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Preparation, Reactivity and Synthetic Applications of Bis(iminophosphoranes): New Entries to Fused 1,3,5-Benzotriazepines, 1,3-Benzodiazepines and Indole Derivatives[1]

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Key Words: Bis(iminophosphoranes); Aza Wittig-type Reaction; Fused 1,3,5-Benzotriazepines; 1,3-Benzodiazepines; Indole Derivatives

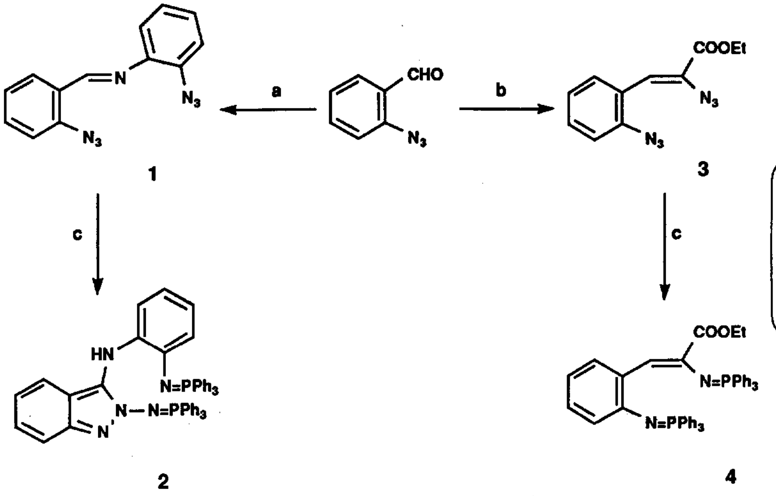
Abstract: *An aza-Wittig-type reaction of bis(iminophosphorane) **2** with two moles of alkyl or aryl iso(thio)cyanates leads to indazolo[2'3':1,5][1,2,4]triazolo[4,3-a][1,3,5]benzotriazepines **7**. The bis(iminophosphorane) **4** reacts with aromatic iso(thio)cyanates to give the corresponding iminophosphoranes **13** derived from the indole ring. Compound **4** also reacts with acyl chlorides to give [1,3]-benzodiazepines **19**. The crystal structure of compound **13c** has been determined.*

Iminophosphorane-mediated synthesis of heterocyclic ring systems has developed dramatically in recent years, which can be attributed in good measure to the rapid progress in the preparation of functionalized iminophosphoranes, and the versatility of these iminophosphoranes in organic synthesis has been well-recognized[2]. However, the chemistry of the bis(iminophosphoranes) has been much less investigated; it has only been briefly mentioned[3] that bis(iminophosphorane) derived from *o*-phenylenediamine reacts with diethyl acetylenecarboxylate to give a quinoxaline derivative. One of the important goals achieved in iminophosphorane chemistry is the formation of functionalized heterocumulenes which exhibit a rich chemistry of unusual synthetic promise. In this context, bis(iminophosphoranes) could be valuable building blocks; they can compose a reaction system in which the two iminophosphorane units can react either with a reagent having two functionalities or with two separate reagents bearing the same functionality; in this case the bis(iminophosphorane) serves as a conjunctive substrate, combining two reagents. It is expected that the utility of the bis(iminophosphoranes) could be enhanced if the two iminophosphorane moieties show different reactivity towards the same functionality.

In this paper we describe the preparation and reactivity of bis(iminophosphoranes) **2** and **4** bearing two chemically different iminophosphorane groups in aza Wittig-type reactions, thus providing efficient and general routes to fused 1,3,5-benzotriazepines, 1,3-benzodiazepines and indole derivatives.

RESULTS AND DISCUSSION.

The starting diazide **1** was readily prepared in 70% yield by condensation of the *o*-azidobenzaldehyde[4] with *o*-azidoaniline in ethanol in the presence of acetic acid. When a solution of **1** in dichloromethane was treated with triphenylphosphine (TPP) at 0°C, the bis(iminophosphorane) **2** was obtained in 80% yield. The ^{31}P n.m.r. spectrum clearly indicates the presence of two different iminophosphorane groups; it showed two signals at δ 4.53 ppm and δ 17.58 ppm respectively which were in good agreement with previously reported values for N-aryliminophosphoranes[5] and iminophosphoranes derived from N-aminoheterocycles[6]. In the ^{13}C n.m.r. spectrum the chemical shifts of all carbon atoms of the indazole ring were in good agreement with the literature values[7]; the C-3 carbon atom appears as a doublet at δ 129.54 ppm ($^3J_{P\text{-}C}$ 10.7 Hz) and in the phenylamino residue the two ortho-carbon atoms to the iminophosphorane group appear as two doublets at δ 119.40 ppm ($^3J_{P\text{-}C}$ 9.5 Hz) and δ 138.07 ppm ($^3J_{P\text{-}C}$ 20.6 Hz).



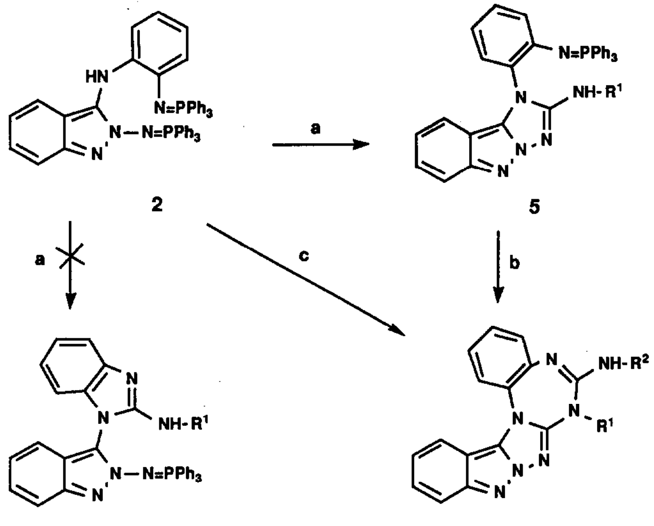
Reagents:
a) *o*-azidoaniline, ethanol, AcOH, r.t.
b) N_3CH_2COOEt, NaOEt, -15°C.
c) TPP, dichloromethane, 0°C.

Scheme I

The formation of **2** shows the different behaviour of the two azide groups in compound **1** towards TPP in the Staudinger reaction; the azido group belonging to the *o*-azidobenzaldehyde fragment reacts to give a phosphazide as intermediate which undergoes cyclization by nucleophilic attack of the central nitrogen atom of the phosphazide moiety on the carbon atom of the azomethine group leading to a zwitterionic intermediate and further transformation of this will lead to the 2H-indazole ring[8], whereas the azido group belonging to the *o*-azidoaniline fragment react in a "normal" fashion to give the iminophosphorane function with nitrogen evolution.

The diazide **3** was prepared in 68% yield by condensation of *o*-azidobenzaldehyde with ethyl azidoacetate. A Staudinger reaction between **3** and TPP at 0°C led to the bis(iminophosphorane) **4** in 88% as a crystalline solid (Scheme I).

The bis(iminophosphorane) **2** reacted with alkyl and aryl iso(thio)cyanates at room temperature to give the iminophosphoranes **5** derived from *1H*-1,2,4-triazolo[2,3-*b*]indazole. The ^{31}P n.m.r. spectra only showed one signal around δ 10 ppm, while the ^{13}C n.m.r. spectra clearly showed that three carbon atoms (two quaternaries and one CH) belonging to the phenyl group were coupled with the phosphorus atom of the iminophosphorane moiety; in addition coupling of the C-3a carbon atom of the indazole ring with the phosphorus atom was not observed. These data are consistent with the proposed structure **5** and rule out the alternative structure **6**. Compounds **5** reacted with a second mol of iso(thio)cyanate in toluene at room temperature to give the previously unreported 1,3,5-benzotriazepines **7**; the yields of the isolated products were higher than 50% (Scheme II).



Entry	R^1
5a	C_2H_5
5b	C_6H_5-CH_2
5c	4-CH_3-C_6H_4
5d	4-CH_3O-C_6H_4
5e	4-F-C_6H_4

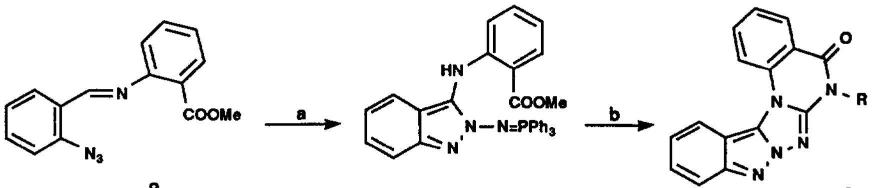
Entry	R^1	R^2
7a	C_2H_5	C_2H_5
7b	C_2H_5	4-CH_3O-C_6H_4
7c	4-CH_3O-C_6H_4	C_2H_5
7d	4-CH_3O-C_6H_4	4-CH_3O-C_6H_4
7e	4-CH_3-C_6H_4	4-CH_3-C_6H_4
7f	4-F-C_6H_4	4-F-C_6H_4

Reagents:
a) 1 equiv. R^1-NCS, dichloromethane, r. t.
b) 1 equiv. R^2-NCS, toluene, r. t..
c) i: 1 equiv. R^1-NCS, dichloromethane, r. t
ii: 1 equiv. R^2-NCS, dichloromethane, reflux

Scheme II

1,3,5-Benzotriazepines **7** can also be prepared from the precursor bis(iminophosphorane) **2** by treatment with two moles of iso(thio)cyanate in dichloromethane solution at reflux temperature. Both conversions **2**→**5** and **5**→**7** involve a tandem aza-Wittig/carbodiimide-mediated annelation reaction. The formation of iminophosphoranes **5** from **2** shows for the first time the preferential reactivity of N-iminophosphoranes with respect to aryliminophosphoranes in aza Wittig-type reactions towards iso(thio)cyanates. By changing the sequence of the two initial aza Wittig processes on **2** is possible to reverse the position of the substituents R^1 and R^2 in compounds **7**. The ^1H n.m.r. spectra of compounds **7** suggested the exocyclic NH; e.g. for **7a** one methylene signal appeared as a complex multiplet. In the ^{13}C n.m.r. spectra the 1,2,4-triazolo[2,3-*b*]indazole ring carbon atoms display chemical shifts similar to those observed in compound **5**, and the new quaternary carbon atom C-6 appears in the region δ 144.80-153.68 ppm. The mass spectra show the expected molecular ion peaks in high intensity, other peaks appear at m/z (M^+-R^1NCNR^2) and m/z 156 (indazole ring); very informative peaks were also found at m/z (R^1NCNR^2) and m/z (R^2NHCN).

A conceptually similar reaction involves the formation of fused pyrimidines **10** from the aldimine **8** derived from *o*-azidobenzaldehyde and ethyl anthranilate. Thus, aldimine **8** reacted with triphenylphosphine at 0°C to give the iminophosphorane **9** in moderate yield (40%). Aza Wittig-type reaction of iminophosphorane **9** with several aliphatic isothiocyanates in dry toluene at reflux temperature for 8h led directly to the previously unreported fused pyrimidines **10**; the reaction with aryl isothiocyanates was carried out under milder conditions, at room temperature for 16h (Scheme III). The reaction seems to be quite general and the yield were higher than 60%. The conversion **9**→**10** involves initial aza Wittig-type reaction between the iminophosphorane and the isothiocyanate to give a highly reactive intermediate carbodiimide which undergoes cyclization by nucleophilic attack of the exocyclic amino group on the central carbon atom of the carbodiimide moiety to give the triazole ring followed by intramolecular amidation. In compounds **10** a central guanidine moiety is forming part of two cycles; recently this type of bicyclic guanidines have received much attention because they serve as binding sites for anionic functional groups[9].



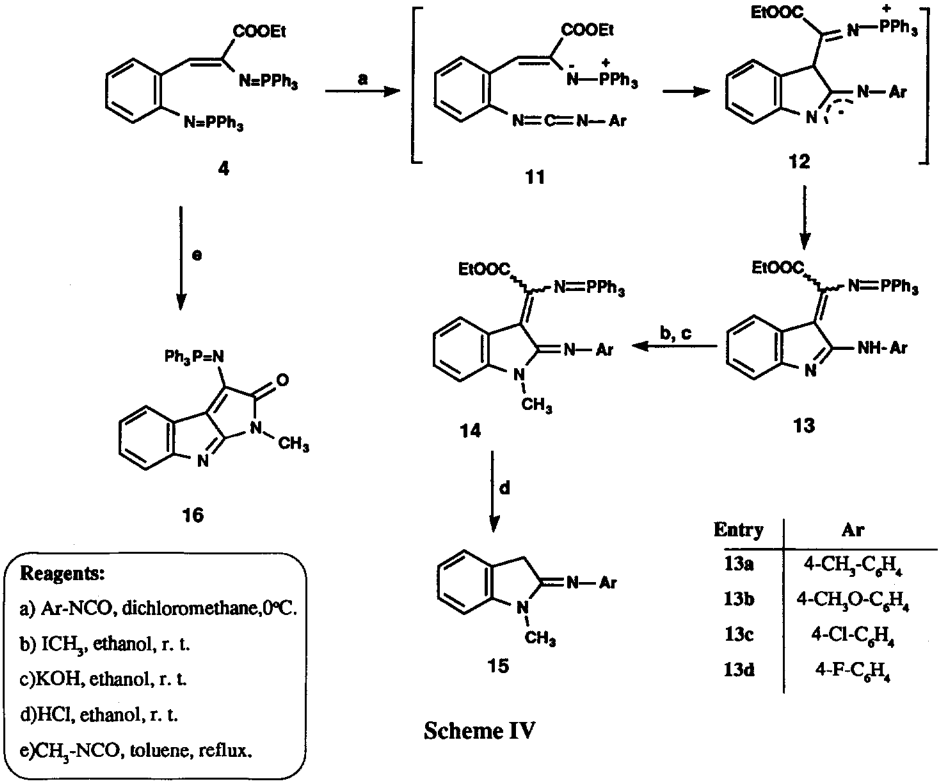
8 **9** **10**

Reagents:
a) TPP, CH_2Cl_2, 0°C.
b) R-NCS, toluene, reflux, 8h
or dichloromethane, r. t., 16h.

Scheme III

Entry	R
10a	C_2H_5
10b	C_6H_5-CH_2
10c	4-CH_3-C_6H_4
10d	4-CH_3O-C_6H_4
10e	4-F-C_6H_4

On the other hand, bis(iminophosphorane) **4** reacted with aromatic isocyanates in dry dichloromethane at 0°C to give the mono iminophosphoranes **13** derived from the indole ring in moderate to good yields (36-60%). The conversion **4**→**13** can be rationalized in terms of aza Wittig-type reaction between the iminophosphorane group linked to the aromatic ring and the isocyanate to give a carbodiimide **11** which undergoes cyclization by nucleophilic attack of the β-carbon atom at the unsaturated *ortho*-substituent leading to the zwitterionic intermediate **12**. Further transformations of **12** will lead to the indoles **13**. This conversion shows for the first time that an aryl iminophosphorane group is more reactive than a β-styryl iminophosphorane in aza Wittig-type reactions towards isocyanates.



Reagents:
a) Ar-NCO, dichloromethane,0°C.
b) ICH_3, ethanol, r. t.
c)KOH, ethanol, r. t.
d)HCl, ethanol, r. t.
e)CH_3-NCO, toluene, reflux.

Entry	Ar
13a	4-CH_3-C_6H_4
13b	4-CH_3O-C_6H_4
13c	4-Cl-C_6H_4
13d	4-F-C_6H_4

Scheme IV

In order to identify unambiguously the structure of compounds **13** an X-ray structure determination of crystalline compound **13c** has been determined. The main geometrical characteristics of **13c** are given in Table I following the number scheme of Figure 1. There, the values of the bond lengths and angles give a representation of the molecule with a constitution well defined in terms of the localization of the double character at the bonds N1=C2, C3=C18, C19=O20 and N24=P25 (for the last one see ref. 10).

The molecule adopts a conformation that is determined by the packing, in such a way that the A and B forms of the phenyl rings are adopted to avoid short contacts. On the other hand the fused rings and the PPh_3 group avoid intramolecular crowding; thus the N=PPh_3 group adopt a conformation between the parallel and the perpendicular one[11] with the rings away from the most frequent C3 conformation[10].

Sequential treatment of iminophosphoranes **13** with methyl iodide and bases in ethanol at room temperature led to **14** which underwent hydrolytic cleavage to give the indole derivatives **15** (Scheme IV).

Bis(iminophosphorane) **4** also reacted with methyl isocyanate in toluene at reflux temperature to afford pyrrolo[2,3-*b*]indole derivatives **16**. The conversion **4**→**16** can be understood by initial formation of an intermediate of the type **13** followed by intramolecular acylation of the exocyclic amino group.

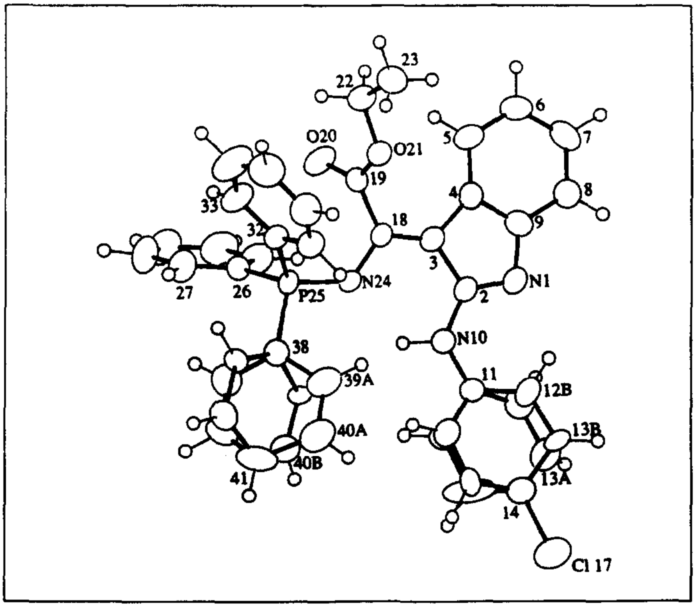


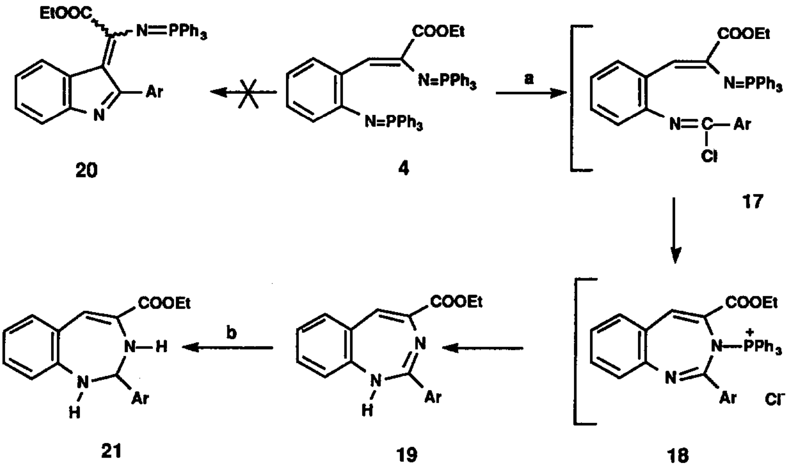
Table I. Selected geometrical characteristics (Å, degrees).

N1-C2	1.294(11)	N1-C9	1.399(12)	C9-C4	1.400(12)
C4-C3	1.456(12)	C3-C2	1.483(12)	C2-N10	1.399(12)
C11-N10	1.397(11)	C14-Cl 17	1.751(12)	C3-C18	1.340(11)
C18-N24	1.388(11)	N24-P25	1.600(6)	C26-P25	1.804(9)
C32-P25	1.818(9)	C38-P25	1.803(9)	C18-C19	1.514(9)
C19-O20	1.212(12)	C19-O21	1.318(12)	C22-O21	1.465(12)

C9-N1-C2	104.9(8)	N1-C2-C3	114.9(8)	C2-C3-C4	101.6(7)
C3-C4-C9	105.6(8)	C4-C9-N1	113.0(8)	C2-N10-C11	126.7(8)
N1-C2-N10	125.0(8)	C2-C3-N10	120.1(8)	C2-C3-C18	126.7(8)
C4-C3-C18	130.6(8)	C3-C18-N24	123.0(8)	C3-C18-N24	123.0(8)
C3-C18-C19	120.5(8)	N24-C18-C19	116.5(7)	C18-N24-P25	128.0(6)
N24-P25-C26	114.0(4)	N25-P25-C32	113.0(4)	N24-P25-C38	105.5(4)
C18-C19-O20	123.3(8)	C18-C19-O21	111.9(7)	O21-C19-O20	124.8(8)

N1-C2-N10-C11	12.7(15)	C2-N10-C11-C12A	-34.2(19)
C2-N10-C11-C12B	8.2(17)	C3-C2-N10-C11	-165.4(8)
N10-C2-C3-C18	1.3(14)	C2-C3-C18-N24	-8.8(14)
C3-C18-N24-P25	-179.3(7)	C3-C18-C19-O21	-66.3(11)
C18-C19-O21-C22	176.7(8)	C19-O21-C22-C23	177.8(8)
C18-N24-P25-C26	79.5(8)	N24-P25-C26-C31	2.2(9)
C18-N24-P25-C32	-46.5(8)	N24-P25-C32-C37	-51.8(8)
C18-N24-P25-C38	-163.8(7)	N24-P25-C38-C39A	28.4(11)
N24-P25-C38-C39A	-36.0(12)		

Finally, bis(iminophosphorane) **4** reacted with aroyl chlorides in dry dichloromethane in the presence of triethylamine at room temperature to give 1,3-benzodiazepines **19** in 55-65% yields with no evidence of indole **20** formation. Presumably, the formation of **19** involves initial formation of an imidoyl chloride[12] **17** as intermediate which cleanly undergoes cyclization by nucleophilic attack of the nitrogen atom of the iminophosphorane portion followed by P-N bond cleavage to give **19** (Scheme V). Compounds **19** were characterized on the basis of their spectroscopic data and mass spectroscopy. In addition, reduction with sodium borohydride led to the dihydro derivative **21**. In the ^{1}H n.m.r. spectra the H-2 appears at around δ 5.18 ppm as a double doublet and the two amino protons appear as doublets at around δ 5.80 and 6.87 ppm. In the ^{13}C spectra the C-2 carbon atom appears at δ 67.62-68.55 ppm.



Entry	Ar
21a	4-CH_3-C_6H_4
21b	4-Cl-C_6H_4
21c	4-Br-C_6H_4

Entry	Ar
19a	C_6H_5
19b	4-CH_3-C_6H_4
19c	4-CH_3O-C_6H_4
19d	4-Cl-C_6H_4
19e	4-Br-C_6H_4
19f	4-F-C_6H_4

Reagents:
a) Ar-COCl, Et_3N, r. t.
b) $NaBH_4$, methanol.

Scheme V

In conclusion, we have developed simple but effective routes for the synthesis of a variety of 1,3,5-benzotriazepines, 1,3-benzodiazepines and indole derivatives from readily available bis(iminophosphoranes). Several trends have surfaced from our studies. First, the order of reactivity of iminophosphoranes towards iso(thio)cyanates in aza Wittig-type reactions is the following: N-iminophosphorane>aryl-iminophosphorane. Second, bis(iminophosphorane) **2** reacts with iso(thio)cyanates to give fused 1,3,5-benzotriazepines through two consecutive aza Wittig/electrocyclic ring-closure processes. Third, aza Wittig-type reactions of bis(iminophosphorane) **4** may be driven towards the production of indole derivatives or 1,3-benzodiazepines by changing the nature of the reagent.

EXPERIMENTAL.

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions on a Nicolet-5DX spectrophotometer. NMR spectra were recorded on a Bruker AC-200 (200 MHz). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer. Microanalyses were performed on a Perkin-Elmer 240C instrument.

X-Ray crystallography. The main characteristics of the X-ray analysis are listed in Table II. The final atomic coordinates for the non-hydrogen atoms are reported in Table III. The C11...C16 and C38...C43 phenyl rings appear to be disordered between two positions, corresponding to different twist of the rings, Table I and Figure I. The population parameters are pp (C12A) = pp (C13A) = pp (C15A) = pp (C16A) = 0.59 (4), pp (C40A) = pp (C42A) = pp (C43A) = 0.57 (3) and 0.41 (4) and 0.43 (3) for the B arrangements. All hydrogen atoms but those of the disordered phenyl rings were derived from difference synthesis but were kept fixed in the last cycles of refinement. Neutral scattering factors were taken from the International Tables[13]. Data processing and computation were carried out on a Vax 6410 computer using the following set of programs: XRay80 System[14], Pesos[15], Parst[16], Xtal3.0[17].

Table II. Crystal analysis parameters at room temperature.

Crystal data	
Formula	$C_{36}H_{29}N_3O_2PCl$
Crystal habit	Orange plates
Crystal size (mm)	0.50x0.33x0.17
Symmetry	Triclinic, P21/c
Unit cell determination:	Least-squares fit from 81 reflections (θ<45°)
Unit cell dimension (Å, °)	a=9.3962(3) b=33.5209(23) c=9.8020(3) 90, 102.975(3), 90
V (Å), Z	3.008.5(3), 4
Dc (g/cm^3), M, F (000)	1.329, 602.07, 1256
μ (cm^{-1})	19.33
Experimental data	
Technique	Four circle diffractometer: Philips PW1100 Bisecting geometry Graphite oriented monochromator: CuKα ω/2θ scans, scan width: 1.4° θmax. 65° 1min. /reflections
Number of reflections:	
Independent	5111
Observed	3350 (3σ (I) criterion)
Standard reflections:	2 reflections every 90 minutes No variation
Min-max. abs. correction:	1.2603-0.745

Solution and refinement

Solution	Patterson
Refinement	Least-Squares on Fo, 2 blocks
Parameters:	
Numbers of variables	4.62 (H atoms fixed)
Degrees of freedom	2888
Ratio of freedom	7.3
H atoms	Difference synthesis (see experimental)
Final shift/error	0.16
Weighting-scheme	Empirical as to give no trends in $<w\Delta^2F>$ vs. $<$ Fobs $>$ and $<\sin\theta/\lambda>$
Max. thermal value	U33 (C15B) = 0.19(7)Å^2
Final ΔF peaks	0.71 e/Å^3
Final R and Rw	0.114, 0.144

Preparation of diazide 1.

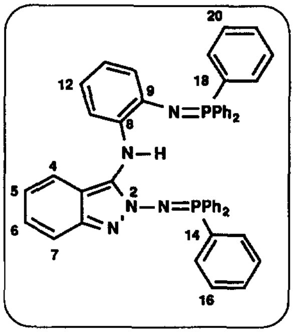
To a well stirred solution of *o*-azidobenzaldehyde (0.735 g, 5mmol) in anhydrous ethanol (20 ml), a solution of *o*-azidoaniline (0.737 g, 5.5 mmol) in the same solvent (10 ml) and acetic acid (0.5 ml) were added. The mixture was stirred at room temperature for 7h. After this the separated solid was collected by filtration, washed with cold ethanol and recrystallized from ethanol to afford 1 (70%), m.p. 88-89°C as yellow prisms. (Found: C, 59.3; H, 3.3; N, 37.4. $C_{13}H_9N_7$ requires: C, 59.3; H, 3.5; N, 37.2); i.r. (Nujol) 2122, 2095, and 1618 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 7.02-7.26 (m, 6H), 7.48 (ddd, 1H, J=8.5 Hz,J= 7.0 Hz, J=1.3 Hz), 8.20 (dd, 1H, J=8.4 Hz, J=1.3 Hz), 8.75 (s, 1H, CH=N); ^{13}C n.m.r. δ ($CDCl_3$): 118.42, 119.37, 120.31, 125.06, 125.49, 126.95 (q), 127.10, 128.41, 132.71, 133.65 (q), 140.63 (q), 144.36 (q), 155.59 (CH=N); m/z (%): 263 (M^+, 3), 207 (39), 206 (49), 103 (41), 76 (100).

Preparation of Ethyl α-Azido-β(*o*-azidophenyl)acrylate 3.

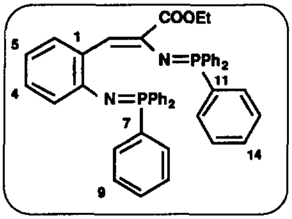
To a well-stirred solution containing sodium (0.92 g) in anhydrous ethanol (50 ml), a solution of ethyl azidoacetate (5.16 g, 4 mmol) and *o*-azidobenzaldehyde (0.147 g, 1 mmol) in the same solvent (50 ml) was added dropwise at -15°C under nitrogen. The reaction mixture was stirred at this temperature for 4h. After this it was poured into aqueous 30% ammonium chloride (25 ml) and extracted with diethyl ether (3x100 ml). The combined organic layer was dried ($MgSO_4$) filtered and concentrated to dryness. The remaining solid was slurried with hexane (2x10 ml) and recrystallized from ethanol to give 3 (68%), m.p. 98-99°C as colourless crystals. (Found: C, 50.9; H, 4.1; N, 32.4. $C_{11}H_{10}N_6O_2$ requires: C, 51.2; H, 3.9; N, 32.5); i.r. (Nujol) 2135, 2078, and 1710 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.37 (t, 3H, J=7.1 Hz), 4.34 (q, 2H, J=7.1 Hz), 7.10-7.25 (m, 2H), 7.44 (t, 1H, J=8.0 Hz), 8.13 (s, 1H, CH=N), 8.20 (d, 1H, J=7.8 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 13.76 (CH_3), 61.89 (CH_2), 117.67, 118.17, 123.82 (q), 124.29, 126.03 (q), 130.23, 130.38, 138.14 (q), 162.42 (C=O); m/z (%): 258 (M^+, 2), 121 (100), 118 (48), 93 (90).

Preparation of Bis(iminophosphoranes) 2 and 4.

A solution of TPP (2.62 g, 10 mmol) in dry dichloromethane (20 ml) was added dropwise under nitrogen to a well-stirred solution of the corresponding diazide 1 or 3 (5 mmol) in the same solvent (30 ml) at 0°C. After the stirring was continued for 1h at the same temperature, the mixture was slowly warmed to room temperature for 7h (for compound 2) or for 16h (for compound 4), and then the solvent was removed under reduced pressure. The resultant crude product was chromatographed on a silica gel column, eluting with ethyl acetate/hexane (3:1) (for compound 2) or dichloromethane/hexane (1:2) (for compound 4) to give 2 and 4 respectively.



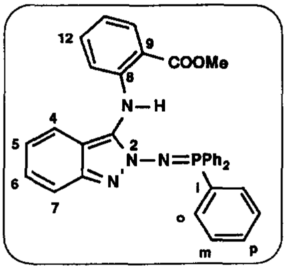
Bis(iminophosphorane) 2 (80%), yellow prisms m.p. 189-190°C. (Found: C, 77.3; H, 5.2; N, 9.4. $C_{49}H_{39}N_5P_2$ requires: C, 77.5; H, 5.2; N, 9.2); i.r. (Nujol) 1620, 1559, and 1112 cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$): 6.41-6.49 (m, 3H), 6.69-6.81 (m, 2H), 7.01-7.16 (m, 6H), 7.29-7.55 (m, 15H), 7.61-7.86 (m, 12H), 8.06 (s, 1H, NH); ^{13}C n.m.r. δ (CDCl$_3$): 111.91 (C-13), 112.74 (C-3a), 115.51 (C-7), 116.89 (C-12), 117.88 (C-11), 118.17 (C-5), 119.40 ($^3J_{P\text{-}C}$=9.5 Hz, C-10), 120.19 (C-4), 123.13 (C-6), 128.21$^{\Delta}$ ($^3J_{P\text{-}C}$=12.0 Hz, C-16), 128.55$^{\Delta}$ ($^3J_{P\text{-}C}$=11.8 Hz, C-20), 128.63* ($^1J_{P\text{-}C}$=97.6 Hz, C-14), 129.54 ($^3J_{P\text{-}C}$=10.7, C-3), 130.90* ($^1J_{P\text{-}C}$=99.1 Hz, C-18), 131.63† ($^4J_{P\text{-}C}$=2.7 Hz, C-17), 131.72† ($^4J_{P\text{-}C}$=2.8 Hz, C-21), 132.59$^\#$ ($^2J_{P\text{-}C}$=9.8 Hz, C-15), 133.26$^\#$ ($^2J_{P\text{-}C}$=9.5 Hz, C-19), 137.54 (C-9), 138.07 ($^3J_{P\text{-}C}$=20.6 Hz, C-8), 142.97 (C-7a). Values assigned by decoupling methods and 2D ^{1}H-^{13}C correlation techniques; ^{31}P n.m.r. δ (CDCl$_3$): 4.53, 17.58; m/z (%): 759 (M$^+$, 5), 183 (100).



Bis(iminophosphorane) 4 (88%), yellow prisms m.p. 199-200°C. (Found: C, 77.5; H, 5.3; N, 4.0. $C_{47}H_{40}N_2O_2P_2$ requires: C, 77.7; H, 5.4; N, 3.8); i.r. (Nujol) 1687, 1568, and 1109 cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$): 1.09 (t, 3H, ^{3}J=7.1 Hz, CH$_3$), 3.93 (q, 2H, ^{3}J=7.1 Hz, CH$_2$), 6.46 (d, 1H, ^{3}J=7.7 Hz, H-3), 6.60 (t, 1H, ^{3}J=7.2 Hz, H-5), 6.70 (td, 1H, ^{3}J=7.3 Hz, ^{4}J=1.7 Hz, H-4), 7.33-7.51 (m, 18H), 7.72-7.82 (m, 12H), 8.04 (d, 1H, ^4J_P=7.6 Hz, CH=C), 9.12 (dt, 1H, ^{3}J=7.6 Hz, ^{4}J=1.7 Hz, H-6); ^{13}C n.m.r. δ(CDCl$_3$): 14.38 (CH$_3$), 60.32 (CH$_2$), 115.31 (^3J_P=18.9 Hz, *CH*=C), 116.83 (C-5), 120.86 (^3J_P=10.2 Hz, C-3), 126.02 (C-6), 127.91* (^2J_P=12.0 Hz, C-8), 128.38* (^2J_P=11.9 Hz, C-12), 130.50$^\#$ (^4J_P=2.8 Hz, C-10), 131.34$^\#$ (^4J_P=2.7 Hz, C-14), 131.80$^{\Delta}$ (^1J_P=97.2 Hz, C-7), 131.18$^{\Delta}$ (^1J_P=100.3 Hz, C-11), 132.50† (^3J_P=9.1 Hz, C-9), 132.68† (^3J_P=9.1 Hz, C-13), 132.77 (C-4), 133.46 (^3J_P=7.3 Hz, C-1), 134.89 (CH=*C*), 149.04 (C-2), 168.79 (^3J_P=6.7 Hz, C=O); m/z (%) 726 (M$^+$, 1), 277 (37), 199 (28), 183 (100).

Preparation of Iminophosphorane 9.

To a solution of *o*-azidobenzaldehyde (0.735 g, 5 mmol) in anhydrous ethanol (30 ml), a solution of methyl anthranilate (0.82 g, 5.5 mmol) in the same solvent (10 ml) and acetic acid (0.5 ml) was added. The reaction mixture was stirred at room temperature for 14h. Then the solvent was removed and the residual material was washed with 5% NaCO$_3$H aqueous solution (2x15 ml), water (2x15 ml), and extracted with diethyl ether (3x20 ml). The combined organic layer was dried (MgSO$_4$) and the solvent evaporated. The remaining product was slurried with hexane (20 ml) and the separated solid was filtered to give the crude aldimine **8** which was used without purification to the next step. A solution of TPP (1.31 g, 0.5 mmol) in dry dichloromethane (20 ml) was added dropwise under nitrogen to a well-stirred solution of the aldimine **8** (1.4 g, 5 mmol) in the same solvent (30 ml) at 0°C. After the stirring was continued for 1h at the same temperature, the mixture was slowly warmed to room temperature for 16h. The solvent was removed and the residual material was recrystallized from diethyl ether/hexane (1:1) to give **9** (40%), yellow prisms m.p. 161-162°C. (Found: C, 72.9; H, 5.2; N, 10.2. $C_{33}H_{27}N_4O_2P$ requires: C, 73.0; H, 5.02; N, 10.3); i.r. (Nujol) 3330, 1682, and 1581 cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$): 3.92 (s, 3H, CH$_3$O), 6.60 (d, 1H, ^{3}J=8.4 Hz, H-13), 6.68 (t, 1H, ^{3}J=7.6 Hz, H-11), 6.85 (t, 1H, ^{3}J=7.6 Hz, H-5), 7.03-7.12 (m, 2H, H-6, H-12), 7.31-7.49 (m, 11H), 7.75 (ddd, 6H, ^3J_P=12.0 Hz, ^{3}J=7.0 Hz, ^{4}J=1.4 Hz, Ho), 7.96 (dd, 1H, ^{3}J=7.9 Hz, ^{4}J=1.3 Hz, H-10); ^{13}C n.m.r. δ (CDCl$_3$): 51.63 (CH$_3$O), 111.65 (C-3a), 114.39 (C-9), 114.98 (C-13), 115.86 (C-7), 116.95 (C-11), 118.46 (C-5), 118.51 (C-4), 123.22 (C-6), 125.57 (^3J_P=11.0 Hz, C-3),



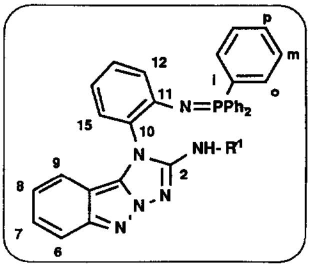
128.30 (^1J_P=98.3 Hz, Ci), 128.35 (^3J_P=12.1 Hz, Cm), 130.95 (C-10), 132.01 (^4J_P=2.8 Hz, Cp), 133.32 (^2J_P=9.6 Hz, Co), 133.89 (C-12), 142.64 (C-7a), 147.36 (C-8), 168.64 (C=O); m/z (%): 542 (M^+, 19), 276 (100), 183 (69), 108 (24).

General Procedure for the Preparation of Iminophosphoranes 5.

To a solution of bis(iminophosphorane) 2 (0.5 g, 0.66 mmol) in dry dichloromethane (15 ml) was added dropwise the appropriate isothiocyanate (0.66 mmol) and the reaction mixture was stirred at room temperature for 7h. The solvent was removed under reduced pressure and the residual material was chromatographed on a silica gel column, eluting with dichloromethane/ethyl acetate (3:1) to afford 5 as crystalline solids.

5a: R^1=C_2H_5 (43%), white prisms m.p. 241-242°C. (Found: C, 73.8; H, 5.3; N, 15.3. $C_{34}H_{29}N_6P$ requires C, 73.9; H, 5.3; N, 15.2); i.r. (Nujol): 3375, 1635, 1591, 1497, 1482, 1438, 1349, 1108, 1051, 1018, 999, 758, 719, and 690 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 0.92 (t, 3H, ^3J= 7.3 Hz, CH_3), 3.24-3.35 (m, 2H, CH_2), 6.60 (s, 1H; NH), 6.71 (d, 1H, $^3J_{12,13}$=7.3 Hz, H-12), 6.80-6.89 (m, 2H, H-14, H-8), 7.02 (td, 1H, ^3J=7.7 Hz, $^4J_{13,15}$=1.6 Hz, H-13), 7.21 (td, 1H, ^3J=8.5, Hz $^4J_{7,9}$=1.3 Hz, H-7), 7.34 (d, 1H, $^3J_{9,8}$=8.5 Hz, H-9), 7.37-7.64 (m, 16H), 7.70 (d, 1H, $^3J_{6,7}$=8.7 Hz, H-6); ^{13}C n.m.r. δ ($CDCl_3$): 14.35 (CH_3), 38.24 (CH_2), 103.50 (C-9a), 116.16 (C-6), 117.10 (C-8), 117.28 (C-9), 118.48 (C-14), 123.41 (^3J_P=9.9 Hz, C-12), 124.01 (C-7), 125.97 (C-15), 128.60 (^3J_P=9.9 Hz, C-10), 128.79 (C-13), 128.91 (^3J_P=12.2 Hz, Cm), 129.37 (^1J_P=100.5 Hz, Ci), 129.60 (C-9b), 132.24 (^2J_P=10.0 Hz, Co), 132.33 (^4J_P=2.8 Hz, Cp), 145.04 (C-11), 148.42 (C-5a), 154.81 (C-2); m/z (%): 553 (M^++1, 5), 552 (M^+, 12), 483 (16), 455 (11), 262 (40), 198 (6), 185 (20), 184 (24), 183 (100), 152 (13), 108 (60), 107 (18), 91 (16), 77 (26).

5b: R^1=C_6H_5-CH_2 (53%) white prisms m.p. 200-201°C. (Found: C, 76.3; H, 5.0: N, 13.5. $C_{39}H_{31}N_6P$ requires C, 76.2; H, 5.1: N, 13.7); i.r. (Nujol) 3370, 3166, 1638, 1594, 1493, 1438, 1354, 1338, 1110, 1054, 1017, 747, 722, 694, and 647 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 4.17 (d, 1H, ^2J=13.0 Hz), 4.57 (dd, 1H, ^2J=13.0 Hz, ^3J=8.5 Hz), 6.62 (d, 1H, ^3J=8.0 Hz, H-15), 6.80-7.59 (m, 27H, ArH+NH), 7.75 (d, 1H, ^3J=8.7 Hz, H-6); ^{13}C n.m.r. δ ($CDCl_3$): 47.88 (CH_2), 103.49 (C-9a), 116.23 (C-6), 117.22 (C-8), 117.37 (C-9), 118.28 (C-14), 123.06 (^3J_P=11.8 Hz, C-12), 124.15 (C-7), 125.72 (^4J_P=1.8 Hz, C-15), 127.25, 128.22, 128.46, 128.48 (C-10), 128.66 (C-13), 128.89 (^1J_P=100.5 Hz, Ci), 129.67 (C-9b), 129.90 (^3J_P=12.2 Hz, Cm), 132.24 (^2J_P=9.9 Hz, Co), 132.30 (^4J_P=2.8 Hz, Cp), 137.80 (q), 144.50 (C-11), 148.48 (C-5a), 154.59 (C-2); ^{31}P n.m.r. δ ($CDCl_3$): 8.83; m/z (%): 615 (M^++1, 2), 484 (4), 456 (3), 262 (14), 185 (16), 184(14), 183 (100), 152 (14), 133 (7), 108 (45), 107 (19), 91 (64), 77 (15).



5c: R^1=4-CH_3-C_6H_4 (82%), white prisms m.p. 187-188°C. (Found: C, 76.1; H, 5.2; N, 13.8. $C_{39}H_{31}N_6P$ requires: C, 76.2; H, 5.1; N, 13.7); i.r. (Nujol) 3370, 3234, 1606, 1592, 1575, 1561, 1494, 1224, 1107, 759, 720, and 697 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 2.17 (s, 3H, CH_3), 6.73 (d, 1H, ^3J=8.0 Hz), 6.79-6.91 (m, 4H), 6.96-7.07 (m, 3H), 7.20 (ddd, 1H, $^3J_{7,6}$=8.7 Hz, $^3J_{7,8}$=6.8 Hz, $^4J_{7,9}$=0.9 Hz, H-7), 7.28-7.69 (m, 18H), 9.52 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$): 20.60 (CH_3), 103.35 (C-9a), 116.24 (C-6), 117.37 (C-8), 117.42 (C-9), 117.48, 118.86 (C-14), 123.80 (^3J_P=9.7 Hz, C-12), 124.42 (C-7), 126.01 (^4J_P=1.1 Hz, C-15), 128.48 (^3J_P=9.7 Hz, C-10), 128.96 (^1J_P=100.6 Hz, Ci), 129.00 (^3J_P=12.2 Hz, Cm), 129.02 (C-13), 129.28, 129.98 (C-9b), 130.84 (q), 132.28 (^2J_P=10.0 Hz, Co), 132.42 (^4J_P=2.8 Hz, Cp), 137.00 (q), 144.81 (^2J_P=1.0 Hz, C-11), 148.69 (C-5a), 150.52 (C-2); ^{31}P n.m.r. δ ($CDCl_3$): 10.43; m/z (%): 614 (M^+, 2), 483 (7), 455 (5), 262 (39), 185 (22), 184 (24), 183 (100), 152 (14), 132 (11), 131 (15), 117 (13), 116 (11), 108 (56), 107 (19), 91 (17), 77 (19).

5d: R^1=4-CH_3O-C_6H_4 (76%), colourless prisms m.p. 216-217°C. (Found: C, 74.1; H, 4.8; N, 13.4. $C_{39}H_{31}N_6OP$ requires C, 74.3; H, 4.9; N, 13.3); i.r. (Nujol) 3404, 3143, 1604, 1592, 1576, 1511, 1495, 1330, 1241, 1111, 1030, 1020, 825, 741, 720, and 695 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 3.73 (s, 3H, CH_3O), 6.68 (d, 2H, ^3J=8.9 Hz), 6.78 (d,1H, $^3J_{12,13}$=8.0 Hz, H-12), 6.86-6.94 (m, 2H, H-8, H-14), 7.06 (td, 1H, ^3J=7.5 Hz, $^4J_{13,15}$=1.5 Hz, H-13), 7.10 (d, 2H, ^3J=8.9 Hz), 7.26 (t, 1H, ^3J=7.2 Hz, H-7), 7.35-7.67 (m, 17H), 7.73 (d, 1H, $^3J_{6,7}$=8.6 Hz, H-6), 9.54 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$): 55.48 (CH_3), 103.40 (C-9a), 114.15, 116.34 (C-6), 117.36 (C-8), 117.44 (C-9), 118.98 (C-14), 119.14, 123.91 (^3J_P=9.6 Hz, C-12), 124.41 (C-7), 126.12 (C-15), 128.66 (^3J_P=9.9 Hz, C-10), 129.04 (^3J_P=12.2 Hz, Cm), 129.05 (C-13), 129.14 (^1J_P=100.6 Hz, Ci), 132.34 (^2J_P=9.9 Hz, Co), 132.44 (^4J_P=2.8 Hz, Cp), 133.06 (q), 144.91 (C-11), 148.76 (C-5a), 150.93 (C-2), 154.59 (q), C-9b not observed; m/z (%): 630 (M^+, 2), 629 (3), 483 (4), 455 (4), 262 (34), 261 (14), 185 (19), 184 (22), 183 (100), 152 (11), 147 (10), 133 (14), 108 (43), 77 (10).

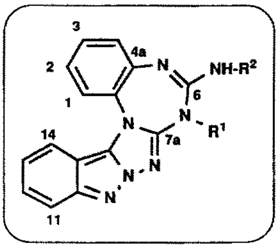
5e: R^1=4-F-C_6H_4 (63%), colourless prisms m.p. 203-204°C. (Found: C, 73.6; H, 4.5; N, 13.4 $C_{38}H_{28}FN_6P$ requires: C, 73.8; H, 4.6; N, 13.6); i.r. (Nujol) 3375, 1617, 1581, 1510, 1493, 1224, 1175, 1108, 998, 827, 756, 720, and 695 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 6.75-7.74 (m, 27H), 9.95 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$): 103.29 (C-9a), 115.22 (^2J_F=22.5 Hz), 116.24 (C-6), 117.33* (C-9), 117.52* (C-8), 118.83 (^3J_F=7.7 Hz), 119.03 (C-14), 123.77 (^3J_P=11.4 Hz, C-12), 124.49 (C-7), 125.89 (C-15), 128.45 (^3J_P=9.6 Hz, C-10), 128.87 (^1J_P=100.7 Hz, Ci), 128.94 (C-13, C-9b), 129.00 (^3J_P=12.3 Hz, Cm), 132.23 (^2J_P=10.0 Hz, Co), 132.48 (^4J_P=2.8 Hz, Cp), 135.62 (^4J_F=2.4 Hz, q), 144.62 (^2J_P=1.0 Hz, C-11), 148.74 (C-5a), 150.43 (C-2), 157.67 (^1J_F=240.1 Hz, q); m/z (%): 617 (M^+-1, 4), 482 (11), 454 (8), 262 (32), 185 (18), 184 (21), 183 (100), 152 (14), 136 (7), 121 (35), 109 (10), 108 (63), 95 (7), 94 (15), 77 (14).

General Procedure for the Preparation of 7-Alkyl(aryl)-6-alkyl(aryl)aminoindazolo[2',3':1,5][1,2,4]triazolo[4,3-*a*][1,3,5]benzotriazepines 7.

Method A.- To a solution of iminophosphorane **5** (0.5 mmol) in dry toluene (25 ml) the appropriate isothiocyanate (0.5 mmol) was added, and the reaction mixture was stirred at room temperature for 24h. After cooling, the solvent was removed and the residue was chromatographed on a silica gel column, eluting with dichloromethane/ethyl acetate (3:1) to give **7**.

Method B.- To a solution of bis(iminophosphorane) **2** (0.6 g, 0.8 mmol) in dry dichloromethane (15 ml) the appropriate isothiocyanate (0.8 mmol) was added and the reaction mixture was stirred at room temperature until the isothiocyanate was consumed (evidenced by TLC). Then, the second isothiocyanate (0.8 mmol) was added and the resultant solution was heated at reflux temperature for 24h. After cooling, the solvent was removed under reduced pressure and the residual material was purified as in Method A.

7a: R^1=R^2=C_2H_5 (70%), colourless prisms m.p. 260-261°C. (Found: C, 65.9; H, 5.6; N, 28.2. $C_{19}H_{19}N_7$ requires: C, 66.1; H, 5.5; N, 28.4); i.r. (Nujol) 3200, 1641, 1600, 1552, 1531, 1497, 1433, 1361, 1244, 1178, 756, 749, 738, and 680 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 1.28 (t, 3H, ^3J=6.9 Hz), 1.31 (t, 3H, ^3J=7.1 Hz), 3.51-3.56 (m, 2H), 3.79 (q, 2H, ^3J=7.1 Hz), 5.41 (br. s, 1H, NH), 7.07 (t, 1H, ^3J=7.6 Hz), 7.16-7.41 (m, 4H), 7.64-7.77 (m, 3H); ^{13}C n.m.r. δ ($CDCl_3$): 13.50 (CH_3), 14.48 (CH_3), 37.76 (CH_2), 43.02 (CH_2), 103.50 (C-14a), 116.58 (C-11), 117.82 (C-14), 119.02 (C-13), 119.73, 123.50 (C-12), 125.70, 127.29 (q), 127.59 (q), 127.75, 127.96, 140.41 (q), 149.16 (C-10a), 151.11 (C-7a), 153.68 (C-6); m/z (%): 346 (M^++1, 13), 345 (M^+, 54), 330 (6), 248 (16), 247 (65), 233 (14), 232 (19), 220 (36), 219 (58), 218 (38), 130 (8), 129 (20), 118 (13), 117 (17), 116 (11), 115 (12), 103 (12), 102 (30), 92 (31), 91 (51), 90 (100), 89 (31).



7b: R^1=C_2H_5, R^2=4-CH_3O-C_6H_4 (50%), colourless prisms m.p. 228-229°C. (Found: C, 68.2; H, 5.1; N, 23.3. $C_{24}H_{21}N_7O$ requires: C, 68.1; H, 5.0; N, 23.1); i.r. (Nujol) 3330, 1659, 1555, 1510, 1240, 1181, 1032, 844, 830, 760, 750, 721, and 653 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 1.48 (t, 3H, ^3J=6.7 Hz), 3.79 (s, 3H), 4.20 (q, 2H, ^3J=6.8 Hz), 6.29 (s, 1H, NH), 6.84-7.00 (m, 5H), 7.05 (d, 1H, ^3J=7.6 Hz), 7.26-7.40 (m, 3H), 7.62 (d, 1H, ^3J=8.3 Hz), 7.72-7.83 (m, 2H); ^{13}C n.m.r. δ ($CDCl_3$): 13.24 (CH_3), 44.67 (CH_2), 55.39 (CH_3O), 102.84 (C-14a), 115.04, 116.90 (C-11), 117.23 (C-14), 118.96 (C-13), 120.52, 121.84 (C-12), 122.81, 125.60, 125.79, 126.71 (q), 127.06 (q), 128.50, 132.37 (q), 139.70 (q), 149.27 (C-10a), 149.61 (C-6), 150.72 (C-7a), 156.09 (q); m/z (%): 424 (M^++1, 32), 423 (M^+, 100), 247 (18), 179 (10), 178 (7), 177 (8), 176 (8), 163 (10), 148 (13), 147 (19), 122 (11), 105 (16), 104 (11), 103 (24), 102 (34), 92 (32), 91 (21), 90 (73), 89 (14).

7c: R^1=4-CH_3O-C_6H_4, R^2=C_2H_5 (52%), colourless prisms m.p. 253-254°C. (Found: C, 67.9; H, 5.1; N, 23.0. $C_{24}H_{21}N_7O$ requires C, 68.1; H, 5.0; N, 23.1); i.r. (Nujol) 3392, 1646, 1595, 1544, 1509, 1492, 1302, 1246, 1225, 1169, 1030, 808, 765, 733, and 618 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.16 (t, 3H, ^3J=7.2 Hz, CH_3), 3.43 (q, 2H, ^3J=7.2 Hz, CH_2), 3.78 (s, 3H, CH_3O), 4.75 (br. s, 1H, NH), 6.88 (d, 2H, ^3J=8.9 Hz), 7.06 (t, 1H, ^3J=7.7 Hz), 7.18-7.39 (m, 4H), 7.57 (d, 2H, ^3J=8.9 Hz), 7.68-7.77 (m, 3H); ^{13}C n.m.r. δ ($CDCl_3$): 14.25 (CH_3), 37.90 (CH_2), 55.53 (CH_3O), 103.26 (C-14a), 114.63, 116.87 (C-11), 117.79 (C-14), 118.98 (C-13), 120.42, 123.78 (C-12), 125.75, 126.18, 127.03 (q), 127.25 (q), 128.02, 128.19, 131.48 (q), 140.19 (q), 149.51 (C-10a), 150.18 (C-6), 150.65 (C-7a), 158.50 (q); m/z (%) 424 (M^++1, 24), 423 (M^+, 83), 276 (23), 248 (15), 247 (31), 220 (42), 219 (45), 218 (26), 177 (8), 148 (33), 147 (31), 134 (10), 133 (54), 116 (9), 103 (11), 102 (26), 92 (40), 91 (48), 90 (100), 77 (40).

7d: R^1=R^2=4-CH_3O-C_6H_4 (55%), colourless prisms m.p. 240-241°C. (Found: C, 69.4; H, 4.5; N, 19.4. $C_{29}H_{23}N_7O_2$ requires: C, 69.4; H, 4.6; N, 19.5); i.r. (Nujol) 3353, 1642, 1595, 1542, 1514, 1492, 1428, 1212, 1171, 1032, 837, 773, 749, 743, and 734 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 3.66 (s, 3H), 3.72 (s, 3H), 6.81-6.89 (m, 4H), 7.04-7.39 (m, 7H), 7.63-7.81 (m, 5H), 9.75 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 54.96 (CH_3), 55.06 (CH_3), 102.54 (C-14a), 113.51, 114.25, 116.01 (C-11), 117.78 (C-14), 118.54 (C-13), 119.54, 120.64, 121.54, 123.92 (C-12), 125.61, 125.71 (q), 127.12 (q), 127.50, 128.14, 132.49 (q), 133.35 (q), 138.83 (q), 145.69 (C-6), 147.82 (C-7a), 148.67 (C-10a), 155.29 (q), 155.88 (q); m/z (%) 502 (M^++1, 8), 501 (M^+, 24), 355 (24), 354 (100), 340 (9), 339 (24), 255 (11), 254 (36), 247 (16), 239 (43), 148 (49), 147 (50), 123 (17), 122 (19), 116 (9), 108 (25), 107 (10), 77 (76).

7e: R^1=R^2=4-CH_3-C_6H_4 (62%), colourless prisms m.p. 230-231°C. (Found: C, 74.0; H, 4.8; N, 21.0. $C_{29}H_{23}N_7$ requires: C, 74.2; H, 4.9; N, 20.9); i.r. (Nujol) 3364, 1648, 1597, 1544, 1518, 1493, 1431, 1401, 1333, 1232, 1213, 1136, 816, 758, 748, and 737 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 2.16 (s, 3H), 2.25 (s, 3H), 7.03-7.16 (m, 7H), 7.33-7.43 (m, 4H), 7.66-7.86 (m, 5H), 10.18 (s, 1H, NH); ^{13}C n.m.r. δ (DMSOd_6): 20.05 (CH_3), 20.40 (CH_3), 102.61 (C-14a), 115.96 (C-11), 116.09, 118.04 (C-14), 118.71 (C-13), 119.94, 121.10 (q), 124.38 (C-12), 125.44 (q), 125.92, 127.63 (CH+q), 128.45, 129.02, 129.77, 132.30 (2xq), 136.96 (q), 138.19 (q), 138.50 (q), 144.80 (C-6), 146.71 (C-7a), 148.79 (C-10a); m/z (%) 470 (M^++1, 10), 469 (M^+, 33), 339 (25), 338 (89), 323 (12), 308 (27), 294 (6), 248 (16), 247 (74), 223 (11), 222 (32), 221 (19), 220 (24), 219 (48), 218 (32), 133 (21), 132 (43), 131 (40), 116 (21), 107 (14), 106 (20), 105 (13), 92 (15), 91 (100), 90 (60), 89 (34).

7f: R^1=R^2=4-F-C_6H_4 (60%), colourless prisms m.p. 206-207°C. (Found: C, 68.0; H, 3.7; N, 20.4. $C_{27}H_{17}F_2N_7$ requires: C, 67.9; H, 3.6; N, 20.5); i.r. (Nujol) 3217, 1665, 1544, 1505, 1437, 1323, 1235, 1209, 1154, 832, 812, 776, 750, and 659 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 7.03-7.44 (m, 11H), 7.55-7.86 (m, 5H), 10.27 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 102.61 (C-14a), 115.16 (^2J_F=22.3 Hz), 116.02 (^2J_F=23.0 Hz), 116.11 (C-11), 118.03 (C-14a), 118.65 (^3J_F=7.5 Hz), 118.73 (C-13), 121.18 (q), 121.81 (^3J_F=7.7 Hz), 124.63 (C-10), 125.57 (q), 125.92, 127.60 (CH+q), 128.47, 135.84 (q), 136.65 (^4J_F=2.4 Hz, q), 138.14 (q), 144.75 (C-7a), 146.74 (C-6), 148.79 (C-10a), 158.18 (^1J_F=240.7 Hz, q), 158.39 (^1J_F=240.5 Hz, q); m/z (%) 478 (M^++1, 18), 477 (M^+, 53), 349 (19), 342 (82), 327 (10), 314 (19), 313 (10), 312 (17), 247 (22), 230 (12), 157 (17), 156 (36), 136 (62), 135 (24), 133 (13), 116 (7), 110 (13), 109 (38), 96 (14), 95 (100), 94 (15).

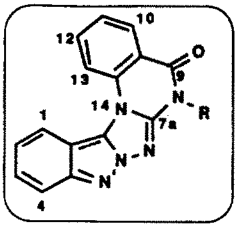
General Procedure for the Preparation of 8-Alkyl(aryl)indazolo[2',3':1,5][1,2,4]triazolo[4,3-*a*]quinazolin-9-ones 10.

Method A.- To the iminophosphorane **9** (0.54 g, 1 mmol) in dry toluene (10 ml), the appropriate aliphatic isothiocyanate (1 mmol) was added. The reaction mixture was heated at reflux temperature for 8h. After cooling, the separated solid was collected by filtration and recrystallized from toluene to give **10a** and **10b**.

Method B.- To a solution of iminophosphorane **9** (0.54 g, 1 mmol) in dry dichloromethane (15 ml), the appropriate aromatic isothiocyanate (1 mmol) was added. The resultant mixture was stirred at room temperature for 16h. The solid was separated by filtration and recrystallized from dichloromethane to give **10c-e**.

10a: R=C_2H_5 (69%), colourless prisms m.p. 282-283°C. (Found: C, 67.4; H, 4.2; N, 23.2. $C_{17}H_{13}N_5O$ requires: C, 67.3; H, 4.3; N, 23.1); i.r. (Nujol) 1688, 1634, 1619, 1605, 1572, 1500, 1437, 1323, 1314, 1260, 1135, 1097, 1074, 761, 732, and 680 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$+TFA): 1.48 (t, 3H, ^3J=7.0 Hz, CH_3), 4.39 (q, 2H, ^3J=7.0 Hz, CH_2), 7.23 (t, 1H, ^3J=8.0 Hz), 7.40 (t, 1H, ^3J=7.7 Hz), 7.63 (t, 1H, ^3J=7.7 Hz), 7.72 (d, 1H, ^3J=8.6 Hz), 8.09 (t, 1H, ^3J=8.0 Hz), 8.22 (d, 2H, ^3J=8.5 Hz), 8.41 (d, 1H, ^3J=7.2 Hz); ^{13}C n.m.r. δ ($CDCl_3$+TFA): 10.95 (CH_3), 40.03 (CH_2), 105.96 (C-14b), 112.56* (C-1), 116.22 (C-13), 116.88 (C-9a), 120.13 (C-4), 125.15 (C-3), 129.06* (C-2), 130.23 (C-10), 130.73 (C-14a), 131.94 (C-13a), 132.43* (C-11), 136.51 (C-12), 141.88 (C-4a), 148.77 (C-7a), 158.17 (C-9); m/z (%): 304 (M^++1, 11), 303 (M^+, 51), 275 (31), 234 (7), 219 (10), 218 (9), 206 (19), 192 (17), 191 (16), 178 (13), 177 (36), 152 (17), 151 (45), 130 (28), 116 (7), 103 (13), 102 (53), 91 (17), 90 (47), 77 (27), 76 (100).

10b: R=C_6H_5-CH_2 (61%), colourless prisms m.p. 318-319°C. (Found: C, 72.4; H, 4.2; N, 19.0. $C_{22}H_{15}N_5O$ requires: C, 72.3; H, 4.1; N, 19.2); i.r. (Nujol) 1682, 1618, 1606, 1573, 1518, 1500, 1439, 1345, 1257, 1141, 983, 753, 736, 712, and 683 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$+TFA): 5.53 (s, 2H, CH_2), 7.27-7.31 (m, 3H), 7.55-7.60 (m, 2H), 7.73 (td, 1H, ^3J=6.8 Hz, ^4J=1.2 Hz), 7.83-7.97 (m, 3H), 8.21 (t, 1H, ^3J=7.1 Hz), 8.29 (d, 1H, ^3J=8.0 Hz), 8.38 (d, 1H, ^3J=8.5 Hz), 8.62 (dd, 1H, ^3J=8.0 Hz, ^4J=1.1 Hz); ^{13}C n.m.r. δ ($CDCl_3$+TFA): 47.97 (CH_2), 105.71 (C-14b), 113.13* (C-1), 116.04 (C-13), 116.78 (C-9a), 119.81 (C-4), 125.79 (C-3), 128.96, 129.15, 129.35, 129.72* (C-2), 130.58 (C-14a), 131.18 (C-10), 131.72 (C-13a), 133.08* (C-11), 133.22 (q), 137.02 (C-12), 141.90 (C-4a), 148.64 (C-7a), 158.36 (C-9); m/z (%) 366 (M^++1, 2), 365 (M^+, 8), 336 (1), 274 (2), 191 (3), 177 (3), 151 (4), 130 (2), 102 (4), 91 (100), 90 (11), 77 (3), 76 (7).



10c: R=4-CH_3-C_6H_4 (62%), colourless prisms m.p. > 340°C. (Found: C, 72.4; H, 4.2; N, 19.1. $C_{22}H_{15}N_5O$ requires: C, 72.3; H, 4.1; N, 19.2); i.r. (Nujol) 1694, 1604, 1566, 1516, 1494, 1438, 1397, 1345, 1323, 1267, 1181, 1154, 880, 810, 788, 759, 738, and 687 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$+TFA): 2.47 (s, 3H, CH_3), 7.31 (d, 2H, ^3J=8.3 Hz), 7.44 (d, 2H, ^3J=8.3 Hz), 7.76 (t, 1H, ^3J=7.2 Hz), 7.81-7.98 (m, 3H), 8.28 (td, 1H, ^3J=7.2 Hz, ^4J=1.0 Hz), 8.38 (d, 1H, ^3J=7.6 Hz), 8.43 (d, 1H, ^3J=8.2 Hz), 8.64 (dd, 1H, ^3J=8.0 Hz, ^4J=0.9 Hz); ^{13}C n.m.r. δ ($CDCl_3$+TFA): 20.88 (CH_3), 105.77 (C-14b), 113.23* (C-1), 116.20 (C-13), 116.85 (C-9a), 119.89 (C-4), 126.00 (C-3), 127.26, 129.27 (q), 129.94* (C-2), 130.81 (C-14a), 131.34, 131.49 (C-10), 132.10 (C-13a), 133.33* (C-11), 137.53 (C-12), 142.05 (C-4a), 142.41 (q), 149.53 (C-7a), 159.65 (C9); m/z (%) 366 (M^++1, 14), 365 (M^+, 47), 336 (3), 322 (2), 234 (8), 206 (48), 192 (16), 178 (17), 177 (70), 152 (29), 151 (100), 131 (19), 130 (27), 102 (42), 91 (23), 90 (16), 77 (49), 76 (70).

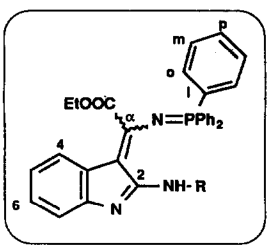
10d: R=4-CH_3O-C_6H_4 (63%), colourless prisms m.p. > 340°C. (Found: C, 69.4; H, 3.9; N, 18.4. $C_{22}H_{15}N_5O_2$ requires: C, 69.3; H, 4.0; N, 18.4); i.r. (Nujol) 1703, 1689, 1606, 1567, 1515, 1496, 1439, 1247, 1176, 1032, 833, 821, 755, 734, and 678 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$+TFA): 3.91 (s, 3H, CH_3O), 7.13 (d, 2H, ^3J=8.9 Hz), 7.37 (d, 2H, ^3J=8.9 Hz), 7.75 (t, 1H, ^3J=7.4 Hz), 7.81-7.97 (m 3H), 8.27 (t, 1H, ^3J=7.6 Hz), 8.37 (d, 1H, ^3J=8.2 Hz), 8.42 (d, 1H, ^3J=8.5 Hz), 8.63 (dd, 1H, ^3J=8.0 Hz, ^4J=0.8 Hz); ^{13}C n.m.r. δ ($CDCl_3$+TFA): 55.69 (CH_3), 105.72 (C-14b), 113.19* (C-1), 115.95, 116.17 (C-13), 116.79 (C-9a), 119.86 (C-4), 124.69 (q), 125.92 (C-3), 128.97, 129.88* (C-2), 130.77 (C-14a), 131.44 (C-10), 132.05 (C-13a), 133.24* (C-11), 137.48 (C-12), 142.00 (C-4a), 149.61 (C-7a), 159.67 (C-9), 161.15 (q); m/z (%) 382 (M^++1, 26), 381 (M^+, 100), 338 (2), 234 (6), 206 (22), 192 (6), 177 (29), 152 (15), 151 (52), 130 (19), 107 (4), 102 (29), 90 (12), 77 (27), 76 (44).

10e: R=4-F-C_6H_4 (65%), colourless prisms m.p. > 340°C. (Found: C, 68.3; H, 3.4; N, 18.3. $C_{21}H_{12}FN_5O$ requires: C, 68.3; H, 3.3; N, 18.3); i.r. (Nujol) 1694, 1630, 1611, 1604, 1571, 1512, 1500, 1439, 1230, 1157, 833, 751, 745, and 738 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$+TFA): 7.22 (t, 1H, ^3J=8.0 Hz), 7.33-7.53 (m, 3H), 7.60- 7.72 (m, 4H), 8.20 (t, 1H, ^3J=7.3 Hz), 8.28-8.46 (m, 3H); ^{13}C n.m.r. δ ($CDCl_3$+TFA): 106.20 (C-14b), 112.85* (C-1), 116.65 (C-13), 116.92 (C-9a), 117.76 (^2J_F=23.7 Hz), 120.38 (C-4), 126.12 (C-3), 128.63 (q), 129.98* (C-2), 130.42 (^3J_F=9.1), 131.20 (C-10), 131.59 (C-14a), 132.55 (C-13a), 133.53* (C-11), 137.86 (C-12), 142.30 (C-4a), 149.95 (C-7a), 159.47 (C-9), 164.51 (^1J_F=252.1 Hz, q); m/z (%) 370 (M$^+$+1, 27), 369 (M$^+$, 100), 340 (6), 234 (5), 206 (20), 192 (5), 177 (30), 164 (5), 152 (13), 151 (53), 130 (21), 102 (32), 95 (16), 90 (11), 77 (14), 76 (60).

General Procedure for the Preparation of Indole Derivatives 13.

To a solution of bis(iminophosphorane) **4** (0.5 g, 0.6 mmol) in dry dichloromethane (20 ml) was added dropwise at 0°C the appropriate isocyanate (0.8 mmol) and the reaction mixture was stirred at this temperature for 1h. The solvent was removed under reduced pressure and the residual material was slurried with diethyl ether (60 ml). The formed solid was separated by filtration and recrystallized from ethanol to afford **13** as crystalline solids.

13a: Ar=4-CH_3-C_6H_4 (50%), orange prisms m.p. 225-226°C. (Found: C, 76.5; H, 5.5; N, 7.3. $C_{37}H_{32}N_3O_2P$ requires: C, 76.4; H, 5.5; N, 7.2); i.r. (Nujol) 3280, 1721, 1562, 1296, 1240, 1217, 1172, 1115, 1036, 1019, 1002, 877, 752, 730, and 690 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 0.95 (t, 3H, ^3J=7.1 Hz), 2.26 (s, 3H), 3.41 (q, 2H, ^3J=7.1 Hz), 6.79 (td, 1H, ^3J=7.9 Hz, ^4J=0.7 Hz), 6.96-7.05 (m, 5H), 7.35 (d, 1H, ^3J=7.6 Hz), 7.52-7.79 (m, 16H), 10.62 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$): 13.23 (CH_3), 20.68 (CH_3), 61.13 (CH_2), 112.50 ($^3J_{P-C}$=20.7 Hz, C-3), 116.69 (C-7), 118.15 (C-4), 118.91, 119.57 (C-5), 125.10 (C-6), 126.72 ($^4J_{P-C}$=2.1 Hz, C-3a), 127.54 ($^1J_{P-C}$=102.6 Hz, Ci), 128.96 ($^3J_{P-C}$=12.6 Hz, Cm), 129.17, 132.85 ($^2J_{P-C}$=10.2 Hz, Co), 132.91 ($^4J_{P-C}$=2.8 Hz, Cp), 138.30 (q), 145.90 ($^2J_{P-C}$=3.9 Hz, Cα), 153.94 (C-9a), 161.80 ($^4J_{P-C}$=1.1 Hz, C-2), 165.56 ($^3J_{P-C}$=9.9 Hz, C=O); ^{31}P n.m.r. δ ($CDCl_3$): 17.03 ppm; m/z (%) 581 (M$^+$, 3), 580 (1), 535 (7), 508 (2), 277 (5), 276 (4), 262 (88), 231 (9), 185 (15), 184 (23), 183 (100), 152 (12), 108 (61), 107 (19), 91 (6), 77 (9).



13b: Ar=4-CH_3O-C_6H_4 (60%), orange prisms m.p. 217-218°C. (Found: C, 72.2; H, 5.7; N, 5.9. $C_{37}H_{32}N_3O_3P$ requires: C, 74.4; H, 5.4; N, 7.0); i.r. (Nujol) 3459, 1727, 1591, 1579, 1562, 1506, 1296, 1245, 1223, 1172, 1104, 996, 877, 832, 752, 724, and 696 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 0.96 (t, 3H, ^3J=7.1 Hz), 3.43 (q, 2H, ^3J=7.1 Hz), 3.75 (s, 3H), 6.75-6.83 (m, 3H), 6.97 (d, 1H, ^3J=7.6 Hz), 7.08 (td, 1H, ^3J=7.9 Hz, ^4J=0.8 Hz), 7.34 (d, 1H, ^3J=7.6 Hz), 7.49-7.79 (m, 17H), 10.57 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$): 13.30 (CH_3), 55.57 (CH_3), 61.18 (CH_2), 112.71 ($^3J_{P-C}$=20.6 Hz, C-3), 114.08, 116.54 (C-7), 118.23 (C-4), 119.54 (C-5), 120.48, 125.23 (C-6), 126.60 ($^4J_{P-C}$=2.2 Hz, C-3a), 127.62 ($^1J_{P-C}$=102.4 Hz, Ci), 129.00 ($^3J_{P-C}$=12.7 Hz, Cm), 132.91 ($^4J_{P-C}$=3.1 Hz, Cp), 132.92 ($^2J_{P-C}$=10.3 Hz, Co), 134.40 (q), 145.61 ($^2J_{P-C}$=3.9 Hz, Cα), 153.99 (C-9a), 154.52 (q), 161.92 ($^4J_{P-C}$=1.3 Hz, C-2), 165.70 ($^3J_{P-C}$=9.9 Hz, C=O); m/z (%) 596 (M$^+$-1, 1), 551 (4), 277 (4), 262 (63), 247 (2), 246 (2), 185 (14), 184 (23), 183 (100), 152 (16), 115 (8), 108 (69), 107 (22), 77 (13).

13c: Ar=4-Cl-C_6H_4 (54%), orange prisms m.p. 218-219°C. (Found: C, 70.3; H, 5.0; N, 7.1. $C_{37}H_{29}ClN_3O_2P$ requires: C, 71.8; H, 4.9; N, 7.0); i.r. (Nujol) 3352, 1727, 1591, 1557, 1517, 1410, 1302, 1245, 1211, 1124, 877, 752, 718, 690, and 639 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 0.95 (t, 3H, ^3J=7.1 Hz), 3.43 (q, 2H, ^3J=7.1 Hz), 6.82 (t, 1H, ^3J=7.3 Hz), 7.00 (d, 1H, ^3J=7.3 Hz), 7.08 (t, 1H, ^3J=7.8 Hz), 7.15 (d, 2H, ^3J=8.7 Hz), 7.36 (d, 1H, ^3J=7.6 Hz), 7.48-7.80 (m, 17H), 10.74 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$): 13.21 (CH_3), 61.24 (CH_2), 112.20 ($^3J_{P-C}$=20.8 Hz, C-3), 116.83 (C-7), 118.24 (C-4), 119.94 (CH+C-5), 125.14 (C-6), 125.74 (q), 126.61 ($^4J_{P-C}$=2.3 Hz, C-3a), 127.27 ($^1J_{P-C}$=102.3 Hz, Ci), 128.50, 129.01 ($^3J_{P-C}$=12.6 Hz, Cm), 132.81 ($^2J_{P-C}$=10.3 Hz, Co), 133.02 ($^4J_{P-C}$=2.9 Hz, Cp), 139.43 (q), 146.57 ($^2J_{P-C}$=3.9 Hz, Cα), 153.32 (C-9a), 161.39 ($^4J_{P-C}$=1.3 Hz, C-2), 165.41 ($^3J_{P-C}$=10.0 Hz, C=O); m/z (%) 615 (M$^+$+2, 5), 613 (M$^+$, 2), 183 (100).

13d: Ar=4-F-C_6H_4 (36%), orange prisms m.p. 191-192°C. (Found: C, 73.7; H, 5.0; N, 7.3. $C_{37}H_{32}N_3O_2P$ requires: C, 73.8; H, 5.0; N, 7.2); i.r. (Nujol) 3205, 1727, 1613, 1579, 1568, 1545, 1506, 1308, 1206, 1104, 1007, 877, 832, 752, 718, and 696 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 0.96 (t, 3H, ^3J=7.1 Hz), 3.44 (q, 2H, ^3J=7.1 Hz), 6.82-7.08 (m, 5H), 7.52-7.79 (m, 18H), 10.68 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$): 13.26 (CH_3), 61.24 (CH_2), 112.47 ($^3J_{P-C}$=21.3 Hz, C-3), 115.13 (^2J_F=22.1 Hz), 116.81 (C-7), 118.26 (C-4), 119.78 (C-5), 120.10 (^3J_F=7.3 Hz), 125.22 (C-6), 126.72 ($^4J_{P-C}$=2.3 Hz, C-3a), 127.52 ($^1J_{P-C}$=102.6 Hz, Ci), 129.03 ($^3J_{P-C}$=12.4 Hz, Cm), 132.78 ($^2J_{P-C}$=10.1 Hz, Co), 137.06 (^4J_F=2.5 Hz), 146.09 ($^2J_{P-C}$=4.1 Hz, Cα), 153.73 (C-9a), 157.68 (^1J_F=239.6 Hz), 161.76 (C-2), 165.57 ($^3J_{P-C}$=9.9 Hz, C=O), Cp not observed;

^{31}P n.m.r. δ ($CDCl_3$): 17.69 ppm; m/z (%) 585 (M^+, 3), 584 (1), 540 (3), 539 (8), 512 (2), 262 (94), 214 (8), 185 (14), 184 (25), 183 (100), 152 (12), 108 (63), 107 (17), 77 (6).

Preparation of compound 14.

To a solution of indole derivative **13b** (Ar=4-CH_3O-C_6H_4) (0.5 g, 0.8 mmol) in ethanol (25 ml), methyl iodide (5 ml) was added. The mixture was stirred at room temperature for 16h, then potassium hydroxide (0.05 g, 0.8 mmol) was added and the solution was stirred at room temperature for 10 min. The precipiteted solid was collected by filtration, air-dried and recrystallized from ethanol to give **14** (98%), orange prisms m.p. 203-204°C. (Found: C, 74.5; H, 5.5; N, 6.7. $C_{38}H_{34}N_3O_3P$ requires: C, 74.6; H, 5.6; N, 6.9); i.r. (Nujol) 1710, 1630, 1557, 1500, 1398, 1251, 1228, 1104, 996, 911, 832, 741, 724, and 696 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 0.78 (t, 3H, ^3J=7.1 Hz), 2.88 (s, 3H, CH_3N), 3.19 (q, 2H, ^3J=7.1 Hz), 3.73 (s, 3H, CH_3O), 6.66 (d, 1H, ^3J=7.3 Hz, H-7), 6.71* (d, 2H, ^3J=7.2 Hz), 6.76* (d, 2H, ^3J=7.2 Hz), 6.93 (t, 1H, ^3J=7.2 Hz, H-5), 7.07 (t, 1H, ^3J=7.3 Hz, H-6), 7.43-7.59 (m, 9H, Hm, Hp), 7.99 (ddd, 6H, ^3J_p=12.5 Hz, ^3J=6.7 Hz, ^4J=1.4 Hz, Ho), 8.26 (d, 1H, ^3J=7.0 Hz, H-4); ^{13}C n.m.r. δ ($CDCl_3$): 13.53 (CH_3), 32.41 (NCH_3), 55.42 (OCH_3), 60.26 (CH_2), 106.08 (C-7), 110.23 (^3J=23.6 Hz, C-3), 113.65, 114.51 (C3a), 120.18 (C-5), 121.84 (C-4), 121.89, 124.55 (C-6), 126.65 (q), 128.49 (^3J=12.4 Hz, Cm), 128.99 (^1J=102.2 Hz, Ci), 132.16 (^4J=2.7 Hz, Cp), 133.08 (^2J=10.2 Hz, Co), 144.66 (C-7a), 147.26 (C-2), 153.15 (^2J=3.4 Hz, Cα), 153.36 (q), 166.81 (^3J=9.4 Hz, C=O); m/z (%) 611 (M^+, 3), 537 (2), 335 (2), 334 (5), 305 (5), 304 (23), 288 (4), 287 (18), 277 (38), 276 (17), 201 (23), 199 (26), 183 (100), 152 (30), 143 (10), 122 (14), 115 (11), 114 (7), 108 (43), 107 (25), 77 (47).

1-Methyl-2-(*p*-methoxyphenyl)imino-2,3-dihydroindole 15.

To a suspension of compound **14** (0.3 g, 0.5 mmol) in ethanol (20 ml), concentrated hydrochloric acid (5 ml) was added. The resultant mixture was stirred at room temperature for 16h. Then, the solvent was removed under reduced pressure and the residual material was recrystallized from diethyl ether/ethanol (2:1) to afford **15** (30%), colourless prisms m.p. 214-215°C. (Found: C, 76.0; H, 6.4; N, 11.2. $C_{16}H_{16}N_2O$ requires: C, 76.2; H, 6.4; N, 11.1); i.r. (Nujol) 1659, 1619, 1511, 1251, 1228, 1030, 929, 843, 764, and 752 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+DMSO-d_6): 3.84 (s, 3H, CH_3O), 3.88 (s, 3H, CH_3N), 4.13 (s, 2H, CH_2), 7.01 (d, 2H, ^3J=8.3 Hz), 7.20-7.50 (m, 6H); ^{13}C n.m.r. δ ($CDCl_3$+DMSO-d_6): 30.94 (CH_3N), 35.57 (CH_2), 55.09 (CH_3O), 110.09 (C-7), 114.62, 124.09, 124.67, 126.30 (CH+C3a), 128.16 (q), 128.22, 143.70 (C7a), 158.99 (q), 168.24 (C2); m/z (%) 253 (9), 252 (M^+, 48), 238 (4), 237 (23), 131 (79), 130 (31), 121 (100), 118 (30), 117 (18), 116 (14), 91 (25), 77 (27).

Preparation of Pyrrolo[2,3-b]indole derivative 16.

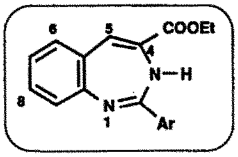
To a solution of bis(iminophosphorane) **4** (0.5 g, 0.6 mmol) in dry toluene (20 ml) was added methyl isocyanate (0.04 g, 0.6 mmol) and the reaction mixture was heated at reflux temperature for 4h. After cooling, the solvent was removed and the residue was chromatographed on a silica gel column, eluting with ethyl acetate/*n*-hexane (3:1) to give **16** (40%), red prisms m.p. 103-104°C. (Found: C, 76.0; H, 4.8; N, 9.2. $C_{29}H_{22}N_3OP$ requires: C, 75.8; H, 4.8; N, 9.1); i.r. (Nujol) 1738, 1636, 1562, 1319, 1104, 888, 752, 718, 690, and 667 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 3.05 (s, 3H), 6.80 (td, 1H, ^3J=7.4 Hz, ^4J=0.7 Hz), 6.98-7.04 (m, 2H), 7.24 (d, 1H, ^3J=7.3 Hz), 7.48-7.58 (m, 9H), 7.76 (ddd, 6H, $^3J_{P-C}$=12.1 Hz, ^3J=7.7 Hz, ^4J=1.6 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 25.82 (CH_3), 118.73, 121.12, 122.82, 125.69, 126.35 (q), 128.79 ($^3J_{P-C}$=12.6 Hz, Cm), 129.18 ($^1J_{P-C}$=12.6 Hz, Ci), 132.40 ($^4J_{P-C}$=12.6 Hz, Cp), 132.84 ($^2J_{P-C}$=12.6 Hz, Co), 132.99 (q), 143.75 (q), 159.61 (q), 171.18 (J=14.4 Hz, q), 173.71 (q); m/z (%) 460 (17) 459 (M^+, 50), 430 (2), 403 (1), 262 (77), 261 (11), 185 (11), 184 (18), 183 (100), 108 (52), 107 (23), 77 (9), 57 (4).

General Procedure for the Preparation of Ethyl 2-Aryl-1,3-1*H*-benzodiazepine-4-carboxylates 19.

To a solution of bis(iminophosphorane) 4 (0.508 g, 0.7 mmol) in dry dichloromethane (25 ml), the corresponding aroyl chloride (7 mmol) and triethylamine (0.07 g, 0.7 mmol) were added dropwise. The reaction mixture was stirred at room temperature for 7h. The solvent was removed and dry benzene (15 ml) was added. The precipitated triethylammonium chloride was separated by filtration and the solvent was removed from the filtrate. The residual material was chromatographed on a silica gel column, eluting with ethyl acetate/hexane (1:2) to give **19** which were recrystallized from the appropriate solvents.

19a: Ar=C_6H_5 (55%), red prisms from ethanol m.p. 119-120°C. (Found: C, 73.8; H, 5.5; N, 9.7. $C_{18}H_{16}N_2O_2$ requires: C, 73.9; H, 5.5; N, 9.6); i.r. (Nujol) 3364, 1688, 1667, 1644, 1589, 1449, 1301, 1287, 1245, 1224, 1210, 1129, 1062, 1018, 960, 904, 878, 862, 769, 704, 674, and 663 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.36 (t, 3H, ^3J=7.3 Hz), 4.29 (q, 2H, ^3J=7.3 Hz), 6.46 (s, 1H, H-5), 6.61 (s, 1H, NH), 6.75 (d, 1H, ^3J=7.3 Hz, H-6), 6.89 (t, 1H, ^3J=7.9 Hz, H-7), 6.92 (d, 1H, ^3J=7.3 Hz, H-9), 7.12 (t, 1H, ^3J=7.3 Hz, H-8), 7.37-7.46 (m, 3H), 7.86 (d, 2H, ^3J=6.8 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 14.24 (CH_3), 62.23 (CH_2), 121.64 (C-5), 125.68 (C-7), 127.67, 128.60, 129.49 (C-9), 130.18 (C-4), 130.55 (C-8), 131.22, 131.52 (C-6), 133.51 (C-5a), 136.21 (q), 149.56 (C-9a), 159.25 (C-2), 163.29 (C=O); m/z (%) 293 (7), 292 (M^+, 30), 220 (9), 219 (58), 218 (100), 217 (7), 193 (23), 192 (10), 165 (22), 143 (12), 115 (10), 89 (16), 77 (6).

19b: Ar=4-CH_3-C_6H_4 (65%), red prisms from ethanol m.p. 79-80°C. (Found: C, 74.5; H, 6.0; N, 9.2. $C_{19}H_{18}N_2O_2$ requires: C, 74.5; H, 5.9; N, 9.1); i.r. (Nujol) 3387, 1704, 1667, 1643, 1590, 1441, 1303, 1281, 1273, 1241, 1223, 1210, 1183, 1157, 1098, 1061, 1023, 962, 901, 864, 829, 760, 718, and 678 cm^{-1}; ^1H n.m.r.δ ($CDCl_3$): 1.30 (t, 3H, ^3J=7.1 Hz), 2.31 (s, 3H), 4.24 (q, 2H, ^3J=7.1 Hz), 6.41 (s, 1H, H-5), 6.54 (s, 1H, NH), 6.70 (d, 1H, ^3J=7.0 Hz, H-6), 6.78-6.87 (m, 2H, H-9, H-7), 7.06 (td, 1H, ^3J=7.0 Hz, ^4J=1.4 Hz, H-8), 7.14 (d, 2H, ^3J=8.1 Hz), 7.69 (d, 2H, ^3J=8.1 Hz); ^{13}C n.m.r.δ ($CDCl_3$): 14.25 (CH_3), 21.45 (CH_3), 62.15 (CH_2), 121.71 (C-5), 125.44 (C-7), 127.72, 129.32 (C-9+CH), 130.15 (C-4), 130.54 (C-8), 131.48 (C-6), 133.33* (q), 133.38* (C-5a), 141.68 (q), 149.77 (C-9a), 159,43 (C-2), 163.43 (C=O); m/z (%) 307 (21), 306 (M^+, 100), 233 (38), 232 (65), 231 (15), 218 (8), 207 (30), 206 (16), 204 (11), 179 (16), 143 (30), 118 (10), 116 (15), 115 (22), 114 (14), 91 (13), 90 (15), 89 (58), 88 (14), 77 (6).



19c: Ar=4-CH_3O-C_6H_4 (65%), red prisms from ethanol m.p. 96-97°C. (Found: C, 70.9; H, 5.7; N, 8.7. $C_{19}H_{18}N_2O_3$ requires: C, 70.8; H, 5.6; N, 8.7); i.r. (Nujol) 3375, 1700, 1673, 1635, 1603, 1589, 1568, 1509, 1442, 1307, 1248, 1176, 1129, 1062, 1025, 843, 808, 766, 724, and 675 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.37 (t, 3H, ^3J=7.3 Hz), 3.83 (s, 3H), 4.31 (q, 2H, ^3J=7.3 Hz), 6.53 (s, 1H, H-5), 6.59 (s, 1H, NH), 6.79 (d, 1H, ^3J=7.3 Hz, H-6), 6.87-6.93 (m, 4H), 7.13 (td, 1H, ^3J=7.8 Hz, ^4J=1.4 Hz, H-8), 7.84 (d, 2H, ^3J=8.7 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 14.31 (CH_3), 55.47 (CH_3), 62.20 (CH_2), 113.95, 121.93 (C-5), 125.29 (C-7), 128.34 (q), 129.09 (C-9), 129.59, 130.20 (C-4), 130.53 (C-8), 131.48 (C-6), 133.66 (C-5a), 149.79 (C-9a), 159.32 (C-2), 162.23 (q), 163.57 (C=O); m/z (%) 323 (21), 322 (M^+, 100), 249 (29), 248 (35), 237 (27), 234 (10), 233 (22), 223 (17), 208 (28), 205 (12), 143 (25), 135 (37), 115 (11), 114 (8), 90 (10), 89 (25), 77 (12).

19d: Ar=4-Cl-C_6H_4 (60%), red prisms from ethanol m.p. 101-102°C. (Found: C, 66.1; H, 4.6; N, 8.7. $C_{18}H_{15}ClN_2O_2$ requires: C, 66.2; H, 4.6; N, 8.6); i.r. (Nujol) 3387, 1693, 1668, 1645, 1590, 1441, 1397, 1302, 1282, 1241, 1221, 1208, 1128, 1113, 1089, 1059, 1024, 1013, 900, 865, 837, 764, and 725 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.35 (t, 3H, ^3J=7.3 Hz), 4.28 (q, 2H, ^3J=7.3 Hz), 6.43 (s, 1H, H-5), 6.52 (s, 1H, NH), 6.74 (d, 1H, ^3J=6.8 Hz, H-6), 6.85-6.95 (m, 2H, H-9, H-7), 7.11 (t, 1H, ^3J=7.3 Hz, H-8), 7.35 (d, 2H, ^3J=8.3 Hz), 7.79 (d, 2H, ^3J=8.3 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 14.22 (CH_3), 62.27 (CH_2), 121.76 (C-5), 125.83 (C-7), 128.77, 129.06, 129.51 (C-9), 130.05 (C-4), 130.63 (C-8), 131.59 (C-6), 133.27 (C-5a), 134.61 (q), 137.36 (q), 149.26 (C-9a), 157.90 (C-2), 163.32 (C=O); m/z (%) 329 (4), 328 (M^++2, 20), 327 (11), 326 (M^+, 64), 255 (14), 254 (41), 253 (39), 252 (100), 229 (14), 228 (14), 227 (48), 226 (20), 219 (15), 218 (39), 217 (34), 216 (16), 201 (18), 200 (8), 199 (51), 192 (9), 191 (32), 190 (41), 143 (44), 139 (12), 115 (43), 114 (28), 90 (13), 89 (67), 88 (18), 77 (4).

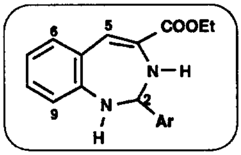
19e: Ar=4-Br-C_6H_4 (56%), red prisms from ethanol m.p. 113-114°C. (Found: C, 58.1; H, 4.0; N, 7.6. $C_{18}H_{15}BrN_2O_2$ requires: C, 58.2; H, 4.1; N, 7.5); i.r. (Nujol) 3375, 1693, 1668, 1643, 1559, 1443, 1304, 1283, 1245, 1225, 1213, 1127, 1070, 1057, 1006, 867, 838, 766, and 721 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 1.36 (t, 3H, ^3J=7.3 Hz), 4.29 (q, 2H, ^3J=7.3 Hz), 6.45 (s, 1H, H-5), 6.51 (s, 1H, NH), 6.75 (d, 1H, ^3J=7.3 Hz, H-6), 6.87 (d, 1H, ^3J=7.3 Hz, H-9), 6.91 (td, 1H, ^3J=7.8 Hz, ^4J=1.4 Hz, H-7), 7.11 (td, 1H, ^3J=7.8 Hz, ^4J=1.4 Hz, H-8), 7.52 (d, 2H, ^3J=8.3 Hz), 7.71 (d, 2H, ^3J=8.7 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 14.21 (CH_3), 62.22 (CH_2), 121.83 (C-5), 125.81 (C-7), 129.22, 129.49 (C-9), 130.00 (C-4), 130.64 (C-8), 131.58 (C-6), 131.72, 135.10 (q), 149.15 (C-9a), 157.84 (C-2), 163.36 (C=O); m/z (%) 373 (19), 372 (M$^+$+2, 95), 371 (21), 370 (M$^+$, 100), 299 (23), 298 (56), 297 (20), 296 (51), 273 (14), 272 (7), 271 (13), 270 (6), 218 (22), 217 (20), 216 (9), 191 (26), 190 (25), 185 (9), 183 (10), 165 (10), 164 (9), 143 (31), 115 (37), 114 (22), 90 (10), 89 (62), 77 (7).

19f: Ar=4-F-C_6H_4 (58%), orange prisms from ethanol m.p. 94-95°C. (Found: C, 69.8; H, 4.8; N, 9.1. $C_{18}H_{15}FN_2O_2$ requires: C, 69.7; H, 4.9; N, 9.0); i.r. (Nujol) 3370, 1693, 1667, 1635, 1603, 1587, 1514, 1441, 1368, 1304, 1246, 1226, 1171, 1128, 1061, 1015, 848, 823, 768, 718, 688, and 674 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 1.36 (t, 3H, ^3J=7.1 Hz), 4.30 (q, 2H, ^3J=7.1 Hz), 6.49 (s, 1H, H-5), 6.76 (d, 1H, ^3J=6.9 Hz, H-6), 6.90 (t, 2H, ^3J=7.5 Hz), 7.02-7.17 (m, 4H, H-8, H-9, H-7, NH), 7.86 (dd, 2H, ^3J=8.8 Hz, ^4J_F=5.3 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 14.14 (CH_3), 62.16 (CH_2), 115.52 (^2J_F=21.8 Hz), 122.06 (C-5), 125.62 (C-7), 129.01 (C-4), 129.91 (^3J_F=8.8 Hz), 130.58 (C-8), 131.50 (C-6), 132.16 (^4J_F=2.9 Hz, q), 133.55 (C-5a), 149.13 (C-9a), 158.18 (C-2), 163.41 (C=O), 164.66 (^1J_F=251.9 Hz, q); m/z (%) 311 (6), 310 (M$^+$, 31), 237 (41), 236 (100), 212 (9), 211 (48), 210 (27), 184 (10), 183 (65), 149 (34), 143 (31), 123 (65), 122 (17), 121 (20), 115 (42), 114 (24), 95 (28), 90 (13), 89 (61), 77 (16).

General Procedure for the Preparation of Ethyl 2-Aryl-1,2-dihydro-1,3-benzodiazepine-4-carboxylates 21.

To a well stirred solution of the appropriate benzodiazepine 19 (0.3 mmol) in anhydrous methanol (10 ml), sodium borohydride (0.02 g, 0.45 mmol) was added at 0°C. After the stirring was continued for 1h at the same temperature, the mixture was slowly warmed to room temperature for 3h. The solvent was removed and the residual material was washed with water (20 ml) and extracted with dichloromethane (2x15 ml). The combined organic layers were dried ($MgSO_4$) and concentrated to dryness to afford the crude product 21 which was recrystallized from a suitable solvent.

21a: Ar=4-CH_3-C_6H_4 (80%), yellow prisms from methanol m.p. 125-126°C. (Found: C, 74.1; H, 6.5; N, 9.0. $C_{19}H_{20}N_2O_2$ requires: C, 74.0; H, 6.5; N, 9.1); i.r. (Nujol) 3392, 3375, 1691, 1629, 1601, 1495, 1368, 1290, 1262, 1241, 1202, 1031, 826, 772, and 743 cm^{-1}; ^{1}H n.m.r. δ (DMSO-d_6): 1.25 (t, 3H, ^3J=7.2 Hz), 2.28 (s, 3H), 4.21 (q, 2H, ^3J=7.2 Hz), 5.04 (dd, 1H, $^3J_{2,1}$=$^3J_{2,3}$=2.7 Hz, H-2), 5.54 (s. broad, 1H, H-3), 6.36 (d, 1H, ^4J=1.5 Hz, H-5), 6.63 (ddd, 1H, ^3J=7.8 Hz, ^3J=6.6 Hz, ^4J=2.1 Hz, H-7), 6.74 (d, 1H, ^3J=2.1 Hz, H-1), 6.84-6.91 (m, 2H, H-8, H-9), 7.06 (d, 1H, ^3J=7.8 Hz, H-6), 7.18 (d, 2H, ^3J=8.1 Hz), 7.28 (d, 2H, ^3J=8.1 Hz); ^{13}C n.m.r. δ (DMSO-d_6): 14.14 (CH_3), 20.67 (CH_3), 61.15 (CH_2), 68.55 (C-2), 109.95 (C-5), 117.96 (C-9), 118.63 (C-7), 122.06 (C-4), 126.68 (C-8), 127.27, 129.12, 132.05 (C-6), 132.65 (C-5a), 137.24 (q), 138.31 (q), 148.30 (C-9a), 164.94 (C=O); m/z (%) 309 (7), 308 (M$^+$, 32), 279 (28), 262 (13), 236 (17), 235 (100), 234 (17), 233 (42), 232 (11), 219 (27), 218 (15), 208 (40), 207 (16), 193 (14), 119 (24), 118 (17), 117 (20), 116 (18), 115 (10), 92 (9), 91 (97), 90 (9), 89 (18).



21b: Ar=4-Cl-C_6H_4 (78%), yellow prisms from methanol m.p.155-156°C. (Found: C, 65.8; H, 5.2; N, 8.7. $C_{18}H_{17}ClN_2O_2$ requires: C, 65.7; H, 5.2; N, 8.5); i.r. (Nujol) 3392, 3375, 1690, 1635, 1599, 1488, 1369, 1292, 1261, 1242, 1200, 1088, 1031, 1016, 838, 769, and 747 cm^{-1}; ^{1}H n.m.r. δ (DMSO-d_6): 1.24 (t, 3H, ^3J=7.1 Hz), 4.23 (q, 2H, ^3J=7.1 Hz), 5.19 (dd, 1H, $^3J_{2,1}$=$^3J_{2,3}$=3.3 Hz, H-2), 5.88 (s. broad, 1H, H-3), 6.34 (s, 1H, H-5), 6.63 (t, 1H, ^3J=7.2 Hz, H-7), 6.83 (d, 1H, ^3J=7.5 Hz, H-9), 6.87-6.96 (m, 2H, H-1, H-8), 7.03 (d, 1H, ^3J=7.9 Hz, H-6), 7.40 (s, 4H); ^{13}C n.m.r. δ (DMSO-d_6): 14.14 (CH_3), 61.15 (CH_2), 67.67 (C-2), 109.89 (C-5), 118.07 (C-9), 118.81 (C-7), 122.45 (C-4), 126.73 (C-8), 128.41, 129.30, 131.91 (C-6), 132.41 (q), 132.47 (C-5a), 140.39 (q), 147.96 (C-9a), 164.93 (C=O); m/z (%) 330 (M$^+$+2, 9), 328 (M$^+$, 25), 301 (6), 299 (18), 257 (34), 256 (19), 255 (100), 254 (18), 253 (28), 252 (12), 144 (8), 143 (26), 141 (11), 139 (28), 90

(11), 89 (24).

21c Ar: 4-Br-C_6H_4 (65%), yellow prisms from methanol m.p. 138-139°C. (Found: C, 57.8; H, 4.5; N, 7.4. $C_{18}H_{17}BrN_2O_2$ requires: C, 57.9; H, 4.6; N, 7.5); i.r. (Nujol) 3420, 3358, 1710, 1636, 1619, 1591, 1484, 1303, 1285, 1240, 1098, 1070, 1013, 832, 753, and 725 cm^{-1}; ^{1}H n.m.r. δ (DMSO-d_6): 1.30 (t, 3H, ^3J=6.9 Hz), 4.21 (q, 2H, ^3J=6.9 Hz), 5.17 (dd, 1H, $^3J_{2,1}$=$^3J_{2,3}$=3.6 Hz, H-2), 5.90 (s. broad, 1H, H-3), 6.32 (s, 1H, H-5), 6.62 (td, 1H, ^3J=7.1 Hz, ^3J=6.6 Hz, ^4J=0.9 Hz, H-7), 6.81 (dd, 1H, ^3J=7.2 Hz, ^4J=0.9 Hz, H-9), 6.85-6.92 (m, 2H, H_1, H-8), 7.02 (d, 1H, ^3J=7.2 Hz, H-6), 7.29 (d, 2H, ^3J=8.1 Hz), 7.53 (d, 2H, ^3J=8.1 Hz); ^{13}C n.m.r. δ (DMSO-d_6): 14.15 (CH_3), 61.16 (CH_2), 67.62 (C-2), 109.85 (C-5), 118.12 (C-9), 118.78 (C-7), 120.98 (q), 122.48 (C-4), 126.80 (C-8), 129.74, 131.36, 131.94 (C-6), 140.86 (q), 148.01 (C-9a), 164.96 (C=O). C-5a not observed; m/z (%) 373 (M$^+$+2, 11), 372 (8), 371 (M$^+$, 11), 358 (17), 356 (18), 344 (3), 342 (3), 301 (22), 300 (97), 299 (23), 298 (100), 296 (9), 278 (16), 277 (36), 273 (29), 271 (28), 219 (39), 191 (31), 190 (30), 185 (22), 183 (25), 164 (18), 163 (18), 144 (5), 143 (11), 89 (18).

*, $^{\#}$, †, $^{\Delta}$: interchangeable assigment.

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