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INVESTIGATIONS ON DIAZO COMPOUNDS AND AZIDES- LXII.[1] SYNTHESIS AND REACTIONS OF α-DIAZO PHOSPHONATES WITH A CONJUGATED 1,3-DIENE UNIT

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Abstract. - α-Diazo phosphonates with a conjugated 1,3-diene unit are synthesised by the Bamford-Stevens reaction (2 → 4 → 3). They undergo [4+2]-cycloadditions with the dienophile 5 to form the tetrahydrotriazolopyridazines 8, which possess an unchanged diazo group. In contrast, dimethyl acetylenedicarboxylate (9) reacts exclusively with the diazo dipole of 3 to yield the 3H-pyrazoles 10, which rearrange to 11 by sigmatropic PO-shifts and hydrolyse to form 13. The diazo compound 3b isomerises to the pyrazole 16 when heated in benzene.

α,β-Unsaturated diazo compounds are mostly prepared by the Bamford-Stevens reaction [2] or by photochemical ring-opening of 3H-pyrazoles [2]; the latter starting materials can be regenerated by [1,5]-cyclisation of the products.

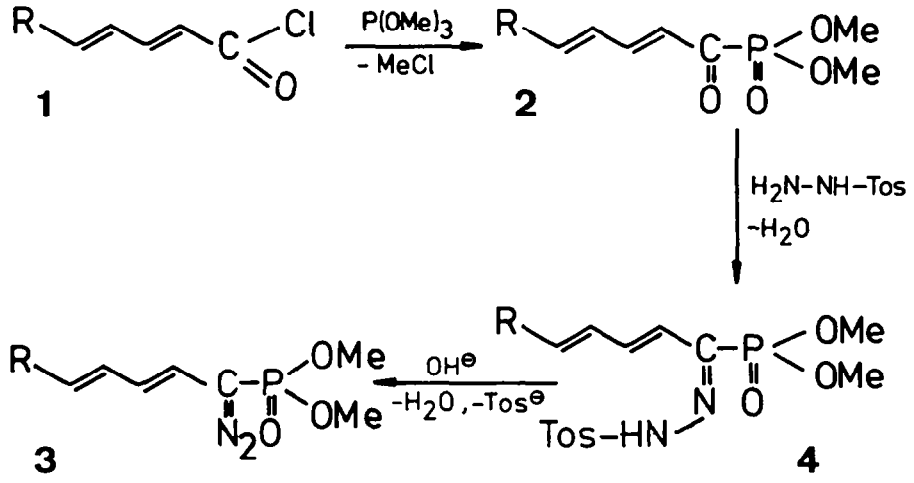
In contrast, our knowledge of the properties of α,β,γ,δ-unsaturated diazo compounds is very limited [3]. With the exception of the thermal isomerisation of trifluoromethyl-substituted 2,3-diazabicyclo[3.2.0]hepta-2,6-dienes [4], it appears that only the alkaline cleavage of the corresponding tosylhydrazones has been employed for the generation of such unsaturated diazo compounds. In these products, the γ,δ-double bond is often part on an aromatic system; it is generally not possible to isolate such compounds as they undergo [1,7]-cyclisation to give diazepines (in analogy to 3 → 15) under the thermal conditions necessary for their generation [3,5]. In some individual cases, the diazo intermediates can be trapped before ring closure as phosphazines [6].

As α-diazo phosphonates are accessible in weakly alkaline media at room temperature by the Bamford-Stevens reaction [7], our present studies are concerned with the synthesis of derivatives with a conjugated 1,3-diene unit using the same methodology. In addition, we were interested in the question as to whether cycloaddition partners attack the diene or the diazo part of these molecules.

RESULTS

Diazo Compounds

The synthesis of the diazo compounds 3a and b starts from the doubly unsaturated carboxylic acid chlorides 1a and b, which are converted to the dimethyl α-oxo phosphonates 2a and b by the Michaelis-Arbusov reaction with trimethyl phosphite in benzene. The oils, obtained in analytically pure form, are condensed with tosylhydrazide in methanol/hydrochloric acid to give the tosylhydrazones 4a and b.



1-4	a	b
R	Ph	Me

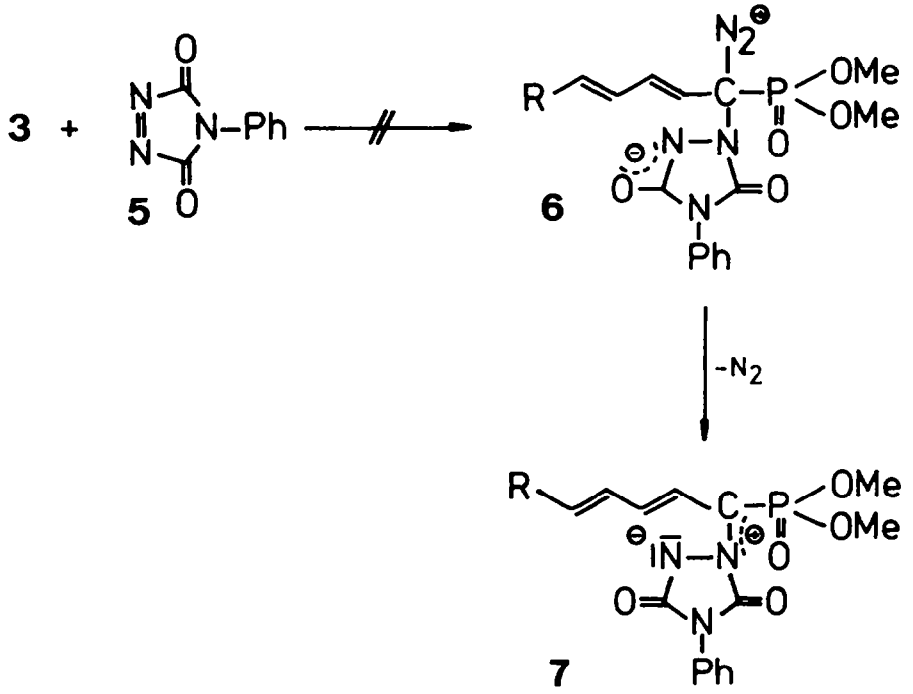
The anti-configuration of the C/N double bond is indicated by the appearance of the NH-absorption in the IR spectra (3425 and 3440 cm^{-1}, respectively); this would not be detectable for the syn-isomers as a result of chelation with the PO group [7]. The NH resonance in the ^{1}H-NMR spectra is observed at relatively high field (δ = 8.95 and 9.60, respectively, 20% solution); on dilution a diamagnetic shift of about 0.6 ppm, as is known for anti-α-tosylhydrazonophosphonates [7], is observed.

Aqueous sodium carbonate solution causes clean tosylhydrazone cleavage and gives the doubly unsaturated α-diazo phosphonates 3a and b; evidence for the constitution is given, among others, by the appearance of the diazo valency vibration at 2098 and 2079 cm^{-1}, respectively, in the IR spectra [8].

Cycloadducts

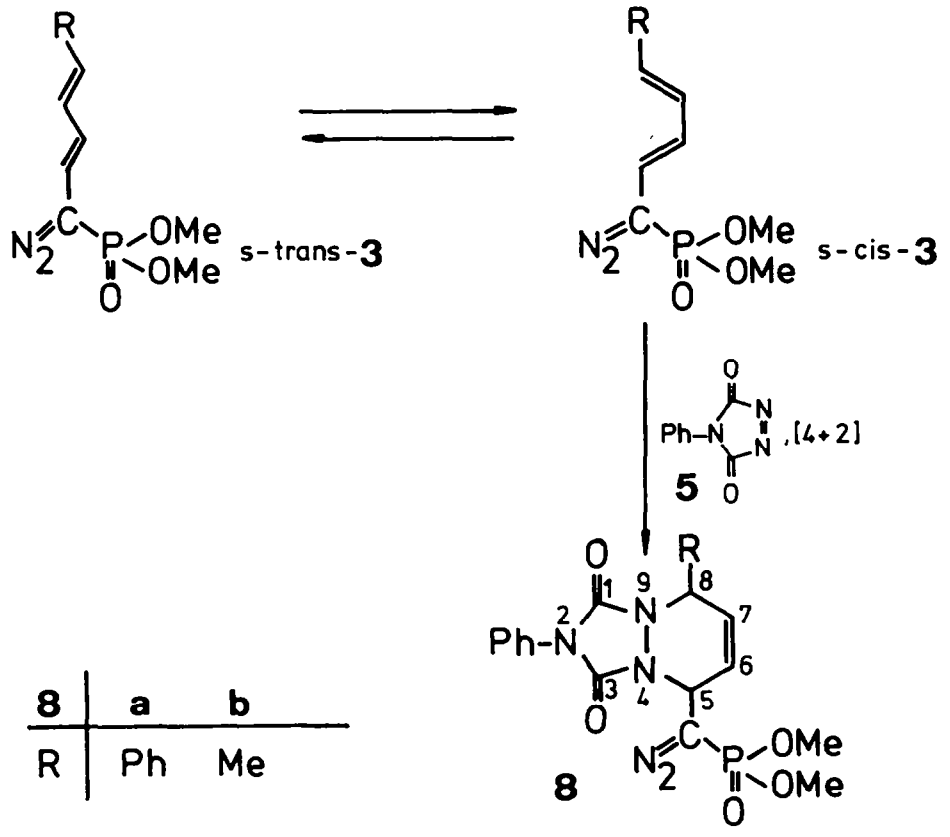
Firstly we studied the reaction of 3a and b with 4-phenyl-3H-1,2,4-triazole-3,5(4H)-dione (5). It is known that the latter reacts on the one hand with 1,3-dienes in a Diels-Alder reaction [9] and, on the other hand, with diazo compounds to give azomethine imine dipoles with cleavage of

nitrogen [10]. In the case of 3, the latter reaction would lead to the formation of 7 through the intermediacy of the diazonium triazolide 6.



Evidence against the above reaction course is given by the fact that the reaction of 3 with 5 proceeds in dichloromethane at room temperature without the evolution of nitrogen. The elemental composition and the IR spectra of the yellow products show unequivocally the retention of the diazo nitrogen atoms ($\nu_{C=N_2}$ = 2090 and 2083 cm^{-1}), respectively). Thus, the products apparently have the Diels-Alder structures 8a and b.

Final evidence for the structure is given by the chemical shifts and multiplicities in the ^{1}H-NMR spectra. As a representative the spectrum of 8b is discussed in detail. As expected, the resonance of the methyl group is seen at highest field (δ = 1.61) and, as a result of vicinal coupling, is split (J = 6.6 Hz). Noteworthy is the resonance of the methoxy groups of the phosphonic ester moiety in the form of 2 doublets (δ = 3.78 and 3.80, respectively, $^3J_{H,P}$ = 11.7 Hz). This is due to the chirality centre at C-5 which is responsible for the diastereotopy of the two methoxy groups [11]. The two olefinic hydrogen atoms H-6 and H-7 together with the tertiary hydrogen atoms H-5 and H-8 comprise an ABXY system [12] which has been unambigously analysed by means of double resonance experiments. The protons H-6 and H-7 show a cis-coupling of 10.4 Hz. For H-6, an additional vicinal coupling with H-5 ($^3J_{H,H}$ = 4.0 Hz) and a further allylic coupling with H-8 ($^4J_{H,H}$ = 1.7 Hz) are observed. The corresponding couplings of H-7 with H-8 ($^3J_{H,H}$ = 2.6 Hz) and with H-5 ($^4J_{H,H}$ = 1.5 Hz) are somewhat smaller. Both tertiary hydrogen atoms H-5 and H-8 also show a long-range coupling of 2.2 Hz. The hetero-coupling of H-5 with phosphorus was found to be 9.8 Hz, and is, of course, not detectable in the phosphorus decoupled ^{1}H-NMR spectrum.

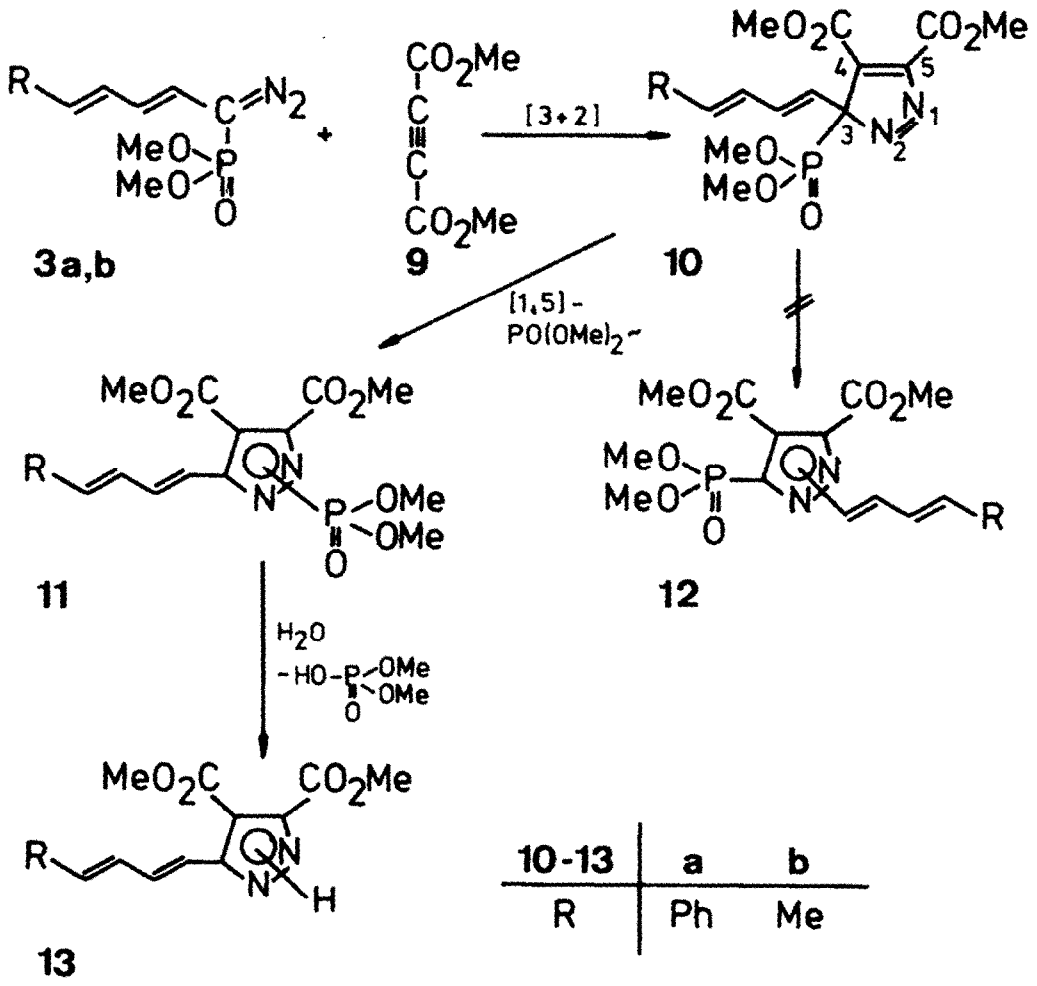


The reason why the triazoledione 5 reacts specifically with the 1,3-diene unit of 3 to form 8 instead of the azomethine imine dipole is mainly due to the marked dienophilic character [9] of 5. In addition, however, it must be noted that the phosphoryl group decreases the electron density at the diazo carbon atom, thus making the primary step (3 + 5 → 6) [10] more difficult, which indirectly favours the Diels-Alder reaction. It can be assumed that the cycloaddition process starts from s-cis-3.

The behaviour of 3 towards dimethyl acetylenedicarboxylate (9) is completely different; the reaction proceeds solely in the sense of a 1,3-dipolar cycloaddition and no evidence for a competitive Diels-Alder reaction can be detected. Thus, the NH-pyrazole 13b is obtained from the reaction of 3b with 9 at room temperature. The formation of 13b can be interpreted with certainly by initial formation of the 3H-pyrazole 10b which undergoes a [1,5]-sigmatropic shift of the dimethoxyphosphoryl group to give the thermodynamically more stable isomer 11b. There is no evidence for the theoretically possible sigmatropic shift of the 1,3-diene unit (10b → 12b). The isolation of 11b is not possible as the traces of water apparently present rapidly solvolyse the N/PO bond to give 13b. There are many analogous examples for this last step which are of preparative importance in phosphorylation [13] processes. Dimethyl phosphate is solvolytically cleaved and has been separated and identified as its tert-butylammonium salt [14].

When the 6-phenyl substituted diazo compound 3a is reacted with 9 under identical conditions and the reaction is stopped after 24 h, the primarily formed 3H-pyrazole 10a can be isolated as yellow crystals in 66% yield. Work-up of the filtrats after a further 24 h gives, in addition,

the NH-pyrazole 13a in 12% yield. As already mentioned for 13b, it is also possible here to identify the dimethyl phosphate, formed by hydrolysis of 11a, as its tert-butylammonium salt [14].

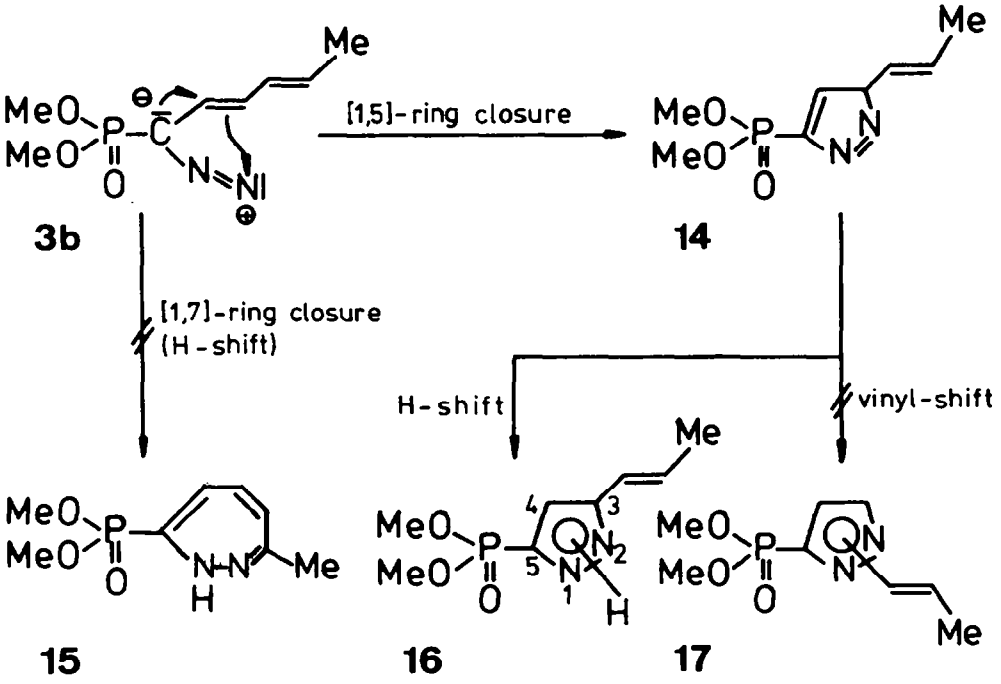


The pyrazoles 13a and b are colourless solids. The IR spectra show broad NH-absorptions (3240 and 3215 cm^{-1}, respectively); the absence of PO-absorptions confirms the hydrolytic cleavage of the phosphoryl groups. In contrast, the IR spectrum of 10a contains an intensive PO-absorption at 1225 cm^{-1} and no NH-bands. Evidence for the N=N structural unit in the 3H-pyrazole 10a is given by the UV maximum (CH_2Cl_2) at λ = 330 nm, which is ascribed to an $n \rightarrow \pi^*$ transition, as has been found for other 3H-pyrazoles. ^{1}H-NMR evidence for the constitution of the primary adduct 10a is given by the diastereotopy [11] of the two OCH_3 groups of the phosphoryl unit (δ = 3.78 and 3.91 ppm, respectively, $^3J_{H,P}$ = 11.5 Hz), which is attributed to the chirality centre at C-3. The ^{13}C-NMR resonance for this carbon atom is observed at δ = 112.7, i.e., at relatively low field, which is to be expected as a result of the substitution pattern. The diastereotopy of the two OCH_3 groups of the phosphoryl unit is also seen in the ^{13}C-NMR spectrum as a doubling of the signals (δ = 52.6 and 56.1 ppm, respectively, $^2J_{C,P}$ = 6.6 Hz). The other two pyrazole carbon atoms C-4 an C-5, in contrast to the unsaturated side chain, show no C/H coupling and thus can be easily

identified among the other olefinic carbon atoms.

Isomerisation of 3b

When 3b is heated in benzene, the red colour disappears but no evolution of nitrogen is detectable; subsequent work up gives the NH-pyrazole 16 in 62% yield. The formation of 16 must proceed via [1,5]-ring closure to give 14 which aromatises by H-shift. The also possible vinyl-shift (14 → 17) apparently has no chance of competing with the H-shift. There is also no evidence that, in addition to the [1,5]-ring closure, 3b can undergo a [1,7]-ring closure to form the azepine 15, although analogous examples have been reported (see, e.g., Ref. [5]).



The pyrazole 16 shows signals for the NH group in the IR (3420 cm^{-1}) and ^{1}H-NMR spectrum (δ = 10.95 ppm). The methyl group resonance appears at δ = 1.88 ppm in the ^{1}H-NMR spectrum and this signal is split (J = 5.2 Hz). The magnitude of this coupling is only difficultly compatible with the isomer 15. The observed vinylic AB-system (δ = 6.30 and 6.42 ppm) with a coupling of 16 Hz, which is typical for trans-hydrogen atoms, and the resonance of H-4 in the aromatic region are in accord with the suggested structure 16.

Finally, analysis of the ^{13}C-NMR spectrum conclusively confirms the structure 16 for the isomerisation product. The resonances of the pyrazole carbon atoms C-3, C-4, and C-5 are observed at δ = 144.6, 107.9, and 138.1 ppm, respectively, with increasing coupling with phosphorus (11.6, 23.9, and 230.8 Hz, respectively). The relatively low field resonances for C-3 and C-5 are explained by the electronegativity of the ring nitrogen atoms. The resonances for the carbon atoms of the vinylic side chain are observed at δ = 118.7 and 129.8 ppm.

EXPERIMENTAL SECTION

Melting points (not corrected): melting point apparatus Mettler FP 61 (heating rate 1°C/min). Microanalyses: Perkin-Elmer Analyzer 240. IR spectra: Beckman IR-20A. UV spectra: Zeiss CMR 10. ^{1}H-NMR spectra: Varian EM 390 and Bruker WP 200 (tetramethylsilane as internal standard). ^{13}C-NMR spectra: Bruker WP 200 (tetramethylsilane as internal standard). All solvents were anhydrous and destilled before use.

Synthesis of the Diazo Compounds 3a and b

Dimethyl 1-oxo-5-phenyl-2,4-pentadienephosphonate (2a). To 38.52 g (0.20 mol) of 1a [16] in 120 ml of benzene is added dropwise at room temperature with starring during 30 min 26.10 g (0.21 mol) of trimethyl phosphite. The clear solution rapidly acquires a yellow colour. After 1 h, the solution is evaporated at 30°C/20 torr to give 47.92 g (90%) of 2a as a yellow oil which is used for further reactions without purification.- IR(film): 1570, 1611, 1717, 1750 (C=O/C=C), 1265 (P=O, broad), 1040 cm^{-1} (POC, broad).- ^{1}H-NMR ($CDCl_3$): δ = 3.80 (d, $^3J_{H,P}$ = 12.0 Hz, 6H, OCH_3), 5.85-7.10, 7.70-8.05 (2m, 4H, olefinic H), 7.20-7.50 (m, 5H, aromatic H).- $C_{13}H_{15}O_4P$ (266.23) calc. C, 58.65; H, 5.68. Found C, 59.0; H, 5.58%.

Dimethyl 1-oxo-2,4-hexadienephosphonate (2b). Starting from 26.12 g (0.20 mol) of 1b [17] in 120 ml of benzene and 26.10 g (0.21 mol) of trimethyl phosphite as described above for 2a, 35.90 g (88%) of 2b are obtained as a yellow oil.- IR(film): 1580, 1620, 1664 (C=O/C=C), 1270 (P=O), 1040 cm^{-1} (POC).- ^{1}H-NMR ($CDCl_3$): δ = 1.88 (d, $^3J_{H,H}$ = 6.2 Hz, 3H, CH_3), 3.82 (d, $^3J_{H,P}$ = 12.0 Hz, 6H, OCH_3), 6.00-6.57, 7.50-7.86 (2m, 4H, olefinic H).- $C_8H_{13}O_4P$ (204.16) calc. C, 47.07; H, 6.42. Found C, 46.8; H, 6.21%.

Dimethyl anti-1-tosylhydrazono-5-phenyl-2,4-pentadienephosphonate (4a). A suspension of 26.62 g (0.10 mol) of 2a and 18.62 g (0.10 mol) of tosylhydrazide [18] in 100 ml methanol/10 ml concentrated hydrochloric acid is stirred for 26 h at room temperature. Filtration and recrystallisation of the residue from methanol gives 32.60 g (75%) of 4a as colourless crystals with mp 140°C.- IR(KBr): 3425 (broad, NH), 1594, 1613 (C=C), 1167, 1350 (SO_2), 1231 (P=O), 1026, 1072 cm^{-1} (POC).- ^{1}H-NMR ($CDCl_3$): δ = 2.42 (s, 3H, CH_3), 3.78 (d, $^3J_{H,P}$ = 12.0 Hz, 6H, OCH_3), 6.00-7.20 (m, 4H, olefinic H), 7.22-7.85 (m, 9H, aromatic H), 8.95 (s, broad, 1H, NH, disappears on addition of D_2O).- $C_{20}H_{23}N_2O_5PS$ (434.45) calc. C, 55.29; H, 5.34; N, 6.45. Found C, 55.0; H, 5.35; N, 6.4%.

Dimethyl anti-1-tosylhydrazono-2,4-hexadienephosphonate (4b). Starting from 20.42 g (0.10 mol) of 2b and 18.62 g (0.10 mol) of tosylhydrazide [18] in 100 ml methanol/10 ml concentrated hydrochloric acid as described above for 4a, 29.80 g (80%) of 4b are obtained as colourless crystals with mp 168°C.- IR(KBr): 3440 (broad, NH), 1610, 1650 (C=C), 1179, 1360 (SO_2), 1244 (P=O), 1032, 1060, 1080 cm^{-1} (POC).- ^{1}H-NMR ($CDCl_3$): δ = 1.77 (d, $^3J_{H,H}$ = 6.2 Hz, 3H, CH_3), 2.39 (s, 3H, tosyl-CH_3), 3.71 (d, $^3J_{H,P}$ = 12.0 Hz, 6H, OCH_3), 5.90-7.15 (m, 4H, olefinic H), 7.55 (AA'XX' system, 4H, aromatic H), 9.60 (s, broad, 1H, NH, disappears on addition of D_2O).- $C_{15}H_{21}N_2O_5PS$ (372.38) calc. C, 48.38; H, 5.68; N, 7.52. Found C, 48.1; H, 5.69; N, 7.5%).

Dimethyl 1-diazo-5-phenyl-2,4-pentadienephosphonate (3a). 2.17 g (5.00 mmol) of 4a and 0.60 g (6.00 mmol) of sodium carbonate in 40 ml of water are covered with 100 ml of ether and the mixture is stirred at room temperature for 8 h. The ether phase is separated, the aqueous phase is re-extracted with 50 ml of ether, the combined organic phases are dried with magnesium sulphate, and concentrated at 30 °C/20 torr. Recrystallisation of the residue from ether at -20°C gives 1.20 g (86%) of 3a as red crystals with mp 68 °C.- IR(KBr): 2098 (C=N_2), 1600, 1630 (C=C), 1255 (P=O), 1034 cm^{-1} (POC).- ^{1}H-NMR ($CDCl_3$): δ = 3.80 (d, $^3J_{H,P}$ = 12.0 Hz, 6H, OCH_3), 5.50-7.48 (m, 9H, olefinic H/aromatic H).- $C_{13}H_{15}N_2O_3P$ (278.25) calc. C, 56.12; H, 5.43; N, 10.07. Found C, 56.2; H, 5.45; N, 9.9%.

Dimethyl 1-diazo-2,4-hexadienephosphonate (3b). Starting from 1.86 g (5.00 mmol) of 4b and 0.60 g (6.00 mmol) of sodium carbonate as described above for 3a, 0.91 g (84%) of 3b is obtained as a red oil which could not be induced to crystallise.- IR(film): 2079 (C=N_2), 1600, 1630 (C=C), 1258 (P=O), 1022 cm^{-1} (broad, POC).- ^{1}H-NMR ($CDCl_3$): δ = 1.76 (d, $^3J_{H,H}$ = 6.2 Hz, 3H, CH_3), 3.77 (d, $^3J_{H,P}$ = 12.0 Hz, 6H, OCH_3), 5.25-6.20 (m, 4H, olefinic H).- $C_8H_{13}N_2O_3P$ (216.18) calc. C, 44.45; H, 6.06; N, 12.96. Found C, 43.9; H, 5.98; N, 9.5%.

Cycloadducts 8 and 13

Dimethyl diazo-{1,3-dioxo-2,8-diphenyl-2,3,5,8-tetrahydro-1H-[1,2,4]triazolo[1,2-a]pyridazin-5-yl}-methanephosphonate (8a). To a solution of 2.78 g (10.00 mmol) of 3a in 50 ml of dichloromethane is added dropwise at room temperature 1.75 g (10.00 mmol) of 5 [19] in 50 ml of the same solvent, whereupon the solution looses its colour. The rate of addition should be so adjusted that an excess of the triazoledione in the reaction mixture is avoided. Concentration of the reaction mixture at 30 °C/20 torr and recrystallisation of the residue from ethyl acetate affords 3.26 g (72%) of 8a as light yellow crystals with mp 178 °C.- IR(KBr): 2945-3087 (CH), 2090 (C=N_2), 1713, 1777 (C=O), 1490 (NPh), 1411 (OC-N), 1261 (P=O), 1010, 1050 cm^{-1} (POC).- ^{1}H-NMR ($CDCl_3$): δ = 3.83, 3.85 (2d, $^3J_{H,P}$ = 11.7 Hz, 6H, OCH_3), 5.16 (Y part of an ABXY system, $^3J_{H-5,H-6}$ = 4.2 Hz, $^3J_{H-5,P}$ = 10.5 Hz, 1H, H-5), 5.47 (X part of an ABXY system, $^3J_{H-8,H-7}$ = 1.7 Hz, 1H, H-8), 6.07 (AB part of an ABXY system, 2H, H-6/H-7), 7.27-7.46 (m, 10 H, aromatic H).- $C_{21}H_{20}N_5O_5P$ (453.40) calc. C, 55.63; H, 4.45; N 15.45. Found C, 55.5; H, 4.50; N, 15.5%.

Dimethyl diazo-{1,3-dioxo-8-methyl-2-phenyl-2,3,5,8-tetrahydro-1H-[1,2,4]triazolo[1,2-a]pyridazin-5-yl}methanephosphonate (8b). Starting from 2.16 g (10.00 mmol) of 3b and 1.75 g (10.00 mmol) of 5 [19], as described above for 8a, 3.13 g (80%) of 8b are obtained as light yellow crystals with mp 132 °C.- IR(KBr): 2840-3075 (CH), 2083 (C=N_2), 1710, 1770 (C=O), 1485 (NPh), 1405 (OC-N), 1252, 1270 (P=O), 1021, 1046 cm^{-1} (POC).- ^{1}H-NMR ($CDCl_3$): δ = 1.61 (d, $^3J_{H,H}$ = 6.6 Hz, 3H, CH_3), 3.78, 3.80 (2d, $^3J_{H,P}$ = 11.7 Hz, 6H, OCH_3), 4.46 (Y part of an ABXY system, $^3J_{H-8,CH_3}$ = 6.6 Hz, $^3J_{H-8,H-7}$ = 2.6 Hz, $^4J_{H-8,H-6}$ = 1.7 Hz, $^5J_{H-8,H-5}$ = 2.2 Hz, 1H, H-8), 5.13 (X part of an ABXY system, $^3J_{H-5,H-6}$ = 4.0 Hz, $^3J_{H-5,P}$ = 9.8 Hz, $^4J_{H-5,H-7}$ = 1.5 Hz, $^5J_{H-5,H-8}$ = 2.2 Hz, 1H, H-5), 5.88, 5.99 (AB part of an ABXY system, $^3J_{H-6,H-7}$ = 10.4 Hz, $^3J_{H-6,H-5}$ = 4.0 Hz, $^4J_{H-6,H-8}$ = 1.7 Hz, $^3J_{H-7,H-8}$ = 2.6 Hz, $^4J_{H-7,H-5}$ = 1.5 Hz, 2H, H-6/H-7), 7.38-7.56 (m, 5H, aromatic H).- $C_{16}H_{18}N_5O_5P$ (391.32) calc. C, 49.11; H, 4.64; N, 17.90. Found C, 49.1; H, 4.66; N, 17.6%.

Reaction of 3a with Dimethyl acetylenedicarboxylate (9). A solution of 0.78 g (2.80 mmol) of 3a and 0.40 g (2.80 mmol) of dimethyl acetylenedicarboxylate 9 in 20 ml of ether is stirred at room temperature for 24 h whereupon a precipiate forms. Suction filtration and recrystallisation from ethyl acetate affords 0.78 g (66%) of dimethyl 3-dimethoxyphosphoryl-3-(4-phenyl-1,3-butadienyl)-3H-pyrazole-4,5-dicarboxylate (10a) as pale yellow crystals with mp 140 °C.- IR(KBr): 1720 (C=O), 1615, 1625 (N=N/C=C), 1225 (P=O), 1000, 1010, 1040 cm^{-1} (POC).- UV (CH_2Cl_2): λ_{max}(log ε) = 330 nm (2.3).- ^{1}H-NMR ($CDCl_3$): δ = 3.78, 3.91 (2d, $^3J_{H,P}$ = 11.5 Hz, 6H, P-OCH_3), 3.90, 3.93 (2s, 6H, C-OCH_3), 6.70-7.55 (m, 9H, olefinic H/aromatic H).- ^{13}C-NMR ($CDCl_3$): δ = 51.9, 55.6 (C-O$\underline{C}H_3$), 52.6, 56.1 (2d, $^2J_{C,P}$ = 6.6 Hz, P-O$\underline{C}H_3$), 112.7 (d, $^1J_{C,P}$ = 182.6 Hz, C-3), 116.4-139.3 olefinic C-2, -3, and -4), 127.0-128.8 (aromatic C), 136.5 (C-5), 147.2 (d, $^2J_{C,P}$ = 12.7 Hz, olefinic C-1), 148.6 (d, $^2J_{C,P}$ = 12.5 Hz, C-4), 161.9, 164.0 (CO).- $C_{19}H_{21}N_2O_7P$ (420.36) calc. C, 54.29; H, 5.04; N, 6.66. Found C, 53.9; H, 5.07; N, 6.6%.

The filtrate from above is stirred at room temperature for a further 24 h, concentrated at 30 °C/20 torr, and the pale yellow residual oil taken up in a small amount of benzene. Cooling at -7 °C for several hours affords 0.10 g (12%) of dimethyl 3-(4-phenyl-1,3-butadienyl)-pyrazole-4,5-dicarboxylate (13a) as colourless crystals with mp 182 °C.- IR(KBr): 3240 (broad, NH), 1720 (C=O), 1620, 1641 cm^{-1} (C=C/C=N).- ^{1}H-NMR ($CDCl_3$): δ = 3.89, 3.91 (2s, 6H, OCH_3), 6.68-7.46 (m, 10 H, olefinic H/aromatic H/NH).- $C_{17}H_{16}N_2O_4$ (312.33) calc. C, 65.38; H, 5.16; N, 8.97. Found C, 64.3;

H, 5.11; N, 8.9%.

The mother liquor from 14a is concentrated at 30 °C/20 torr and the residue treated with 0.20 g (2.80 mmol) of tert-butylamine to give tert-butylammonium dimethyl phosphate as colourless crystals with m.p. 137 °C (Lit.[14]: 136 °C).- IR(KBr): 3015 (NH_3^+), 1269 (P=O), 1041 cm^{-1} (POC).

Dimethyl 3-(1,3-pentadienyl)-pyrazole-4,5-dicarboxylate (13b). A solution of 0.61 g (2.80 mmol) of 3b and 0.40 g (2.80 mmol) of dimethyl acetylenedicarboxylate (9) in 20 ml of ether is stirred at room temperature for 48 h whereupon a precipitate forms. Suction filtration and recrystallisation from ethyl acetate affords 0.36 g (52%) of 13b as colourless crystals with mp 151 °C.- IR(KBr): 3215 (broad, NH), 1700, 1717 (C=O), 1618, 1635 cm^{-1} (C=C/C=N).- ^{1}H-NMR ($CDCl_3$): δ = 1.80 (d, $^3J_{H,H}$ = 6.0 Hz, 3H, CH_3), 3.82, 3.84 (2s, 6H, OCH_3), 5.58-7.00 (m, 4H, olefinic H), 10.14 (s, broad, 1H, NH, disappears on addition of D_2O).- $C_{12}H_{14}N_2O_4$ (250.25) calc. C, 57.60; H, 5.64; N, 11.19. Found C, 57.2; H, 5.56; N, 11.2%.

The filtrate from 13b is treated with 0.20 g (2.80 mmol) tert-butylamine as described above to give 0.42 g (75%) of tert-butylammonium dimethyl phosphate as colourless crystals with mp 137 °C (Lit.[14]: 136 °C).

Isomerisation of 3b → 16

Dimethyl 3-(1-propenyl)-pyrazole-5-phosphonate (16). A solution of 1.08 g (5.00 mmol) of 3b in 40 ml of benzene is heated under reflux for 90 min during which time the colour lightens. Concentration at 30 °C/20 torr and recrystallisation of the residue from ethyl acetate affords 0.68 g (62%) of 16 as colourless crystals with mp 100 °C.- IR(KBr): 3420 (broad, NH), 2955-3150 (CH), 1660 (C=C/C=N), 1230 (P=O), 1015, 1054 cm^{-1} (POC).- ^{1}H-NMR ($CDCl_3$): δ = 1.88 (d, $^3J_{H,H}$ = 5.2 Hz, 3H, CH_3), 3.81 (d, $^3J_{H,P}$ = 11.5 Hz, 6H, OCH_3), 6.30 (part of an AB system, $^3J_{H-1,H-2}$ = 16.0 Hz, $^3J_{H,H}$ = 5.2 Hz, 1H, olefinic H-2), 6.42 (part of an AB system, $^3J_{H-1,H-2}$ = 16.0 Hz, 1H, olefinic H-1), 6.71 (d, $^3J_{H,P}$ = 1.7 Hz, 1H, H-4), 10.95 (s, broad, 1H, NH, disappears on addition of D_2O).- ^{13}C-NMR ($CDCl_3$): δ = 18.5 (CH_3), 53.3 (d, $^2J_{C,P}$ = 5.4 Hz, OCH_3), 107.9 (d, $^2J_{C,P}$ = 23.9 Hz, C-4), 118.7 (olefinic C-1), 129.8 (olefinic C-2), 138.1 (d, $^1J_{C,P}$ = 230.8 Hz, C-5), 144.6 (d, $^3J_{C,P}$ = 11.6 Hz, C-3).- $C_8H_{13}N_2O_3P$ (216.18) calc. C, 44.45; H, 6.06; N, 12.96. Found C, 44.4; H, 5.94; N, 12.6%.

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