Pergamon

Tetrahedron, Vol. 52, No. 43, pp. 13695-13702, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00821-6

An Efficient Procedure for the Synthesis of *N*-Alkenyl Derivatives of Six-Membered and Larger 1,2-Diaza Heterocycles.

Graziano Baccolini*, Athanase Munyaneza and Carla Boga

Dipartimento di Chimica Organica,"A. Mangini", Università, Viale Risorgimento 4, I-40136 Bologna, Italy

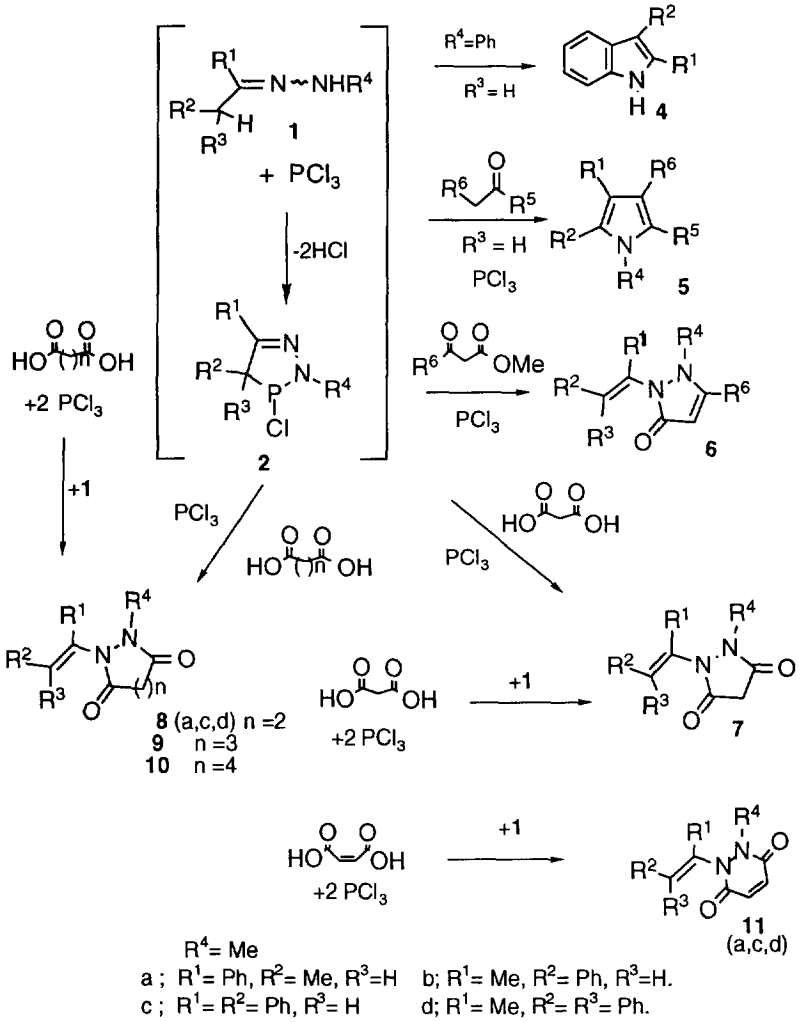
Abstract: The use of diazaphosphole derivatives generated in situ or the PCl_3/hydrazone combination can be applied in a novel efficient one-pot procedure for the synthesis at room temperature of the title six-, seven - and eight-membered rings using always high concentration of the reagents (0.2-0.5M). *N*-alkenyl derivatives of 1,2-diazaheterocycles such as **8** (perhydro-pyridazine-3,6-diones), **9** (perhydro-1,2-diazepin-3,7-diones), **10** (perhydro-1,2-diazocin-3,8-diones) and **11** (1,2-dihydro-pyridazine-3,6-diones) were obtained by reaction of PCl_3, ketone methylhydrazones and succinic, glutaric, adipic and maleic acids respectively. Changing the order of addition of reagents, or their simultaneous addition, gave identical results. In all the procedures the yields were good. The exclusive or prevalent formation of the *E* isomer was always observed. The *E*-configuration of the exocyclic double bond was deduced from some NOE experiments carried out on a *E,Z* mixture obtained by isomerization of the *E* isomer. Mechanism for the reaction is also proposed. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The most useful synthesis of pyridazines[1] (1,2-diazines) and their derivatives is the reaction between maleic anhydride or its substituted analogs and hydrazines or substituted hydrazines to give maleic hydrazides (1,2-dihydro-pyridazine-3,6-diones). Suitable reaction conditions can give either the corresponding pyridazinones directly or the intermediates are cyclized thermally in a subsequent step. With the saturated analogs, i.e. succinic anhydride and its derivatives, perhydro-pyridazine-3,6-diones are formed only in few cases[1b]. These perhydropyridazines are obtained by reduction of the corresponding maleic hydrazides. Cyclocondensation at several reaction conditions (100-150°C) between hydrazines and dicarboxylic acid derivatives is an obvious route to 1,2-diazepine[2] or 1,2-diazocine systems[2b]; however high dilution techniques are necessary in order to avoid polymerization . In this paper we describe a novel efficient one-pot procedure for the synthesis at room temperature of the above six-, seven - and eight-membered rings using always high concentrations of the reagents.

Some years ago we devised[3] that the reaction between a phenylhydrazone **1** (R^4= Ph) and PCl_3 gives indoles **4** in good yields after few minutes at room temperature. Successively we discovered[5] that chlorodiazaphospholine such as **2** or its ionic forms[4] are intermediates for a one-pot two steps synthesis of unsymmetrically substituted pyrroles **5**. When in the second step we used methyl acetoacetate, 1,2-dihydro-2-alkenyl-3*H*-pyrazol-3-ones **6** were obtained[6] (See Scheme 1). Recently we discovered[7] that when we use malonic acid the *N*-alkenylpyrazolidine-3,5-dione derivatives **7** are formed (75-85% yields) with the exclusive

formation of one isomer with the *E*-configuration of the *N*-alkenyl group when R^3= H. Moreover, changing the order of addition of reagents, or their simultaneous addition, gave identical results.



Scheme 1

RESULTS AND DISCUSSION

Objective of this study was the possible extension of the above reaction to the higher dicarboxylic acids to obtain the title six-membered and larger rings. At the beginning of this research it was difficult to find the best conditions to have good results. Obviously, the first experiments were carried out at the same or lower concentrations of the reagents than we did with malonic acid (0.05M) in order to avoid polymerization as in the conventional methods, but at these concentrations the corresponding dicarboxylic anhydride was observed as the major product. Surprisingly, good results were obtained as we decided to increase the concentration of the

reagents. Then, when we used succinic acid (0.2-0.5M), the perhydro-2-alkenyl-pyridazine-3,6-dione derivatives **8a,c,d** were formed (55-75% yields) (Scheme 1).

As previously reported in the case of malonic acid changing the order of addition of the reagents gave practically identical results. Then different procedures can be used. A first typical procedure consists of addition of a THF solution of succinic acid and equimolar amounts of PCl_3 to a dichloromethane solution of hydrazone **1** and equimolar amounts of PCl_3. Depending on the structure of the reactants, the time required for completion of the reaction is in a range of 2h to 5h. It should be noted that it is not necessary to expect the complete formation of **2** to have the best results.

A second and more simple procedure consists in the addition of a THF solution of hydrazone **1** to a THF solution of succinic acid and two equiv. of PCl_3 to give **8** with the same high yields.

Subsequently we have carried out the reaction with glutaric acid and adipic acid and afforded the corresponding seven- and eight-membered diazaheterocycles **9** and **10** at room temperature in about 60% and 50% yields respectively. The reaction can be performed in the above two ways using always high concentration of the reactants (0.5M) and the time required is in a range of 4-5h. Only small amounts of by-products due probably to polimerization were observed. On heating the reaction mixture in THF under reflux compounds **9** and **10** were obtained in the same yields but in minor time (1-2h).

A slow hydrolysis of **9** and **10** was also observed during the work up, noting their convertion into the ketone of starting hydrazone.

With the same procedures maleic hydrazides **11** were also obtained and high concentrations of the reagents were needed in order to avoid the anhydride formation. Obviously the reaction with fumaric acid does not give compounds **11**. Compounds **8, 9, 10** and **11** were purified by silica gel column chromatography. Their structures were established from their spectroscopic properties (See Table). The presence of carbonyl groups was easily detected through the IR absorption at about 1670-1650 cm^{-1}. In the cases **a,b** and **c** the prevalent formation of the *E*-isomer was observed. (*E/Z* ratio of about 9: 1 at the end of reaction). It should be noted that in the early part of the reaction only the *E*-isomer was detected. The Z-isomer was formed by isomerization in the acidic reaction medium . The *E*-configuration was deduced from NOE experiments carried out on a *E,Z* mixture of some compounds.

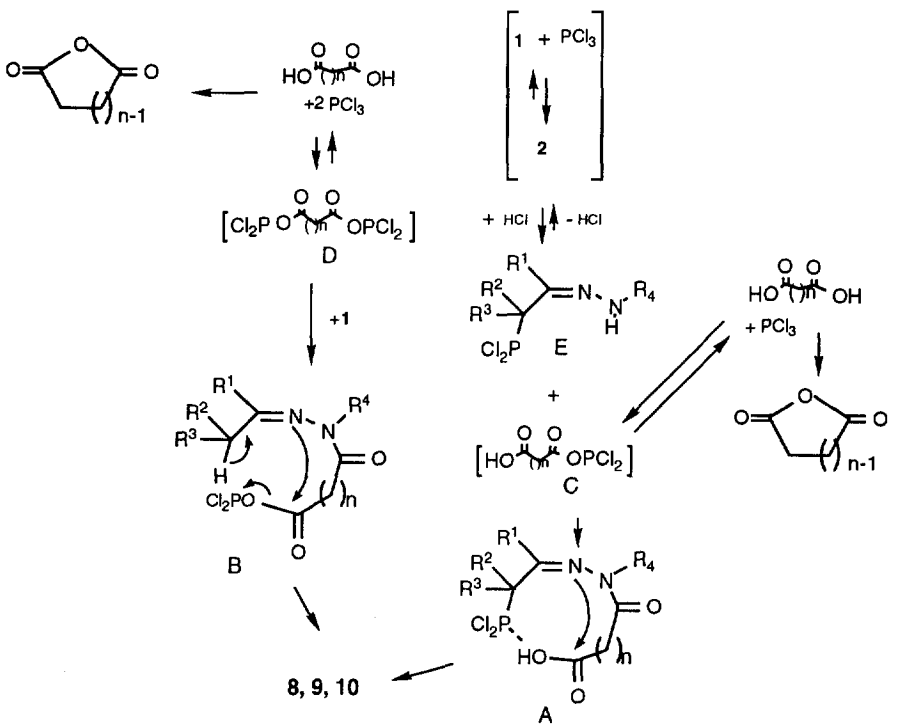
Compounds **8, 9, 10** and **11** are new series of perhydro-pyridazine-3,6-diones, perhydro-4H-1,2-diazepin-3,7-diones, perhydro-1,2-diazocin-3,8-diones and 1,2-dihydro-pyridazine-3,6-diones respectively and, bearing a *N*-alkenyl group, are likely to be difficult to prepare by conventional methods.

The explanation of this facile formation of larger rings without the use of high dilution techniques is probably due to the different nature of the two nitrogen atoms in **1** or in the ring opened intermediate **E** derived from **2** (See Scheme 2). The amine nitrogen in **1** or **E** is more prone to react with the activated carboxylic acid **D** or **C** respectively than the less nucleophilic immine nitrogen. Consequently only after the first attack which gives intermediates such as **A** or **B** the imine nitrogen is activated to give the second attack with consequent cyclization. In this manner the intramolecular cyclization is favoured more than a possible polymerization. Presumably these intermediates lower the entropic factors which disfavour the seven-membered and larger rings closure.

The necessity of high concentration of the reagents (0.1-1M) is due to the fact that in this manner the condensation to give **A** or **B** is favoured over the competing reaction which gives the corresponding dicarboxylic anhydride (See Scheme 2). In fact , comparisons at the same high concentrations were made of the rate of

formation of the 1,2-diaza heterocycles and of formation of the corresponding anhydrides from dicarboxylic acids and PCl_3. These experiments confirmed a significantly faster reaction in the case of 1,2-diaza heterocycles formation. When we used low concentrations after several hours only the anhydride was observed. These results indicate also that the anhydride cannot be an intermediate of the cyclocondensation which gives the 1,2-diaza heterocycles. It should be noted that high concentrations are not required with malonic acid because malonic anhydride is disfavoured by ring strain.

In addition, the reaction between the anhydrides and hydrazones **1** does not give the corresponding diaza heterocycles even if the reaction is carried out for several hours in refluxing THF. This fact confirms that the true intermediates derived from dicarboxylic acid and PCl_3 cannot be either the anhydride or the acid chloride as reported[7] previously. Presumably intermediates such as **D** or **C** (or similar forms) are operative in this reaction and the $OPCl_2$ group activates the carbonyl group to undergo a nucleophilic attack.



Scheme 2

In conclusion, the results reported here reveal that the use of PCl_3/hydrazone combination provides an efficient route to six-, seven-, and eight-membered 1,2-diaza heterocycles and the proposed mechanism suggests that this method could be used with other bifunctional reagents to produce a large number of new *N*-alkenyl - 1,2-diaza heterocycles.

Table : HRMS and ^{1}H NMR[a] Data of **8,9,10** and **11**

Comp.	Exact Mass (calc.)	δ_H(CDCl3)
E-8a	244.1212 (244.1210)	1.85 (d, 3H, J = 7.0 , CH_3-CH=), 2.70-2.95 (m, 4H, $(CH_2)_2$, 3.03 (s, 3H, 1-Me), 6.30 (q, J=7.0 , 1H, CH=), 7.25-7.45 (m, 5H, ArH).
Z-8a[b]	244.1212 (244.1210)	1.90(d, 3H, J = 7.4 , CH_3CH=), 2.55-2.80 (m, 4H, $(CH_2)_2$), 3.10 (s, 3H, 1-Me), 6.10 (q, J = 7.4 , 1H, -CH=), 7.20-7.40 (m,5H, ArH).
E-8c	306.1368 (306.1362)	2.58-2.65 (m, 2H, CH_2), 2.74-2.81 (m, 2H, CH_2), 3.14 (s, 3H, 1-Me), 6.85 (s, 1H, PhCH=), 7.05-7.40 (m, 10H, ArH).
8d	320.1525 (320.1523)	1.90-2.13 (m, 2H, CH_2), 2.11 (s, 3H, Me-C=), 2.40-2.60 (m, 2H, CH_2), 3.14 (s, 3H, 1-Me), 7.11-7.40 (m, 10H, ArH).
E-9a	258,1365 (258,1368)	1.74 (d, 3H, J=7.2 , CH_3CH=), 2.10-2.70 (m, 6H, $(CH_2)_3$), 3.19 (s, 3H, 1-Me), 5.91 (q, 1H, J=7.0 , -CH=), 7.21-7.39 (m, 5H, ArH).
Z- 9a[b]		1.76 (d, 3H, J=7.0 , CH_3CH=), 2.15-2.80 (m, 6H, $(CH_2)_3$), 3.12 (s, 3H, 1-Me), 5.95 (q, 1H, J=7.0, -CH=) 7.22-7.33 (m, 5H, ArH).
E- 9b	258,1366 (258,1368)	2.10 (s, 3H, CH_3-C=), 2.20-2.90 (m, 6H, $(CH_2)_3$), 3.13 (s, 3H, 1-Me), 6.50 (s, 1H, CH=), 7.22-7.38 (m, 5H, ArH).
E-9c	320,1522 (320,1525)	2.1-2.7 (m, 6H, $(CH_2)_3$), 3.24 (s, 3H, 1-Me), 6.68 (s, 1H, -CH=), 6.90-7.40 (m, 10H, ArH).
Z -9c[b]		2.00-2.70 (m, 6H, $(CH_2)_3$), 2.97 (s, 3H, 1-Me), 6.81 (s, 1H, -CH=), 7.30-7.50 (m, 10H, ArH).
E-9d	334,1679 (334,1681)	1.99 (s, 3H, CH_3C=), 2.06-2.44 (m, 6H, $(CH_2)_3$), 3.00 (s, 3H, 1-Me) 7.20-7.30 (m, 10H, ArH).
E-10a	272,1524 (272,1525)	1.72 (d, 3H, J=7.2 Hz, CH_3CH=), 1.74-2.52 (m, 8H, $(CH_2)_4$), 3.21 (s, 3H, 1-Me), 5.87 (q, 1H, J=7.2 , -CH=), 7.20-7.40 (m, 5H, ArH).
E-10b	272,1526 (272,1525)	1.59-2.44 (m, 8H, $(CH_2)_4$), 2.06 (s, 3H, CH_3C=), 3.09 (s, 3H, 1-Me), 6.36 (s, 1H, CH=), 7.12-7.31 (m, 5H, ArH).
E-10c	334,1680 (334,1681)	1.80-2.50 (m, 8H, $(CH_2)_4$), 3.29 (s, 3H, 1-Me), 6.65 (s, 1H, -CH=), 6.94-7.40 (m, 10H, ArH).
E-10d	348,1837 (348,1838)	1.54-2.31 (m, 8H, $(CH_2)_4$), 1.94 (s, 3H, CH_3C=), 3.00 (s, 3H, 1-Me), 7.19-7.35 (m, 10H, ArH).
E-11a	242, 1055 (242, 1057)	2.07 (d, J=7;4), 3H, CH_3C=), 3.35 (s, 3H, 1-Me), 6.20 (q, J =7.4, 1H, -CH=), 7.05-6.90 (AB system , 2H, 2 -CH=), 7.25-7.45 (m, 5H, ArH).
E-11c	304,1212 (304,1210)	3,41 (s , 3H,1-Me), 6.6- 6.97 (AB system, 2H, 2 CH=), 7.15-7.30 (m, 10H, ArH).
11d	318,1368 (318,1362)	2.15 (s, 3H, CH_3C=), 3.50 (s, 3H, 1-Me), 6.89-6.91 (AB system, 2H, 2 -CH=), 7.15-7.35 (m, 10H, ArH).

[a] ^{1}H-NMR spectra were obtained from $CDCl_3$ solution. δ with respect to $SiMe_4$ as internal standard (J values are in Hz). [b]Spectrum obtained from a *E,Z* mixture (9:2).

EXPERIMENTAL SECTION

General. All chemicals and solvents were of reagent grade. ^{1}H-NMR spectra were recorded at 200 MHz with a Gemini 200 instrument. Chemical shifts are given in ppm from Me_4Si. Mass spectra were recorded with a VG 7070 spectrometer or with an HP-5890 gas-chromatograph equipped with a methyl silicone capillary column and by an HP-5970 mass detector. IR spectra were obtained in CH_2Cl_2 in a Perkin Elmer 1600 spectrophotometer. Mps were determined with a Buchi apparatus. The purity of all the products was checked by TLC, GC-MS and ^{1}H-NMR spectra. Commercial PCl_3 was used without further purification. Yields are based on starting quantities of the dicarboxylic acid. Flash chromatography was performed in a Gilson apparatus.

Hydrazones. These were obtained by heating the respective hydrazine and ketone together in equivalent amounts in benzene solution at reflux for *ca.* 2 h. under Dean-Stark conditions. After drying and removal of the solvent the crude products were used immediately to avoid their decomposition.

First Typical Procedure for the Synthesis of 8, 9, 10 and 11. Phosphorus trichloride (10 mmol) was added at room temperature to a stirred dichloromethane solution (10 ml) of a hydrazone (10 mmol). The mixture was allowed to react at room temperature for few minutes. After about 10-15 min a THF solution (15 ml) of dicarboxylic acid(10 mmol) and further PCl_3 (10 mmol) were added to the mixture which was kept at room temperature for about 2-5h. The course of this stage of the reaction was followed by GC-MS analysis and TLC. Evaporation under reduced pressure using a Rotavapor was operated to remove the solvent . The crude oil or solid was dissolved in dichloromethane and washed with water and then with saturated sodium carbonate and dried over sodium sulfate. The solvent was evaporated under reduced pressure to give crude product **8, 9, 10** and **11** which were purified by crystallization or by silica gel column chromatography. These compounds were characterized essentially by ^{1}H NMR, mass spectrometry (see Table 1).

Second Typical Procedure for the Synthesis of 8, 9, 10 and 11. To a THF solution (15 ml) of dicarboxylic acid (10 mmol) was added PCl_3 (20 mmol) and the mixture was allowed at room temperature; after few minutes a THF solution (50 ml) of hydrazone **1** was added to the reaction mixture and stirred for about 2-5 h. Compounds **8, 9 ,10** and **11** were isolated by the same procedure used above. It should be noted that the concentration of the reagents can vary into a range of 0.2-0.5M depending on the solubility of the dicarboxylic acid being used. Both procedures give practically identical results. However, the second procedure might be preferred as the simplest one.

1-Methyl-2-(1-phenylprop-1-enyl)perhydro-pyridazine-3,6-dione (*E*-8a);

After 5h of reaction ***E*-8a**, impure of traces of the *Z*-isomer, was obtained as white solid (66 %yield), R_f 0.34 (diethyl ether-dichloromethane 2:1 as eluent); IR: ν(CO) 1673 cm^{-1}. (Found: C, 68.4; H, 6.6; N,11.5. $C_{14}H_{16}N_2O_2$ requires C, 68.8; H, 6.6; N,11.2).

1-Methyl-2-(1,2-diphenylvinyl)perhydro-pyridazine-3,6-dione(*E*-8c);

After 5h of reaction ***E*-8c** impure of traces of the *Z*-isomer was obtained as pale yellow solid (73 %yield), R_f 0.41 (diethyl ether -dichloromethane 2:1 as eluent). IR: ν(CO) 1679 cm^{-1} (Found: C, 74.8; H, 5.8; N, 9.0.$C_{19}H_{18}N_2O_2$ requires C, 74.5; H, 5.9, N, 9.1).

1-Methyl-2-(1-methyl-2,2-diphenylvinyl)perhydro-pyridazine-3,6-dione (8d);
After 6h of reaction **8d** was obtained as pale yellow solid, m.p. 107-108°C (75 %yield), Rf 0.42 (diethyl ether-dichloromethane 2:1 as eluent) IR : ν(CO) 1673 cm^{-1}. (Found: C, 74.6; H, 6.2; N, 8.6. $C_{20}H_{20}N_2O_2$ requires C, 75.0; H, 6.3; N, 8.6).

1-Methyl-2-(1-phenylprop-1-enyl)perhydro-1,2-diazepine-3,7-dione (*E*-9a);
After 3h of reaction ***E*-9a** was obtained as white solid, m.p. 142-143°C (45 % yield), Rf 0.25 (diethyl ether - dichloromethane 3:1 as eluent); IR: ν(CO) 1674 cm^{-1}. ***Z*-9a** (Rf 0.26) was isolated as white solid (20 % yield), impure of traces of the *E*-isomer . (Found: C, 69.5; H, 7.1; N, 10.9. $C_{15}H_{18}N_2O_2$ requires C, 69.7; H, 7.0, N, 10.9).

1-Methyl-2-(1-methyl-2-phenylvinyl)perhydro-1,2-diazepine-3,7-dione (*E*-9b);
After 3h of reaction ***E*-9b** was obtained as white solid, m.p. 108-109°C (55 % yield), Rf 0.25 (diethyl ether - dichloromethane 3:1 as eluent); IR: ν(CO) 1674 cm^{-1} ***Z*-9b** (Rf 0.26) was obtained in very small amounts and impure of the *E*-isomer. (Found: C, 69.5; H, 7.1; N, 10.9. $C_{15}H_{18}N_2O_2$ requires C, 69.7; H, 7.0, N, 10.9).

1-Methyl-2-(1,2-diphenylvinyl)perhydro-1,2-diazepine-3,7-dione (*E*-9c);
After 3h of reaction ***E*-9c** was obtained as white solid, m.p. 156-157°C (55 % yield), Rf 0.28 (diethyl ether - dichloromethane 3:1 as eluent); IR: ν(CO) 1674 cm^{-1}. ***Z*-9c** (Rf 0.35) was obtained in very small amounts (8%) and impure of the *E*-isomer.
(Found: C, 74.6; H, 6.2; N, 8.6. $C_{20}H_{20}N_2O_2$ requires C, 75.0; H, 6.3; N, 8.6).

1-Methyl-2-(1-methyl-2,2-diphenylvinyl)perhydro-1,2-diazepine-3,7-dione (9d);
After 4h of reaction **9d** was obtained as white solid, m.p. 172-173°C (65 % yield), Rf 0.35 (diethyl ether - dichloromethane 3:1 as eluent); IR: ν(CO) 1665 cm^{-1}, (Found: C, 75.5; H, 6.5; N, 8.4. $C_{21}H_{22}N_2O_2$ requires C, 75.4; H, 6.6, N, 8.4).

1-Methyl-2-(1-phenylprop-1-enyl)perhydro-1,2-diazocine-3,8-dione (*E*-10a);
After 4h of reaction ***E*-10a** was obtained as white solid, m.p. 112-133°C, (45 % yield) Rf 0.32 (diethyl ether - dichloromethane 3:1 as eluent); IR: ν(CO) 1660 cm^{-1}. ***Z*-10a** was isolated impure of the *E*-isomer . (Found: C, 71.1; H, 7.2; N, 10.0. $C_{16}H_{20}N_2O_2$ requires C, 70.6; H, 7.4, N, 10.3).

1-Methyl-2-(1-methyl-2-phenylvinyl)perhydro-1,2-diazocine-3,8-dione (*E*-10b);
After 3h of reaction ***E*-10b** was obtained as white solid, impure of traces of Z-isomer (55 % yield), Rf 0.29 (diethyl ether -dichloromethane 3:1 as eluent); IR: ν(CO) 1661 cm^{-1}. ***Z*-10b** (Rf 0.31) was obtained in very small amounts and impure of the *E*-isomer. (Found: C, 71.0; H, 7.5; N, 10.0. $C_{16}H_{20}N_2O_2$ requires C, 70.6; H, 7.4, N, 10.3).

1-Methyl-2-(1,2-diphenylvinyl)perhydro-1,2-diazocine-3,8-dione (*E*-10c)
After 4h of reaction ***E*-10c** was obtained as white solid, m.p. 129-130°C (55 % yield), Rf 0.32 (diethyl ether - dichloromethane 3:1 as eluent); IR: ν(CO) 1656 cm^{-1}. ***Z*-10c** (Rf 0.35) was obtained in very small amounts (8%) and impure of the *E*-isomer. (Found: C, 75.1; H, 6.9; N, 8.4. $C_{21}H_{22}N_2O_2$ requires C, 75.4; H, 6.7; N, 8.4).

1-Methyl-2-(1-methyl-2,2-diphenylvinyl)perhydro-1,2-diazepine-3,7-dione (10d);
After 5h of reaction **10d** was obtained as white solid, m.p. 158-159°C, (64 % yield) Rf 0.36 (diethyl ether - dichloromethane 3:1 as eluent); IR: ν(CO) 1656 cm^{-1}. (Found: C, 76.2; H, 6.8; N, 7.8. $C_{22}H_{24}N_2O_2$ requires C, 75.8; H, 7.0, N, 8.0).

1-Methyl-2-(1-phenylprop-1-enyl)1,2-dihydro-pyridazine-3,6-dione (*E*-11a);
After 5h of reaction ***E*-8a**, impure of traces of the Z-isomer, was obtained as white solid (66 %yield), Rf 0.34 (diethyl ether-dichloromethane 2:1 as eluent); IR: ν(CO) 1652 cm^{-1} (Found: C, 69.0; H, 5.7; N,11.5. $C_{14}H_{14}N_2O_2$ requires C, 69.4; H, 5.8; N,11.6).

1-Methyl-2-(1,2-diphenylvinyl)1,2-dihydro-pyridazine-3,6-dione (*E*-11c);
After 5h of reaction ***E*-11c** impure of traces of the Z-isomer was obtained as pale yellow solid (73 %yield), Rf 0.41 (diethyl ether-dichloromethane 2:1 as eluent). IR: ν(CO) 1656 cm^{-1} (Found: C, 75.5; H, 5.2; N, 9.2. $C_{19}H_{16}N_2O_2$ requires C, 75.0; H, 5.3, N, 9.2).

1-Methyl-2-(1-methyl-2,2-diphenylvinyl)1,2-dihydro-3,6-pyridazinedione (8d);
After 6h of reaction **8d** was obtained as pale yellow solid, m.p. 107-108°C (75 %yield). Rf 0.42 (diethyl ether-dichloromethane 2:1 as eluent), IR: ν(CO) 1655 cm^{-1} (Found: C, 75.0; H, 5.6; N, 8.6. $C_{20}H_{18}N_2O_2$ requires C, 75.4; H, 5.7; N, 8.8.)

Acknowledgements. This work has been carried out in the frame of the "Progetto di Finanziamento Triennale, Ateneo di Bologna". Thanks are also due to Consiglio Nazionale delle Ricerche (CNR-Roma) and Ministero della Ricerca Scientifica e Tecnologica (MURST) for financial support.

REFERENCES AND NOTES

1. Tisler, M.; Stanovnik, B., Pyridazines and their Benzo Derivatives. In *Comprehensive Heterocyclic Chemistry,* Pergamon Press, New York 1984, Vol 3 Katrizky, A.R; Rees, C.W., Eds.; pp. 1-56 and references cited therein. b) Feuer, H.; Bachman, G.B.; White, E. H., *J. Am. Chem. Soc.*, **1951**, *73*, 4716.
2. Sharp, J.T., Seven-membered Rings with Two or More Heteroatoms. In *Comprehensive Heterocyclic Chemistry,* Pergamon Press, New York 1984, Vol 7 Katrizky, A.R.; Rees, C.W., Eds. Part 5 Lwowski, W. Ed.; pp. 594-615. (b) More, J. A; Anet, F.A. Eight-membered Rings. In *Comprehensive Heterocyclic Chemistry,* Pergamon Press, New York 1984, Vol 7 Katrizky, A. R; Rees, C.W., Eds. Part 5 Lwowski, W. Ed; pp 66-671.
3 (a) Baccolini, G.; Dalpozzo, R.; Errani, E. *Tetrahedron,* **1987**, *43,* 2775-2760 and references cited therein.; (b) Baccolini, G.; Dalpozzo; R.; Todesco, P.E. *J. Chem. Soc., Perkin. Trans. 1,* **1988**, 971-973.
4. Chlorodiazaphospholine **2** should be in equilibrium with the corresponding phosphenium chloride as reported by Luber, J. and Schmidpeter, A. *Angew . Chem. Int . Ed . Engl .* **1976**, *18*, 112-113.
5. Baccolini, G., *J. Chem. Soc., Perkin Trans. 1,* **1989**, 1053-1056.
6. (a) Baccolini, G.; Sgarabotto, P. *J.Chem. Soc.,Chem.Commun.*, **1991**, 34-35; (b) Baccolini, G.; Evangelisti, D.; Rizzoli, C.; Sgarabotto, P. *J. Chem. Soc., Perkin. Trans.1,* **1992**, 1729-1733. c) Baccolini, G.; Biondi, D. *Heteroatom Chem.* **1993**, *4* , 497-502.
7. Baccolini, G.; Gianelli, M., *Tetrahedron,* **1995**, *51,* 9487-*9492.*

(*Received in UK* 18 *July* 1996; *revised* 10 *September* 1996; *accepted* 12 *September* 1996)