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A Convenient Synthesis of Quinazoline Ring by Tandem Aza-Wittig Reaction/Electrocyclic Ring Closure

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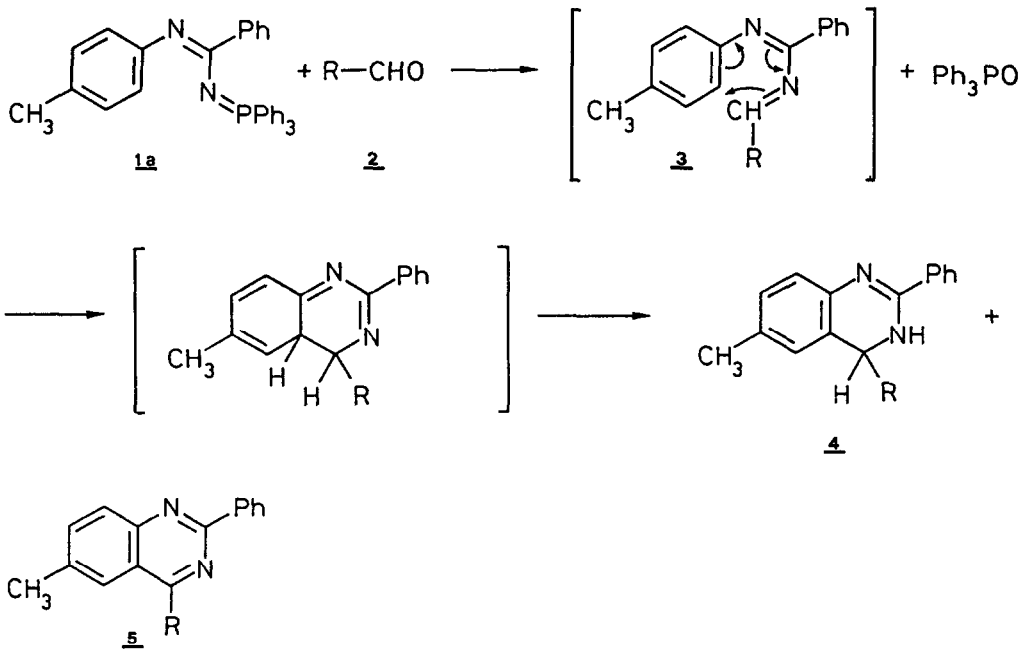
Abstract: 3,4-Dihydroquinazolines and Quinazolines were prepared starting from N'-aryl-N-(triphenylphosphoranilidene)-carboximidamides and aliphatic or aromatic aldehydes. The mechanism of the reaction is discussed.

In a recent short comunication[1] we reported a new synthesis of quinazolines from N'-(4-methylphenyl)-N-(triphenylphosphoranilidene)-benzenecarboximidamide **1a** and aldehydes **2**. The reaction, which procedes in high yields, under non-acidic conditions, probably involves an aza-Wittig reaction followed by a 6π-electrocyclic ring closure of the 1,3-diazabuta-1,3-diene intermediate **3**. Subsequent [1,5] sigmatropic hydrogen shift results in the formation of the 3,4-dihydroquinazoline **4** which may aromatize, in the reaction conditions, to quinazoline **5**. (SCHEME 1).

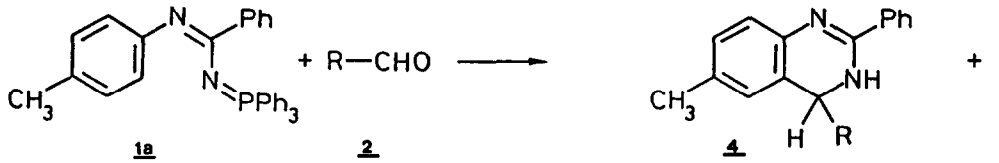


SCHEME 1

In this work we extended the reaction to a variety of different substituted aliphatic and aromatic aldehydes and to a new iminophosphorane (**1b**) bearing an electron-withdrawing substituent on the N-aryl group. The aim of this work was to study the effect of substituents, in both the aldehydic and the iminophosphorane moiety on the reaction rate and product distribution. Furthermore, in order to achieve a better understanding of the mechanism involved, some donor and acceptor-substituted 1,3-diazabuta-1,3-diene intermediates **3** were prepared using a new procedure. The capability of these compounds to undergo 6π-electrocyclic ring closure and the influence of substituents on the electron-cyclization rate have also been evaluated.

RESULTS AND DISCUSSION

The reaction of iminophosphorane **1a** and aldehydes **2** was performed in boiling xylene using three equivalents of aldehyde. The crude reaction mixture gave, after chromatographic purification over silica gel, the 3,4-dihydroquinazolines **4** and/or the quinazolines 5, (SCHEME 2, Table 1).



1a 2 4

5

2-5	R	Reaction time (h)	Yield 4	Yield 5
a	C_6H_{13}	40	31	42
b	$PhCH_2CH_2$	24	40	50
c	$4\text{-}(CH_3)_2NC_6H_4$	90	20	-[1]
d	$4\text{-}CH_3OC_6H_4$	90	53	9[2]
e	C_6H_5	48	71	-
f	$4\text{-}ClC_6H_4$	25	85	12
g	$4\text{-}FC_6H_4$	25	79	15
h	$4\text{-}CNC_6H_4$	20	62	33
i	$4\text{-}CF_3C_6H_4$	12	74	25
j	$2\text{-}NO_2C_6H_4$	12	-	45[3]
k	$4\text{-}NO_2C_6H_4$	12	-	70

1) Unreacted **1a** 70%.
2) Unreacted **1a** 30%.
3) In the reaction between **1a** and **2j** it was possible to isolate also a small amount (15%) of 4-(2'-aminophenyl)-6-methyl-2-phenylquinazoline which probably came from an intramolecular reaction of oxido-reduction (see Ref. 1).

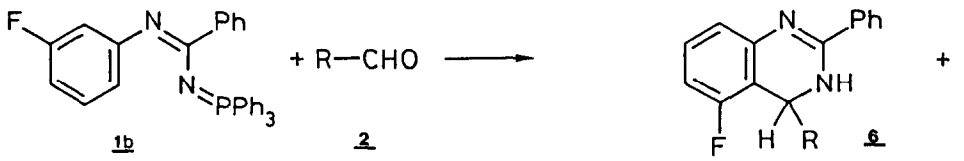
SCHEME 2

As shown in SCHEME 2, the reaction times and the yields depend strictly on the nature of the aldehyde employed. When R = alkyl, phenyl or when R is an aryl group bearing an electron-withdrawing substituent the yields are very high and reaction times decrease with the increasing electron-withdrawing power of R On the other hand, when R is an aryl group bearing an electron-donating substituent, even after prolonged reaction times, a certain amount of iminophosphorane **1a** was recovered unreacted and subsequently yields are lower.

The ratio between compounds **4** and **5** also depends on the nature of R. When R is an aliphatic group an equimolecular distribution between compounds **4** and **5** is observed. In the aromatic series, increasing the electron-withdrawing power of R, the aromatizaton process is favoured,

probably owing to the greater acidity of the hydrogen bond at C(4). In fact in the case of the reaction involving ortho- or para- nitrobenzaldehyde **2h** and **2i** the quinazolines **5j** and **5k** are the sole reaction products.

The reaction of iminophosphorane **1b** and aldehydes **2d,e,f,h,i,k** was performed as described above for the iminophosphorane **1a**, (SCHEME 3, Table 2). However, in this case the reaction products are, as expected, two pairs of isomers, the 3,4-dihydroquinazolines **6** and **6'** and the quinazolines **7** and **7'**, which were both obtained as a 1 1 mixture after chromatographic purification over silica gel.



1b 2 6

6' 7, 7'

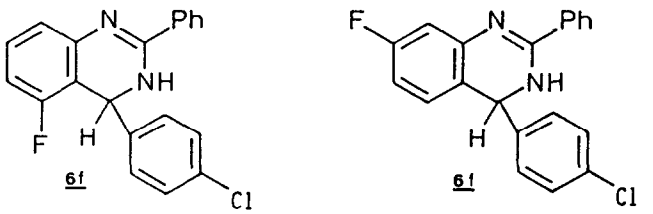
2-7	R	Reaction time (h)	Yield % 6	6'	7	7'
d	4-$CH_3OC_6H_4$	90	20	20	14	
e	C_6H_5	48	43	42	10	
f	4-ClC_6H_4	25	47	38	10	
h	4-CNC_6H_4	20	48	37	10	
i	4-$CF_3C_6H_4$	12	40	44	10	
k	4-$NO_2C_6H_4$	12	34	10	9	40

SCHEME 3

The results summarized in SCHEME 3 indicate that the presence of an electron-withdrawing substituent on the N-aryl group of **1b** has very little effect on the reaction course. In fact both the reaction times and the yields are unchanged in comparison with the results obtained in the reaction between the same aldehydes and the iminophosphorane **1a**. However, the dihydroderivatives **6** and **6'** seem to be more stable to oxidation than

the dihydroquinazolines **4**; in most cases it was possible to isolate only a little amount (about 10%) of the quinazolines **7** and **7'**. Only in the reaction between iminophosphorane **1b** and 4-nitrobenzaldehyde **2k** was an equimolecular distribution between compound **6,6'** and **7,7'** observed.

The isomeric compounds **7** and **7'** have been separated only in the case of reaction with 4-nitrobenzaldehyde **2k**, on the other hand the isomeric 3,4-dihydroquinazolines **6** and **6'** have been separated in all cases by column chromatography over silica gel using an high ratio crude product /silica gel (1 150). The structure of 4-aryl-5-fluoro-2-phenyl-4,5-dihydroquinazoline **6** and 4-aryl-7-fluoro-2-phenyl-4,5-dihydroquinazoline **6'** were assigned by ^{1}H and ^{19}F-NMR spectral analysis of the aromatic protons and fluorine atom, respectively, on the basis of the coupling costants reported in literature[2]. For example (Fig. 1), the ^{1}H-NMR spectrum of 4-(4'-chlorophenyl)-5-fluoro-2-phenyl-3,4-dihydroquinazoline **6f** shows, centered at 6.53 ppm, a double triplet which can be attributed to H(6) with $J_{orthoH-H}$ and $_{H-F}$= 8.8 Hz and $J_{metaH-H}$= 1.0 Hz. The ^{1}H-NMR spectrum of the isomeric 4-(4'-chlorophenyl)-7-fluoro-2-phenyl-3,4-dihydroquinazoline **6'f** shows instead, centered at 6.34 ppm, a double doublet which can be attributed to H(5) with $J_{orthoH-H}$= 8.4 Hz and $J_{metaH-F}$= 6.0 Hz, and at 6.54 ppm a double triplet attributed to H(6) with $J_{orthoH-H}$ and $_{H-F}$ = 8 4 Hz and $J_{metaH-H}$= 2.7 Hz



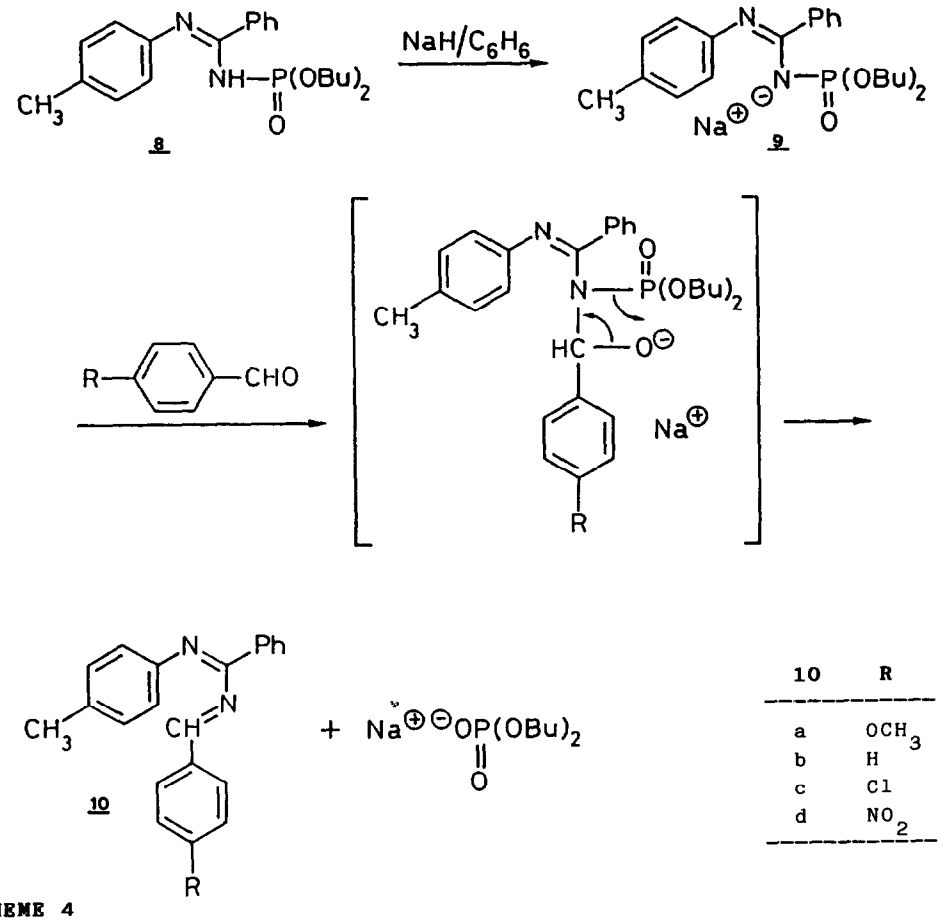
6f 6'f

FIGURE 1

The ^{19}F-NMR spectrum of compound **6f** shows at -120.13 ppm a broad singlet, instead the ^{19}F-NMR spectrum of compounds **6'f** shows at -114.58 a twelve line system which, for line intensity and coupling constants, can be attributed to the fluorine atom at C(7) in the quinazoline ring with J_{meta}= 10.8 Hz, J_{ortho}= 7.4 Hz and a long-range coupling (0.8 Hz) which probably involves the H(4).

The proposed mechanism for the reaction of iminophosphoranes **1a** and **1b** with aldehydes is shown in SCHEME 1. The first stage of the reaction results in the formation of the 1,3-diazabuta-1,3-diene intermediate **3** and is in agreement with previously reported results regarding the reactions of iminophosphorane and carbonyl compounds[3] as well as with the experimental evidence of triphenylphosphineoxide formation.

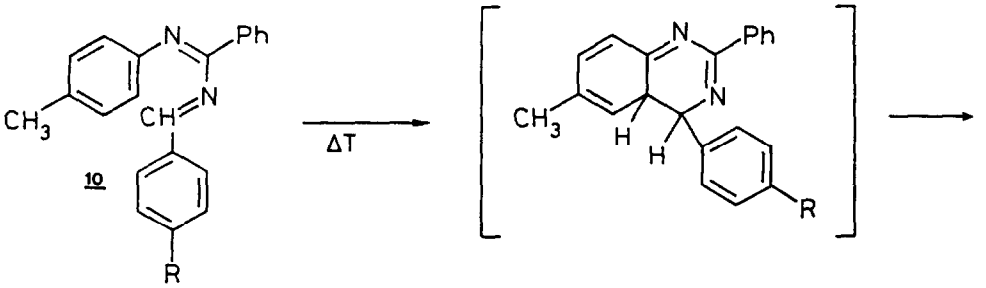
In the second stage the diene intermediate **3** undergoes 6π-electrocyclic ring closure followed by a fast [1,5] hydrogen shift, with rearomatization to 3,4-dihydroquinazoline **4**, the dihydroderivative **4** is then partially oxidized to quinazoline **5**, probably by air. In fact , when the reaction is performed with degassed solvent under nitrogen atmosphere only the 3,4-dihydroderivative **4** may be detected in the reaction mixture. Furthermore, the aldehyde, which is present in large excess, is not involved in the redox reaction the GLC analysis of the crude did not show any signal which could be attributed to the corresponding alcohol. The capability of compounds **3** to undergo electrocyclic ring closure was proven by an independent and original synthesis of the diene system There are only a few reports about the synthesis of the 1,3-diazabuta-1,3-diene system [4, 5,6,7,8] and none of the reported methods was useful for our purpose. We therefore chose a novel approach to such derivatives using a new and more reactive nitrogen-phosphorus ylide derived from benzamidine system (SCHEME 4). The dibutyl-N-[α-(4'-methylphenylimino)]benzyl phosphoramidate **8** is a new compound which was prepared following the reported procedure[9] for aliphatic and aromatic amines, starting from N-(4-methylphenyl)-benzamidine and dibutylphosphite The reactive ylide **9** was then generated in situ by treating **8** with sodium hydride in benzene and reacted with the appropiate aldehyde. The reaction, which proceeds at room temperature, gave, after elimination of the corresponding phosphate ester, the 1,3-diazabuta-1,3-dienes **10a-d** which were isolated in preparative yields after chromatographic purification over silica gel The compounds prepared and their physico-chemical properties are listed in Table 3.

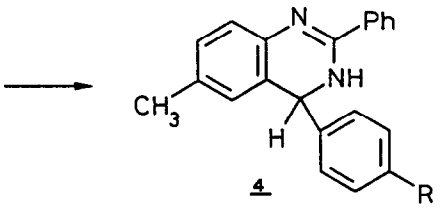


10	R
a	OCH_3
b	H
c	Cl
d	NO_2

SCHEME 4

The behaviour of these compounds in thermal electrocyclic reactions was studied in refluxing toluene or xylene solution (ca. 10^{-2}M), the reaction being monitored by tlc, the results are collected in SCHEME 5. The 1,3-diazabuta-1,3-dienes **10a-d** gave quantitatively the corresponding 3,4-dihydroquinazolines **4**, reaction times are also shown in SCHEME 5.





4

10	R	Solvent	Reaction time (h)
a	OCH_3	toluene	65
a	OCH_3	xylene	22
b	H	toluene	12
b	H	xylene	6.5
c	Cl	toluene	7.5
c	Cl	xylene	4.5
d	NO_2	toluene	2.5
d	NO_2	xylene	1

SCHEME 5

The reaction products were identified by comparison (tlc) with an authentic sample, except for compound **10d** the reaction product of which was unknown and therefore isolated. The structure of 6-methyl-2-phenyl-4-(4'-nitrophenyl)-3,4-dihydroquinazoline **4k** was assigned to this compound on the basis of analytical and spectral data.

This experimental evidence supports the proposed mechanism for the second stage of the reaction also. We feel that the cyclization is strictly thermally induced, since the reaction occurs in an inert solvent under non-catalytic conditions, and since an alternative electrophilic mechanism is incompatible with these experimental conditions Besides, when a -I group is present on the aromatic ring involved in the cyclization, a hypothetical electrophilic reaction would not be favoured. Instead no variation was observed in the reaction performed with the iminophosphorane **1b** bearing a fluorine substituent on the N-aryl group. Furthermore it is interesting to note that the cyclization rates are affected by substitution thus an electron-donating substituent on the aryl group at C(4) lowers the electro cyclization rate whereas an electron-withdrawing substituent enhances it

In conclusion, the reaction between N'-aryl-N-(triphenylphosphoranilidene)-benzenecarboximidamides and aldehydes provides easily and in high yields 3,4-dihydroquinazolines and quinazolines under non-acidic conditions. Moreover, we think that the amidine-ylide approach could be useful for the synthesis of a variety of nitrogen-containing rings, we are working toward the development of these and related compounds in heterocyclic synthesis

Table 1. 3,4-Dihydroquinazolines **4** and Quinazolines **5**

N°	Eluent for chromatography	m.p. °C (solvent)[a]	^{1}H-NMR ($CDCl_3$) δ from TMS, J = Hz[b]
4a	cyclohexane/Et_3N 8 2	79-82 PE[c]	0.83-1.03(m,3H,CH_3),1.07-1.84(m,10H,CH_2),2.30(s,3H,CH_3), 4.65(t,1H,CH,J=5),4.55(bs,1H,NH),6.70-7.60(m,6Harom),7.68-8.00(m,2Harom).
4b	cyclohexane/Et_3N 8 2	134-136 benzene	1 75-2 20(m,2H,CH_2),2 27(s,3H,CH_3),2.57-3.15(m,2H,CH_2),4.65 (t,1H,CH,J=6),6.70-7.52(m,12H,arom+NH),7.60-7.87(m,2Harom).
4c	cyclohexane/benzene/ Et_3N 6 2.2	143-146 Et_2O/PE[c]	2.30(s,3H,CH_3),3.00(s,6H,CH_3),5.88(s,1H,CH),6.70-7.75(m, 11H,arom+NH),7.90-8 20(m,2Harom).
4d	cyclohexane/benzene/ Et_3N 4 4 2	138-140 cyclohexane/ benzene	2.20(s,3H,CH_3),3.75(s,3H,OCH_3),5.70(s,1H,CH),6.55-7.50(m, 11H,arom+NH),7.65-7.85(m,2Harom).
4e	EtOAc/benzene 7·3	165-168 benzene	2.12(s,3H,CH_3),5.72(s,1H,CH),6.58(s,1H,H5),6.80-7.50(m,11H, arom+NH),7.60-7.85(m,2Harom).
4f	cyclohexane/benzene/ Et_3N 4:4:2	158-160 i-Pr_2O/PE[c]	2 12(s,3H,CH_3),5.63(s,1H,CH),6.55(s,1H,H5),6.85-7.45(m, 9Harom+NH),7.50-7.75(m,2Harom).
4g	cyclohxane/benzene/ Et_3N 4 4 2	162-164 cyclohexane	2 12(s,3H,CH_3),5.73(s,1H,CH);6.60(s,1H,H5),6.80-7.50(m, 10H,arom+NH),7.65-7.90(s,2Harom).
4h	cyclohexane/benzene/ Et_3N 6·2:2	106-111 cyclohexane	1.78(s,3H,CH_3),5.74(s,1H,CH),6.65(s,1H,H5),7.00-7.55(m,10H, arom+NH),7.60-7 85(m,2Harom).
4i	cyclohexane/benzene/ Et_3N 4 4 2	145-148 cyclohexane	2.20(s,3H,CH_3),5.80(s,1H,CH),6.63(s,1H,H5),7.05-7.55(m,10H, arom+NH),7.60-7.85(m,2Harom).
5a	cyclohexane/ Et_3N 8 2	61-63 pentane	0.60-0 87(m,3H,CH_3),0.97-2.23(m,8H,CH_2),2.30(s,3H,CH_3);3.10 (t,2H,CH_2,J=8),7.27-8.00(m,6Harom),8.40-8.63(m,2Harom).
5b	cyclohexane/ Et_3N 8 2	120-125 EtOH	2.45(s,3H,CH_3),3.10-3.80(m,4H,CH_2),7.07-8.10(m,11Harom), 8.50-8.85(m,2Harom).
5d	cyclohexane/benzene/ Et_3N 4 4 2	160-165 EtOH	2.35(s,3H,CH_3),3.70(s,3H,OCH_3),7.00-7.65(m,10Harom),8.46-8.75(m,2Harom).

Table 1. Continued.

N°	Eluent for chromatography	m.p. °C (solvent)[a]	^{1}H-NMR ($CDCl_3$) δ from TMS, J = Hz[b]
5f	cyclohexane/benzene/ Et_3N 4 4 2	181-183 PE[c]	2.50(s,3H,CH_3),7.45-8.10(m,10Harom),8.40-8.85(m,2Harom).
5g	cyclohexane/benzene/ Et_3N 4 4 2	152-156 cyclohexane	2.50(s,3H,CH_3),7.00-8.10(m,10Harom),8.50-8.86(m,2Harom)
5h	cyclohexane/benzene/ Et_3N 4·4 2	185-188 i-Pr_2O	2 50(s,3H,CH_3),6.85-8.10(m,10Harom),8.50-8.85(m,2Harom).
5i	cyclohexane/benzene/ Et_3N 4 4 2	194-196 cyclohexane	2 50(s,3H,CH_3),6.90-8.10(m,10Harom),8.50-8.85(m,2Harom).
5j	CH_2Cl_2	214-217 EtOAc	2.50(s,3H,CH_3),7 42-8.25(m,8Harom),8.41(d,2Harom,J=9),8.45-8.78(m,2Harom).
5k	CH_2Cl_2	189-190 EtOAc	2.41(s,3H,CH_3),7.20-7.80(m,7Harom),7.85-8.30(m,3Harom), 8 38-8 76(m,2Harom).

a) Microanalyses were in good agreement with calculated values
b) Recorded at 60MHz on a Varian EM360 Spectrometer
c) PE = petroleum ether bp 50-70°C.

Table 2. 3,4-Dihydroquinazolines 6, 6' and Quinazolines 7, 7'.

N°	Eluent for chromatography	m.p. °C (solvent)[a]	^{1}H-NMR (C_6D_6) δ from TMS, J = Hz[b]
6d	cyclohexane/benzene/ Et_3N 4 4.2	125-130 cyclohexane	3.18(s,3H,CH_3),5.25(bs,1H,NH);5.65(bs,1H,CH),6.56(t,1H,H6, J=8.4),6.60(d,2Harom,J=8.6),6.9(q,1H,H7,J=6.6),7.00-7.25(m, 5Harom,7 42(m,1Harom),7.70(dd,2Harom,J=7,1.5).
6'd	cyclohexane/benzene/ Et_3N 4 4 2	85-100[c] cyclohexane	3.25(s,3H,CH_3),5.10(bs,1H,NH),5.29(bs,1H,CH),6.48(dd,1H,H5, J=8.3,6),6.57(dt,1H,H6,J=8.4,2.5),6.68(d,2Harom,J=7),7.00-7.25(m,5Harom),7.42(m,1Harom),7.65(m,2Harom,J=7,1.5).
6e	cyclohexane/benzene/ Et_3N 4 4 2	123-125 benzene/EP[d]	3.50(bs,1H,NH);5.45(bs,1H,CH),6.53(dt,1H,H6,J=8.9,1),6.75-7.45(m,10Harom),7.65(dd,2Harom,J=7,1.5).
6'e	cyclohexane/benzene/ Et_3N 4.4 2	156-160 Et_2O	3.63(s,1H,NH),5.3(s,1H,CH),6.44(dd,1H,H5,J=8.4,6.2),6.54 (dt,1H,H6,J=8.2,2.4),7.00-7.45(m,9Harom),7.65(dd,2Harom, J=7,1.5).
6f	cyclohexane/benzene/ Et_3N 2.7.1	184-186 $CHCl_3$/EP[d]	5.05(bs,1H,NH),5.46(bs,1H,CH),6.53(dt,1H,H6,J=8.8,1);6.82-7.15(m,8Harom),7.4(m,1Harom),7.65(dd,2Harom,J=7,1.5).
6'f	cyclohexane/benzene/ Et_3N 2·7 1	148-151 cyclohexane	4.92(bs,1H,NH),5.10(bs,1H,CH),6.34(dd,1H,H5,J=8.4,6),6.54 (dt,1H,H6,J=8.4,2.7),6.78-7.15(m,7Harom),7.40(m,1Harom), 7.66(dd,2Harom,J=7,1.6).
6h	cyclohexane/benzene/ Et_3N 2·7 1	182-185 EtOAc/EP[d]	4.97(bs,1H,NH),5.42(bs,1H,CH),6.51(t,1H,H6,J=9.3),6.8-7.47 (m,9Harom);7.65(dd,2Harom,J=7,1.4).
6'h	cyclohexane/benzene/ Et_3N 2 7 1	35-80[c] cyclohexane	5.12(bs,2H,CH+NH),6.28(dd,1H,H5,J=8.4,5.8),6.54(dt,1H,H6, J=8.4,2.5),6.70-7.45(m,8Harom),7.68(dd,2Harom,J=7.3,1.8).
6i	cyclohexane/benzene/ Et_3N 2 7 1	153-156 cyclohexane	5.07(d,1H,NH,J=2),5.5(d,1H,CH,J=2),6.55(t,1H,H6,J=8.8);6.90 (q,1H,H7,J=8.1),7.10-7.44(m,8Harom),7.69(dd,2Harom, J=7.4,1.6).
6'i	cyclohexane/benzene/ Et_3N 2.7 1	172-174 i-Pr_2O	5.07(s,1H,NH),5.12(s,1H,CH),6.33(dd,1H,H5,J=8,6.1),6.58 (dt,1H,H6,J=8.2,2.6),6.85-7.45(m,8Harom),7.67(dd,2Harom, J=7.4,1.3).

Table 2. Continued.

N°	Eluent for Chromatography	m.p. °C (solvent)[a]	^{1}H-NMR (C_6D_6) δ from TMS, J = Hz[b]
6k	$CHCl_3$/EtOAc 8 2	157-160 i-Pr_2O/ EtOAc[c]	5.00(bs,1H,NH),5.43(bs,1H,CH),6.53(t,1H,H6,J=8.9),6.70-7.25 (m,6Harom),7.35(m,1Harom);7.6(d,2Harom,J=8.4),7.68(dd, 2Harom,J=7.5,1.5).
6'k	$CHCl_3$/EtOAc 8 2	196-198 Et_2O	3.10(bs,1H,NH),5.20(s,1H,CH),6.29(dd,1H,H5,J=8.4,6),6.56 (dt,1H,H6,J=8.3,2.6),6.82(d,2Harom,J=8.7),7.0-7.25(m, 4Harom),7.67(dd,2Harom,J=7.3,1.6),7.72(d,2Harom,J=8.8).
7k	$CHCl_3$/EtOAc 8 2	184-187 benzene	6.78(dt,1H,H6,J=8.4,2.6);7.12-7.53(m,4Harom),7.64-7.94(m, 5Harom),9.11(dd,2Harom,J=7.1,1.6).
7'k	$CHCl_3$/EtOAc 8 2	205-208 benzene	6.76(dt,1H,H6,J=8.2,2.5);7.15-7.43(m,6Harom),7.72(dd,1H,H8, J=9.7,2 5),7.89(d,2Harom,J=8.8),9.00(dd,2Harom,J=8,1.5).

a) Microanalyses were in good agreement with calculated values.
b) Recorded at 200 MHz on a Gemini-Varian Spectrometer.
c) Amorphous powder.
d) PE = petroleum ether bp 50-70°C.

Table 3. 1,3-Diazabuta-1,3-dienes **10a-d.**

N°	Reaction time (h)	Eluent for chromatography	Yield[a] %	m.p.[b] (°C) (solvent)	Molecular formula	Elemental analysis, %[c] C	H	N	^{1}H-NMR ($CDCl_3$)[d] δ from TMS
10a	90	cyclohexane/ Et_3N 8 2	28	109-112 i-Pr_2O	$C_{22}H_{20}N_2O$ (328.39)	80.66 (81.20)	6.36 (6.14)	8.17 (8.53)	2.22(s,3H,CH_3),3.85(s, 3H,OCH_3),6.88 and 7.68 (AA'BB'sys,J=8.8),6.91 and 7.00(AA'BB'sys,J= 8.1)7.3-7.5(m,3Harom), 7.94(dd,2Harom,J=7.6, 1.7),8.08(s,1H,CH).
10b	48	cyclohexane/ benzene/Et_3N 4 4 2	71	80-84 i-Pr_2O	$C_{21}H_{18}N_2$ (298 37)	83.82 (84.53)	6.28 (6.08)	9.08 (9.39)	2.22(s,3H,CH_3),6.88and 7.01(AA'BB'sys,J=8.2), 7.3-7.5(m,6Harom),7.73 (dd,2Harom,J=7.6,1.7), 7.95(dd,2Harom,J=7.6, 1.7),8.18(s,1H,CH)
10c	22	cyclohexane/ Et_3N 8 2	70	oil	$C_{21}H_{17}N_2Cl$ (332.82)	75.25 (75 78)	5.32 (5.15)	8.30 (8.42)	2.22(s,3H,CH_3),6.86and 7.01(AA'BB'sys,J=8), 7.39 and 7 66(AA'BB' sysJ=8.4),7.3-7.5(m, 3Harom),7.92(dd,2H arom,J=7.5,1.6),8.12 (s,1H,CH).
10d	4	cyclohexane/ benzene/Et_3N	65	80-84 Et_2O	$C_{21}H_{17}N_3O_2$ (343.37)	72.98 (73.45)	4.95 (4.99)	12.20 (12.24)	2.22(s,3H,CH_3),6.84and 7.01(AA'BB'sys,J=7.5); 7.4-7.5(m,3Harom),7.90 and 8.28(AA'BB'sys, J=8.5),7.8-8.0(m,2H arom),8.24(s,1H,CH).

a) Of isolated analytically pure product. b) Uncorrected.
c) Calculated values in parentheses. d) Recorded at 200MHz on a Gemini-Varian Spectrometer.

EXPERIMENTAL

N'-aryl-N-(triphenylphosphoranilidene)-carboximidamides **1a** and **1b**.

The N-imidoyliminotriphenylphosphorane **1a** is a known compound and was prepared by the method described in Ref. 1. The N-imidoyliminotriphenylphosphorane **1b** is new and was prepared according to the procedure described in Ref.1 Yield 61%, m.p. 139-142°C (ethyl acetate/diisopropylether, 1 1), elem. anal., found % (calcd for $C_{31}H_{25}N_2FP$) C 77.92 (78.30), H 5.24 (5.30), N 5.83 (5.90).

Quinazolines **5, 7, 7'** and 3,4-Dihydroquinazolines **4, 6, 6'**.

A mixture of the N-imidoyliminotriphenylphosphorane **1a** or **1b** (6mmol), the aldehyde **2** (18mmol), and dry xylene (40ml) was heated under reflux for 12-90h. The solvent was then removed under reduced pressure and the crude reaction mixture was chromatographed over a silica gel (70-130 mesh) column (ratio crude product/silica gel, 1 40) yielding progressively, for the reaction with the iminophosphorane **1a**, the quinazolines **5a-k** and the 3,4-dihydroquinazolines **4a-i**. For data see Table 1. When the reaction involves the iminophosphorane **1b** a mixture of the isomeric quinazolines **7** and **7'd-k** and a mixture of the isomeric 3,4-dihydroquinazolines **6** and **6'd-k** were obtained after usual chromatographic purification performed using the following eluents for the reaction with **2d** cyclohexane/benzene /TEA, 4 4:2, with **2e** and **2i** cyclohexane/ethyl acetate, 7 3, with **2f** and **2h** ethyl ether/PE, 7 3, with **2k** dichloromethane/ethylether, 9 1 The isomeric compounds **7** and **7'** have been separated only in the reaction with 4-nitrobenzaldehyde **2k** Instead a pure sample of both isomers **6** and **6'** was obtained in all cases performing a second chromatography over a silica gel column using a ratio crude product/silica gel, 1 150 For data see Table 2.

Dibutyl-N-[α-(4'-methylphenylimino)]benzyl phosphoramidate **8**.

To a well stirred solution of N-(4-methylphenyl)benzamidine (12.4g, 59mmol) and triethylamine (6 55g, 65mmol) in dry CCl_4 (125ml) a solution of dibutyl phosphite (12.62g, 65mmol) in dry CCl_4 (125ml) was added dropwise at room temperature Stirring was continued for 24h, then the

reaction mixture was washed with water (2x100ml), the organic layer was dried over anhydrous sodium sulfate and freed from the solvent under reduced pressure. The crude product was purified by crystallization from petroleum ether (bp = 50-70°C). Yield 70%, m.p. 71-73°C, elem.anal., found (calcd for $C_{22}H_{31}N_2O_3P$): C 65.34 (65.65), H 7.67 (7.76), N 7.07 (6.96). ^{1}H-NMR (60MHz, $CDCl_3$/TMS) 0.90(t,6H,CH_3),1.40(six lines,4H, $\underline{CH_2}$-CH_3),1.65(five lines,4H,CH_2);2.25(s,3H,CH_3),4.00(q,4H,OCH_2),6.90 bs,1H,NH),6.95-7.05(m,4Harom),7.20-7.35(m,3Harom),7.45-7.55(m,2Harom).

4-Aryl-1-(4'-methylphenyl)-2-phenyl-1,3-diazabuta-1,3-dienes **10a-d.**

To a stirred slurry of sodium hydride, 50% in mineral oil (0.72g, 14.5mmol) in dry benzene (3ml) a solution of **8** (5g, 1.24mmol) in dry benzene (50ml) was added dropwise, at 40°C under nitrogen. After hydrogen evolution ceased the mixture was cooled to room temperature and a bimolecular amount of the appropiate aldehyde was added. The reaction mixture was stirred for 4-90h and then washed with a cold sat. sol of $NaHCO_3$ (20ml). The organic layer was dried over anhydrous sodium sulfate and freed from the solvent under reduced pressure without heating. The crude product was then purified by chromatography over a silica gel (70-120 mesh) column (ratio crude product/silica gel, 1 40) yielding the 1,3-diazabuta-1,3-dienes **10a-d**. For data see Table 3.

6-Methyl-2-phenyl-4-(4'-nitrophenyl)-3,4-dihydroquinazoline **4k.**

A solution of 1-(4'methylphenyl)-4-(4'-nitrophenyl)-2-phenyl-1,3-diazabuta-1,3-diene **10d** (0.5g, 1.45mmol) in dry xylene (5ml) was heated under reflux for 1h. The mixture was then freed from the solvent under reduced pressure and the crude was purified by crystallization from ethyl ether/ diisopropyl ether, 2 1. Yield 85%, m.p. 143-145°C, elem. anal., found (calcd for $C_{21}H_{17}N_3O_2$) C 72.66 (73.45), H 4.88 (5.00), N 12 04 (12.24). ^{1}H-NMR (200MHz, $CDCl_3$/TMS) · 2.22(s,3H,CH_3),5.70(bs,1H,NH),5.92(s,1H,CH), 6.62(bs,1Harom),7.05(m,1Harom),7.20(m,1Harom),7 38-7 48(m,3Harom),7.54 and 8.20 (AA'BB' system,J=8.5),7 82(dd,2Harom,J=7.5,1.5).

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