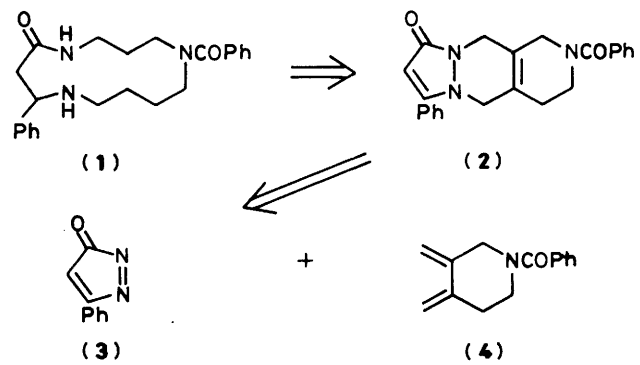
Azo Dienophiles. Diels–Alder Reactions of 4-Phenyl-1,2,4-triazole-3,5-dione and 5-Phenylpyrazol-3-one with Functionalised Dienes

Matthew P. Johnson and Christopher J. Moody*
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

4-Phenyl-1,2,4-triazole-3,5-dione (PTAD) undergoes a Diels–Alder reaction with a variety of functionalised dienes. The adduct (**9**) from 2,3-bis(iodomethyl)butadiene gives, on treatment with zinc–copper couple, the diene 2,3,5,6,7,8-hexahydro-6,7-dimethylene-2-phenyl-1*H*-[1,2,4]triazolo[1,2-*a*]-pyridazine-1,3-dione (**10**) which then reacts with dienophiles in a tandem Diels–Alder reaction. The unsymmetrical azo dienophile, 5-phenylpyrazol-3-one (**3**), reacts regioselectively with 1-acetoxybutadiene to give, after hydrolysis, the alcohol 5,8-dihydro-8-hydroxy-3-phenyl-1*H*-pyrazolo[1,2-*a*]-pyridazin-1-one (**19**).

Azo compounds in which the azo bond is flanked by one or two carbonyl groups, in contrast to aliphatic and aromatic azo compounds, possess a highly reactive N=N bond which readily participates in cycloaddition reactions.[1] This behaviour is typified by 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) which is one of the most reactive dienophiles known.[2] However, in contrast to Diels–Alder reactions involving all-carbon dienes and dienophiles, heterodienophiles,[3] and heterodienes,[4] all of which have found wide application, the Diels–Alder reactions of azo dienophiles have not been extensively exploited in the synthesis of heterocyclic compounds.

We have been interested in the possibility of using the Diels–Alder adducts of cyclic azo dienophiles as precursors to larger rings which could be derived by reductive cleavage of the N–N bond. This general approach is exemplified for the naturally occurring macrocyclic polyamine celabenzine (**1**),[5] which in principle is available from the tricyclic intermediate (**2**) by oxidative cleavage of the central C=C bond followed by reductive cleavage of the N–N bond, and subsequent functional group manipulation. The key intermediate (**2**) could be prepared in a single Diels–Alder reaction from the azo dienophile (**3**) and the diene (**4**) (Scheme 1).

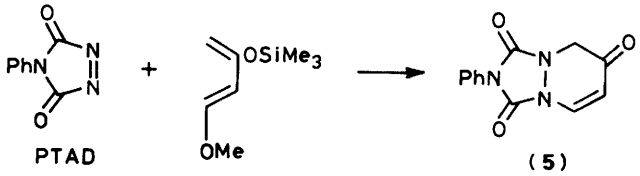


Scheme 1.

As a prelude to testing the feasibility of such a Scheme, and as part of a wider study of the potential of azo dienophiles in heterocyclic synthesis, we have investigated the reactions of cyclic azo dienophiles with functionalised dienes, and the regiochemistry of the Diels–Alder reaction of the unsymmetrical dienophile (**3**).

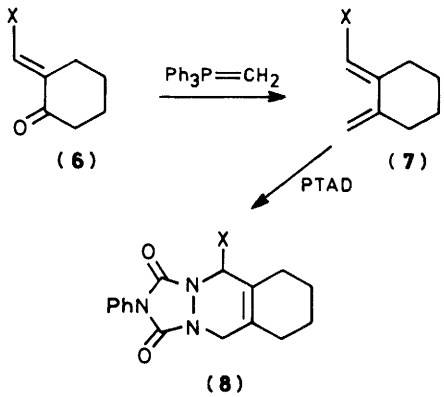
Results and Discussion

Although several cyclic azo dienophiles are known, most of them have to be generated and intercepted *in situ*. However, PTAD is an isolable compound, and therefore the initial studies were performed using this more easily handled dienophile. 1-Methoxy-3-trimethylsiloxybuta-1,3-diene reacted rapidly with PTAD at room temperature to give, after work-up, the expected enone (**5**) (84%).



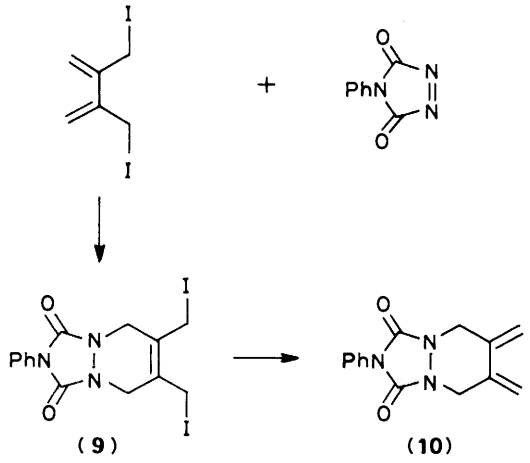
Cycloaddition of PTAD to the bis-*exo*-methylene cyclohexanes (**7a**) and (**7b**), prepared in poor yield from 2-(n-butylthiomethylene)cyclohexanone (**6a**)[6] and 2-(acetoxymethylene)-cyclohexanone (**6b**)[7] by Wittig reaction with methylenetriphenylphosphorane, also occurred readily at room temperature, although the yields of the adducts (**8**) were only moderate. The allylic acetate (**8b**) was hydrolysed to the alcohol (**8c**) on attempted chromatography on silica gel.

Recently there has been considerable interest in tandem Diels–Alder reactions involving various 2,3-disubstituted butadienes,[8,9] and therefore in order to investigate this type of reaction in the azo series, the reaction of PTAD with 2,3-bis-



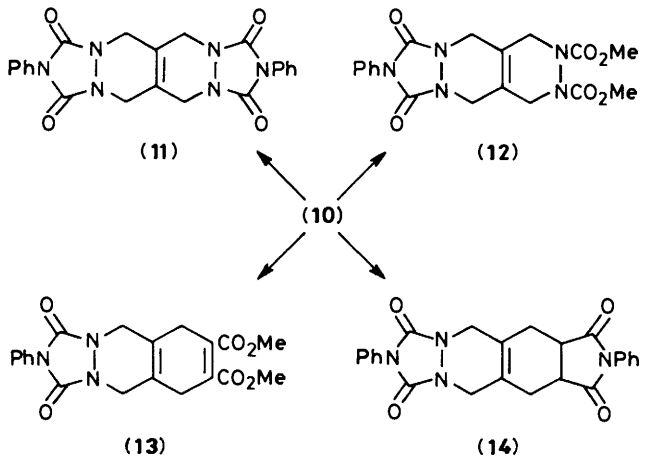
a; X = SBu; **b**; X = OAc; **c**; X = OH

(iodomethyl)buta-1,3-diene[10] was studied. Although reaction occurred readily at 0 °C, no Diels–Alder adduct was isolated. The required adduct (**9**) was isolated, however, as an unstable solid (60%) by carrying out the Diels–Alder reaction at −50 °C. Conversion of (**9**) into the diene (**10**) proved to be troublesome. Thus, treatment of (**9**) with zinc dust or zinc–copper couple in ether, with and without sonication, was unsatisfactory, although varying amounts of the required diene could be detected by n.m.r. spectroscopy. The only set of conditions which gave the diene (**10**) in high (97%) and reproducible yield employed a freshly prepared zinc–copper couple in a mixture of dimethylformamide (DMF), diethyl ether, and tetrahydrofuran (THF).[11]



(**9**) (**10**)

The diene (**10**) reacted with more PTAD to give the tandem Diels–Alder adduct (**11**) (54%) as an amorphous powder. The diene (**10**) also reacted with dimethyl azodicarboxylate, dimethyl acetylenedicarboxylate, and *N*-phenylmaleimide to give the expected adducts (**12**), (**13**), and (**14**) in yields of 76, 86, and 87% respectively (Scheme 2).

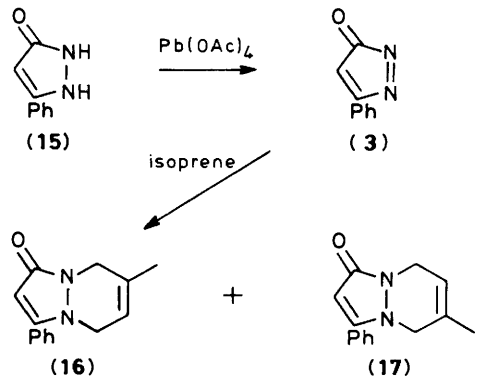


Scheme 2.

In contrast to the Diels–Alder reaction of unsymmetrical carbon dienes and dienophiles, the regiochemistry of which has been widely studied, nothing is known about the regiochemistry of Diels–Alder reactions involving unsymmetrical azo dienophiles. Since a regioselective Diels–Alder reaction is a key step in the strategy outlined in Scheme 1, the reaction of the cyclic azo dienophile (**3**) with unsymmetrical model dienes was investigated.

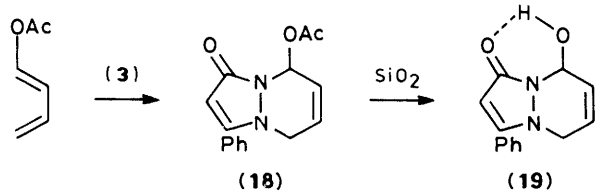
The generation of the azo compound (**3**) by oxidation of the pyrazolinone (**15**), and of its sodium salt, was studied under various conditions. Although successful in the oxidation of other hydrazo compounds, t-butyl hypochlorite,[12] dinitrogen tetraoxide,[13] tosyl isocyanate in dimethyl sulphoxide,[14] and nickel peroxide[15] were all unsatisfactory, and lead tetra-acetate[16] was the preferred oxidant in this case.

Thus, oxidation of the pyrazolinone (**15**) in dichloromethane in the presence of isoprene at −10 °C gave a mixture of regioisomeric Diels–Alder adducts (**16**) and (**17**) (78%). By integration of the methyl signals in the ^{1}H n.m.r. spectrum the ratio was determined to be 5:4, although it was not possible to assign the major product by n.m.r. spectroscopy.



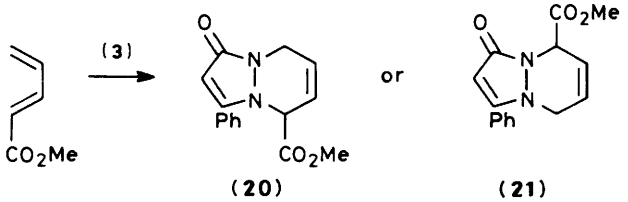
(**15**) (**3**) (**16**) (**17**)

Reaction of compound (**3**) with 1-acetoxybutadiene, however, gave a single Diels–Alder adduct, as detected by n.m.r. spectroscopy. Attempts to purify the adduct by chromatography on silica gel resulted in hydrolysis and formation of the corresponding allylic alcohol. On the basis of its OH stretch in the i.r. spectrum at 3 075 cm^{-1}, indicative of intramolecular hydrogen bonding, the alcohol was assigned the structure (**19**), and hence the initial adduct as (**18**). The diene (**7a**) failed to give an adduct with the azo compound (**3**) under a variety of conditions.



(**18**) (**19**)

Methyl penta-2,4-dienoate also gave a single Diels–Alder adduct on reaction with azo dienophile (**3**). However, on the basis of the n.m.r. spectral data the structure could not be assigned as (**20**) or (**21**) unambiguously.



(**20**) (**21**)

Thus, in common with the all-carbon Diels–Alder reaction, reactions of dienes containing conjugatively electron-releasing or -withdrawing groups with unsymmetrical azo dienophiles appear to exhibit high regioselectivity.

Experimental

I.r. spectra were recorded for liquids as thin films, and for solids as solutions in chloroform, unless otherwise stated, on a Perkin-Elmer 298 spectrophotometer, and calibrated against polystyrene. ^{1}H N.m.r. spectra were recorded on a Bruker WM250 (at 250 MHz), Perkin Elmer R32 (90 MHz), or Varian EM360 (60 MHz) spectrometer. Mass spectra were recorded using a VG Micromass 7070B mass spectrometer operating at 70 eV using a direct-insertion probe. Ether refers to diethyl ether, and light petroleum refers to that fraction with b.p. 40—60 °C. All solvents were dried by standard procedures.

2,3,5,6-*Tetrahydro*-2-*phenyl*-1H-[1,2,4]*triazolo*[1,2-a]*pyridazine*-1,3,6-*trione* (**5**).—1-Methoxy-3-trimethylsiloxybuta-1,3-diene was added dropwise to a stirred solution of PTAD (106 mg) in dichloromethane (10 ml) at room temperature until the deep red colour disappeared. The solvent was evaporated off to leave crystals of the *title compound* (**5**) (124 mg, 84%), m.p. 167—170 °C (from dichloromethane–light petroleum) (Found: C, 59.5; H, 3.7; N, 17.0. $C_{12}H_9N_3O_3$ requires C, 59.3; H, 3.7; N, 17.3%); $\nu_{max.}$ 1 790, 1 730, 1 690, and 1 600 cm^{-1}; δ (60 MHz; $CDCl_3$) 4.45 (2 H, s), 5.75 (1 H, d, *J* 8 Hz), 7.55 (5 H, s), and 7.85 (1 H, d, *J* 8 Hz); *m/z* 243 (M^+), 188, 148, 119 (base), and 96.

5-(*n-Butylthio*)-2,3,5,6,7,8,9,10-*octahydro*-2-*phenyl*-1H-[1,2,4]*triazolo*[1,2-b]*phthalazine*-1,3-*dione* (**8a**).—n-Butyllithium (1.66M in hexane; 3.0 ml, 5 mmol) was stirred in dry ether (16 ml), and methyltriphenylphosphonium bromide (1.80 g, 5 mmol) was added. The solution was stirred for 4 h, and then 2-(n-butylthiomethylene)cyclohexanone (**6a**)[6] (1.0 g, 5.1 mmol) was added dropwise. The dark coloured reaction mixture was heated under reflux for 16 h, and then filtered. The filtrate was concentrated, and the residue was distilled to give 1-(*n-butylthiomethylene*)-2-*methylenecyclohexane* (**7a**) (0.22 g, 22%) as a pale yellow oil, b.p. 75—80 °C at 0.02 mmHg (Kugelrohr) (Found: M^+, 196.1276. $C_{12}H_{20}S$ requires *M*, 196.1285).

A solution of the diene (**7a**) (220 mg, 1.12 mmol) in dichloromethane (1 ml) was added dropwise to a stirred solution of PTAD (200 mg, 1.14 mmol) in dichloromethane (10 ml) at room temperature. After the addition, the mixture was stirred for a further 3 h. The solvent was evaporated off, and the residue was chromatographed on silica gel. Elution with ether–light petroleum (1:1) gave the *title compound* (**8a**) (80 mg, 19%) as crystals, m.p. 132—135 °C (Found: C, 64.6; H, 6.8; N, 11.3. $C_{20}H_{25}N_3O_2S$ requires C, 64.7; H, 6.8; N, 11.3%); $\nu_{max.}$(Nujol) 1 770 and 1 710 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.90 (3 H, t), 1.40—2.20 (11 H, m), 2.55 (1 H, m), 2.75 (1 H, m), 2.95 (1 H, m), 4.05 (2 H, AB quartet), 5.34 (1 H, s), and 7.30—7.60 (5 H, m); *m/z* 371 (M^+), 282 (base), 163, 134, and 120.

2,3,5,6,7,8,9,10-*Octahydro*-5-*hydroxy*-2-*phenyl*-1H-[1,2,4]-*triazolo*[1,2,-b]*phthalazine*-1,3-*dione* (**8c**).—1-(Acetoxymethylene)-2-methylenecyclohexane (**7b**) was prepared (3%) from 2-(acetoxymethylene)cyclohexanone (**6b**)[7] by a similar method to that described for the diene (**7a**).

A solution of PTAD in dichloromethane was added dropwise to a stirred solution of the diene (**7b**) (28.5 mg, 0.17 mmol) in dichloromethane until the solution remained slightly pink. The solvent was evaporated off, and the residue was chromatographed on silica gel. Elution with ether gave the *title compound* (**8c**) (24 mg, 47%), m.p. 203—206 °C (Found: C, 64.3; H, 5.7; N, 13.9. $C_{16}H_{17}N_3O_3$ requires C, 64.2; H, 5.7; N, 14.0%); $\nu_{max.}$ 3 320br, 1 770, 1 710, and 1 600 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.5—2.4 (8 H, m), 4.05 (2 H, AB quartet, *J* 16 Hz), 5.60 (1 H, s), and 7.3—7.6 (5 H, m); *m/z* 299 (M^+), 281, 270, 178, 177, 122 (base), and 119.

2,3,5,8-*Tetrahydro*-6,7-*bis*(*iodomethyl*)-2-*phenyl*-1H-[1,2,4]-*triazolo*[1,2-a]*pyridazine*-1,3-*dione* (**9**).—A solution of PTAD (63 mg, 0.36 mmol) in dry dichloromethane (5 ml) was slowly added to a stirred solution of 2,3-bis(iodomethyl)buta-1,3-diene[10] (120 mg, 0.36 mmol) in dry dichloromethane (10 ml) at −50 °C. The reaction mixture was stirred at −50 °C for 15 min, and then stored at −20 °C overnight. After the mixture had warmed to room temperature the solvent was evaporated off, and the residue was triturated to give the *title compound* (**9**) (108 mg, 60%) as a yellow solid, m.p. 157—163 °C (decomp.) (Found: C, 33.3; H, 2.5; N, 8.3. $C_{14}H_{13}I_2N_3O_2$ requires C, 33.0; H, 2.6; N, 8.25%); $\nu_{max.}$ 1 770, 1 710, and 1 600 cm^{-1}; δ (90 MHz; $CDCl_3$) 3.90 (4 H, s), 4.20 (4 H, s), and 7.40 (5 H, m); *m/z* 509 (M^+), 255, 128 (base), 127, and 119.

2,3,5,6,7,8-*Hexahydro*-6,7-*dimethylene*-2-*phenyl*-1H-[1,2,4]-*triazolo*[1,2-a]*pyridazine*-1,3-*dione* (**10**).—Zinc powder (3.25 g, 50 mg-atom) and hydrated copper(II) sulphate (1.25 g, 5 mmol) were ground together into an intimate mixture. This mixture was stirred together under nitrogen at 0 °C, and DMF (2.5 ml) was added. The cooling bath was removed, and dry ether (20 ml) was added to the mixture. To this stirred, black suspension of zinc–copper couple was added dropwise a solution of compound (**9**) (270 mg, 0.53 mmol) in dry THF (25 ml). The reaction mixture was stirred for 2 h, filtered through Celite, and the filtrate was concentrated. Ether (50 ml) was added, and the organic layer was washed with saturated aqueous sodium hydrogen carbonate (25 ml), dried ($MgSO_4$), and evaporated. Chromatography of the residue on silica gel gave the *title compound* (**10**) (132 mg, 97%), m.p. 124—126 °C (from ether) (Found: C, 65.7; H, 5.2; N, 16.2. $C_{14}H_{13}N_3O_2$ requires C, 65.9; H, 5.1; N, 16.5%); $\nu_{max.}$ 1 770 and 1 715 cm^{-1}; δ (90 MHz; $CDCl_3$) 4.25 (4 H, br s), 5.15 (2 H, br s), 5.45 (2 H, br s), and 7.45 (5 H, m); *m/z* 255 (M^+, base), 135, and 119.

Diels–Alder Reactions of the Diene (**10**).—(a) *With PTAD.* A stirred solution of diene (**10**) (132 mg, 0.52 mmol) in dichloromethane (3 ml) was treated with a saturated dichloromethane solution of PTAD until the reaction mixture remained pink. The precipitate was filtered off, washed with dichloromethane, and dried to give the *adduct* (**11**) (120 mg, 54%), as an amorphous powder which could not be recrystallised, m.p. >360 °C (starts to darken at 280 °C) (Found: C, 61.0; H, 4.1; N, 19.1%; M^+, 430.1384. $C_{22}H_{18}N_6O_4$ requires C, 61.4; H, 4.2; N, 19.5%; *M*, 430.1389) $\nu_{max.}$(Nujol) 1 760, 1 710, and 1 600 cm^{-1}; δ [90 MHz; $(CD_3)_2SO$] 4.25 (8 H, br s) and 7.45 (10 H, m); *m/z* 430 (M^+, base), 254, 135, and 119.

(b) *With dimethyl azodicarboxylate.* Dimethyl azodicarboxylate (35 mg, 0.24 mmol) was added to a solution of the diene (**10**) (31 mg, 0.12 mmol) in dichloromethane (2 ml). After 24 h, a solid had precipitated from the yellow solution. The solid was filtered off, washed with dichloromethane, and dried to give the *adduct* (**12**) (37 mg, 76%), m.p. 276—282 °C (decomp.) (from acetonitrile) (Found: C, 53.8; H, 4.8; N, 17.4. $C_{18}H_{19}N_5O_6$ requires C, 53.9; H, 4.8; N, 17.45%); $\nu_{max.}$(Nujol) 1 765, 1 725, 1 710, and 1 595 cm^{-1}; δ [90 MHz; $(CD_3)_2SO$] 3.70 (6 H, s), 3.85—4.55 (8 H, m), and 7.50 (5 H, s); *m/z* 401 (M^+), 254 (base), 135, and 119.

(c) *With dimethyl acetylenedicarboxylate.* A mixture of the diene (**10**) (65 mg, 0.25 mmol) and dimethyl acetylenedicarboxylate (72 mg, 0.51 mmol) in chloroform (3 ml) was kept at room temperature for 7 d. The resulting crystals were filtered off, washed, and dried to give the *adduct* (**13**) (87 mg, 86%), m.p.

264—272 °C (decomp.) (Found: C, 60.15; H, 4.8; N, 10.6. $C_{20}H_{19}N_3O_6$ requires C, 60.45; H, 4.8; N, 10.6%); $\nu_{max.}$ 1 775, 1 715, and 1 600 cm^{-1}; δ (90 MHz; $CDCl_3$) 3.00 (4 H, br s), 3.70 (6 H, s), 3.95 (4 H, br s), and 7.25 (5 H, m); *m/z* 397 (M^+, base), 395, 365, 338, 337, 278, and 119.

(d) *With* N-*phenylmaleimide*. A mixture of the diene (**10**) (44 mg, 0.17 mmol) and *N*-phenylmaleimide (30 mg, 0.17 mmol) in chloroform (2 ml) was kept at room temperature for 7 d. The solvent was evaporated off to leave crystals of the *adduct* (**14**) (64 mg, 87%), m.p. 261—264 °C (from chloroform) (Found: M^+, 428.1475. $C_{24}H_{20}N_4O_4$ requires *M*, 428.1484) $\nu_{max.}$ 1 770, 1 710, and 1 600 cm^{-1}; δ (90 MHz; $CDCl_3$) 2.60 (2 H, m), 2.65 (2 H, m), 3.40 (2 H, m), 4.10 (4 H, br s), and 7.35—7.65 (10 H, m); *m/z* 428 (M^+), 202, and 173 (base).

Diels–Alder Reactions of 5-Phenylpyrazol-3-one (**3**).—(a) *With isoprene*. A mixture of 1,2-dihydro-5-phenylpyrazol-3-one (**15**) (1.60 g, 10 mmol) and isoprene (0.70 g, 10 mmol) in dichloromethane (50 ml) was stirred and cooled to −10 °C under nitrogen. Lead tetra-acetate (4.5 g, 10 mmol) was added slowly during 30 min, and the resulting mixture was stirred for a further 3 h. The solution was washed with aqueous sodium carbonate (5%; 25 ml), filtered, washed with water (2 × 50 ml), dried ($MgSO_4$), and evaporated to leave a mixture of the adducts (**16**) and (**17**) (1.76 g, 78%) as a brownish oil, $\nu_{max.}$ 1 685, 1 660, and 1 635 cm^{-1}; δ (60 MHz; CCl_4) 1.70 and 1.80 (total 3 H, br s, ratio 5:4), 3.45—3.80 (2 H, m), 3.85—4.25 (2 H, m), 5.35—5.75 (1 H, m), 5.50 (1 H, br s), and 7.35 (5 H, s); *m/z* 226 (M^+), 225, 211, 102, 86, and 84 (base).

(b) *With* 1-*acetoxybuta*-1,3-*diene*. The pyrazolinone (**15**) (0.80 g, 5 mmol), 1-acetoxybuta-1,3-diene (0.60 g, 5.4 mmol), and lead tetra-acetate (2.3 g, 5.2 mmol) were treated together in dry dichloromethane (50 ml) as described above. Work-up, and evaporation of the mixture, gave the adduct (**18**) (0.90 g, 67%) as a brown solid, m.p. 127—130 °C; $\nu_{max.}$ 1 730, 1 670, and 1 655 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.08 (3 H, s), 3.55 (1 H, br d, *J* 15 Hz), 4.35 (1 H, br d, *J* 15 Hz), 5.76 (1 H, s), 6.20 (2 H, m), 7.05 (1 H, m), and 7.50 (5 H, s); *m/z* 270 (M^+), 211, 210 (base), 102, 81, and 69.

Attempted purification of the above adduct by chromatography on silica gel led to hydrolysis of the acetate, and isolation of 5,8-dihydro-8-hydroxy-3-phenylpyrazolo[1,2-*a*]-pyridazin-1-one (**19**) (0.29 g, 25%) as an unstable solid, $\nu_{max.}$(hexachlorobutadiene) 3 075br, 1 630, and 1 610 cm^{-1}; δ (250 MHz; $CDCl_3$) 3.60 (1 H, br d, *J* 15 Hz), 4.30 (1 H, br d, *J* 15 Hz), 5.65 (1 H, br s), 5.70 (1 H, s), 6.0—6.25 (3 H, m), and 7.50 (5 H, s); *m/z* 228 (M^+), 211, 210, 199, 173, 160, and 119 (base).

(c) *With methyl penta*-2,4-*dienoate*. Lead tetra-acetate (1.62 g, 3.7 mmol) was added to a stirred suspension of the pyrazolinone (**15**) (0.91 g, 5.7 mmol) and methyl penta-2,4-dienoate (0.64 g, 5.7 mmol) in dry dichloromethane (20 ml) at −23 °C. The reaction mixture was stirred at −23 °C for 2 h, and then allowed to warm up to room temperature. The mixture was filtered, and the filtrate was washed successively with saturated aqueous sodium hydrogen carbonate (20 ml) and water (2 × 20 ml), dried ($MgSO_4$), and evaporated to leave a red oil (1.14 g). This oil could not be purified by column chromatography, but extraction with light petroleum gave the adduct (**20**) or (**21**) as a pale orange oil, $\nu_{max.}$ 1 725 and 1 625 cm^{-1}; δ (90 MHz; $CDCl_3$) 3.50 (3 H, s), 4.40 (2 H, AB quartet, *J* 18 Hz), 5.00 (1 H, m), 5.80 (1 H, s), 6.15 (2 H, m), and 7.45 (5 H, m); *m/z* 270 (M^+), 211 (base), 184, 129, 102, and 81.

Acknowledgements

We thank the S.E.R.C. for financial support.

References

1 C. J. Moody, *Adv. Heterocycl. Chem.*, 1982, **30**, 1.
2 R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1967, 1905; M. E. Burrage, R. C. Cookson, S. S. Gupte, and I. D. R. Stevens, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1325.
3 S. M. Weinreb and R. R. Staib, *Tetrahedron*, 1982, **38**, 3087.
4 D. L. Boger, *Tetrahedron*, 1983, **39**, 2869.
5 H. H. Wasserman and J. S. Wu, *Heterocycles*, 1982, **17**, 581; J. S. McManis and B. Ganem, *J. Org. Chem.*, 1980, **45**, 2041; H. Yamamoto and K. Maruoka, *J. Am. Chem. Soc.*, 1981, **103**, 6133.
6 *Cf.* R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, 1962, **27**, 1615.
7 R. Jacquier, C. Petrus, F. Petrus, and M. Valentin, *Bull. Soc. Chim. Fr.*, 1970, 2678.
8 Y. Gaoni and S. Sadeh, *J. Org. Chem.*, 1980, **45**, 870.
9 B. M. Trost and M. Shimizu, *J. Am. Chem. Soc.*, 1982, **104**, 4299.
10 D. P. G. Hamon and P. R. Spurr, *Synthesis*, 1981, 873.
11 R. O. Angus and R. P. Johnson, *J. Org. Chem.*, 1983, **48**, 273.
12 R. C. Cookson, S. S. Gupte, I. D. R. Stevens, and C. T. Watts, *Org. Synth.*, 1971, **51**, 121; A. B. Evnin, A. Y. Lam, J. J. Maher, and J. J. Blyskal, *Tetrahedron Lett.*, 1969, 4497.
13 J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, 1966, **31**, 3444.
14 J. A. Moore, R. Muth, and R. Sorace, *J. Org. Chem.*, 1974, **39**, 3799.
15 S. Takase and T. Motoyama, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 3926.
16 B. T. Gillis and R. Weinkam, *J. Org. Chem.*, 1967, **32**, 3321.

Received 6th April 1984; *Paper* 4/573