2,4-Bisimino-1,3-diazetidines: Iminophosphoranes, Carbodiimides and Related Betaines

Pedro Molina,*,[a] Mateo Alajarin,[a] Carmen Lopez-Leonardo,[a] Felix Hernandez Cano,*,[b] Antonio L. Llamas-Saiz,[b] Concepcion Foces-Foces,[b] Rosa Maria Claramunt[c] and Jose Elguero[c]

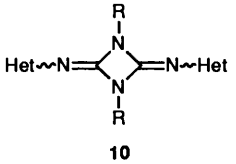
[a] *Departamento de Quimica Organica, Facultad de Ciencias, Campus de Espinardo, 30071 Murcia, Spain*
[b] *U.E.I. de Cristalografia, Instituto de Quimica Fisica 'Rocasolano', CSIC, Serrano, 119, 28006 Madrid, Spain*
[c] *UNED and CSIC, Departamento de Quimica Organica and Instituto de Quimica Medica, Facultad de Ciencias, Ciudad Universitaria, 28040 Madrid, Spain*

Iminophosphoranes **2** and **3** derived from 4-amino-6-methyl-3-methylthio-4,5-dihydro[1,2,4]triazin-5-one react with primary isocyanates or isothiocyanates to give the betaines **8** and **9**, respectively; however, the reaction with isopropyl and *tert*-butyl isocyanate leads to the corresponding carbodiimides **6**. Thermal treatment of betaines **8** affords diazetidines **10**.

The crystal structures of betaines **8d** and **8i** have been determined. The relationship between the rotation about the $[P \cdots N]^+$ bond and the hybridization of the nitrogen is perturbated by the intramolecular phenyl–phenyl 'stacking type' interaction in **8d** and by the steric hindrance of the isopropyl substituent in **8i**. This steric effect precludes the bipyramidalization of P(1) in **8i**, which loses the intermediate character between the open-chain betaine and the ring-chain 1,3,2-diazaphosphetidine, present in the other betaines. In contrast, **8d** has the lowest P ··· N/P–N ratio found. A careful ^1H and ^{13}C NMR study of betaines and diazetidines reveals that in betaines **9** carrying a PPh_2Me substituent, the phenyl groups are diastereotopic and present differences in the ^{13}C–^{31}P coupling constants and that in diazetidines **10** the major isomer is *E,E* when the 1,3-substituent is either a benzyl or an isopropyl group. We propose, tentatively, how the title compounds are mechanistically related which includes a possible formation of diazetidines different from carbodiimide dimerization, the experimental evidence that betaines result from the reaction of carbodiimides with iminophosphoranes and that this last reaction is reversible.

In six previous papers,[1–6] we have discussed the synthesis and reactivity of 2,4-bisimino-1,3-diazetidines, and also the structural aspects of these and related compounds using X-ray crystallography and nuclear magnetic resonance spectroscopy (^1H and ^{13}C). In this final paper we wish to report our new results, and to provide a comprehensive view of the chemistry and structure of diazetidines and related betaines. For this, a brief summary of the results already obtained is necessary.

1 Het-NH_2



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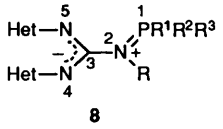

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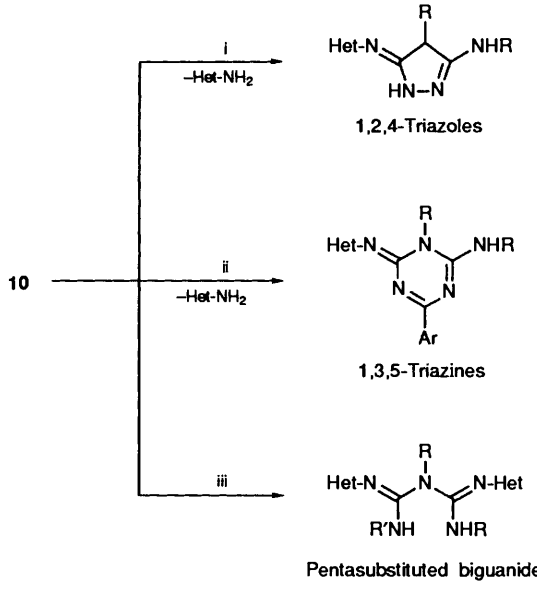
In the first paper,[1] we described the transformation of *N*-aminoheterocycle **1** into an iminophosphorane Het–N=PPh_3 **2**, which reacted with aromatic isocyanates (R = Ar) to afford diazetidines **10** with a *Z,Z* configuration. These diazetidines thermally rearranged to triazolotriazinones with loss of Het–NH_2, CO_2 and MeSH. The formation of diazetidines was supposed to proceed through a carbodiimide Het–N=C=N–R **6**, formed by an aza-Wittig reaction followed by a $[\pi_s^2 + \pi_a^2]$ cyclodimerization.

Diazetidines **10** reacted as an activated biuret synthon towards hydrazine,[2] arylamidines,[3] and amines.[4] In Scheme 1 these reactions are represented.



Scheme 1 *Reagents:* i, NH_2NH_2; ii, $ArC(NH_2)$=NH; iii, $R'NH_2$ (RR'NH).

The X-ray structure of two such polysubstituted biguanides, a penta ($R'NH_2$) and a hexa-substituted (RR'NH) biguanide was reported in the last publication.[6] It was also found that a minor amount of *E,E*-isomer is observed in some cases together with the *Z,Z*-isomer of **10** (R = aryl).

When iminophosphorane **2** reacted with aliphatic isocyanates, betaines **8** ($R^1 = R^2 = R^3 = Ph$) were obtained instead of diazetidines **10**.[5] It was discovered and theoretically supported that there is a relationship between the rotation about the $[P \cdots N]^+$ bond and the pyramidalization of the nitrogen. This relationship is summarized in Fig.1, where the conformations are viewed along the P–N bond.

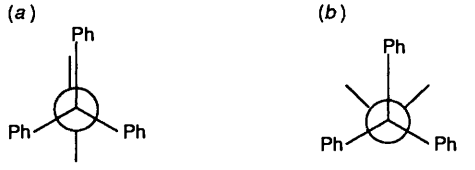


Fig. 1 (*a*) Parallel conformation (‖)[7] sp^2 nitrogen; (*b*) perpendicular conformation (⊥)[7] sp^2–sp^3 nitrogen.

Results and Discussion

Iminophosphorane **2** reacts with isopropyl and *tert*-butyl isocyanate in dry benzene at room temperature for 24 h to give the carbodiimides **6i** (45%) and **6j** (60%), respectively. However, the reaction of **2** with isopropyl isocyanate in benzene at reflux temperature leads to the diazetidine **10i** isolated as a mixture of isomers *E,E–Z,Z* (93:7) in 40% yield. Cycloaddition of **6i** to give **10i** does not occur in dry benzene at reflux temperature even in the presence of tributylphosphine, which normally promotes this type of reaction. However, compound **6i** reacts with iminophosphorane **2** in dry benzene at room temperature to give the betaine **8i** as a crystalline solid in 89% yield.

Iminophosphorane **2** also reacts with benzyl isothiocyanates to give the corresponding betaines **8d–8h** in excellent yields (85–96%). In the same way, iminophosphorane **3** reacts with alkyl and benzyl isothiocyanates to give the related betaines **9a–9d** in good yields (60–98%). Thermal treatment of betaines **8d–8h** leads to iminophosphorane **2** and the corresponding diazetidines **10d–10h** in moderate to good yields as a mixture of isomers *E,E–Z,Z* (85:15). Finally, betaines **9a–9c** undergo hydrolytic cleavage to give *N,N″*-bis(heteroaryl)-*N′*-alkyl guanidines **12** and diphenylmethylphosphine oxide **13**.

Scheme 2 represents all the information we have gathered on these compounds; its central part contains the core of the problem: carbodiimides **6**, 1,3,2-diazaphosphetidine **7**, betaines **8** and **9**, and 2,4-bisimino-1,3-diazetidines **10**.

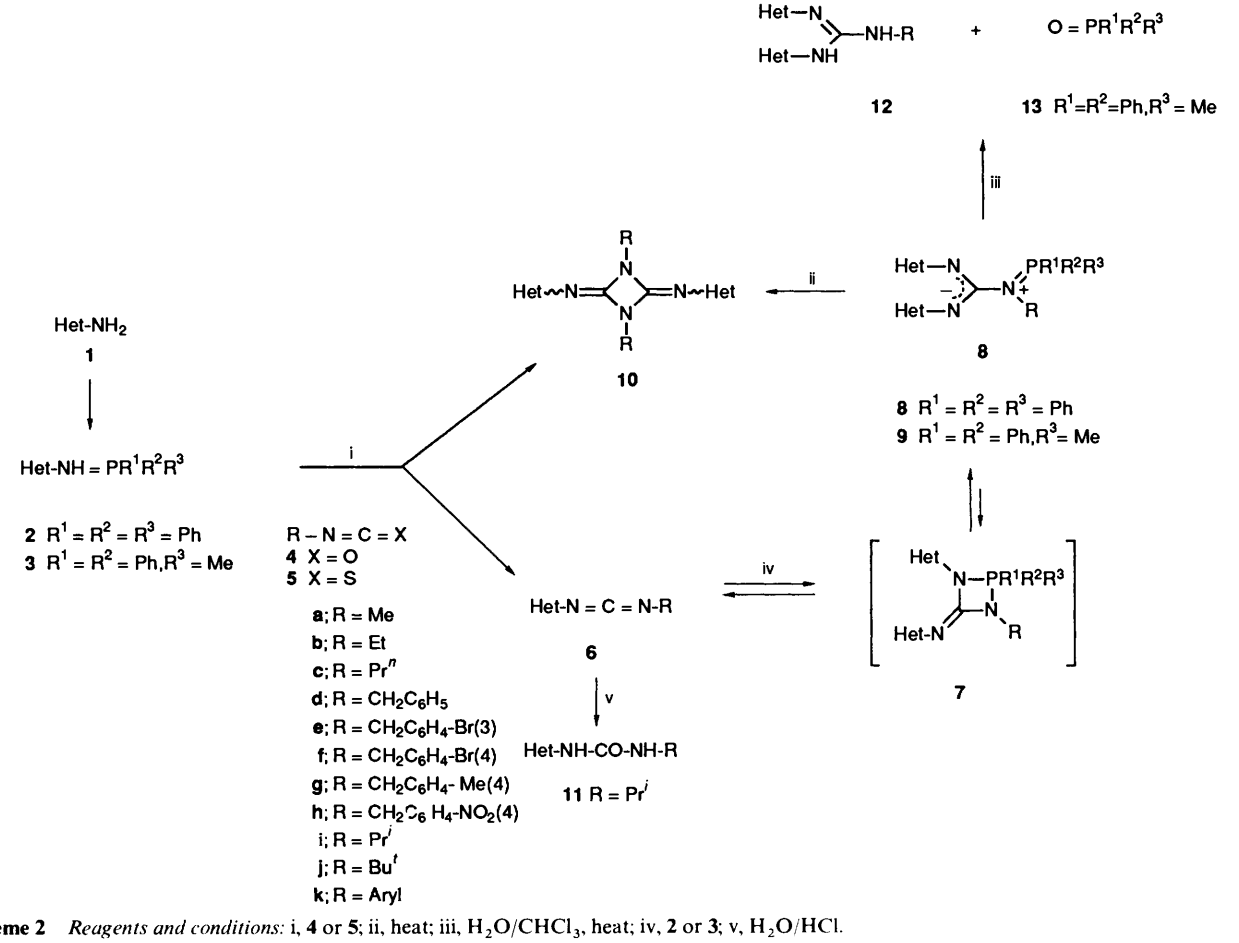
Molecular Structure of Betaines **8d** *and* **8i**.—The structures of the three betaines **8a**•C, **8a**•D and **8c** were previously reported.[5] The new structures we report here (Fig. 2) differ from the previous ones only by the substituent R on the nitrogen N(2): R = Me in **8a**, Pr in **8c**, while we have here Pr^i in **8i** and benzyl in **8d**. The letters C and D in **8a** stand for the chloroform and dioxane co-crystallizing molecules. The new compounds were selected because their ^1H NMR spectra present some interesting features (see later).

Five points, concerning the conclusions of the previous work,[5] are to be discussed in the new structures.

(i), The negative charge is localized in the N(4)–C(3)–N(5) moiety and the positive charge in the P(1)–N(2) bond, which is shorter than the standard single bond value. This conclusion is also valid here for **8i** and **8d**, with small variations in the geometric description of this effect (see Table 1).

(ii), Atoms P(1), N(2), C(3) and N(5) form quite a planar pseudocycle. Now, **8i** presents a puckering in this pseudocycle, the torsion around C(3)–N(2) having high value, thus allowing for the lengthening of the bond; this is due to the steric hindrance from the isopropyl substituent to the N(2) atom.

(iii), The tetrahedron at P(1) appears distorted towards a



Scheme 2 *Reagents and conditions:* i, **4** or **5**; ii, heat; iii, $H_2O/CHCl_3$, heat; iv, **2** or **3**; v, H_2O/HCl.

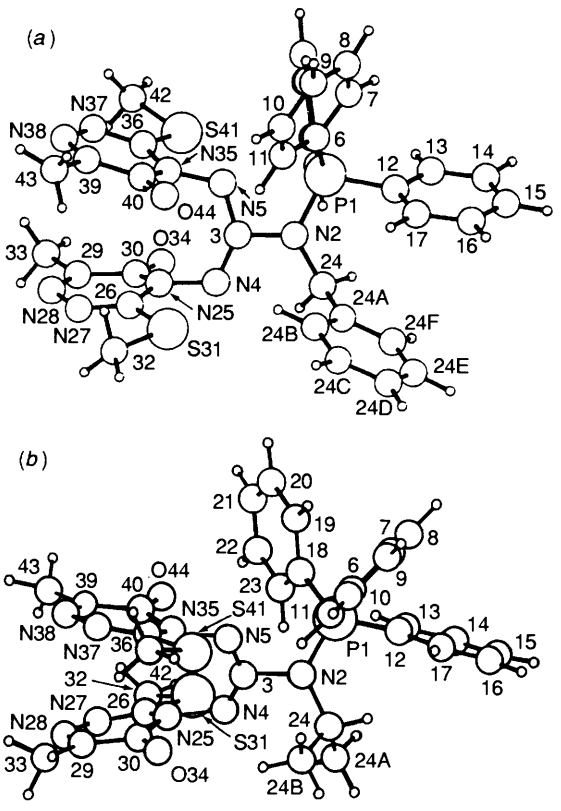


Fig. 2 (*a*) and (*b*) View of the molecules **8d** and **8i**, respectively, showing the atomic numbering used in the crystallographic analysis. Compounds **8a** and **8c** are analogous but with a methyl or an isopropyl substituent at N(2).

bipyramid, suggesting a N(5)···P(1) interaction at an apical position. Now we have again, P(1)–N(2) bond lengths supporting the pyramidalization, somehow precluded in **8i**, owing to the above mentioned steric effect. With no such hindrance, **8d** presents the higher degree of pyramidalization of the five structures.

(iv), Concerning the ring-chain isomerism between **8** and **7**, in the solid state, the structures **8a**·C, **8a**·D and **8c** correspond to the former, presenting the mentioned P(1)···N(2) interaction, with a ratio of this length over the usual P–N bond of 1.60, 1.58 and 1.66, respectively; these values indicate that the interaction can modulate the 1,3,2-diazaphosphetidine character. We see now that in **8i** this P(1)···N(2) distance elongates up to 2.885(5) Å as a consequence of the precluded pyramidalization of P(1). However, **8d** presents the shortest contact, 2.592(7) Å.

(v), In relation to the result represented in Fig. 1, the geometry around N(2) suggests an sp^2 hybridization in **8i**, and some sp^3 character in **8d**, but now the sp^2 character is related to a perpendicular conformation around P(1)–N(2) and the sp^3 character to a parallel one; this fact seems to be in contradiction with our previous result (Fig. 1 and ref. 5), but some new effects, not previously present, are now affecting the angular geometry around N(2) (see Fig. 3).

Thus, in **8i** the above mentioned hindrance breaks the analogy with **8c**, as it is affecting the position of C(3), for example, opening the C(3)–N(2)–C(24) angle and increasing the C(3)–N(2)–P(1)–C(Ph) torsion values. So, the perpendicular conformation and the sp^3 character of N(2) are still present, but distorted by the bulky substituent. As far as **8d** is concerned, examination of the geometry around N(2) and C(24) (see Table 1) leads to the conclusion that some interaction exists between the Ph ring at C(24) and that Ph(C-12–17), distorting the geometry of the sp^2 hybridization and that of the parallel conformation of the type present in **8a**.

The conclusion concerning the structure of betaines **8** in the solid state is that in all cases there is a P(1)···N(5) interaction, with the corresponding bipyramidalization of P(1) and delocalization of the charges. The rule, 'parallel conformation about P(1)–N(2) related to sp^2 hybridization and perpendicular conformation related to sp^2–sp^3 hybridization', always holds but could be blurred by other interactions such as those present in **8i** (steric hindrance), and in **8d** (phenyl–phenyl 'stacking' interaction). Concerning the chemical reaction path,[8] relating betaines **8** to 1,3,2-diazaphosphetidines **7**, as defined by the ratio P(1)···N(5)/P(1)–N(2) (*vide supra*), we have found a smooth variation: 1.54 **8d** < 1.58 **8a**·D < 1.60 **8a**·C < 1.66 **8c** < 1.76 **8i**.*

NMR Spectroscopy of Betaines.—The ^1H, ^{13}C and ^{31}P NMR spectra of betaines **8a**, **8b** and **8c** have been already reported.[5] The ^1H and ^{13}C NMR spectra of compounds **8d–8h** are gathered in Tables 2 and 3, respectively.

One of the most interesting features of compounds **8b** (R = Et) and **8c** (R = Pr) was that the prochiral protons of the first methylene group were diastereotopic [$\Delta\delta$ 0.48 and 0.61 ppm for **8b** and **8c**, respectively]. This observation was related with the quasibipyramidal structure of the $NPPh_3$ group.† The anisochrony is larger in the *N*-benzyl series ($\Delta\delta$ 1.07, 1.21, 1.13, 1.03 and 1.24 ppm). Due to this fact, we suspected that these betaines could be in a more 'closed' form [shorter N(5)···P(1) distance]. Although the X-ray structure confirms this, a conformational origin for the increase of $\Delta\delta$ cannot be excluded.

Since the observation of this phenomenon requires a prochiral group on the nitrogen, it should be observed also on the *P*-phenyl groups if instead of a $NPPh_3$ group (series **8**) there is a $NPPh_2Me$ group (series **9**). In ^1H NMR, there is no clear answer (not even at 300 MHz) but in ^{13}C NMR (50 MHz) compounds **9b** (R = Et) and **9d** (R = $PhCH_2$) (see Experimental section) show two groups of signals for the phenyl rings. Thus, for the compound **9b** the anisochrony is quite small ($\Delta\delta$:C_i, 0.11; C_o, 0.81; C_m, 0.17; and C_p, 0.64 ppm), but the ^{13}C–^{31}P coupling constants show clear differences in some cases (ΔJ: ^1J, 11.9; ^2J, 1.0, ^3J, 1.4, ^4J, 0.5). Still more remarkable, one of the phenyl rings **P** presents signals (δ, J) very similar to those of compounds **8** and the other, **P′**, is quite different.

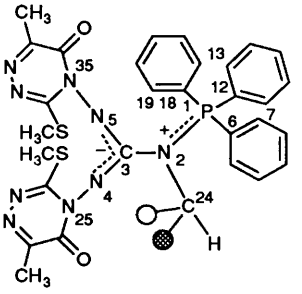
In compounds **8** the three phenyl rings show isochronicity for protons and carbons of equivalent positions due to rapid rotation about the P(1)–N(2) bond in the NMR time scale. The differences observed for one of the phenyl rings of **9** can be associated with the hybridization of the nitrogen (Fig. 1) or, more probably, with differences in the C(*ortho*)–C(*ipso*)–P(1)–N(2) dihedral angle. A situation like that depicted in Fig. 4 explains the results. In compounds **8**, the average involves 2**P** + **P′**, thus the 'normal' phenyl group in **9** should be **P** and the 'different' one should be **P′**. The proximity of the methyl group to the N–CH_2 protons is probably why $\Delta\delta$ in **9d** attains only 0.28 ppm.

The last betaine which deserves comment is **8i** (R = Pr^i). It is much more labile than the others (see Chemical section) to the point that we suspected that this compound should not be a betaine. The X-ray structure proves that actually it is a

* See page 210 for 'Note added in proof'.

† A referee has suggested an alternative explanation. According to him the source of asymmetry is the N(2) atom which could become pyramidal on going from solid state [planar, see Σ(N̂2), Table 1] to chloroform solution.

Table 1 Selected geometrical characteristics (Å, deg). For comparison purposes, those values corresponding to the five compounds, **8a**•C, **8a**•D, **8c**, **8d** and **8i** are included.



8	R	○	●
a	Me	H	H
c	Pr^n	H	Et
d	Bz	H	Ph
i	Pr^i	CH_3	Me

Compound	8a•C	8a•D	8c	8d	8i
P(1)–N(2)–C(3)–N(5)	−0.4(4)	2.5(5)	−8.7(5)	−7.5(9)	−44.1(5)
N(5)···P(1)	2.658(3)	2.610(4)	2.741(7)	2.592(7)	2.885(4)
N(5)···P(1)–N(2)	57.2(1)	57.8(2)	55.4(3)	58.3(3)	51.3(2)
N(5)···P(1)–C(6)	85.3(1)	84.2(2)	73.0(4)	87.9(3)	79.5(2)
N(5)···P(1)–C(18)	83.9(1)	84.0(2)	94.4(3)	81.0(3)	90.1(2)
N(5)···P(1)–C(12)	161.8(1)	162.2(2)	157.2(4)	164.3(3)	158.3(2)
P(1)–C(12)	1.806(3)	1.809(5)	1.801(11)	1.801(9)	1.808(5)
P(1)–C(6)	1.794(3)	1.790(5)	1.790(9)	1.798(7)	1.774(5)
P(1)–C(18)	1.789(4)	1.790(5)	1.779(10)	1.807(10)	1.783(5)
C(12)–P(1)–N(2)	104.8(2)	104.5(2)	106.4(5)	106.2(4)	107.1(2)
C(12)–P(1)–C(6)	102.7(2)	103.4(2)	107.0(5)	101.5(4)	109.3(2)
C(12)–P(1)–C(18)	107.1(2)	107.2(3)	106.1(5)	105.9(4)	104.1(2)
N(2)–P(1)–C(18)	111.9(2)	113.5(2)	111.9(4)	114.1(4)	115.4(2)
N(2)–P(1)–C(6)	115.6(2)	149.9(2)	112.6(5)	113.4(4)	108.8(2)
C(6)–P(1)–C(18)	113.5(2)	112.2(2)	112.3(5)	114.3(4)	111.9(2)
N(4)–C(3)–N(5)	139.7(3)	138.5(5)	138.2(9)	139.5(8)	140.6(5)
N(2)–C(3)–N(4)	111.4(3)	113.3(4)	112.0(8)	113.4(7)	110.1(4)
N(2)–C(3)–N(5)	109.0(3)	108.2(4)	109.8(8)	107.2(7)	109.3(4)
C(3)–N(5)	1.326(4)	1.318(6)	1.330(14)	1.346(11)	1.319(6)
C(3)–N(4)	1.312(5)	1.332(6)	1.322(14)	1.307(12)	1.316(6)
C(3)–N(2)	1.431(4)	1.427(6)	1.429(10)	1.421(11)	1.449(6)
P(1)–N(2)	1.662(3)	1.656(4)	1.651(8)	1.681(7)	1.638(4)
C(3)–N(2)–P(1)	118.3(2)	117.4(3)	121.0(6)	116.8(5)	119.9(3)
C(24)–N(2)–P(1)	123.1(2)	123.5(3)	119.1(6)	121.2(5)	121.0(3)
C(3)–N(2)–C(24)	118.2(3)	118.5(4)	117.5(7)	119.4(6)	118.5(4)
Σ(N̂2)	359.6(4)	359.9(6)	357.6(11)	357.4(9)	359.4(6)
C(3)–N(2)–P(1)–C(6)	−65.1(3)	−66.4(4)	−42.9(8)	−64.7(7)	−36.1(4)
C(3)–N(2)–P(1)–C(12)	−177.3(3)	−179.0(3)	−159.8(7)	−177.9(6)	−154.1(4)
C(3)–N(2)–P(1)–C(18)	67.0(3)	64.5(4)	84.7(8)	65.9(7)	90.6(4)
C(24)–N(2)–P(1)–C(6)	122.4(3)	122.6(4)	155.1(7)	131.3(6)	153.1(4)
C(24)–N(2)–P(1)–C(12)	10.2(3)	9.9(4)	38.2(8)	20.7(7)	35.1(4)
C(24)–N(2)–P(1)–C(18)	−105.6(3)	−106.6(4)	−77.3(7)	−95.5(7)	−80.2(4)
N(2)–P(1)–C(6)–C(7)	−169.7(3)	−173.4(4)	139.2(10)	−166.1(7)	137.3(4)
N(2)–P(1)–C(18)–C(19)	−139.3(3)	−135.0(4)	−20.6(9)	−140.5(8)	−15.2(4)
N(2)–P(1)–C(12)–C(13)	−110.8(3)	−111.4(5)	−84.8(10)	−122.2(8)	−91.0(5)

Table 2 ^1H NMR shifts (ppm) and coupling constants (Hz) of betaines **8** in $CDCl_3$

Compound	C-Me	S-Me	CH_2	PPh_3	Ar
8d	2.14 (s)	2.32 (s)	4.50 (dd, H_A, *J* 12.5, −16.5), 5.57 (dd, H_B, *J* 20.5, −16.5)	7.8–7.2 (m, 15 H)	7.8–7.2 (m, 15 H)
8e	2.14 (s)	2.33 (s)	4.38 (dd, H_A, *J* 11.9, −16.5), 5.59 (dd, H_B, *J* 20.5, −16.5)	7.8–6.8 (m, 15 H)	7.8–6.8 (m, 4 H)
8f	2.14 (s)	2.32 (s)	4.41 (dd, H_A, *J* 12.4, −16.5), 5.54 (dd, H_B, *J* 20.4, −16.5)	7.8–7.3 (m, 15 H)	7.31 (d, 2 H), 7.13 (d, 2 H)
8g	2.14 (s)	2.31 (s)	4.46 (dd, H_A, *J* 13.1, −16.5), 5.49 (dd, H_B, *J* 20.4, −16.5)	7.8–7.2 (m, 15 H)	7.10 (d, 2 H), 7.00 (d, 2 H) 2.34 (s, 3 H): 4-H_3C–C_6H_4
8h	2.14 (s)	2.33 (s)	4.48 (dd, H_A, *J* 11.5, −17.1), 5.72 (dd, H_B, *J* 18.4, −17.1)	7.8–7.4 (m, 15 H)	8.11 (d, 2 H), 7.32 (d, 2 H)

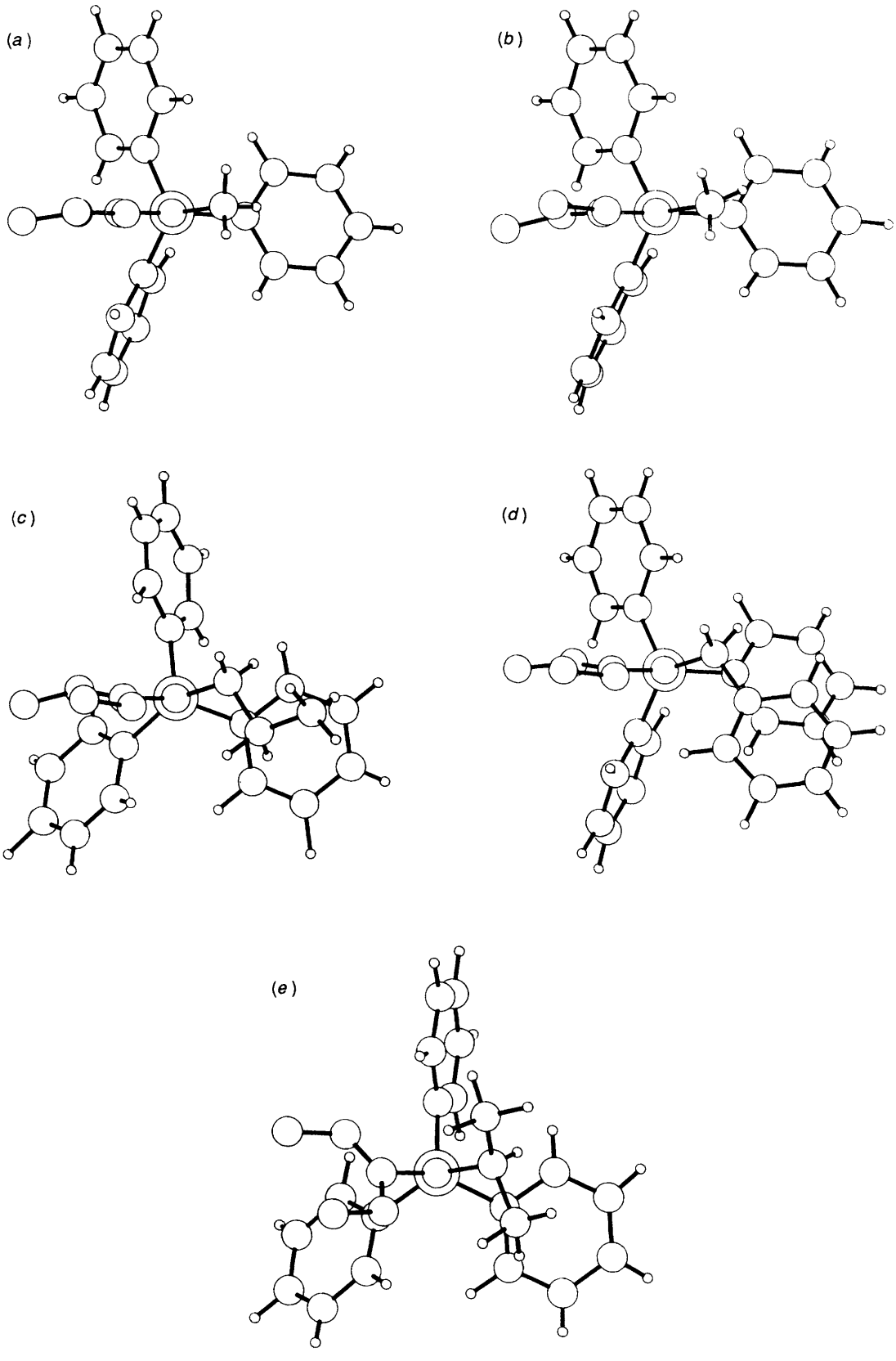
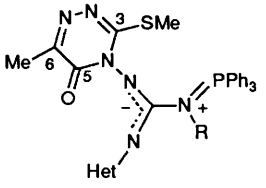


Fig. 3 (*a*)–(*e*) Newman projections along the N(2)–P(1) bond for the five compounds **8a**-C, **8a**-D, **8c**, **8d** and **8i**, respectively. For the sake of clarity, only the first atoms of the heterocyclic moieties are shown.

betaine, although a rather distorted one. The NMR parameters in solution are rather difficult to obtain, since the signals corresponding to **2** and **6i** appeared and rapidly increased in intensity. However, by recording the spectrum at different times, it is possible to identify all the signals of **8i** (see Experimental section). For this compound we also recorded the ^{13}C NMR spectrum in the solid state (75 MHz, CP–MAS technique). The spectrum does not change with time and the chemical shifts nicely agree with those in solution (see Experimental section). The most remarkable fact about the spectroscopy of **8i** is the

Table 3 ^{13}C NMR values of betaines **8** in $CDCl_3$

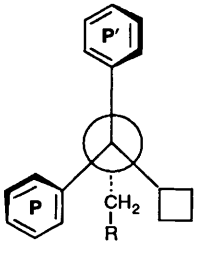


Compound	C-3/C-5/C-6	S-Me	C-Me	C^-	CH_2	PPh_3	Ar
8d	160.57 148.82 152.18	14.61	17.19	152.98 ($^2J_{CP}$ 5.1)	51.05 ($^2J_{CP}$ 2.7)	C_i 124.33 ($^1J_{CP}$ 107.1) C_o 133.92 ($^2J_{CP}$ 10.8) C_m 129.11 ($^3J_{CP}$ 13.6) C_p 133.12 ($^4J_{CP}$ 3.1)	C_i 138.63 C_o, C_m: 128.25, 127.63 C_p 127.20
8e	160.47 148.61 152.19	14.65	17.24	152.68 ($^2J_{CP}$ 5.5)	50.54 ($^2J_{CP}$ 3.4)	C_i 123.70 ($^1J_{CP}$ 107.0) C_o 133.82 ($^2J_{CP}$ 10.8) C_m 129.20 ($^3J_{CP}$ 13.6) C_p 133.35 ($^4J_{CP}$ 3.0)	C-1(CCH_2) 141.03 C-3(CBr) 121.89 C-2,C-4 129.06, 129.00 C-5, 129.34, C-6 126.69
8f	160.43 148.74 152.27	14.57	17.14	152.98 ($^2J_{CP}$ 5.2)	50.52 ($^2J_{CP}$ 2.7)	C_i 124.13 ($^1J_{CP}$ 107.0) C_o 133.89 ($^2J_{CP}$ 10.8) C_m 129.25 ($^3J_{CP}$ 13.6) C_p 133.29 ($^4J_{CP}$ 3.0)	C_i 127.26 C_o 131.37 C_m 128.34 C_p 137.80
8g	160.58 148.83 152.20	14.62	17.19	152.98 ($^2J_{CP}$ 5.6) 152.97 ($^2J_{CP}$ 6.0)	50.86 ($^2J_{CP}$ 2.9)	C_i 124.48 ($^1J_{CP}$ 107.2) C_o 133.94 ($^2J_{CP}$ 10.8) C_m 129.06 ($^3J_{CP}$ 13.8) C_p 133.04 ($^4J_{CP}$ 3.0)	C_i 136.79 C_o, C_m: 128.93, 127.65 C_p 135.56 4-H_3C: 21.13
8h	160.27 148.70 152.31	14.59	17.17		50.66 ($^2J_{CP}$ 3.1)	C_i 123.86 ($^1J_{CP}$ 106.8) C_o 133.86 ($^2J_{CP}$ 10.8) C_m 129.39 ($^3J_{CP}$ 13.7) C_p 133.57 ($^4J_{CP}$ 3.1)	C_i, C_p: 147.37, 146.25 C_o 128.36 C_m 123.47

Table 4 ^1H NMR shifts (ppm) and coupling constants (Hz) of diazetidines **10**[a]

	C-Me	S-Me	CH_2	Ar
10d (*E,E*)	2.41 (s)	2.45 (s)	4.41 (s)	7.3–7.0 (m)
10d (*Z,Z*)	2.29 (s)	2.47 (s)	4.09 (s), 4.77 (s)	7.3–7.0 (m)
10e (*E,E*)	2.46 (s)	2.51 (s)	4.44 (s)	7.6–7.0 (m)
10e (*Z,Z*)	2.33 (s)	2.54 (s)	4.09 (s), 4.73 (s)	7.8–6.8 (m)
10f (*E,E*)	2.55 (s)	2.60 (s)	4.38 (s)	6.99 (d, *J* 8.4), 7.52 (d, *J* 8.4)
10f (*Z,Z*)	2.49 (s)	2.58 (s)	4.06 (s), 4.71 (s)	6.91 (d, *J* 8.3), 7.38 (d, *J* 8.3) 7.40 (d, *J* 8.4), 7.60 (d, *J* 8.4)
10g (*E,E*)	2.55 (s)	2.60 (s)	4.38 (s)	6.98 (d, *J* 8.0), 7.17 (d, *J* 8.0) 2.35 (s, 4-H_3C–C_6H_4)
10g (*Z,Z*)	2.47 (s)	2.58 (s)	4.07 (s), 4.72 (s)	6.80 (d, *J* 7.9), 7.04 (d, *J* 7.9) 7.26 (d, *J* 8.1), 7.39 (d, *J* 8.1) 2.27 (s, 4-H_3C–C_6H_4), 2.35 (s, 4-H_3C–C_6H_4)

[a] Compounds **10d** and **10e** in $CDCl_3$ solution, **10f** and **10g** in $CDCl_3$–CF_3CO_2H solution.



8 R = Ph
9 R= Me

Fig. 4 (⊥)

large anisochrony of the methyl groups of the *N*-Pr^i substituent: $\Delta\delta$ 0.18 (^1H), 2.53 (^{13}C, solution) and 2.90 ppm (^{13}C, solid state). According to the X-ray structure, the spectacular splitting observed in ^{13}C NMR is due to the proximity of C(24A) (δ_C 20.87) to the centroid of the phenyl ring labelled [C(12)–C(13)–···] [d_2 4.001(7) Å, deviation from the normal to the ring, θ = 29.8(2)°] (see Fig. 1). The effect is less apparent in ^1H NMR spectroscopy because the rotation of the isopropyl group averages the shielding.

NMR Spectroscopy of Diazetidines.—In contrast to the betaines, the NMR spectroscopy of 2,4-bisimino-1,3-diazetidines was carefully studied in our last publication.[6] Thus, only the most salient facts of NMR data of diazetidines **10** in $CDCl_3$ solution, summarized in Tables 4 and 5, will be commented upon.

(i), Regarding the signals of the *N*-benzyl substituent, the comparison of *E,E* and *Z,Z* pairs shows that those of the *E,E* isomer roughly correspond to the average of those of the *Z,Z* isomer, for instance, the *N*-CH_2 signals of **10d** (*E,E*), δ_H 4.41 and δ_C 47.61, are comparable to those obtained by averaging the signals of **10d** (*Z,Z*), δ_H 4.09 and 4.77 and δ_C 48.09 and

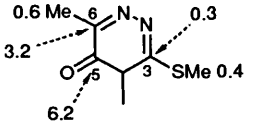
Table 5 ^{13}C NMR values of diazetidines **10**[a]

	C-3	C-5	C-6	S-Me	C-Me	C=N	CH_2	Ar
10d (*E,E*)	158.38	154.26	157.72	14.59	17.70	148.92	47.61	C_i 134.15, C_o 126.67, C_m 129.27, C_p 128.54
10d (*Z,Z*)	157.84	154.37	157.67	14.47	17.60	149.13	48.09 47.08	134.05, 133.30, 129.06, 128.91, 128.52, 128.43, 125.74[b]
10e (*E,E*)	158.02	154.33	157.30	14.60	17.69	149.04	46.76	C-1(CCH_2) 136.31, C-3(CBr) 123.47, C-2 130.80, C-4 129.71, C-5 131.86, C-6 125.24
10e (*Z,Z*)	157.72	154.39	157.02	14.63	17.61	149.20	47.24 46.38	136.01, 135.61, 131.82, 130.73, 130.42, 129.70, 128.98, 127.34, 125.12, 124.23, 123.29, 123.17
10f (*E,E*)	163.57	154.02	158.17	14.80	16.06	149.06	47.58	C_i 132.45, C_o 128.45, C_m 132.98, C_p 123.64
10f (*Z,Z*)	163.51	154.09	157.37	14.72	15.97	149.40	48.15 46.87	132.74, 132.55, 132.39, 132.25, 131.79, 130.33, 127.70, 123.17
10g (*E,E*)	164.30	154.14	159.79	14.65	15.81	149.31	48.08	C_i 139.82, C_o 126.00, C_m 130.42, C_p 130.50 4-H_3C-C_6H_4: 20.95

[a] Compounds **10d** and **10e** in $CDCl_3$ solution, **10f** and **10g** in $CDCl_3$–CF_3COOH solution. [b] Not observed.

47.08. This means that the effect of the Het substituents are additive. Regarding the ^1H NMR signals of the Het residue, those of the S–Me are quite insensitive to the stereochemistry while those of the C–Me always appear shielded in the *Z,Z* isomer. This observation agrees with that reported[6] for the *N,N'*-diaryl series.

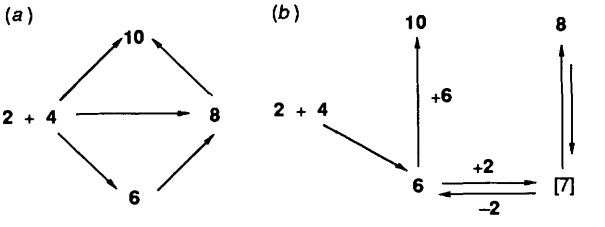
(ii), The comparison of the *N,N'*-dibenzyldiazetidines **10d** and **10e** (the *N,N'*-diisopropyl derivative **10i** is very similar) with the *N,N'*-diaryl series **10k** shows clear differences in the position of the Het signals. In ^1H NMR spectroscopy the *C*-methyl is shielded by about 0.4 ppm in the aryl *Z,Z* derivatives compared with the benzyl ones, due to the ring currents of the two aryl rings (the effect is lower for the *E,E* pairs and relatively greater when the isopropyl derivative **10i** is used for comparison). In ^{13}C NMR spectroscopy, the following averaged effects are observed (δN-benzyl − δN-aryl):



These cannot be explained by ring current effects of the phenyl rings in the **10k** series, but necessarily imply modification of electron density in the whole diazetidine. The carbon of the four-membered ring is also affected, by about 4 ppm, but in the opposite sense. This last effect is much smaller and diamagnetic instead of paramagnetic in related diacetamides: δ_C CO of $PhN(COMe)_2$ 172.3, δ_C CO of $PhCH_2N(COMe)_2$, 173.05.[9]

The Chemistry of Iminophosphoranes, Carbodiimides, Betaines and Diazetidines.—Up to this moment we have used Scheme 2 to represent the relationships between these four classes of molecules. There is no difference in reactivity between isocyanates **4** and isothiocyanates **5**, which can be used interchangeably (benzylisothiocyanates **5d–5h** are more easy to prepare). There is also no difference between iminophosphoranes **2** and **3** although there is between the corresponding betaines **8** and **9**, since only the latter are hydrolysed to guanidines **12**. The iminophosphorane moiety of compounds **9** is much more reactive towards nucleophiles due to the presence of the methyl substituent.[10] With these two considerations, the discussion can be simplified to the triphenyl series **2** and **8** and to the isocyanates **4**. The hydrolytic reactions (formation of **11** and **12**) are not essential for this discussion.

Thus, it is possible to simplify Scheme 2 in Scheme 3. On the left side [3(*a*)] are summarized the experimental evidences and in the right side [3(*b*)] the underlying mechanistic relationships.



Scheme 3

Influence of the nature of R *in the isocyanate* **4**. As **2** is always the same, the formation of **6**, **8** or **10** will depend only on R: (i) for R = alkyl and benzyl groups, *i.e.* for isocyanates of the $R'CH_2$–N=C=O type with R' = H, Me, Et or Ph, betaines **8a–8h** are formed; (ii) for R = Pr^i, at room temperature carbodiimide **6i** is formed, and at reflux in benzene, diazetidine **10i** (93% *E,E*–7% *Z,Z*) is isolated; (iii) for R = Bu^t, the reaction, in all conditions, yield carbodiimide **6j**; (iv) finally, for R = Ar, the *Z,Z* diazetidines **10k** are always obtained, in some cases, accompanied by small amounts of the *E,E* isomers.

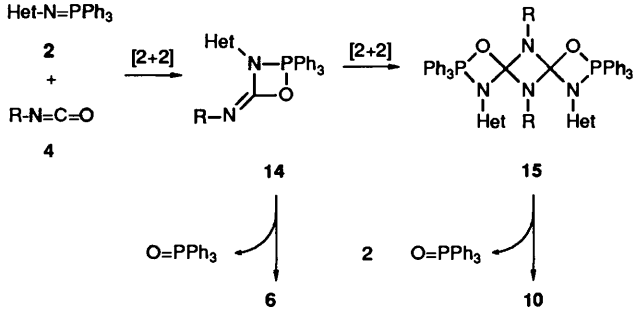
Mechanistically, we have postulated[1] that the reaction initially leads to the carbodiimide **6** which can be stable, and then reacts with itself to form **10** or reacts with another molecule of iminophosphorane to form the betaine **8** by ring opening of the diazaphosphetidine **7**. Concerning the first possibility, *i.e.* **6** + **6** → **10**, in the only two cases where the carbodiimide **6i** and **6j**, was isolated, it could not be transformed into the diazetidine. Moreover, the diazetidine **10i** can be prepared 'directly' but not from the carbodiimide which either remains unaltered or, in strong conditions, is hydrolysed to the urea **11**.

All these evidences suggest that, at least in some cases, the reaction **2** + **4** → **10** does not proceed through **6** but by another mechanism. Taking into account what has been proposed for the mechanism of the reaction of iminophosphoranes with carbonyl compounds,[11] we propose that represented in Scheme 4 to explain the direct formation of diazetidines.

Concerning the second possible mechanism of the reaction of carbodiimides, *i.e.* **6** + **2** ⇌ [7] ⇌ **8**, which we postulated[5] to explain the formation of betaines, we now have experimental evidence. When carbodiimide **6i** is allowed to react with iminophosphorane, betaine **8i** was formed. The other carbodiimide **6j** (R = Bu^t) does not react under the same conditions. We have calculated that if the methine proton of the isopropyl residue of betaine **8i** was replaced by a methyl group, the resulting betaine **8j** would be so overcrowded {contacts of the 'new' methyl group with the carbons of the Ph[C(12)–C(13)···] down to 2.2 Å} that it could not be formed.

Table 6 Crystal analysis parameters at room temperature

Compound	**8d**	**8i**
Crystal data		
Formula	$C_{36}H_{34}N_9O_2PS_2 \cdot CHCl_3 \cdot H_2O$	$C_{34}H_{34}N_9O_2PS_2$
Crystal habit	Transparent plate	Transparent prism
Crystal size/mm	0.26 × 0.10 × 0.03	0.10 × 0.13 × 0.23
Symmetry	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
Unit cell determination:	Least-squares fit from 71 reflexions ($\theta < 45°$)	Least-squares fit from 78 reflexions ($\theta < 45°$)
Unit cell dimensions/Å, deg	*a* 15.3878(15)	*a* 17.3260(15)
	b 11.7449(11)	*b* 17.9563(16)
	c 13.3338(9)	*c* 10.6655(9)
	86.952(7)	90
	104.946(6)	91.562(6)
	111.481(8)	90
Packing: V/Å^3, Z	2146.3(4), 2	3316.9(5), 4
Dc/g cm^{3}· M, F(000)	1.315, 857.21, 888	1.345, 671.77, 1408
μ/cm^{-1}	35.670	22.46
Experimental data		
Technique	Four circle diffractometer: Philips PW1100 Bisecting geometry Graphite oriented monochromator: CuKα $\omega/2\theta$ scans, scan width: 1.4° Detector apertures 1 × 1°	
Total measurement		
θ_{max}	60°	65°
Speed	1 min/reflex	
Number of reflexions		
Independent	6398	5672
Observed	3863 [$3\sigma(I)$ criterion]	3267 [$3\sigma(I)$ criterion]
Standard reflexions	2 reflexions every 90 minutes no variation	
Max–min transmission factors	1.355–0.724 (DIFABS[12])	1.247–0.783
Solution and refinement		
Solution	Direct methods	
Refinement	Least-squares on F_0 with 2 blocks	
Parameters:		
Number of variables	496 (H atoms fixed)	551
Degrees of freedom	3367	2716
Ratio of freedom	7.8	5.9
H atoms	Difference synthesis	
Final shift/error	0.50	0.21
Weighting-scheme	Empirical as to give no trends in $\langle w\Delta^2F \rangle$ *vs* $\langle \lvert F_{obs} \rvert \rangle$ and $\langle \sin\theta/\lambda \rangle$	
Max. thermal value	U22 (C152) = 0.43(1) Å^2	*U*22 (C32) = 0.19(1) Å^2
Final ΔF peaks	0.60 e Å^{-3}	0.29 e Å^{-3}
Final R and R_w	0.099, 0.115	0.063, 0.061
Computer and programs	Vax 6410, XRAY80,[13] SIR88,[14] PLUTO[15]	
Scattering factors	Int. Tables for X-Ray Crystallography[16]	



Scheme 4

This part of Scheme 3(*b*) is necessary to explain the formation of diazetidines from some betaines. Betaines **8d**–**8h** on heating are transformed into the corresponding diazetidines **10d**–**10h**. The mechanism should be: **8** → [7] → **6** + **2** and then **6** dimerizes. The iminophosphorane **2** was also isolated.

It remains to explain why in some cases carbodiimides dimerize and in others do not, and why the diazetidines of the aryl series **10k** are ⩾ 90% *Z,Z* whereas those of the benzyl series **10d**-**10h** are ⩾ 80% *E,E* (**10i** is 93% *E,E*). There are too many possibilities (like **14** reacting with **6** or other isomers of **15**) to be more precise.

In these series of papers we have explored the chemistry of iminophosphoranes **2** and **3**, of isocyanates **4** and isothiocyanates **5**, of carbodiimides **6**, of betaines **8** and **9**, and of bisiminodiazetidines **10**. The diazaphosphetidine **7** has proved elusive, but indirect proofs have been gathered about its existence. From a structural point of view, the effort has centred on betaines and on diazetidines, compounds rather neglected before this work was started. In summary, the knowledge of the structure and reactivity of the –N=C and N=P bonds has been greatly improved.

Experimental

M.p.s were determined with a Kofler hot-stage microscope and are uncorrected. Spectral studies were performed with the following instruments: IR, Nicolet FT-5DX; ^{1}H and ^{13}C NMR,

Table 7 Final atomic coordinates for compound **8d**

Atom	*x/a*	*y/b*	*z/c*
P(1)	0.7161(1)	0.2975(2)	0.5770(2)
N(2)	0.6908(4)	0.1658(6)	0.5120(5)
C(3)	0.7135(6)	0.0715(7)	0.5713(7)
N(5)	0.7405(5)	0.1090(6)	0.6720(5)
N(4)	0.7028(5)	−0.0222(6)	0.5143(5)
C(6)	0.8434(5)	0.3805(7)	0.6275(6)
C(7)	0.8733(7)	0.5018(8)	0.6621(8)
C(8)	0.9692(7)	0.5737(9)	0.6941(9)
C(9)	1.0377(7)	0.5255(11)	0.6885(10)
C(10)	1.0091(7)	0.4064(10)	0.6501(11)
C(11)	0.9121(7)	0.3332(9)	0.6195(8)
C(12)	0.6837(6)	0.3989(7)	0.4811(7)
C(13)	0.6172(7)	0.4508(9)	0.4864(8)
C(14)	0.6027(8)	0.5384(10)	0.4187(9)
C(15)	0.6505(7)	0.5725(10)	0.3437(9)
C(16)	0.7173(8)	0.5233(10)	0.3381(8)
C(17)	0.7357(6)	0.4378(8)	0.4053(7)
C(18)	0.6451(6)	0.2834(7)	0.6691(6)
C(19)	0.6824(7)	0.3433(9)	0.7658(7)
C(20)	0.6247(8)	0.3340(10)	0.8292(8)
C(21)	0.5272(9)	0.2627(11)	0.7989(9)
C(22)	0.4883(7)	0.2016(10)	0.7014(8)
C(23)	0.5456(6)	0.2103(9)	0.6363(8)
C(24)	0.6211(6)	0.1339(7)	0.4067(6)
C(24A)	0.6674(7)	0.1606(8)	0.3186(7)
C(24B)	0.7493(8)	0.1394(10)	0.3180(10)
C(24C)	0.7834(12)	0.1661(14)	0.2273(16)
C(24D)	0.7363(22)	0.2123(22)	0.1411(14)
C(24E)	0.6582(17)	0.2322(17)	0.1460(11)
C(24F)	0.6214(9)	0.2077(14)	0.2306(8)
N(25)	0.7155(5)	−0.1220(6)	0.5726(5)
C(26)	0.7815(6)	−0.1672(8)	0.5533(7)
N(27)	0.7982(6)	−0.2590(7)	0.6011(7)
N(28)	0.7484(6)	−0.3146(7)	0.6720(7)
C(29)	0.6790(7)	−0.2848(8)	0.6853(7)
C(30)	0.6522(6)	−0.1874(7)	0.6277(7)
S(31)	0.8399(2)	−0.0929(2)	0.4592(2)
C(32)	0.9187(9)	−0.1768(11)	0.4651(11)
C(33)	0.6267(9)	−0.3471(10)	0.7648(9)
O(34)	0.5819(5)	−0.1633(6)	0.6325(5)
N(35)	0.7808(5)	0.0396(6)	0.7449(5)
C(36)	0.7403(6)	0.0004(7)	0.8257(6)
N(37)	0.7733(6)	−0.0612(7)	0.9029(6)
N(38)	0.8548(7)	−0.0851(8)	0.9005(7)
C(39)	0.8995(6)	−0.0428(9)	0.8310(7)
C(40)	0.8691(6)	0.0283(7)	0.7461(7)
S(41)	0.6398(2)	0.0351(2)	0.8237(2)
C(42)	0.6120(9)	−0.0349(12)	0.9425(9)
C(43)	0.9879(9)	−0.0711(14)	0.8303(11)
O(44)	0.9117(4)	0.0725(6)	0.6799(5)
Cl(50)	0.2516(4)	0.1713(5)	0.8247(3)
Cl(51)	0.3764(5)	0.3728(5)	0.9583(4)
Cl(52)	0.1751(7)	0.3299(10)	0.8958(8)
C(53)	0.2601(14)	0.2641(16)	0.9261(14)
O(54)	0.9293(19)	0.3051(36)	0.9407(24)

Table 8 Final atomic coordinates for compound **8i**

Atom	*x/a*	*y/b*	*z/c*
P1	0.312 32(7)	0.382 96(7)	0.700 92(12)
N(2)	0.349 9(2)	0.358 5(2)	0.567 9(4)
C(3)	0.318 0(3)	0.296 0(3)	0.498 0(5)
N(4)	0.310 8(2)	0.313 1(2)	0.378 2(4)
N(5)	0.304 8(2)	0.240 6(2)	0.575 8(4)
C(6)	0.210 9(3)	0.369 7(3)	0.689 8(5)
C(7)	0.169 8(3)	0.338 1(3)	0.788 5(6)
C(8)	0.090 1(4)	0.334 5(4)	0.780 4(7)
C(9)	0.051 5(4)	0.362 1(4)	0.675 4(8)
C(10)	0.090 9(4)	0.390 8(4)	0.575 8(7)
C(11)	0.170 5(3)	0.394 1(3)	0.582 8(6)
C(12)	0.332 8(3)	0.480 9(3)	0.723 4(5)
C(13)	0.282 7(4)	0.535 3(3)	0.676 8(5)
C(14)	0.301 1(5)	0.610 1(4)	0.690 8(6)
C(15)	0.368 7(5)	0.630 3(3)	0.756 1(6)
C(16)	0.418 4(4)	0.577 0(4)	0.800 7(6)
C(17)	0.400 6(3)	0.502 4(3)	0.786 2(5)
C(18)	0.353 8(3)	0.339 6(3)	0.837 2(5)
C(19)	0.338 5(3)	0.370 2(3)	0.956 6(5)
C(20)	0.376 1(4)	0.342 6(4)	1.062 0(5)
C(21)	0.428 9(4)	0.286 6(4)	1.050 4(6)
C(22)	0.445 3(4)	0.256 3(4)	0.934 9(7)
C(23)	0.406 5(3)	0.282 2(3)	0.827 3(5)
C(24)	0.424 5(3)	0.392 3(3)	0.525 8(5)
C(24A)	0.410 4(4)	0.450 8(4)	0.425 5(6)
C(24B)	0.481 3(3)	0.332 3(4)	0.489 5(6)
N(25)	0.284 4(2)	0.256 3(2)	0.295 3(4)
C(26)	0.223 7(3)	0.276 0(4)	0.216 7(5)
N(27)	0.195 8(3)	0.233 7(4)	0.129 3(5)
N(28)	0.228 4(4)	0.164 1(4)	0.114 2(6)
C(29)	0.291 2(4)	0.145 9(4)	0.177 2(6)
C(30)	0.328 0(4)	0.193 8(3)	0.270 6(5)
S(31)	0.186 8(1)	0.364 3(1)	0.244 0(2)
C(32)	0.111 0(6)	0.367 2(7)	0.125 7(8)
C(33)	0.325 1(6)	0.069 9(5)	0.158 2(9)
O(34)	0.390 0(3)	0.182 0(2)	0.323 6(4)
N(35)	0.269 4(2)	0.177 1(2)	0.521 7(4)
C(36)	0.306 7(3)	0.110 6(3)	0.542 6(5)
N(37)	0.281 2(3)	0.045 7(3)	0.505 3(5)
N(38)	0.212 1(3)	0.043 8(3)	0.438 7(5)
C(39)	0.170 8(3)	0.104 5(3)	0.422 4(6)
C(40)	0.194 1(3)	0.176 8(3)	0.471 8(5)
S(41)	0.393 3(1)	0.118 5(1)	0.628 5(2)
C(42)	0.418 4(6)	0.021 4(4)	0.641 0(12)
C(43)	0.096 0(5)	0.099 0(6)	0.351 6(10)
O(44)	0.154 2(2)	0.232 6(2)	0.469 1(4)

Bruker AC-200 ($SiMe_4$ internal reference; all chemical shifts expressed as δ values, all J values in Hz); ^{31}P NMR, Varian FT-80A (H_3PO_4 external reference); mass (70 eV), Hewlett-Packard 5993C. Combustion analyses were performed with a Perkin-Elmer 240C instrument.

The single crystal samples used in the X-ray crystallographic analysis were obtained by evaporation from chloroform. As a result **8d** includes two chloroform and two water molecules per unit cell. Crystal data for **8d**·$CHCl_3$·H_2O and **8i** are given in Table 6.

Selected geometrical characteristics for compound **8d** and **8i** are given in Table 1, where the corresponding parameters for **8a**·C and **8c** are included for comparison purposes. The numbering scheme is presented in Fig. 2. Final atomic coordinates for the non-hydrogen atoms are given in Tables 7 and 8.

Reagents.—All solvents were dried according to standard procedures, distilled and stored over activated molecular sieves (4 Å). 4-Amino-6-methyl-3-methylthio-4,5-dihydro-1,2,4-triazin-5-one[17] **1** and 6-methyl-3-methylthio-4-triphenylphosphoranylideneamino-4,5-dihydro-1,2,4-triazin-5-one[1] **2** were prepared by previously reported procedures. Isocyanates **4a–c**, **4i** and **4j**, and isothiocyanate **5d** were commercially available. Substituted benzyl isothiocyanates **5e–h** were obtained in 60–70% overall yield starting from the commercially available substituted benzyl bromides, by a sequence involving its conversion into the corresponding benzyl azides by treatment with Amberlite IRA-400 (N_3 form),[18] Staudinger reaction[19] with triphenylphosphine, and refluxing of the obtained iminophosphoranes with an excess of carbon disulphide in benzene solution;[20] all of them were purified by vacuum distillation and showed the expected spectral data.

4-*Diphenyl(methyl)phosphoranylideneamino*-6-*methyl*-3-*methylthio*-4,5-*dihydro*-1,2,4-*triazin*-5-*one* **3**.—This was prepared by the same method described[1] for the preparation of compound **2**, but using diphenyl(methyl)phosphine, in 91% yield, as brown prisms from benzene–hexane, m.p. 162–164 °C (Found: C, 58.4; H, 5.2; N, 15.0. $C_{18}H_{19}N_4OPS$ requires C,

58.37; H, 5.17; N, 15.13%); ν_{max}(Nujol)/cm^{-1} 1636vs, 1438m, 1342s, 1308m, 1285m, 1240s, 1109m, 1070m, 1019m, 906m, 889m, 753m, 742s and 696m; δ_H($CDCl_3$) 7.8–7.4 (10 H, m, Ar), 2.60 (3 H, s, C–CH_3), 2.50 (3 H, d, *J* 13.2, P–CH_3) and 2.30 (3 H, s, S–CH_3); δ_C($CDCl_3$) 160.83 (C-3), 150.98 (C-5), 153.30 (C-6), 131.85 (C_i, *J* 100.5), 131.70 (C_p, *J* 2.9), 131.19 (C_o, *J* 9.6), 128.74 (C_m, *J* 12.1), 18.35 (P–CH_3, *J* 68.0), 17.30 (C–CH_3) and 14.80 (S–CH_3); δ_P($CDCl_3$) 21.04; *m/z* 370 (M^+, 7), 369 (36), 228 (10), 214 (10), 213 (30), 201 (15), 200 (100), 199 (14), 185 (24), 183 (38), 152 (6), 122 (6), 121 (9), 107 (5), 100 (6), 77 (8), 73 (10) and 45 (5).

General Procedure for the Preparation of Carbodiimides **6i** *and* **6j**.—To a solution of 6-methyl-3-methylthio-4-triphenylphosphoranylideneamino-4,5-dihydro-1,2,4-triazin-5-one **2** (5 g, 0.0116 mol) in dry benzene (100 cm^3), the appropriate isocyanate (0.0116 mol) was added. The reaction mixture was stirred for 24 h at room temperature, the solvent was evaporated off under reduced pressure, and the resulting residue treated with cold hexane (60 cm^3). The precipitated triphenylphosphine oxide was separated by filtration, and concentration of the filtrate afforded the corresponding *carbodiimide* **6**. The following compounds were obtained.

Compound **6i**, 45% yield, as colourless prisms, m.p. 86–88 °C (Found: C, 45.25; H, 5.4; N, 29.2. $C_9H_{13}N_5OS$ requires C, 45.17; H, 5.48; N, 29.27%); ν_{max}(Nujol)/cm^{-1} 2100vs, 1664vs, 1528w, 1331m, 1308m, 1274w, 1189m, 1104m, 1070m, 968m, 769w, 752w, 724w and 696m; δ_H($CDCl_3$) 4.03 (1 H, sept, *J* 6.5, CH), 2.59 (3 H, s, S–CH_3), 2.48 (3 H, s, C–CH_3) and 1.42 (6 H, d, *J* 6.5; 2 CH_3); δ_C($CDCl_3$) 156.94 (C-3), 152.64 (C-6), 150.93 (C-5), 137.13 (NCN), 51.98 (CH), 23.27 (2 CH_3), 17.37 (C–CH_3) and 14.80 (S–CH_3); *m/z* 239 (M^+, 11), 224 (13), 223 (16), 209 (15), 208 (16), 199 (58), 198 (13), 193 (33), 185 (20), 184 (14), 183 (41), 172 (35), 170 (10), 156 (48), 152 (39), 115 (21), 87 (14), 86 (21), 85 (38), 73 (30), 55 (17) and 47 (100).

Compound **6j**, 60% yield, as colourless prisms, m.p. 102–103 °C (Found: C, 47.35; H, 6.1; N, 27.75. $C_{10}H_{15}N_5OS$ requires C, 47.41; H, 5.97; N, 27.65%); ν_{max}(Nujol)/cm^{-1} 2100vs, 1671vs, 1535w, 1331s, 1280w, 1195m, 1070m, 979w, 747m, 725w and 668m; δ_H($CDCl_3$) 2.59 (3 H, s, S–CH_3), 2.48 (3 H, s, C–CH_3) and 1.48 (9 H, s, CH_3); δ_C($CDCl_3$) 157.00 (C-3), 152.72 (C-6), 151.00 (C-5), 136.11 (NCN), 59.72 [*C*(3)–Me], 30.26 (3-CH_3), 17.39 (C–CH_3) and 14.50 (S–CH_3); *m/z* 253 (M^+, 9), 240 (6), 239 (13), 238 (100), 199 (5), 198 (12), 197 (60), 170 (12), 157 (7), 156 (57), 155 (10), 143 (15), 128 (12), 127 (6), 125 (7), 115 (11), 114 (14), 102 (9), 87 (11), 83 (6), 73 (10), 57 (35) and 47 (9).

When a solution of carbodiimide **6i** (0.5 g, 0.0021 mol) in 80% aqueous ethanol (15 cm^3) was heated at reflux temperature for 2 h, in the presence of a catalytic amount of conc. hydrochloric acid, and then cooled to room temperature, a white solid precipitated which was collected by filtration and crystallized from dimethyl sulfoxide to give the *urea* **11** (0.5 g, 93%) as colourless prisms, m.p. 242–244 °C (Found: C, 42.15; H, 5.75; N, 27.3. $C_9H_{15}N_5O_2S$ requires C, 42.01; H, 5.88; N, 27.22%); ν_{max}(Nujol)/cm^{-1} 3296m, 1710s, 1664vs, 1568m, 1483m, 1342m, 1313m, 1246m, 1160w, 1064m, 985w, 854w, 832w, 803w, 758w and 718w; δ_H[$(CD_3)_2SO$] 9.07 (1 H, s, Het–NH), 6.48 (1 H, d, CH–N*H*), 3.95 (1 H, sept, CH), 2.49 (3 H, s, S–CH_3), 2.40 (3 H, s, C–CH_3) and 1.17 (6 H, d, 2 CH_3); *m/z* 258 (M^+ + 1, 7), 257 (M^+, 9), 199 (7), 173 (16), 172 (96), 157 (10), 156 (100), 128 (10), 125 (8), 114 (10), 86 (10), 74 (30), 73 (16), 69 (22), 58 (34), 57 (16) and 46 (41).

Preparation of Betaine **8i**.—A solution of *N*-isopropyl-*N'*-(6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazin-4-yl)carbodiimide **6i** (0.5 g, 0.0021 mol) in dry benzene (10 cm^3) was added at once to a stirred solution of 6-methyl-3-methylthio-4-triphenylphosphoranylideneamino-4,5-dihydro-1,2,4-triazin-5-one **2** (0.9 g, 0.0021 mol) in the same solvent (25 cm^3), and the reaction mixture was stirred at room temperature for 2 h. The precipitated solid was collected by filtration, dried, and crystallized from dichloromethane–ether to give *betaine* **8i** (1.25 g, 89%), as pale-yellow prisms, m.p. 166–168 °C (Found: C, 57.3; H, 5.15; N, 18.7. $C_{32}H_{34}N_9O_2PS_2$ requires C, 57.21; H, 5.10; N, 18.76%); ν_{max}(Nujol)/cm^{-1} 1681vs, 1664m, 1535s, 1438m, 1319m, 1302m, 1274s, 1217m, 1194w, 1149w, 1109m, 1070m, 756m, 746m, 735m, 717s, and 689 m; δ_H($CDCl_3$) 7.9–7.3 (15 H, m, Ar), 3.64 (1 H, sept, *J* 6.7, CH), 2.34 (6 H, s, S–CH_3), 2.07 (6 H, s, C–CH_3), 1.76 (3 H, d, CH_3) and 1.58 (3 H, d, CH_3); δ_C($CDCl_3$) 160.53 (C-3), 152.29 (C-6), 151.70 (C^-, *J* 6.5), 148.63 (C-5), 133.70 (C_o, *J* 10.15), 133.06 (C_p, *J* 2.9), 129.16 (C_m, *J* 13.4), 124.95 (C_i, *J* 107.2), 51.98 (CH, br), 20.87 (CH_3, *J* 2.8), 23.40 (CH_3, *J* 3.2), 17.07 (C–CH_3) and 14.53 (S–CH_3); δ_C(solid state) 161.9 (C-3), 152.8 (C-6 + C^-, br), 149.0 (C-5), 134.8 (C_o, br), 138 (C_p, br), 131.1 (C_m, *J* – 15), 123.4 (C_i, *J* – 100), 52.9 (CH), 21.6 and 24.5 (CH_3, Pr^i), 17.1 (C–CH_3) and 15.0 (S–CH_3); δ_P($CDCl_3$) 34.02; *m/z* 432 (5), 277 (20), 262 (30), 239 (12), 199 (40), 183 (15), 172 (10), 156 (40), 85 (22), 73 (52) and 47 (100).

General Procedure for the Preparation of Betaines **8d–h** *and* **9a–d**.—To a solution of iminophosphorane **2** or **3** (0.002 mol) in dry benzene (30 cm^3), the appropriate isocyanate **4a–c** or isothiocyanate **5d–h** (0.0022 mol) was added, and the resulting mixture was stirred at room temperature for 24 h. The precipitated solid was collected by filtration, dried and crystallized from the appropriate solvent to give the corresponding betaine **8** as a crystalline solid. Compounds **9** did not precipitate in the reaction mixture, and a slightly different work-up was employed: the solvent was evaporated off under reduced pressure, and the residue was scratched in ether at 0 °C to give a solid which was filtered off and crystallized from the appropriate solvent to give the corresponding betaine **9**. The following compounds were obtained.

Compound **8d**, 96% yield, as white needles from dichloromethane–ether, m.p. 195–197 °C (Found: C, 60.15; H, 4.7; N, 17.45. $C_{36}H_{34}N_9O_2PS_2$ requires C, 60.07; H, 4.76; N, 17.51%); ν_{max}(Nujol)/cm^{-1} 1681vs, 1534s, 1438m, 1308s, 1285s, 1115m, 1075m, 1030m, 996w, 956, 843m, 758m, 731m, 713m and 690s; δ_P($CDCl_3$) 34.22; *m/z* 433 (5), 262 (10), 183 (22), 170 (6), 154 (14), 131 (11), 115 (70), 108 (23), 91 (100), 77 (13), 73 (16), 69 (12), 65 (14) and 47 (15).

Compound **8e**, 87% yield, as white prisms from dichloromethane–ether, m.p. 191–193 °C (Found: C, 54.05; H, 4.1; N, 15.85. $C_{36}H_{33}N_9BrO_2PS_2$ requires C, 54.14; H, 4.16; N, 15.78%); ν_{max}(Nujol)/cm^{-1} 1679vs, 1541vs, 1439m, 1413m, 1326s, 1308s, 1286vs, 1115m, 1070m, 955w, 843m, 833m, 757m, 713m and 683; *m/z* 433 (5), 432 (9), 286 (6), 277 (18), 262 (36), 201 (17), 199 (17), 184 (25), 183 (100), 171 (60), 170 (15), 169 (70), 157 (28), 152 (26), 131 (21), 116 (16), 108 (63), 107 (32), 90 (35), 89 (24), 77 (41), 73 (39), 69 (28), 63 (16), 51 (45) and 47 (73).

Compound **8f**, 93% yield, as white needles from dichloromethane–ether, m.p. 192–194 °C (Found: C, 54.2; H, 4.05; N, 15.8. $C_{36}H_{33}N_9BrO_2PS_2$ requires C, 54.14; H, 4.16; N, 15.78%); ν_{max}(Nujol)/cm^{-1} 1676vs, 1540s, 1438m, 1415m, 1308s, 1291s, 1132w, 1115m, 1104m, 1070m, 1013m, 956w, 860m, 758m, 735m, 713m and 684m; δ_P($CDCl_3$) 34.40; *m/z* 433(5), 432 (12), 286 (5), 277 (10), 262 (28), 184 (14), 183 (52), 171 (95), 170 (13), 169 (100), 157 (16), 156 (7), 155 (5), 152 (14), 108 (33), 107 (17), 90 (31), 89 (26), 78 (5), 77 (24), 73 (24), 69 (17), 63 (12), 59 (18) and 47 (48).

Compound **8g**, 85% yield, as white needles from dichloromethane–ether, m.p. 208–210 °C (Found: C, 60.65; H, 4.9; N, 17.1. $C_{37}H_{36}N_9O_2PS_2$ requires C, 60.56; H, 4.94; N, 17.18%); ν_{max}(Nujol)/cm^{-1} 1681vs, 1540s, 1438m, 1330m, 1313s, 1291s,

1115m, 1070m, 1040m, 996w, 849m, 752m, 718m, and 690m; *m/z* 433 (5), 302 (6), 262 (8), 183 (15), 170 (5), 157 (7), 131 (7), 119 (7), 115 (8), 108 (17), 105 (100), 91 (9), 79 (7), 77 (18), 73 (15), 69 (10), 65 (10) and 47 (20).

Compound **8h**, 85% yield, as white needles from dichloromethane–ether, m.p. 186–188 °C (Found: C, 56.65; H, 4.3; N, 18.4. $C_{36}H_{33}N_{10}O_4PS_2$ requires C, 56.54; H, 4.35; N, 18.31%); ν_{max}(Nujol)/cm^{-1} 1681vs, 1540vs, 1523s, 1438m, 1353m, 1325m, 1308s, 1285s, 1115m, 1070w, 962w, 871m, 736m, 713m and 690m; *m/z* 433 (5), 432 (20), 277 (13), 262 (47), 201 (11), 185 (15), 184 (23), 183 (100), 170 (5), 156 (10), 152 (22), 136 (5), 131 (19), 122 (10), 108 (64), 107 (30), 77 (25), 73 (30), 69 (12), 57 (6), 51 (24) and 47 (29).

Compound **9a**, 60% yield, as white prisms from dichloromethane–ether, m.p. 156–158 °C (Found: C, 51.7; H, 4.8; N, 21.6. $C_{25}H_{28}N_9O_2PS_2$ requires C, 51.62; H, 4.85; N, 21.67%); ν_{max}(Nujol)/cm^{-1} 1676vs, 1535s, 1518s, 1308s, 1189w, 1115m, 1070w, 1000m, 934m, 752m, 696m and 679m; δ_H($CDCl_3$) 7.7–7.3 (10 H, m, Ar), 3.20 (3 H, d, *J* 11.2, N–CH_3), 2.86 (3 H, d, *J* 13.4, P–CH_3), 2.56 (6 H, s, S–CH_3) and 2.44 (6 H, s, C–CH_3); *m/z* 371 (6), 370 (5), 232 (14), 231 (8), 217 (10), 216 (8), 215 (28), 214 (15), 211 (5), 200 (79), 185 (29), 183 (58), 170 (5), 156 (5), 152 (16), 139 (32), 133 (5), 128 (6), 123 (18), 122 (13), 121 (32), 107 (24), 100 (13), 95 (11), 91 (26), 83 (15), 77 (100), 73 (88), 51 (95) and 47 (89).

Compound **9b**, 83% yield, as pale-yellow prisms from dichloromethane–ether, m.p. 181–183 °C (Found: C, 52.4; H, 5.0; N, 21.2. $C_{26}H_{30}N_9O_2PS_2$ requires C, 52.43; H, 5.08; N, 21.16%); ν_{max}(Nujol)/cm^{-1} 1687s, 1545vs, 1438m, 1364m, 1331w, 1189w, 1166w, 1126m, 1075w, 1019m, 905m, 786w, 752m, 718m and 696m; δ_H($CDCl_3$) 7.8–7.3 (10 H, m, Ar), 3.48 (2 H, m, N–CH_2), 2.87 (3 H, d, *J* 13.1, P–CH_3), 2.39 (6 H, s, S–CH_3), 2.19 (6 H, s, C–CH_3) and 1.31 (3 H, t, CH_3); δ_C($CDCl_3$) 160.22 (C-3), 153.52 (C$^=$, *J* 4.9), 152.08 (C-6), 149.02 (C-5), 133.72 (C_p, **P**, *J* 2.3), 133.08 (C_p, **P′**, *J* 2.8), 132.21 (C_o, **P**, *J* 10.4), 131.40 (C_o, **P′**, *J* 11.4), 129.42 (C_m, **P′**, *J* 12.4), 129.25 (C_m, **P**, *J* 13.8), 125.33 (C_i, **P′**, *J* 96.0), 125.22 (C_i, **P**, *J* 107.9), 42.64 (CH_2, br), 16.90 (C–CH_3), 16.85 (P–CH_3, *J* 75.7), 15.66 (CH_3–CH_2) and 14.24 (S–CH_3); *m/z* 370 (47), 232 (9), 226 (11), 225 (33), 214 (26), 219 (66), 201 (31), 200 (100), 199 (22), 185 (40), 183 (71), 170 (8), 156 (21), 152 (12), 139 (12), 121 (20), 115 (15), 91 (14), 77 (38), 73 (92), 69 (43) and 47 (75).

Compound **9c**, 69% yield, as pale-yellow prisms from ether, m.p. 140–142 °C (Found: C, 53.25; H, 5.15; N, 20.6. $C_{27}H_{32}N_9O_2PS_2$ requires C, 53.19; H, 5.29; N, 20.68%); ν_{max}(Nujol)/cm^{-1} 1681vs, 1534s, 1438m, 1325m, 1308m, 1291m, 1115m, 1075w, 1019m, 917w, 883w, 752m and 696m; δ_H($CDCl_3$) 7.8–7.3 (10 H, m, Ar), 3.46 (2 H, m, N–CH_2), 2.87 (3 H, d, *J* 13.1, P–CH_3), 2.39 (6 H, s, S–CH_3), 2.18 (6 H, s, C–CH_3), 1.81 (2 H, m, CH_2) and 0.63 (3 H, t, CH_3); *m/z* 371 (12), 370 (5), 239 (5), 215 (25), 214 (24), 210 (92), 201 (23), 200 (80), 199 (16), 185 (32), 183 (47), 156 (8), 152 (13), 139 (15), 122 (14), 121 (20), 115 (18), 109 (6), 107 (15), 100 (15), 99 (10), 96 (61), 88 (15), 83 (22), 73 (88), 69 (55), 55 (31) and 47 (100).

Compound **9d**, 98% yield, as white prisms from benzene–hexane, m.p. 176–178 °C (Found: C, 56.7; H, 4.8; N, 19.7. $C_{31}H_{32}N_9O_2PS_2$ requires C, 56.61; H, 4.90; N, 19.64%); ν_{max}(Nujol)/cm^{-1} 1681vs, 1545s, 1438s, 1421m, 1325s, 1038s, 1291s, 1115m, 1092w, 1075w, 1036w, 968w, 917m, 894m, 843w, 752m, 703m and 690m; δ_H($CDCl_3$) 7.8–7.2 (15 H, m, Ar), 5.02 (1 H, dd, *J* 17.0, −16.5, CH_AH_B), 4.74 (1 H, dd, *J* 16.0, −16.5, CH_AH_B), 2.74 (3 H, d, *J* 13.0, N–CH_3), 2.37 (6 H, s, S–CH_3) and 2.18 (6 H, s, C–CH_3); δ_C($CDCl_3$) 160.43 (C-3), 154.10 (C$^=$, *J* 5.5), 152.22 (C-6), 149.07 (C-5), 138.20 (C_i), 133.48 (C_p, **P**, *J* 2.6), 133.03 (C_p, **P′**, *J* 3.1), 132.30 (C_o, **P**, *J* 10.6), 131.31 (C_p), 130.60 (C_o, **P′**, *J* 10.6), 129.24 (C_m, **P**, *J* 14.2), 129.05 (C_m, **P′**, *J* 12.7), 128.31 (C_o), 127.34 (C_m), 125.11 (C_i, **P**, *J* 108.1), 124.80 (C_i, **P′**, *J* 98.9), 50.76 (CH_2, br), 17.12 (C–CH_3), 16.68 (P–CH_3, *J* 76.0) and 14.46 (S–CH_3); *m/z* 371 (11), 370 (42), 287 (15), 211 (6), 210 (14), 200 (81), 199 (22), 185 (27), 183 (48), 170 (7), 156 (9), 152 (11), 91 (30), 77 (100), 73 (70), 69 (43) and 47 (89).

General Procedure for Preparation of 1,3-*Diazetidines* **10d–g**.—A solution of the appropriate betaine **8d–g** (0.001 mol) in dry benzene (40 cm^3) was heated at reflux temperature for 24 h. After being cooled to room temperature, the solvent was evaporated under reduced pressure, and the solid residue was treated with boiling dry ethanol (20 cm^3) to give the corresponding 1,3-*diazetidine* **10d–g** as a white solid, collected by filtration and dried. Concentration of the filtrate and cooling to 0 °C yielded iminophosphorane **2** as yellow prisms m.p. 219–220 °C (lit.,[2] 220–221 °C).

The following compounds were obtained.

1,3-*Dibenzyl*-2,4-*bis*[(6-*methyl*-3-*methylthio*-5-*oxo*-4,5-*dihydro*-1,2,4-*triazin*-4-*yl*)*imino*]-1,3-*diazetidine* **10d**, 67% yield, isomer ratio *E,E–Z,Z* 88:12; (Found: C, 54.2; H, 4.5; N, 24.45. $C_{26}H_{26}N_{10}O_2S_2$ requires C, 54.34; H, 4.56; N, 24.37%); ν_{max}(Nujol)/cm^{-1} 1693vs, 1625vs, 1472m, 1410m, 1347w, 1308m, 1070m, 1030w, 979w, 860w, 758m, 735m and 701m; *m/z* 287 (M$^+$/2, 5), 222 (11), 157 (12), 156 (5), 131 (7), 115 (8), 91 (100), 77 (12), 69 (13), 65 (15) and 47 (20).

1,3-*Bis*(3-*bromobenzyl*)-2,4-*bis*[(6-*methyl*-3-*methylthio*-5-*oxo*-4,5-*dihydro*-1,2,4-*triazin*-4-*yl*)*imino*]-1,3-*diazetidine* **10e**, 54% yield, isomer ratio *E,E–Z,Z* 81:19 (Found: C, 42.75; H, 3.2; N, 19.05. $C_{26}H_{24}N_{10}Br_2O_2S_2$ requires C, 42.63; H, 3.30; N, 19.12%); ν_{max}(Nujol)/cm^{-1} 1692vs, 1630vs, 1467s, 1409m, 1341m, 1326m, 1307s, 1208m, 1072m, 958m, 948w, 864m, 836w, 778m, 753m, 736s and 686m; *m/z* 378 (5), 365 (M$^+$/2, 6), 172 (8), 171 (100), 169 (94), 157 (24), 156 (8), 132 (72), 116 (15), 115 (5), 110 (7), 105 (5), 90 (60), 89 (44), 77 (27), 74 (15), 71 (14), 69 (40), 63 (20) and 47 (89).

1,3-*Bis*(4-*bromobenzyl*)-2,4-*bis*[(6-*methyl*-3-*methylthio*-5-*oxo*-4,5-*dihydro*-1,2,4-*triazin*-4-*yl*)*imino*]-1,3-*diazetidine* **10f**, 43% yield, isomer ratio *E,E–Z,Z* 84:16 (Found: C, 42.55; H, 3.4; N, 19.15. $C_{26}H_{24}N_{10}Br_2N_2S_2$ requires C, 42.63; H, 3.30; N, 19.12%); ν_{max}(Nujol)/cm^{-1} 1687vs, 1625vs, 1538m, 1492m, 1391m, 1336m, 1305m, 1202m, 1084m, 1007m, 977m, 959w, 940w, 864m, 824m, 793m and 760m; *m/z* 379 (5), 365 (M$^+$/2, 13), 172 (6), 171 (98), 170 (6), 169 (100), 157 (10), 132 (14), 116 (8), 115 (5), 91 (7), 90 (30), 89 (18), 77 (8), 74 (9), 69 (20), 55 (6), 51 (8) and 47 (30).

1,3-*Bis*(4-*tolyl*)-2,4-*bis*[(6-*methyl*-3-*methythio*-5-*oxo*-4,5-*dihydro*-1,2,4-*triazin*-4-*yl*)*imino*]-1,3-*diazetidine* **10g**, 48% yield, isomer ratio *E,E–Z,Z* 90:10 (Found: C, 55.75; H, 5.1; N, 23.15. $C_{28}H_{30}N_{10}O_2S_2$ requires C, 55.80; H, 5.02; N, 23.24%); ν_{max}(Nujol)/cm^{-1} 1687vs, 1625vs, 1534m, 1517m, 1398m, 1342m, 1325m, 1308s, 1206w, 1070m, 1036m, 979m, 939w, 866m, 809w, 764m, 752m and 662w; *m/z* 301 (M$^+$/2, 8), 250 (9), 249 (15), 157 (13), 120 (16), 106 (21), 105 (100), 91 (32), 79 (7), 77 (12), 69 (14), 55 (10) and 47 (20).

1,3-*Diisopropyl*-2,4-*bis*[(6-*methyl*-3-*methylthio*-5-*oxo*-4,5-*dihydro*-1,2,4-*triazin*-4-*yl*)*imino*]-1,3-*diazetidine* **10i**.—A mixture of 6-methyl-3-methylthio-4-triphenylphosphoranylideneamino-4,5-dihydro-1,2,4-triazin-5-one (0.50 g, 0.001 16 mol), isopropyl isocyanate (0.1 g, 0.001 16 mol) and dry benzene (20 cm^3) were stirred at reflux temperature for 24 h. A white solid gradually appeared in the reaction mixture. After being cooled, the precipitated solid was isolated by filtration and repeatedly crystallized from dichloromethane to give the *title* 1,3-*diazetidine* **10i** (0.11 g; 40%) as a mixture of isomers in the ratio *E,E–Z,Z* 93:7 (Found: C, 45.25; H, 5.4; N, 29.15. $C_{18}H_{26}N_{10}O_2S_2$ requires C, 45.17; H, 5.48; N, 29.27%); ν_{max}(Nujol)/cm^{-1} 1698vs, 1620s, 1540m, 1308m, 1211w, 1132m, 1070w, 996w, 962w and 758w; δ_H($CDCl_3$): (*E,E*) 3.2 (1 H, sept, *J* 6.8, CH), 2.63 (3 H, s, S–CH_3), 2.50 (3 H, s, C–CH_3)

and 1.32 (6 H, d, *J* 6.8, $2CH_3$); (*Z,Z*) 4.03 (1 H, sept, *J* 6.8, CH), 3.12 (1 H, sept, *J* 6.9, CH), 2.63 (6 H, s, S–CH_3), 2.40 (6 H, s, C–CH_3), 1.54 (6 H, d, *J* 6.8, 2 CH_3) and 0.88 (6 H, d, *J* 6.9, 2 CH_3); $\delta_C(CDCl_3)$: (*E,E*) 158.52 (C-3), 157.49 (C-6), 154.63 (C-5), 148.58 (C=N), 49.69 (CH), 20.50 (2 CH_3), 17.63 (C–CH_3) and 14.47 (S–CH_3); *m/z* 239 ($M^+/2$, 41), 224 (46), 198 (13), 156 (23), 126 (76), 84 (100), 83 (26), 79 (30) and 43 (68).

General Procedure for the Preparation of N-*Alkyl*-N′,N″-*bis*(6-*methyl*-3-*methylthio*-5-*oxo*-4,5-*dihydro*-1,2,4-*triazin*-4-*yl*)*guanidines* **12a–c**.—A stirred solution of the appropriate betaine **9a–c** (0.0015 mol) in commercial chloroform (30 cm^3) was heated at reflux temperature for 6 h. After being cooled, the white solid which gradually precipitated out was collected by filtration, dried and crystallized from the adequate solvent to give the corresponding *guanidine* **12a–c**. The filtrate was evaporated under reduced pressure and the residue crystallized from hexane to give diphenyl(methyl)phosphine oxide as colourless prisms m.p. 110 °C (lit.,[21] m.p. 111–112 °C).

The following compounds were prepared.

N-*Methyl* **12a**, 61% yield, as white prisms from dimethyl sulfoxide, m.p. 208–210 °C (Found: C, 37.45; H, 4.55; N, 32.95. $C_{12}H_{17}N_9O_2S_2$ requires C, 37.59; H, 4.47; N, 32.87%); ν_{max}(Nujol)/cm^{-1} 3300m, 1710vs, 1693vs, 1591m, 1562m, 1415m, 1325m, 1308s, 1223m, 1211m, 1070w, 968w, 764w, 725w and 667w; $\delta_H[(CD_3)_2SO + CF_3CO_2H]$ 2.80 (3 H, s, CH_3), 2.55 (6 H, s, S–CH_3) and 2.35 (6 H, s, C–CH_3); *m/z* 383 (M^+, 5), 336 (5), 212 (29), 181 (14), 180 (48), 179 (6), 158 (15), 157 (21), 156 (9), 152 (12), 151 (11), 124 (6), 116 (17), 115 (60), 110 (13), 98 (17), 88 (14), 82 (63), 74 (40), 69 (83), 57 (48) and 47 (100).

N-Ethyl **12b**, 54% yield, as white prisms from dimethyl sulfoxide, m.p. 210–211 °C (Found: C, 39.35; H, 4.85; N, 31.85. $C_{13}H_{19}N_9O_2S_2$ requires C, 39.28; H, 4.82; N, 31.71%); ν_{max}(Nujol)/cm^{-1} 3225m, 1718s, 1692vs, 1607s, 1544m, 1329m, 1310m, 1292s, 1257m, 1221w, 1146w, 1125w, 1074m, 980w and 747w; $\delta_H[(CD_3)_2SO + CF_3CO_2H]$ 2.95 (2 H, m, CH_2), 2.55 (6 H, s, S–CH_3), 2.35 (6 H, s, C–CH_3) and 1.10 (3 H, t, CH_3); *m/z* 397 (M^+, 10), 350 (18), 227 (6), 226 (35), 195 (15), 194 (21), 193 (8), 179 (21), 158 (18), 157 (20), 156 (13), 135 (11), 129 (12), 116 (18), 115 (61), 112 (23), 110 (21), 97 (19), 83 (28), 74 (35), 71 (37), 69 (83), 55 (69) and 47 (100).

N-Propyl **12c**, 41% yield, as white prisms dimethyl sulfoxide–water, m.p. 190–192 °C (Found: C, 40.75; H, 5.05; N, 30.75. $C_{14}H_{21}N_9O_2S_2$ requires C, 40.86; H, 5.14; N, 30.63%); ν_{max}(Nujol)/cm^{-1} 3296m, 1715s, 1693vs, 1596s, 1551m, 1319m, 1308s, 1257m, 1206w, 1143w, 1126w, 1070m, 979w, 758w and 747w; $\delta_H[(CD_3)_2SO + CF_3CO_2H]$ 3.10 (2 H, m, N–CH_2), 2.50 (6 H, s, S–CH_3), 2.30 (6 H, s, C–CH_3), 1.50 (2 H, m, CH_2) and 0.90 (3 H t, CH_3); *m/z* 411 (M^+, 5), 364 (10), 240 (8), 215 (11), 201 (7), 179 (10), 157 (15), 116 (17), 110 (19), 91 (7), 74 (25), 69 (38) and 47 (100).

Supplementary Data Available.—(See Section 5.6.3 of Instructions for Authors, January issue): lists of the structure factors, thermal components, hydrogen parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

Note added in proof. Recently (J. Breker, P. G. Jones and R. Schmutzler, *Z. Naturforsch.*, 1990, **45B**, 1407) the X-ray structure of a phosphadiazetidinone was reported. Due to the pyramidal character of the phosphorus, the two intracyclic P–N bonds are different, the equatorial is 1.68 Å whereas the axial is 1.82 Å. The ratio (1.08) is still far from our betaines.

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