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X=Y-ZH SYSTEMS AS POTENTIAL 1,3-DIPOLES. PART 13[1].

PROTOTROPIC GENERATION OF AZOMETHINE IMINES FROM HYDRAZONES

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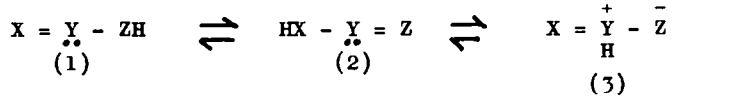
Abstract - Hydrazones of aldehydes and ketones undergo intermolecular cycloaddition to electronegative olefins via azomethine imines, formed by a formal 1,2-prototropic shift, in low to moderate yield on heating in xylene or ethanol. In some instances the reaction is diverted to give products derived (at least formally) from an ene reaction. Similar intramolecular cycloadditions occur with unactivated terminal alkenes and alkynes.

X=Y-ZH Systems can be divided into four classes (Scheme 1) according to the number of constituent atoms that possess lone pairs of electrons (note that more than one pair may be located on each atom).[1]



Type		No.of lone pair atoms	Examples
I	X=Y-ZH	0	Alkenes
II	X=Y-ZH X=Y-ZH X=Y-ZH	1	Imines, ketones, nitroalkanes
III	X=Y-ZH X=Y-ZH X=Y-ZH	2	Hydrazones, oximes, amidines
IV	X=Y-ZH	3	Triazenes

TABLE 1

We suggested that when the central Y atom in an X=Y-ZH system possesses a lone pair of electrons (Scheme 1, types II-IV), as well as the well known formal 1,3-prototropy (1 ⇌ 2) a new general type of prototropy, 1,2-prototropy (1 ⇌ 3) should occur.[2] The occurrence of 1,2-prototropy in types II-IV X=Y-ZH systems should result in the formation of novel types of 1,3-dipoles (3)[3] which, although expected to be present in only trace amounts (cf enols), should be detectable by 1,3-dipolar cycloaddition trapping experiments. We have reported extensively on such processes in imines (a type II system)[1,4,5] and oximes (type III)[6,7] and briefly on hydrazones.[2,8] We now describe our studies with hydrazones (a type III system) in detail.

Type III systems are potentially ambident nucleophiles and those which possess lone pairs on contiguous atoms such as oximes and hydrazones should show enhanced

nucleophilicity.[9] Furthermore, as with X=Y-ZH systems in general, the potential for prototropy extends beyond the initial X=Y-ZH system. Thus for alkyl hydrazones four species≠ need to be considered (Scheme 1) as potential participants in prototropic equilibria in neutral media.

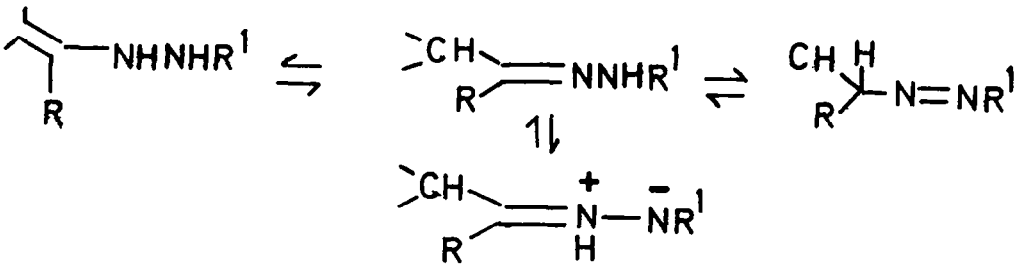
The hydrazone, azo and ene-hydrazine equilibrium has been studied spectroscopically[10] and the equilibria involving azomethine imines is the subject of this paper. The equilibria summarised in Scheme 1 indicate that the reaction of hydrazones with electronegative olefins could proceed via Michael addition, ene-reaction or cycloaddition. In cases where ene-hydrazine equilibration is absent or unavailable, reaction of hydrazones with electronegative olefins in neutral media could lead to four types of product (Scheme 2).

Path a (Scheme 2) involves Michael addition by the more nucleophilic sp^3-nitrogen centre but is apparently unknown in neutral media although it has been suggested[11] as an intermediate step in some "cycloadditions".
Path b (Scheme 2) could proceed either via a C-Michael addition or a concerted ene-reaction and a number of examples of this process have been reported.[12] Path c (Scheme 2) was first recognised by us[2,4] and path d, though preeminent in oximes[6,7] has not been reported for hydrazones although the reaction of alkylhydrazones (4a) and (4b) with methyl vinyl ketone[12], a particularly good Michael acceptor[13], to give (5a) and (5b) may involve a path d process.

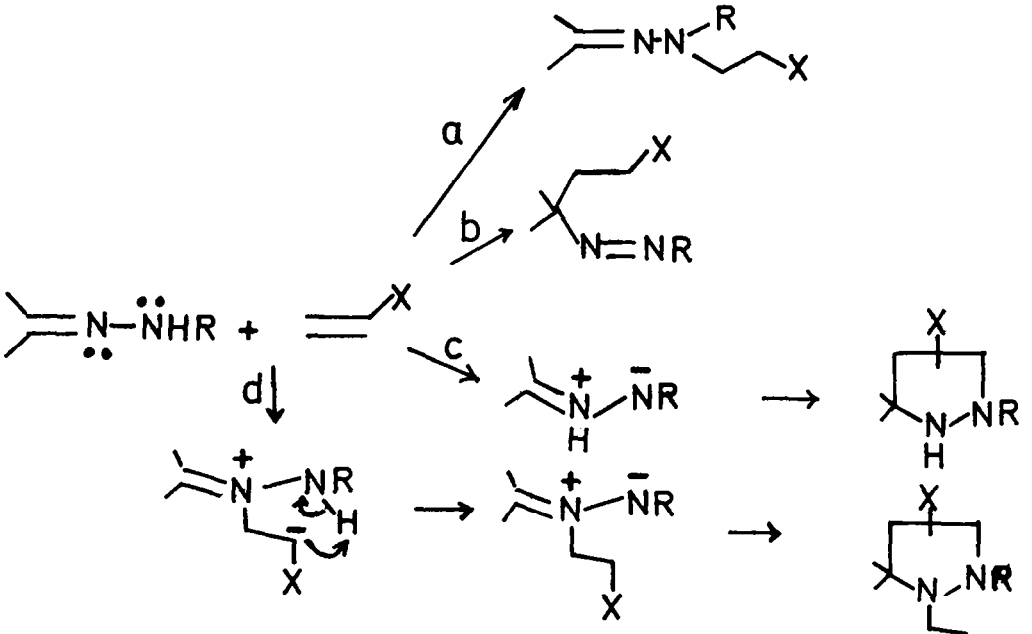
The hydrazone moiety can also potentially undergo $4\pi + 2\pi$ cycloaddition in the neutral (6), protonated (7) or anionic (8) forms. Prior to our work in neutral media Hesse[14] had observed the cycloaddition of aldehyde hydrazones to non-activated olefins in acidic (H_2SO_4-HOAc) media giving pyrazolidines and suggested a two-step mechanism via the imine N-protonated species (7). Related work using a catalytic amount of p-toluenesulphonic acid in boiling xylene showed cycloaddition also occurred to methyl propiolate.[15] It was later suggested that the acid catalysed reaction was an example of a $[3^+ + 2]$ concerted cycloaddition (7, arrows).[16] Subsequent to our preliminary communication[2] on the prototropic generation of azomethine imines (Scheme 2), path c) in neutral media, Hamelin et al. reported regio- and stereo-chemical studies of the cycloaddition of hydrazones to styrene and electronegative olefins in acidic media that supported the previously suggested $[3^+ + 2]$ concerted cycloaddition mechanism[17], and others have recently provided further examples.[18]
Intramolecular Cycloadditions.[2] There are two early reports of the reactions of phenylhydrazones with dimethyl acetylenedicarboxylate (ADE) in the absence of acids.[19,20] Low yields of mixtures of products (pyrazoles, pyrazolines) some of which incorporated two molecules of ADE were reported. The reactive intermediate was believed to be the nitrile imine (9)[19] or the zwitterion (10).[20]

We observe that the arylhydrazones (4c) and (4d) react with N-phenylmaleimide in degassed xylene at ~ 150°C (sealed tube) to give the corresponding pyrazolidines (11a, 84%) and (11b, 87%). When analogous reactions of (4c) and (4e) are carried out in boiling xylene with less rigorous exclusion of air, the pyrazolines (12a) and (12b) are obtained in substantially lower yield (25-48%). Hydrazone (13) reacts similarly to give (14) in ca. 25% yield, whilst (13) and ADE give (15, 41%). Assignment of stereochemistry to (11a), (11b) and (14) was made on the basis of n.O.e. experiments. Thus for (14) irradiation of H_A effects a 13% enhancement of the signal for H_B, whilst irradiation of H_B effects enhancement of H_A (12%) and H_C (15%). The marked drop in product yield when the hydrazones are reacted without rigorous exclusion of air reflects the sensitivity of hydrazones to autoxidation at the high temperatures used to effect the cycloaddition.[21]

≠ Geometrical isomers are ignored for brevity.



SCHEME 1



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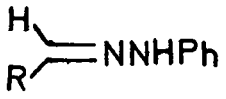
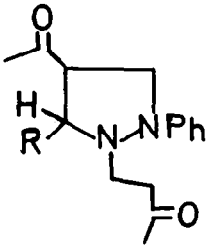
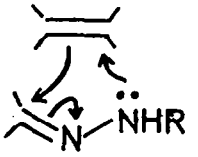


(4) a. R=i-Pr
b. R=Me
c. R=Ph
d. R=p-$MeOC_6H_4$
e. R=2-thienyl



(5) a. R=i-Pr
b. R=Me



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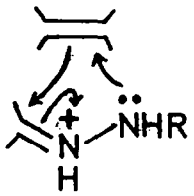

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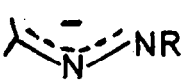


(8)

In the examples discussed so far there is no opportunity for ene-hydrazine equilibration and it was therefore of interest to study some cases where such equilibration might occur, to see if cycloaddition could still be achieved. When ethyl pyruvate was heated with phenylhydrazine and N-phenylmaleimide in ethanol in a sealed tube at 120-130°C the cycloadduct (16a) was obtained in 51% yield. Hydrazone (17) reacted in an analogous manner with N-phenylmaleimide to give (16b, 60%) and with ADE to give (18,44%).

In contrast, formaldehyde phenylhydrazone reacts with N-phenylmaleimide and methyl acrylate in boiling xylene, via path b (Scheme 2), to give the adducts (19, 85%) and (20, 70%) respectively.≠

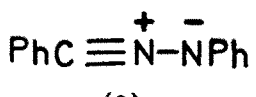
We have also briefly studied the cycloaddition reactions of tosylhydrazones (21a) and (21b) and of carbazone (22). When (21a) and N-phenylmaleimide were heated in boiling xylene for 4h the product (42%) was the cyclopropane derivative (23a). The tosylhydrazone (21b) reacted similarly to give (23b, 40%). The stereochemistry of (23a) and (23b) is assigned on the basis of the cyclopropyl proton coupling constants (J 1-3.5Hz). The cyclopropane derivatives (23a) and (23b) could arise in several ways one of which is 1,3-dipolar cycloaddition to give (24), followed by loss of sulphinic acid giving (25) and finally elimination of nitrogen to give (23). Related cyclopropyl forming reactions have been reported by others[22] and the thermal elimination of nitrogen from pyrazolines is well known.[23]

The carbazone (22) reacted with ADE in boiling xylene over 24h to give a mixture of products from which an ADE adduct formulated as (26) could be isolated in low (20%) yield. One possible route to (26) involves condensation of an initial azomethine imine cycloadduct with a further molecule of the carbazone.

Early work on N,N′-disubstituted hydrazones as precursors of azomethine imines[24] was correctly reinterpreted by Huisgen[25], and Dorn[26], and subsequently Oppolzer[27], showed the versatility and synthetic utility of N-alkyl-N^1-acyl-hydrazines. The low to moderate yields of cycloadducts encountered in our prototropic generation of azomethine imines prompted a comparison of the prototropic route with the in situ generation of azomethine imines from unsymmetrical N,N^1-disubstituted hydrazines (27) and aldehydes. Oppolzer has reported one example of the use of (27a) as an azomethine imine precursor.[27]

Heating (27a) with benzaldehyde and N-methylmaleimide in boiling xylene gave a 2:1 mixture (80%) of cycloadducts (28a) and (29a). Similarly (27a), pyridine 2-carboxaldehyde, and N-methylmaleimide gave a 1:5 mixture (62%) of (28b) and (29b) whilst p-chlorobenzaldehyde reacted with (27a) and N-methylmaleimide to give a 2:1 mixture (70%) of (28c) and (29c). The stereochemistry of (28) and (29) was assigned on the basis of n.O.e. experiments and the observation that the signal for the 4-H proton appears as a doublet (J ~ 8Hz) in (28) but as a singlet or narrowly split doublet (JO-2.5Hz) in (29). In contrast both (27a) and (27b) react with phenylglyoxal and N-methylmaleimide to give a single isomer (29d, 60%) and (29e, 50%) respectively. These latter cycloadditions occurred over 24 and 40h respectively but n.m.r. monitoring of the cycloadditions did not reveal any of the alternative stereoisomers. When cycloadduct (28b) was recycled through the reaction it partially isomerised to a 3.5:1 mixture of (28b) and (29b) suggesting that (29b) is largely formed directly and only a minor amount of (29b) arises by isomerisation. The reaction of (27a) with benzyl acrylate and pyridine 2-carboxaldehyde (xylene, 140°C, 7h) was studied to assess regiospecificity. A 1.3:1.6:1.0:1.6 mixture of (30a), (30b), (31a) and (31b) was obtained showing a total lack of regiospecificity in this case.

≠ Path b (Scheme 2) products can arise via a Michael addition or an ene reaction.



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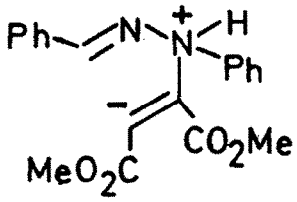

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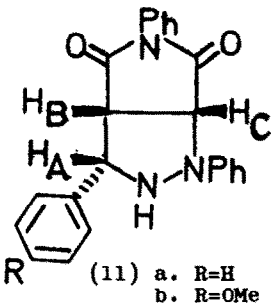
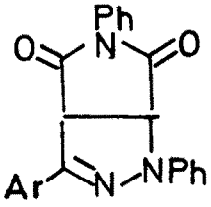
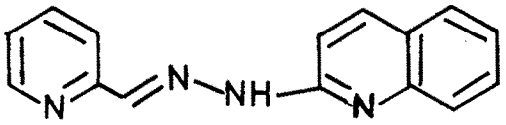


(11) a. R=H
b. R=OMe



(12) a. Ar=Ph
b. Ar=2-thienyl



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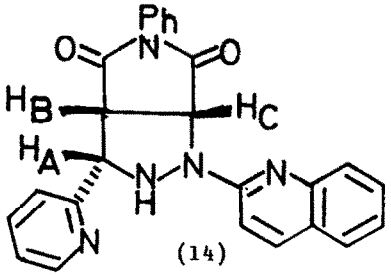

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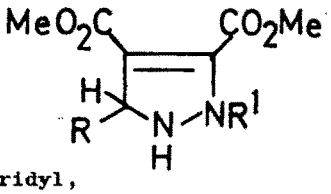
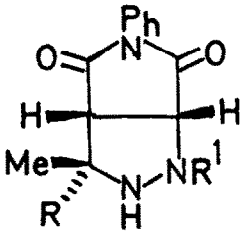
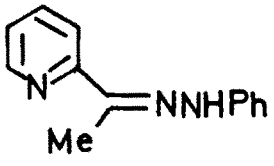


(15) R=2-pyridyl,
R^1=2-quinolinyl



(16) a. R=CO_2Et, R^1=Ph
b. R=2-pyridyl, R^1=Ph



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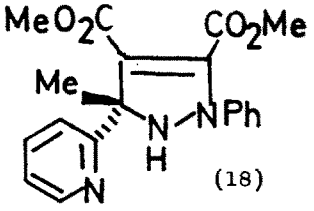

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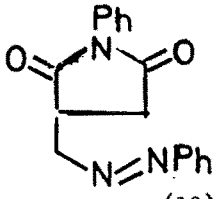

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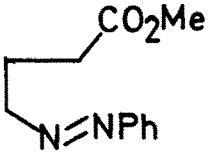

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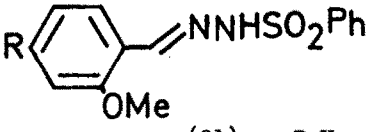
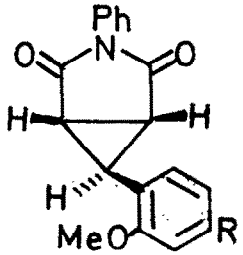
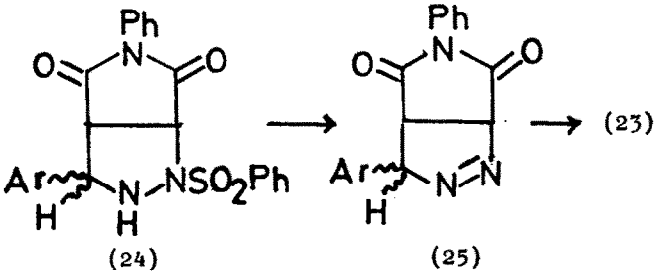


(21) a. R=H
b. R=OMe

(22)



(23) a. R=H
b. R=OMe



(24) (25) (23)

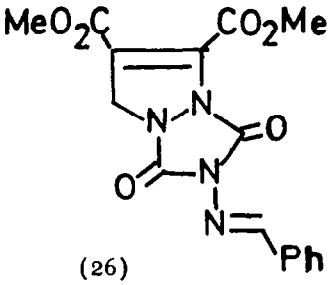
Intramolecular Cycloaddition.[8] The hydrazones (32a-c), (33a) and (33b) were prepared and studied as precursors for intramolecular azomethine imine cycloadditions.

Heating (32a) in boiling xylene for 6dy afforded (34a) in low yield (18%) and the pyridylhydrazone (32b) similarly gave (34b, 25%). The low yields again reflect the instability of hydrazones in air at elevated temperatures and the facile oxidation of pyrazolidines to pyrazolines under these conditions as discussed earlier. The acetylenic hydrazone (33a) gave a small amount (11%) of (34a) under analogous conditions. N.m.r. monitoring of this reaction showed the presence of (35) [δ 5.24(H_A) and 4.69(H_B)], but attempts to isolate this product [(34a):(35) ca 2.7:1] by chromatography were unsuccessful. The corresponding acetylenic pyridyl hydrazone (33b) gave (34b) in 50% yield. A contributing factor to the poor yields encountered in these intramolecular cycloadditions is the poor dipolarphilic reactivity of the unactivated terminal alkene and alkyne groups in (32a,b) and (33a,b). However, when the hydrazone (32c) bearing an activated alkene was heated in boiling xylene cycloaddition did not occur but instead the lactam (36, 66%) was formed. The genesis of (36) involves an intramolecular Michael addition, or an ene reaction,[12] giving (37), followed by azo-hydrazo prototropy giving (38) and finally 6-exo-trig cyclisation to (36). When the aldehyde (39a) was heated with hydrazone (27a) in boiling xylene the product (83%) consisted of a 10:1 mixture of cycloadducts (40a) and (41). The major isomer (40a) arises via an exo transition state. Assignment of stereochemistry to (41) is based on n.O.e. experiments. Thus irradiation of H_A effects a 10% enhancement of the signal for H_B whilst irradiation of H_B effects enhancement of H_A (6%) and CO_2Me (10%). Similarly n.O.e. experiments on (40a) showed an absence of enhancement of H_B when H_A was irradiated, although H_A and H_B are coupled (J 7.3Hz). The cycloaddition of (32c) in acidic media has been reported to give (40b, 45%).[28] When the aldehyde (39b) was heated with hydrazone (27a) in boiling toluene (Dean-Stark trap) for 8h n.m.r. analysis$^{\neq}$ of the reaction mixture showed it to comprise 1.7:1:1 mixture of (40c), (39b) and (32a). In this case the slow cycloaddition permits N-demethylation (42, arrows) to compete with cycloaddition.

Thus in neutral media* we observe that hydrazones react intermolecularly with electronegative olefins mainly by path c of Scheme 2, although in certain instances reaction via path b occurs. In intramolecular cases reaction occurs by path b with electronegative olefins and by path c with unactivated terminal alkenes and alkynes. However, cycloaddition yields are, in general, poor to moderate. Products arising via paths a and d were not observed although Hamelin et al. have reported some evidence for path a reactivity.[11] Our previous studies with imines in neutral[3] and acidic media[5,29] show they react solely by a path analogous to path c (Scheme 2) whilst in basic media imines undergo $4\pi + 2\pi$ anionic cycloadditions,[30,31] together in some cases with competing Michael additions.[31] Oximes in neutral media invariably react by a path analogous to path d (Scheme 2) with a few exceptions which apparently react by a path analogous to path c.[6,7]

$^{\neq}$ Integration of H_B (δ 3.30) for (40c), aldehyde proton (δ 10.54) of (39b) and imine proton (δ 8.13) of (32a).

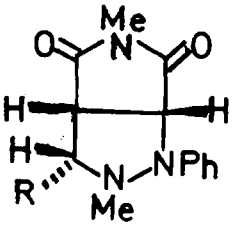
* The contiguous lone pairs present on the amino and imino nitrogen atoms in hydrazones and the lone pairs present on the imino nitrogen atom of imines and oximes render all three basic. This weak basicity is undoubtedly crucial to prototropic processes occurring in otherwise neutral media.



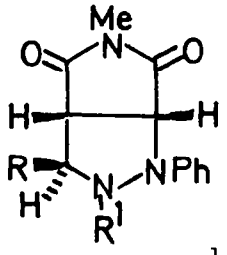
(26)

PhNHNHR

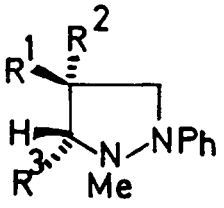
(27) a. R=Me
b. R=CH_2Ph



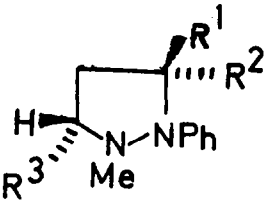
(28) a. R=Ph
b. R=2-pyridyl
c. R=p-ClC_6H_4



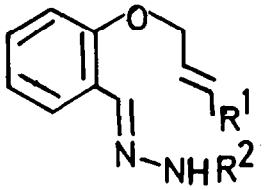
(29) a. R=Ph, R^1=Me
b. R=2-pyridyl, R^1=Me
c. R=p-ClC_6H_4, R^1=Me
d. R=PhCO, R^1=Me
e. R=PhCO, R^1=CH_2Ph



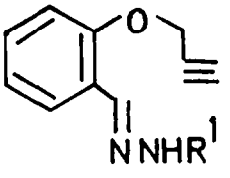
(30)



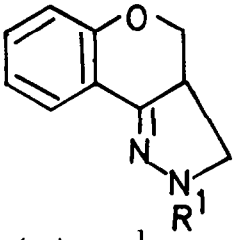
(31)
a. R^1=H, R^2=CO_2CH_2Ph, R^3=2-pyridyl
b. R^1=CO_2CH_2Ph, R^2=H, R^3=2-pyridyl



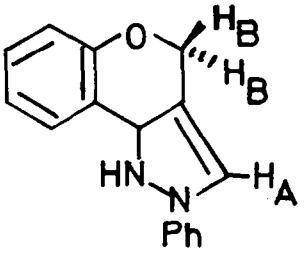
(32) a. R^1=H, R^2=Ph
b. R^1=H, R^2=2-pyridyl
c. R^1=CO_2Me, R^2=Ph



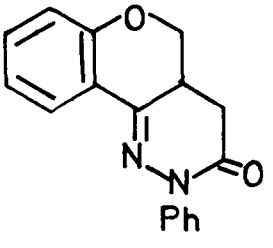
(33) a. R^1=Ph
b. R^1=2-pyridyl



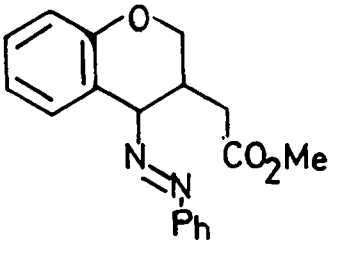
(34) a. R^1=Ph
b. R^1=2-pyridyl



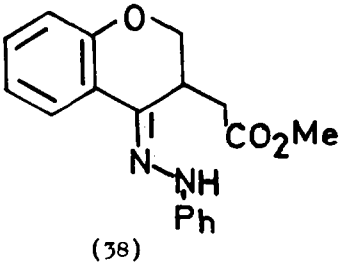
(35)



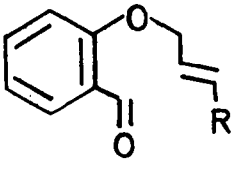
(36)



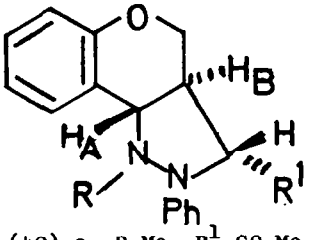
(37)



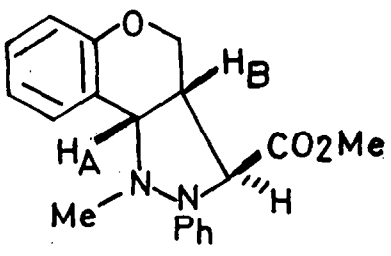
(38)



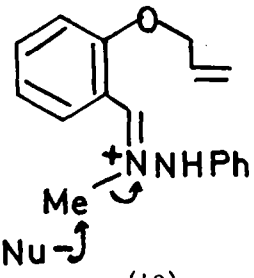
(39) a. R=CO_2Me
b. R=H



(40) a. R=Me, R^1=CO_2Me
b. R=H, R^1=CO_2Me
c. R=Me, R^1=H



(41)



(42)

Experimental. General details were as previously described.[3] Petroleum ether refers to the fraction b.p. 60-80°C. Flash chromatography was performed using Sorbsil C60-40/60 (Crosfields).

2,4,7-Triphenyl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octane (11a). A solution of benzaldehyde phenylhydrazone (196mg, 1 x 10^{-3}mole) and N-phenylmaleimide (170mg, 1 x 10^{-3}mole) in deuteriobenzene contained in an n.m.r. tube was degassed using three freeze-pump-thaw cycles on a vacuum frame and then sealed under vacuum. The solution was then heated at 140-150°C for 54h, monitoring the reaction by n.m.r. After cooling to room temperature the tube was opened, the solvent evaporated, and the residual oil crystallised from methylene chloride-petroleum ether to afford the product (310mg, 84%) as a buff powder, m.p. 74-77°C (Found: C, 74.55; H, 5.25; N, 11.05. $C_{23}H_{19}N_3O_2$ requires C, 74.80; H, 5.20; N, 11.35%); δ ($CDCl_3$ + 1 drop D_2O) 7.52-7.13 (m, 15H, ArH), 5.08 (d, 1H, J 1.7Hz, H_A), 4.77 (d, 1H, J 7.6Hz, H_C) and 4.08 (dd, 1H, H_B); m/z(%) 369 (M^+, 15), 367(50), 233(55) and 173(100).

4-(4-Methoxyphenyl)-2,7-diphenyl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octane (11b). Prepared in an analogous manner to the above from p-anisaldehyde phenylhydrazone (230mg, 1 x 10^{-3}mole). The product (340mg, 87%) precipitated from methylene chloride-petroleum ether as an off white powder, m.p. 80-83°C (Found: C, 72.40; H, 5.30; N, 10.25. $C_{24}H_{21}N_3O_3$ requires C, 72.15; H, 5.30; N, 10.50%); δ ($CDCl_3$ + 1 drop D_2O) 7.50-7.20 (m, 12H, ArH), 6.96 (m, 2H, ArH), 5.00 (d, 1H, J 1.7Hz, H_A), 4.75 (d, 1H, J 7.8Hz, H_C), 4.02 (dd, 1H, H_B) and 3.85 (s,3H,OMe) m/z(%) 399 (M^+, 10), 397(100), 293(20), 250(39) and 226(62).

2,4,7-Triphenyl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]oct-3-ene (12a). A solution of benzaldehyde phenylhydrazone (1.96g, 1 x 10^{-2}mole) and N-phenylmaleimide (1.73g, 1 x 10^{-2}mole) in o-xylene (50ml) was stirred and boiled under reflux for 48h. The solvent was then removed under reduced pressure to leave a brown oil which was triturated with ether-petroleum ether at -20°C to afford a gummy solid (2.2g). Subsequent treatment with charcoal in methylene chloride and crystallisation from methylene chloride-petroleum ether afforded the product (1.8g, 48%) as colourless needles, m.p. 192-194°C (Found: C, 75.10; H, 4.80; N, 11.30. $C_{23}H_{17}N_3O_2$ requires C, 75.20; H, 4.65; N, 11.45%); δ 8.00 (m, 2H, ArH), 7.80-7.00 (m, 13H, ArH), 5.30 (d, 1H, J 11Hz) and 5.00 (d, 1H); m/z(%) 367 (M^+, 100).

4-(2-Thienyl)-2,7-diphenyl-6,8-dioxo-2,3,7--triazabicyclo[3.3.0]oct-3-ene (12b). Prepared from thiophene-2-carboxaldehyde phenylhydrazone (2.02g) and N-phenylmaleimide (1.73g) in boiling xylene (50ml) for 3dy as described above. The product (940mg, 25%) crystallised from methanol as pale yellow plates, m.p. 214-216°C (Found: C, 67.30; H, 4.15; N, 11.10. $C_{21}H_{15}N_3O_2S$ requires C, 67.55; H, 4.05; N, 11.25%); δ 7.75-6.90 (m, 13H, ArH), 5.30 (d, 1H, 11Hz) and 4.90 (d, 1H); m/z(%) 373 (M^+, 100), 226(39), 202(31), 91(21) and 77(19).

2-(2-Quinolinyl)-4-(2-pyridyl)-7-phenyl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octane (14). Prepared from pyridine 2-carboxaldehyde-2-quinolinylhydrazone, and N-phenylmaleimide in boiling argon purged xylene for 2h as described above. The dark semi-solid crude product was triturated with ether-petroleum ether to yield a

white solid which was crystallised from methanol to afford the product (24%) as colourless plates, m.p. 209-211°C (Found: C, 71.50; H, 4.45; N, 16.45. $C_{25}H_{19}N_5O_2$ requires C, 71.25; H, 4.50; N, 16.65%); δ 7.20-7.90 (m, 15H, ArH), 6.90 (d, 1H, J 7.8Hz, H_C), 5.70 (d, 1H, J 12Hz, NH), 4.58 (dd, 1H, H_A) and 3.89 (dd, 1H, J 7.9 and 9.3Hz, H_B); m/z(%) 421 (M^+, 1), 343(1), 173(38) and 170(100).

1-(2-Quinolinyl)-3-(2-pyridyl)-4,5-di(methoxycarbonyl)4-pyrazoline (15a). A solution of pyridine 2-carboxaldehyde-2-quinolinylhydrazone (2.48g, 0.01mole) and ADE (1.44g, 0.01mole) in argon purged xylene (50ml) was boiled under reflux for 2h. Removal of the solvent and trituration of the residue with ether-petroleum ether afforded an orange yellow solid which was crystallised from methanol to afford the product (1.80g, 46%) as pale yellow plates, m.p. 173-174°C(Found: C, 64.65; H, 4.65; N, 14.00. $C_{21}H_{18}N_4O_4$ requires C, 64.60; H, 4.60; N,13.85%); δ 8.00-7.30 (m, 10H, ArH), 7.60 (s, 1H) and 3.73 and 3.61 (2 x s, 2 x 3H, OMe): m/z(%) 390 (M^+, 10), 312(100), 195(16) and 128(40).

Ethyl 4-methyl-2,7-diphenyl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octane 4-carboxylate (16a). A mixture of ethyl pyruvate (80mg, 0.73mmole), phenylhydrazine (74mg, 0.68mmole) and N-phenylmaleimide (89mg, 0.51mmole) in ethanol (3ml) was heated at 120-130°C for 72h in a sealed tube. On cooling yellow crystals of the product separated and were removed by filtration. Additional product was obtained by preparative t.l.c. of the residue obtained by evaporation of the filtrate. The combined fractions were recrystallised from ethanol to afford the product (100mg, 51%) as pale yellow needles, m.p. 174°C (Found: C, 66.65; H, 5.45; N, 11.10. $C_{21}H_{21}N_3O_4$ requires C, 66.50; H, 5.60; N, 11.05%); δ (pyridine-d_5) 7.72-6.93 (m, 10H, ArH), 5.39 (d, 1H, J 7.5Hz, 1-H), 4.40 (q, 2H, CH_2Me), 3.63 (d, 1H, 5-H), 1.45 (s, 3H, Me) and 1.28 (t, 3H, $CH_2\underline{Me}$); m/z(%) 379 (M^+, 52), 306(50), 265(32), 206(46) and 132(100); ν_{max} 3300, 1730 and 1710 cm^{-1}.

4-Methyl-4-(2-pyridyl)-2,7-diphenyl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octane (16b) Prepared from 2-acetylpyridine phenylhydrazone and N-phenylmaleimide in an analogous manner to that above. Heating was continued for 44.5h at 120-130°C. Work-up as above followed by crystallisation from chloroform-ethanol afforded the product (60%) as colourless needles, m.p. 211-212°C (Found: C, 71.30; H, 5.10; N, 14.50. $C_{23}H_{20}N_4O_2$ requires C, 71.85; H, 5.25; N, 14.55%), δ 8.65-6.65 (m, 14H, ArH), 6.05 (s, 1H, NH), 5.02 (d, 1H, 1-H), 3.48 (d, 1H, J 8.0Hz, 5-H) and 1.60 (s, 3H, Me); m/z(%) 384 (M^+, 17), 370(11), 369(41), 211(100) and 194(31).

1-Phenyl-3-(2-pyridyl)--3-methyl-4,5-di(methoxycarbonyl)4-pyrazoline (18). Prepared from 2-acetylpyridine phenylhydrazone and ADE in an analogous manner to that above. Heating was continued for 40 min. at 120-130°C. Preparative t.l.c. (silica, 1:1 hexane-ether) gave the cycloadduct (R_f 0.5) (44%) as a pale brown oil (Found: C, 64.30; H, 5.25; N, 11.70. $C_{19}H_{19}N_3O_4$ requires C, 64.60; H, 5.40; N, 11.90%); δ 8.55-6.65 (m, 9H, ArH), 4.99 (s, 1H, NH), 3.82 and 3.63 (2 x s, 2 x 3H, OMe) and 2.08 (s, 3H, Me); ν_{max}(film) 3350, 1700 and 1580 cm^{-1}.

3-Phenylazomethyl-N-phenylsuccinimide (19). A solution of formaldehyde phenylhydrazone (2g, 167mmole) and N-phenylmaleimide (2.88g, 167mmole) in xylene (40ml) was boiled under reflux under an argon atmosphere for 6h. The solvent was removed and the residual oil dissolved in ethanol and set aside at 0°C for a few hours during which the product crystallised. Recrystallisation from ethanol afforded the product (4.1g, 85%) as bright yellow needles, m.p. 91-93°C (Found: C, 67.75; H, 4.90; N, 14.30. $C_{17}H_{15}N_3O_2$ requires C, 69.60; H, 5.15; N, 14.35%); δ 7.70-7.25 (m, 10H, ArH), 4.60 (m, 2H, CH_2N), 3.52 (m, 1H), and 3.03 and 2.72 (2 x dd, 2 x 1H, J 18.3 and 9.0Hz, and J 18.3 and 5Hz respectively, ring CH_2); m/z(%) 293 (M^+, 2), 119(4), 106(5), 105(65), 91(6), 78(8), 77(100) and 51(11).

Methyl 4-phenylazobutanoate (20). Prepared in an analogous manner to that described above from formaldehyde phenylhydrazone and methyl acrylate. The product (70%) distilled as a pale yellow oil, b.p. 82-84°C/0.05mmHg (Found: C, 64.00; H, 6.80; N, 13.70. $C_{11}H_{14}N_2O_2$ requires C, 64.05; H, 6.85; N, 13.60%); δ 7.72--7.36 (m, 5H, ArH), 4.07 (t, 2H, NCH_2), 3.66 (s, 3H, OMe), 2.49 (m, 2H, CH_2CO_2Me) and 2.27 (m, 2H, CH_2); m/z(%) 206 (M^+, 4), 175(8), 105(40), 101(14), 78(10), 77(100), 59(9) and 51(11).

3-Phenyl-6-(2-methoxyphenyl)-2,4-dioxo-3-azabicyclo[3.1.0]hexane (23a). A solution of o-anisaldehyde tosylhydrazone (0.01mole) and N-phenylmaleimide (0.01mole) in dry xylene (100ml) was boiled under reflux for 4h. The solvent was then removed under reduced pressure and the residue crystallised from ether-petroleum ether to afford the product (42%) as colourless needles, m.p. 121-122°C (Found: C, 73.70; H, 5.15; N, 4.80. $C_{18}H_{15}NO_3$ requires C, 73.60; H, 5.25; N, 4.75%); δ 7.40-6.90 (m, 9H, ArH), 3.86 (s, 3H, OMe), 3.21 (t, 1H) and 2.95 (d, 2H, J 3.3Hz); m/z(%) 293 (M^+, 12), 250(64), 218(23), 173(40) and 125(100).

3-Phenyl-6-(2,4-dimethoxyphenyl)-2,4-dioxo-3-azabicyclo[3.1.0]hexane (23b). Prepared in analogous manner to that described above from 2,4-dimethoxybenzaldehyde tosylhydrazone and N-phenylmaleimide. The product (40%) crystallised from methanol as colourless prisms, m.p. 175-176°C (Found: C, 70.40; H, 5.25; N, 4.80. $C_{19}H_{18}NO_4$ requires C, 70.55; H, 5.30; N, 4.35%); δ 7.52-6.38 (m, 8H, ArH), 3.84 (s, 6H, 2 x OMe), 3.17 (br s, 1H) and 2.9 (br s, 2H); m/z(%) 323 (M^+, 74), 204(100), 176(26), 161(46) and 77(22).

3-Benzylideneimino-6-phenyl-7,8-di(methoxycarbonyl)-2,4-dioxo-1,3,5-triazabicyclo[3.3.0]octane (26). A solution of benzaldehyde ethyl carbazone (1.92g, 1 x 10^{-2}mmole) and ADE (1.42g, 1 x 10^{-2}mmole) in xylene was boiled under reflux for 24h. The solvent was removed under reduced pressure and the residual oil triturated with methylene chloride-petroleum ether to give a solid which was crystallised from the same solvent mixture. The product (550mg, 12.5%) crystallised as colourless prisms, m.p. 175-177°C (Found: C, 60.25; H, 4.20; N, 12.90. $C_{22}H_{18}N_4O_6$ requires C, 60.85; H, 4.20, N, 12.90%); δ 9.40 (s, 1H, CH=N), 8.00-7.21 (m, 10H, ArH), 6.30 (s, 1H, 6-H), and 4.05 and 3.70 (2 x s, 2 x 3H, OMe); m/z(%) 434 (M^+, 100), 365 (M-Ph, 15), and 288 [M-Ph-(CH=N-N=C=O), 20].

2,4-Diphenyl-3,7-dimethyl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octane (28a) and (29a) A solution of N-methyl-N′-phenylhydrazine (600mg, 4.9mmole), benzaldehyde (520mg, 4.9mmole) and N-methylmaleimide (550mg, 4.9mmole) in dry xylene (70ml) was boiled under reflux under a nitrogen atmosphere for 3h. The solvent was then removed under reduced pressure and the residue separated by flash chromatography eluting with 1:1 v/v ether-petroleum ether to afford (28a) (840mg) and (29a) (420mg), a combined yield of 80%.

(28a) Colourless plates from methanol, m.p. 183-185°C (Found: C, 70.70; H, 6.25; N, 13.30. $C_{19}H_{19}N_3O_2$ requires C, 71.00; H, 5.95; N, 13.05%); δ 7.43-7.25 (m, 10H, ArH), 4.74 (d, 1H, J 8.3Hz, 4-H), 4.42 (d, 1H, J 8.6Hz, 1-H), 4.19 (t, 1H, 5-H) and 2.64 and 2.46 (2 x s, 2 x 3H, 2 x NMe); m/z(%) 321 (M^+, 100), 306(17), 221(14), 209(59) and 195(18).

(29a) Colourless plates from methanol, m.p. 151-152°C; δ 7.48-6.82 (m, 10H, ArH), 4.37 (d, 1H, J 2.4Hz, 4-H), 3.95 (d, 1H, J 8.1Hz, 1-H), 2.97 (dd, 1H, 5-H), and 2.61 and 2.25 (2 x s, 2 x 3H, 2 x NMe).

2-Phenyl-3,7-dimethyl-4-(2-pyridyl)-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octane (28b) and (29b). Prepared from N-methyl-N′-phenylhydrazine, pyridine 2-carboxaldehyde and N-methylmaleimide in an analogous manner to that described above. Heating was continued for 5h. The crude product was separated by flash chromatography eluting with 7:3 v/v ether-petroleum to afford (28b) (10%) and (29b) (52%).

(28b) Cream plates from ether-petroleum ether, m.p. 105-107°C; δ 8.4-6.9

(m, 9H, ArH), 4.65 (d, 1H, J 8.4Hz, 4-H), 4.52 (d, 1H, J 8.7Hz, 1-H), 4.13 (t, 1H, 5-H), and 2.68 and 2.41 (2 x s, 2 x 3H, 2 x NMe); m/z(%) 322 (M^+, 51), 213(76), 119(31) and 79(100).

(29b) Colourless plates from methanol, m.p. 123-125°C (Found: C, 66.75; H, 5.50; N, 16.80. $C_{18}H_{18}N_4O_2$ requires C, 67.05; H, 5.65; N, 17.40%); δ 8.30-6.80 (m, 9H, ArH), 4.80 (s, 1H, 4-H), 4.74 (d, 1H, J 8.0Hz, 1-H), 4.62 (d, 1H, 5-H), and 3.09 and 2.67 (2 x s, 2 x 3H, 2 x NMe); m/z(%) 322 (M^+, 10), 233(12), 121(22) and 77(100).

2-Phenyl-3,7-dimethyl-4-(4-chlorophenyl)-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octane (28c) and (29c). Prepared from N-methyl-N -phenylhydrazine, p-chlorobenzaldehyde and N-methylmaleimide in an analogous manner to that described above. Heating was continued for 7h. The crude product was separated by flash chromatography eluting with 1:1 v/v ether-petroleum ether to afford (28c) (46%) and (29c) (24%).

(28c) Colourless plates from methanol, m.p. 180-182°C (Found: C, 64.30; H, 4.95; N, 12.05. $C_{19}H_{18}ClN_3O_2$ requires C, 64.15; H, 5.10; N, 11.80%); δ 7.46-7.24 (m, 9H, ArH), 4.74 (d, 1H, J 8.2Hz, 4-H), 4.40 (d, 1H, J 8.5Hz, 1-H), 4.16 (t, 1H, 5-H), and 2.70 and 2.44 (2 x s, 2 x 3H, 2 x NMe); m/z(%) 355 (M^+, 100), 340(19), 255(13), 245(16) and 243(46).

(29c) Colourless plates from methanol, m.p. 123-125°C; δ 7.10-6.53 (m, 9H, ArH), 3.90 (d, 1H, J 2.3Hz, 4-H), 3.70 (d, 1H, J 8.0Hz, 1-H), 2.53 (dd, 1H, 5-H), and 2.34 and 1.91 (2 x s, 2 x 3H, 2 x NMe).

2-Phenyl-3,7-dimethyl-4-benzoyl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octane (29d). Prepared from N-methyl-N′-phenylhydrazine, phenylglyoxal monohydrate and N-methylmaleimide in an analogous manner to that described above. Heating was continued for 12h. After removal of the solvent under reduced pressure the residue was triturated with ether-petroleum ether and the resulting solid crystallised from methanol to afford the product (60%) as colourless needles, m.p. 209-210°C (Found: C, 68.45; H, 5.65; N, 12.10. $C_{20}H_{19}N_3O_3$ requires C, 68.75; H, 5.50; N, 12.05%); δ 8.00-6.70 (m, 10H, ArH), 4.85 (s, 1H, 4-H), 4.40 (d, 1H, J 8.0Hz, 1-H), 4.00 (d, 1H, 5-H), and 2.70 and 2.50 (2 x s, 2 x 3H, 2 x NMe); m/z(%) 349 (M^+, 22), 244(100), 203(40) and 146(18).

2-Phenyl-3-benzyl-4-benzoyl-7-methyl-6,8-dioxo-2,3,7-triazabicyclo[3.3.0]octane (29e). Prepared from N-benzyl-N′-phenylhydrazine, phenylglyoxal monohydrate and N-methylmaleimide in an analogous manner to that described above. Heating was continued for 40h. The crude product was purified by flash chromatograph, eluting with 2:3 v/v ether-petroleum ether, followed by crystallisation from methanol to afford the product (50%) as colourless plates, m.p. 176-178°C (Found: C, 73.30; H, 5.45; N, 10.00. $C_{26}H_{23}N_3O_3$ requires C, 73.40; H, 5.45; N, 9.90%); δ 7.48-6.77 (m, 15H, ArH), 5.26 (s, 1H, 4-H), 4.83 (d, 1H, J 8Hz, 1-H), 4.30 (d, 1H, 5-H), 4.05 and 3.64 (2 x d, 2 x 1H, NCH_2), and 3.15 (s, 3H, NMe); m/z(%) 425 (M^+, 10), 334(13), 320(22), 105(100), 91(84) and 77(25).

1-Phenyl-2-methyl-3-(2-pyridyl)-4-carbobenzyloxypyrazolidine (30a) and (30b) and 1-phenyl-2-methyl-3-(2-pyridyl)-5-carbobenzloxypyrazolidine (31a) and (31b). Prepared from N-methyl-N′-phenylhydrazone, pyridine 2-carboxaldehyde and benzyl acrylate in an analogous manner to that described above. Heating was continued for 7h. Evaporation of the solvent left a viscous oil whose n.m.r. spectrum showed it to comprise a 1.3:1.6:1.0:1.6 mixture of (30a), (30b), (31a) and (31b). Flash chromatography eluting with 1:1 v/v ether-petroleum ether afforded pure samples of each isomer.

(30a) Colourless gum: δ 8.28-6.67 (m, 14H, ArH), 5.04 (dd, 2H, OCH_2), 4.59 (d, 1H, J 7.1Hz, 3-H), 4.10 (m, 1H, 4-H), 3.92 and 3.6 (2 x t, 2 x 1H, 2 x H-5) and 2.64 (s, 3H, NMe); ^1H NOEDS(%) irradiation of 3-H effects enhancement of 4-H(9); m/z(%) 373 (M^+, 53), 251(12), 238(17), 159(81) and 121(100).

(30b) Colourless plates from ether-petroleum ether, m.p. 81-82°C (Found: C, 74.00; H, 6.60; N, 10.95. $C_{23}H_{23}N_3O_2$ requires C, 73.95; H, 6.20; N, 11.25%); δ 8.30-6.57 (m, 14H, ArH), 5.06 (dd, 2H, OCH_2), 4.83 (d, 1H, J 4.8Hz, 3-H), 4.12 (m, 1H, 4-H), 3.98 and 3.43 (2 x t, 2 x 1H, 2 x 5-H), and 2.53 (s, 3H, NMe); m/z(%) 373 (M^+, 64), 240(17), 222(17) and 121(100).

(31a) Colourless plates from ether-petroleum ether, m.p. 171-173°C; δ (2:1 C_6D_6-$CDCl_3$) 8.39-6.43 (m, 14H, ArH), 4.90 (s, 2H, OCH_2), 4.18 (dd, 1H, J 7.0 and 9.0Hz, 3-H), 4.08 (t, 1H, 5-H), 3.30 and 2.70 (2 x m, 2 x 1H, 2 x 4-H) and 2.28 (s, 3H, NMe); ^{1}H NOEDS(%) irradiation of 4-H (δ 2.70) effects enhancement of 3-H)(11), 4-H (δ 3.30)(20) and 5-H(7); irradiation of 4-H (δ 3.30) only effects an enhancement of 4-H (δ 2.70)(19); m/z(%) 373 (M^+, 25), 214(17), 213(100), 107(45) and 79(99).

(31b) Colourless plates from methanol, m.p. 86-87°C; δ 8.37-6.67 (m, 14H, ArH), 5.15 (dd, 2H, OCH_2), 4.30 (t, 1H, J 5.2Hz, 3-H), 4.04 (t, 1H, J 7.6Hz, 5-H), 2.90 (m, 2H, 2 x 4-H) and 2.74 (s, 3H, NMe); m/z(%) 373 (M^+, 53), 251(13), 238(17) and 159(81).

2-Phenyl-4H-3,3a-dihydropyrazolo[2,3-d]benzo[b]pyran (34a). (a). A solution of 2-allyloxybenzaldehyde phenylhydrazone (7.1g) in xylene (40ml) was boiled under reflux under an argon atmosphere for 6dy. The solvent was removed under reduced pressure and the residual dark red oil chromatographed (SiO_2) eluting with 1:4 v/v ether-petroleum ether to afford the product (1.25g, 18%) as bright yellow rods from ethanol, m.p. 99-100°C (Found: C, 76.90; H, 5.60; N, 11.10. $C_{16}H_{14}N_2O$ requires C, 76.80; H, 5.65; N, 11.20%); δ 7.90-6.90 (m, 9H, ArH), 4.70 (dd, 1H), 4.20 (dd, 1H), 4.10 (dd, 1H), 3.80 (m, 1H) and 3.28 (dd, 1H); m/z(%) 250 (M^+, 100), 249(45), 146(5), 145(5), 130(5), 117(5), 104(8), 91(13) and 77(26).

(b) A solution of 2-(prop-2-ynyloxy)benzaldehyde phenylhydrazone in xylene was boiled under reflux under an argon atmosphere for 3 dy. Work-up as above afforded the product (11%) as bright yellow rods, m.p. 99-100°C.

2-(2-Pyridyl)-4H-3,3a-dihydropyrazolo[2,3-d]benzo[b]pyran (34b). (a) Prepared from 2-alloxybenzaldehyde 2-pyridylhydrazone in manner analogous to that described above. Heating was continued for 8dy at which time unchanged hydrazone (2.5g) and product (1.25g, 50%) were obtained on work-up. The product crystallised from ether-petroleum ether as bright yellow rods m.p. 120-121°C (Found: C, 71.70; H, 5.20; N, 16.70. $C_{15}H_{13}N_3O_3$ requires C, 71.55; H, 5.35; N, 16.55%); δ 8.20-6.70 (m, 8H, ArH), 4.70 (dd, 1H, CHO), 4.54 (t, 1H, CHO), 4.10 (t, 1H, CHN), 3.80 (m, 1H, 3a-H) and 3.5 (t, 1H, CHN); m/z(%) 251 (M^+, 72), 133(100), 79(11) and 78(24).

(b) Repeating the above reaction with 2-(prop-2-ynyloxy)benzaldehyde 2-pyridylhydrazone afforded the product (27%) after 8dy in boiling xylene.

2-Phenyl-3-oxo-4H-4,4a-dihydro-1,2-diazino[2,3-d]benzo[b]pyran (36). A solution of 2[(3-carbomethoxy-2-propenyl)oxy]benzaldehyde phenylhydrazone in xylene (40ml) was boiled under reflux under an argon atmosphere for 3dy. The solution was then concentrated to ca. 20ml and cooled in an ice bath causing precipitation of a pale brown solid which was crystallised from xylene (charcoal) to afford the product (2.0g, 66%) as colourless needles, m.p. 162-164°C (Found C, 73.55; H, 5.15; N, 9.90. $C_{17}H_{14}N_2O_2$ requires C, 73.35; H, 5.05; N, 10.05%); δ 8.11-6.86 (m, 9H, ArH), 4.50 (dd, 1H, J 5.6 and 10.7Hz, CHO), 3.96 (dd, 1H, J 10.7 and 12.0Hz, CHO), 3.50 (m, 1H, 4a-H), 2.79 (dd, 1H, J 6.6 and 16.0Hz, CHC=O) and 2.45 (dd, 1H, J 14.9 and 16.0Hz, CHC=O); m/z(%) 278 (M^+, 100); 236(14), 132(35), 91(16) and 77(34); ν_{max} 1670, 1620 and 1600 cm^{-1}.

1-Methyl-2-phenyl-3-methoxycarbonyl-pyrazolidino[2,3-d]benzo[b]pyran (40a) and (41). An equimolar solution of N-methyl-N′-phenylhydrazine and 2-[carbomethoxy-2-propenyl)oxy]benzaldehyde in xylene was boiled under reflux for 12h. Work-up in

the usual way followed by flash chromatography eluting with 1:1 ether-petroleum ether afforded (40a, 75%) and (41, 7.5%).

(40a) Colourless plates from ether-petroleum ether, m.p. 153-155°C (Found: C, 70.20; H, 6.28; N, 8.65. $C_{19}H_{20}N_2O_3$ requires C, 70.35; H, 6.20; N,8.65%); δ 7.40-6.60 (m, 9H, ArH), 4.30 (d, 1H, H_A), 4.10 (dd, 1H, CHO), 3.60 (m, 2H, CHO and NCHCO$_2$Me), 3.30 (s, 3H, OMe), 2.85 (m, 1H, H_B) and 2.60 (s, 3H, NMe); m/z(%) 324 (M^+, 100), 309(13), 265(67) and 205(3).

(41) Reddish gum, δ 7.00-7.40 (m, 9H, ArH), 4.38 (dd, 1H, H_A), 3.46-4.56 (m, 3H, overlapping signals, CH_2O and CHCO$_2$Me), 3.30 (s, 3H, OMe), 3.20 (m, 1H, H_B),and 2.5 (s, 3H, NMe).

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