199) of the crude material gave *ethylacrolein* N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7c** (1.24 g, 82%) as a colourless oil, b.p. 105 °C at 0.07 mmHg (Found: C, 67.85; H, 9.4; N, 14.3. $C_{11}H_{18}N_2O$ requires C, 68.0; H, 9.3; N, 14.4%); $\nu_{max.}$ (film) 2940, 1670, 1400, 1055 and 900; δ 1.14 (3 H, t, J 7.4 Hz), 2.34-2.48 (4 H, m), 2.86 (2 H, t, J 8.1 Hz), 3.27 (3 H), 4.95-5.12 (2 H, m), 5.30-5.36 (1 H, m), 5.43-5.49 (1 H, m), 5.80-6.00 (1 H, m) and 7.40 (1 H); m/z 194.1417 (M^+) (21%) ($C_{11}H_{18}N_2O$ requires 194.1419), 122 (19), 97 (33), 83 (23), 55 (100) and 41 (30).

Crotonaldehyde N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7d**. Using the same method as for **6**, 1-methyl-1-(pent-4-enoyl)hydrazine **3b** (1.50 g, 11.70 mmol) was condensed with crotonaldehyde (0.82 g, 11.70 mmol). Work-up by flash silica column chromatography with chloroform as eluent gave *crotonaldehyde* N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7d** (1.52 g, 72%) as a pale yellow oil, b.p. 190 °C at 2.5 mmHg (Found: C, 66.8; H, 9.0; N, 15.6. $C_{10}H_{16}N_2O$ requires C, 66.6; H, 8.9; N, 15.5%); $\nu_{max.}$ (film) 2920, 1680, 1405, 1065 and 910; δ 1.91 (3 H, d, J 5.5 Hz), 1.34-1.48 (2 H, m), 2.85 (2 H, t, J 8.2 Hz), 3.25 (3 H), 4.92-5.14 (2 H, m), 5.78-6.35 (3 H, m), 7.36 (1 H, d, J 8.3 Hz, $N{=}C\underline{H}$); m/z 180.1262 (M^+) (28%) ($C_{10}H_{16}N_2O$ requires 180.1263), 165 (9), 97 (13), 83 (46), 68 (12), 55 (100) and 41 (22).

Acrolein N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8a**. By a procedure analogous to that used to prepare **6**, 1-methyl-1-(pent-4-ynoyl)hydrazine **4a** (1.00 g, 7.93 mmol) was condensed with acrolein (0.44 g, 7.86 mmol). Flash silica column chromatography (chloroform) afforded *acrolein* N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8a** (0.51 g, 40%) as colourless crystals, m.p. 46-47 °C, b.p. 122 °C at 0.2 mmHg (Found: C, 65.9; H, 7.4; N, 17.2. $C_9H_{12}N_2O$ requires C, 65.8; H, 7.4; N, 17.1%); $\nu_{max.}$ (nujol) 1705, 1095, 990 and 920 cm^{-1}; δ 1.45 (1 H, t, J 3.3 Hz), 2.00-2.09 (2 H, m), 2.49 (2 H, t, J 8.3 Hz), 3.75 (3 H), 5.03-5.15 (2 H, m), 5.92-6.12 (1 H, m) and 6.86 (1 H, d, J 8.3 Hz, $N{=}C\underline{H}$); m/z 163.0872 (M^+ - 1) (38%) ($C_9H_{11}N_2O$ requires 163.0871), 164 (11), 110 (6), 83 (23), 81 (23) and 53 (100).

Methacrolein N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8b**. By a method analogous to that used to prepare **6**, 1-methyl-1-(pent-4-ynoyl)hydrazine **4a** (2.00 g, 15.86 mmol) was treated with methacrolein (1.12 g, 16.00 mmol). Purification of the crude material by flash silica column chromatography (ethanol-dichloromethane, 1:99) gave *methacrolein* N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8b** (2.41 g, 86%) as colourless crystals, m.p. 59-60 °C (from hexane) (Found: C, 67.6; H, 8.0; N, 15.8. $C_{10}H_{14}N_2O$ requires C, 67.4; H, 7.94; N, 15.7%); $\nu_{max.}$ (nujol) 3300, 1660, 1095 and 940 cm^{-1}; δ 1.96-1.99 (4 H, m), 2.52-2.61 (2 H, m), 3.02 (2 H, t, J 7.5 Hz), 3.28 (3 H), 5.34 (1 H), 5.48 (1 H) and 7.43 (1 H); m/z 177.1026 (M^+ - H) (45%) ($C_{10}H_{13}N_2O$ requires 177.1028), 178 (7), 81 (20), 56 (13), 55 (55), 53 (100) and 41 (15).

Ethylacrolein N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8c**. By a method analogous to that used to prepare **6**, 1-methyl-1-(4-pentynoyl)hydrazine **4a** (1.00 g, 7.93 mmol) was condensed with ethylacrolein (0.67 g, 7.98 mmol). Flash silica column chromatography of the crude material (ethanol-dichloromethane, 1:199) gave *ethylacrolein*-N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8c** (1.43 g, 94%) as colourless crystals, m.p. 42-43 °C, b.p. 110 °C at 0.05 mmHg (Found: C, 68.4; H, 8.3; N, 14.8. $C_{11}H_{16}N_2O$ requires C, 68.7; H, 8.4; N, 14.6%); $\nu_{max.}$ (nujol) 3300, 1670, 1090 and 900 cm^{-1}; δ 1.44 (3 H, t, J 7.4 Hz), 1.97 (1 H, t, J 2.6 Hz), 2.40 (2 H, q, J 7.4 Hz), 2.53-2.59 (2 H, m), 3.01 (2 H, t, J 7.5 Hz), 3.28 (3 H), 5.33 (1 H), 5.46 (1 H) and 7.40 (1 H); m/z 191.1187 (M^+ - H) (67%) ($C_{11}H_{15}N_2O$ requires 191.1184), 192 (10), 111 (27), 82 (32), 81 (24), 53 (100) and 51(10).

Methacrolein N-*(pent-4-ynoyl)hydrazone* **9**. By a method analogous to that used to prepare **6**, pent-4-enoylhydrazine[6] (0.60 g, 5.26 mmol) was condensed with methacrolein (0.37 g, 5.29 mmol). Work-up by flash silica column chromatography (ethanol-dichloromethane, 1:49) gave *methacrolein* N-*(pent-4-enoyl)hydrazone* **9** (0.74 g, 85%) as a colourless wax, m.p. 61-63 °C, b.p.170°C at 1 mmHg; $\nu_{max.}$ (nujol) 3200, 1680, 1410, 1330 and 905 cm^{-1}; δ 1.93 (3 H), 2.45 (2 H, q, J 7.4 Hz), 2.80-2.94 (2 H, m), 4.87-5.14 (2 H, m), 5.34 (1 H), 5.46 (1 H), 5.80-6.00 (1 H, m), 7.56 (1H) and 10.00 (1H, br, N<u>H</u>); m/z 166.1104 (M^+) (10%) ($C_9H_{14}N_2O$ requires 166.1106), 110 (1), 83 (37), 55 (100) and 41 (24).

Methacrolein N-*allyloxycarbonyl*-N-*methylhydrazone* **10**. By a method analogous to that used to prepare **6**, 1-allyloxycarbonyl-1-methylhydrazine **5** (1.80 g, 13.85 mmol) was condensed with methacrolein (1.10 g, 15.71 mmol). Work-up by flash silica column chromatography (ethanol-chloroform, 1:99) gave *methacrolein* N-*allyloxycarbonyl*-N-*methylhydrazone* **10** (1.50 g, 60%), b.p. 180 °C at 0.1 mmHg (Found: C, 59.3; H, 7.8; N, 15.35. $C_9H_{14}N_2O_2$ requires C, 59.3; H, 7.7; N, 15.4%); $\nu_{max.}$ (film) 1705, 1315, 1160, 925 and 760 cm^{-1}; δ 2.00 (3 H), 3.22 (3 H), 4.70-4.76 (2 H, m), 5.20-5.45 (4 H, m), 5.90-6.10 (1 H, m), and 7.43 (1 H); m/z 182.1055 (M^+) (8%) ($C_9H_{14}N_2O_2$ requires 182.1055), 141 (72), 97 (10), 57 (44) and 41 (100).

Ethylacrolein N-*methyl*-N-*propynyloxycarbonylhydrazone* **11**. By a method analogous to that used for **6**, 1-methyl-1-propynyloxycarbonylhydrazine **4b** (1.10 g, 8.59 mmol) was condensed with ethylacrolein (0.72 g, 8.57 mmol). Flash silica column chromatography (dichloromethane) gave *ethylacrolein* N-*methyl*-N-*propynyloxycarbonylhydrazone* **11** (1.24 g, 75%), b.p. 86 °C at 0.6 mmHg; $\nu_{max.}$ (film) 2960, 1705, 1315, 1160, 955 and 775 cm^{-1}; δ 1.14 (3 H, t, J 7.4 Hz), 1.60 (1 H), 2.45 (2 H, q, J 7.4 Hz), 3.32 (3 H), 3.86 (2 H), 5.32 (1 H), 5.43 (1 H) and 7.41 (1 H); m/z 194.1058 (M^+) (1%) ($C_{10}H_{14}N_2O_2$ requires 194.1055), 165 (3), 111 (100), 83 (27), 82 (18) and 55 (14).

Methacrolein benzoylhydrazone **15a**. A solution of benzoylhydrazine (1.00 g, 7.35 mmol) and methacrolein (0.51 g, 7.23 mmol) in ethanol (40 ml) containing conc. HCl (1 ml) was stirred at room temp. for 1 h. It was then was then neutralised with aq. sodium hydroxide and the ethanol was distilled off. The residue was triturated with ether to give a colourless solid which was crystallised to give *methacrolein benzoylhydrazone* **15a** (1.10 g, 81%), m.p. 146 °C (from ethanol) (Found: C, 70.24; H, 6.48; N, 15.10. $C_{11}H_{12}N_2O$ requires C, 70.2; H, 6.4; N, 14.9%); $\nu_{max.}$ (nujol) 3230 and 1650 cm^{-1}; δ 2.04 (3 H), 5.34 (1 H), 5.49 (1 H), 7.39-7.56 (3 H, m), 7.91 (2 H, dd, J 7.5 and 1.5 Hz), 8.09 (1 H) and 10.95 (1 H, br, N<u>H</u>); m/z 188.0951 (M^+) (1%) ($C_{11}H_{12}N_2O$ requires 188.0949) 121 (23) and 105 (100).

Methacrolein toluene-4-sulphonylhydrazone **15b**. By the method used to prepare **15a**, methacrolein (1.4 g) was converted into its *toluene-4-sulphonylhydrazone* **15b** (79%), m.p. 108-110 °C (from ethanol)

(Found: C, 55.4; H, 5.9; N, 11.7. $C_{11}H_{14}N_2O_2S$ requires C, 55.5; H, 5.9; N, 11.8%); $\nu_{max.}$ (nujol) 3170, 1460 and 1170 cm^{-1}; δ 1.88 (3 H), 2.45 (3 H), 5.25 (1 H), 5.44 (1 H), 7.34 (2 H, d, J 8.5 Hz), 7.42 (1 H), 7.76 (1 H, br, NH) and 7.84 (2 H, d, J 8.5 Hz).

Methacrolein 2,4-dinitrophenylhydrazone **15c**. This had m.p. 204 °C (from ethanol) (lit.,[9] m.p. 206-206.5 °C); δ 2.04 (3 H), 5.47 (1 H), 5.62 (1 H), 7.83 (1 H), 7.96 (1 H, d), 8.36 (1 H, dd), 8.43 (1 H, br, NH), and 9.15 (1 H, dd).

Methacrolein phenylhydrazone **15d**. This had m.p. 68-69 °C (from ethanol) (lit.,[9,10] m.p. 73-74 °C); δ 2.01 (3 H), 5.12 (1 H), 5.23 (1 H), 6.79-6.90 (1 H, m), 7.00 (2 H, approx. d), 7.25 (2 H, approx. t), 7.41 (1 H) and 7.43 (1 H, br, NH).

Intramolecular Diels-Alder Reactions

With methacrolein N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7b**. A solution of the hydrazone **7b** (0.51 g, 2.83 mmol) in 1,2-dichlorobenzene (5 ml) was heated under reflux (180 °C) under argon for 48 h. Some charring occurred. The solvent was distilled off under reduced pressure and the residue was subjected to flash column chromatography (silica; ethanol-dichloromethane, 1:99). This gave the starting hydrazone **7b** (0.12 g, 24%) and a yellow oil. On distillation at 170 °C and 0.1 mmHg this oil gave *1,7-dimethyl-4,4a,5,6-tetrahydropyrido-1H-[1,2-b]pyridazin-2(3H)-one* **12a** (0.31 g, 79% based on starting material consumed) as a colourless crystalline solid m.p. 58-60 °C (Found: C, 66.7; H, 9.1; N, 15.55. $C_{10}H_{16}N_2O$ requires C, 66.6; H, 8.9; N, 15.5%); $\nu_{max.}$ (nujol) 1676, 1625, 1415, 1175 and 865 cm^{-1}; δ 1.61 (3 H), 1.75-1.89 (3 H, m), 2.00-2.17 (3 H, m), 2.38-2.46 (2 H, m), 3.11 (3 H), 3.45-3.56 (1 H, m, 4a-H) and 5.74 (1 H, 8-H); m/z 180.1263 (M$^+$) (78%) ($C_{10}H_{16}N_2O$ requires 180.1263), 165 (9) and 137 (100).

A reaction carried out in xylene at 140 °C gave, after 5 days, the hydrazone **7b** (49%) and the pyridopyridazine **12a** (47%; 91% based on starting material consumed).

With ethylacrolein N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7c**. A solution of the hydrazone **7c** (0.40 g, 2.06 mmol) in decalin (15 ml) was heated under reflux (190 °C) under argon for 36 h. The solvent was distilled off under reduced pressure and the residue was subjected to flash column chromatography (silica; ethanol-dichloromethane, 1:99). This gave the starting hydrazone **7c** (0.05 g, 13%) and *7-ethyl-1-methyl-4,4a,5,6-tetrahydropyrido-1H-[1,2-b]pyridazin-2(3H)-one* **12b** (0.31 g, 89% based on starting material consumed) as a yellow oil b.p. 185 °C at 0.7 mmHg (Found: C, 68.0; H, 9.3; N, 14.3. $C_{11}H_{18}N_2O$ requires C, 68.0; H, 9.3; N, 14.4%); $\nu_{max.}$ (nujol) 1663, 1450, 1175 and 886 cm^{-1}; δ 0.99 (3 H, t, J 7.4 Hz), 1.80-2.20 (8 H, m), 2.36-2.49 (2 H, m), 3.11 (3 H), 3.46-3.58 (1 H, m, 4a-H) and 5.74 (1 H, 8-H); m/z 194.1423 (M$^+$) (56%) ($C_{11}H_{18}N_2O$ requires 194.1419), 179, (100), 165 (5) and 151 (40).

With methacrolein N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8b**. A solution of the hydrazone **8b** (0.25 g, 1.40 mmol) in 1,2-dichlorobenzene (10 ml) was heated under reflux (180 °C) under argon for 48 h. Removal of the solvent and flash silica column chromatography (ethanol-chloroform, 1:99, then 1:9) gave the starting hydrazone **8b** (0.10 g, 40%) together with *5-methylpyridine-2-(*N*-methyl)propionamide* **13a** (0.11 g, 73% based on starting material consumed) as a waxy solid, m.p., 66-67°C; $\nu_{max.}$ (nujol) 3180, 1690, 1580, 820 and 725 cm^{-1}; δ 2.31 (3 H), 2.65 (2 H, t, J 7.1 Hz), 2.77 (3 H, d, J 4.8 Hz, NMe), 3.08 (2 H, t, J 7.1 Hz), 6.50 (1 H, br, NH), 7.10 (1 H, d, J 7.9 Hz, 3-H of pyridine), 7.42 (1 H, dd, J 2.2 and 7.9 Hz, 4-H of pyridine), 8.34 (1 H, d, J 2.2 Hz, 6-H of pyridine); m/z 178.1105 (M$^+$) (1%) ($C_{10}H_{14}N_2O$ requires 178.1106), 120 (100), 92 (6) and 77 (5). This compound was further characterised as its *picrate* m.p. 135-136 °C (from ethanol) (Found: C, 46.9; H, 4.1; N, 17.25. $C_{16}H_{17}N_5O_8$ requires C, 47.2; H, 4.2; N, 17.2%); δ 2.55 (3 H), 2.77 (3 H, d, J 4.8 Hz,

NCH_3), 2.82 (2 H, t, J 6.9 Hz), 3.44 (2 H, t, J 6.9 Hz), 6.34 (1H, br, NH), 7.79 (1 H, d, J 8.3 Hz, 3-H of pyridine), 6.1 (1 H, dd, J 2.0 and 8.3 Hz, 4-H of pyridine), 8.49 (1 H, d, J 2.0 Hz, 6-H of pyridine) and 8.97 (2 H).

With ethylacrolein N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8c**. A solution of the hydrazone **8c** (0.45 g, 2.34 mmol) in 1,2-dichlorobenzene (15 ml) was heated under reflux (180 °C) under argon for 48 h. Some charring occurred. Removal of the solvent and flash silica column chromatography (ethanol-chloroform, 1:99 then 1:19) of the residue yielded the starting hydrazone **8c** (0.12 g, 27%) and *5-ethylpyridine-2-(*N-*methyl)propionamide* **13b** (0.29 g, 64%) as a yellow oil, b.p. 200°C at 0.3 mmHg; $\nu_{max.}$ (film) 3190, 1685, 1575, 815 and 730; δ 1.23 (3 H, t, J 6.8 Hz), 2.63 (4 H, overlapping q and t, both J 6.8 Hz), 2.75 (3 H, d, J 4.9 Hz, NCH_3), 3.12 (2 H, t, J 6.8 Hz), 6.5 (1 H, br, NH), 7.15 (1 H, d, J 7.7 Hz, 3-H of pyridine), 7.50 (1 H, dd, J 7.7 and 2.3 Hz, 4-H of pyridine) and 8.30 (1 H, d, J 2.3 Hz, 6-H of pyridine). This compound was characterised as its *picrate*, m.p. 104-105 °C (from ethanol) (Found: C, 48.2; H, 4.4; N, 16.8. $C_{17}H_{19}N_5O_8$ requires C, 48.5; H, 4.55; N, 16.6%); δ 1.36 (3 H, t, J 7.6 Hz), 2.77 (3 H, d, J 4.8 Hz, NMe), 2.82-2.87 (4 H, m), 3.45 (2 H, t, J 6.9 Hz), 6.36 (1 H, br, NH), 7.82 (1 H, d, J 8.3 Hz, 3-H of pyridine), 8.14 (1 H, dd, J 2.6 and 8.3 Hz, 4-H of pyridine), 8.50 (1 H, d, J 2.6 Hz, 6-H of pyridine) and 8.96 (2H).

Intermolecular Cycloaddition to N-*Phenylmaleimide*

With acrolein N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7a**. A solution of the hydrazone **7a** (0.17 g, 1.02 mmol) and *N*-phenylmaleimide (0.18 g, 1.02 mmol) was heated under reflux in mesitylene (10 ml) under argon for 36 h. Removal of the solvent under reduced pressure followed by flash silica column chromatography (ethanol-dichloromethane, 1:99) gave 6-phenylpyrrolo[3,4-b]pyridine-5,7-dione **14a** (0.21 g, 88%), m.p. 208-209 °C (from ethanol) (lit.,[11] m.p. 215-216 °C); δ 7.43-7.56 (5 H, m), 7.71 (1 H, dd, J 5.0 and 7.7 Hz, 3-H of pyridine), 8.29 (1 H, dd, J 1.5 and 7.7 Hz, 4-H of pyridine) and 9.06 (1 H, dd, J 1.5 and 5.0 Hz, 2-H of pyridine).

With ethylacrolein N-*methyl*-N-*(pent-4-enoyl)hydrazone* **7c**. A solution of the hydrazone **7c** (0.30 g, 1.54 mmol) and *N*-phenylmaleimide (0.27 g, 1.54 mmol) in mesitylene (10 ml) was heated under reflux under argon for 36 h. This gave 3-ethyl-6-phenylpyrrolo[3,4-b]pyridine-5,7-dione **14c** (0.37 g, 95%), m.p., 189 - 190 °C (lit.,[3f] m.p. 190-191 °C); δ 1.36 (3 H, t, *J* 8.3 Hz), 2.87 (2 H, q, *J* 8.3 Hz), 7.38-7.58 (5 H, m), 8.10 (1 H, d, *J* 1.9 Hz, 4-H of pyridine) and 8.89 (1H, d, *J* 1.9 Hz, 2-H of pyridine).

With acrolein N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8a**. A solution of the hydrazone **8a** (0.10 g, 0.61 mmol) and *N*-phenylmaleimide (0.10 g, 0.61 mmol) in mesitylene (10 ml) was heated under reflux under argon for 36 h to give 6-phenylpyrrolo[3,4-b]pyridine-5,7-dione **14a** (0.14 g, 93%), m.p. 208-209 °C (from ethanol), identical (n.m.r.) to that produced from hydrazone **7a**.

With methacrolein N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8b**. A solution of the hydrazone **8b** (0.13 g, 0.73 mmol) and *N*-phenylmaleimide (0.13 g, 0.73 mmol) in decalin (10 ml) was heated under reflux under argon for 48 h, during which time charring was observed. Evaporation of the solvent followed by flash silica column chromatography (dichloromethane) gave 3-methyl-6-phenylpyrrolo[3,4-b]pyridine-5,7-dione **14b** (0.09 g, 53%), m.p. 245-246 °C (lit.,[3f] m.p. 244-246 °C); δ 2.60 (3 H), 7.36-7.60 (5 H, m), 8.04 (1 H, 4-H of pyridine) and 8.85 (1 H, 2-H of pyridine).

With ethylacrolein N-*methyl*-N-*(pent-4-ynoyl)hydrazone* **8c**. A solution of the hydrazone **8c** (0.29 g, 1.51 mmol) and *N*-phenylmaleimide (0.31 g, 1.51 mmol) gave 3-ethyl-6-phenylpyrrolo[3,4-b]pyridine-5,7-dione **14c** (0.35 g, 92%), m.p. 189-190 °C (from ethanol).

With methacrolein N-*allyloxycarbonyl*-N-*methylhydrazone* **10**. The hydrazone **10** (0.17 g, 0.93 mmol) and *N*-phenylmaleimide (0.16 g, 0.93 mmol) were heated under reflux in mesitylene (10 ml) under argon to give 3-methyl-6-phenylpyrrolo[3,4-b]pyridine-5,7-dione **14b** (0.18 g, 82%).

With ethylacrolein N-*methyl*-N-*(prop-2-ynyloxycabonyl)hydrazone* **11**. The hydrazone **11** (0.30 g, 1.54 mmol) and *N*-phenylmaleimide (0.27 g, 1.54 mmol) in mesitylene (10 ml) were heated under reflux under argon for 36 h to give 3-ethyl-6-phenylpyrrolo[3,4-b]pyridine-5,7-dione **14c** (0.36 g, 92%).

With methacrolein benzoylhydrazone **15a**. A solution of the hydrazone **12a** (0.50 g, 2.66 mmol) and *N*-phenylmaleimide (0.46 g, 2.66 mmol) in mesitylene (10 ml) was heated under reflux under argon for 36 h. Flash silica chromatography (chloroform) gave 3-methyl-6-phenylpyrrolo[3,4-b]pyridine-5,7-dione **14b** (0.57 g, 91%).

With methacrolein toluene-4-sulphonylhydrazone **15b**. A solution of the hydrazone **15b** (0.70 g, 2.9 mmol) and *N*-phenylmaleimide (0.51 g, 2.9 mmol) in xylene (180 ml) was heated under reflux under argon for 64 h. The solvent was evaporated off. T.l.c. showed the presence of *N*-phenylmaeimide but not of the hydrazone **15b**; the pyridine **14b** was detected together with an unidentified product. The residue was subjected to flash chromatography (dichloromethane) which gave the pyridine **14b** (0.21 g, 31%).

With methacrolein 2,4-dinitrophenylhydrazone **15c**. The hydrazone **15c** (0.50 g, 2.0 mmol) and N-phenylmaleimide (0.35 g, 2.0 mmol) were heated in xylene (50 ml) under reflux under argon for 45 h. After this period t.l.c. showed only traces of starting materials and a spot corresponding to the pyridine **14b**. Flash chromatography gave (with dichloromethane) the pyridine **14b** (0.20 g, 42%).

With methacrolein phenylhydrazone **15d**. The hydrazone **15d** (0.50 g, 3.1 mmol) and N-phenylmaleimide (0.54 g, 3.1 mmol) were heated in xylene (50 ml) under reflux under argon for 18 h. T.l.c. showed only traces of starting materials together with a spot corresponding to the pyridine **14b** and an intense orange spot. This was isolated by flash chromatography (dichloromethane) and was tentatively identified as the dihydropyridine **16** (R = Me) (0.47 g, 63%) m.p. 225-230 °C (from ether) $\nu_{max.}$ (nujol) 3330 (NH) and 1710 (C=O) cm^{-1}; δ 1.71 (3 H),3.18 (2 H), 5.94 (1 H), 6.17 (1 H, br) and 7.20-7.50 (5 H, m); m/z 240.0890 (M^+) (62%) ($C_{14}H_{12}N_2O_2$ requires 240.0899), 239 (100) and 238 (35).

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