1-Aza-1,3-bis(triphenylphosphoranylidene)propane: A Novel =CHCH$_2$N= Synthon

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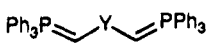
1-Aza-1,3-bis(triphenylphosphoranylidene)propane (**3**), prepared *in situ* by the reaction of 1-[[(triphenylphosphoranylidene)amino]methyl]benzotriazole (betmip, **4**) with methylidenetriphenylphosphorane followed by treatment with butyllithium, enables convenient preparations of 3*H*-2-benzazepine (**7**), 2,3-diarylpyrroles **8**, and primary allylamines **12** and **13**.

Bis(alkylidenetriphenylphosphoranes) **1** (1,2-, 1,3-, and 1,4-bisylides) (see review[1] and references cited therein) and bis(iminophosphoranes) **2** (bisazaylides) have been known for decades.[2] They provide reactive systems in which the two alkylidenetriphenylphosphorane or the two iminophosphorane functionalities can react either with a bis-electrophile or successively with two separate electrophiles. Interesting cyclization reactions involving



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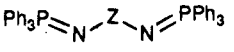
Y = i. $(CH_2)_n$ (n = 0, 1, 2)
ii. O, S
iii. Aromatic ring(s)



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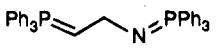
Z = i. Aromatic ring(s)
ii. Direct single bond

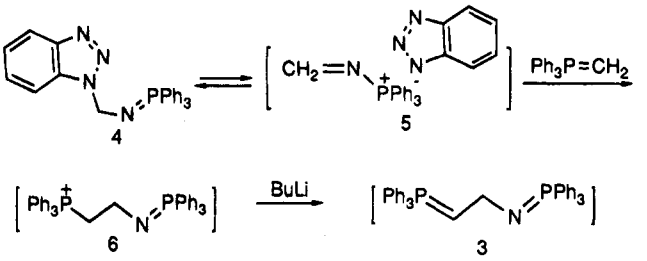


3

bis(alkylidenetriphenylphosphoranes) **1** have been reviewed:[1] they are particularly important in the synthesis of large ring compounds with the ring sizes synthesized ranging from five to 36. Bis(iminophosphoranes) **2** exhibit a rich chemistry of unusual synthetic promise.[2] However, the chemistry of monoazabisphosphorus ylides (analogous reagents containing both a phosphazene and a phosphorus ylide), which should also have considerable synthetic potential, has remained unexplored, and 1,3-mono-aza-bis-ylides of type **3** were unknown prior to our work.

Our preliminary paper[3] reported 1-aza-1,3-bis(triphenylphosphoranylidene)propane (**3**) for the first time and some of its Wittig/aza-Wittig reactions (corresponding to the bis-Wittig reactions) to produce 3*H*-2-benzazepine (**7**) and 2,3-disubstituted pyrroles **8** as well. In contrast to the bisylides **1** and bisazaylides **2**, in which the two phosphorane functionalities are usually of the same reactivity toward electrophiles, we expected that an electrophile could react selectively with the two different

Scheme 1



phosphorane moieties of 1-aza-1,3-bis(triphenylphosphoranylidene)propane (**3**) and thus that the utility should be improved. If this were the case, after a single Wittig reaction, one phosphorane group should survive which could subsequently undergo reaction with another different electrophile. We now disclose details of the previously reported[3] bis-Wittig reactions of **3** with dicarbonyl compounds and of new reactions with aldehydes and ketones. These reactions provide attractive syntheses of **7**, **8**, imine **11**, and primary allylamines **12** and **13**.

Results and Discussion

Betmip, [1-[[(triphenylphosphoranylidene)amino]methyl]-benzotriazole (**4**)], is the first reported equivalent of $CH_2{=}NP^+Ph_3X^-$ (**5**), an analog of vinyltriphenylphosphonium halide ($CH_2{=}CHP^+Ph_3X^-$). We have already demonstrated its utility in the synthesis of nitrogen-containing compounds and heterocycles.[4] It can be conveniently prepared by the reactions of benzotriazole, formaldehyde, sodium azide, and triphenylphosphine on a large scale in 85% overall yield.[4c] The white solid **4** can be stored for at least several months in a dry atmosphere. The compound **3** was synthesized *in situ* by the nucleophilic reaction of betmip **4** with methylidenetriphenylphosphorane via the ion-pair intermediate **5** followed by treatment with butyllithium (Scheme 1). The N=PPh$_3$ functionality in phosphonium salt **6** did not react appreciably with benzaldehyde after 10 h at room tempera-

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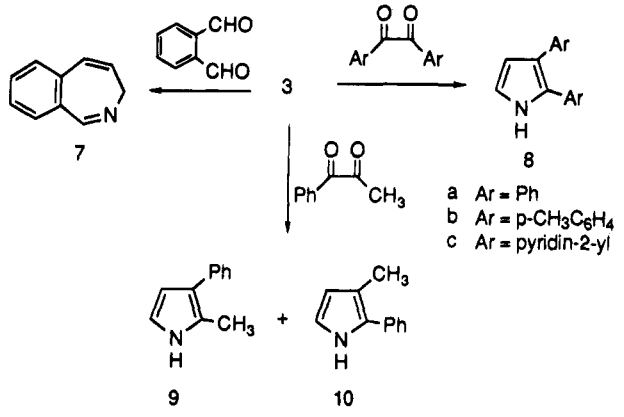
Scheme 2



ture, largely due to the low solubility of **6** in THF. Furthermore, treating this reaction mixture with butyllithium gave 1-phenylpentanol by addition of butyllithium to the unreacted benzaldehyde. Due to the sparing solubility of salt **6**, 2 h at −78 °C and 0.5 at around −30 °C are required to complete deprotonation by butyllithium. The compound **3** thus prepared is stable in THF below −20 °C under argon or nitrogen. At room temperature it slowly decomposes, as evidenced by the formation of triphenylphosphine. Therefore, in all cases, the suspension of **3** was directly reacted with the appropriate electrophile and all reactions were carried out in one pot.

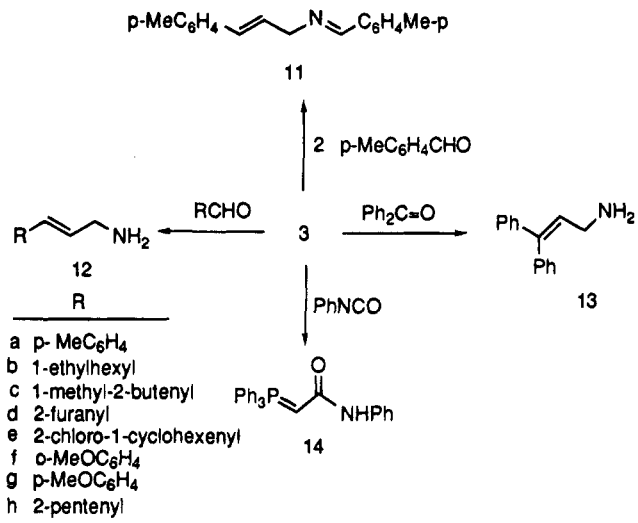
Reactions of 1-Aza-1,3-bis(triphenylphosphoranylidene)propane (3) with Dicarbonyl Compounds: Preparations of 3*H*-2-Benzazepine (7) and 2,3-Disubstituted Pyrroles 8. As already communicated,[3] the yellow suspension of **3** reacted smoothly with phthalic dicarboxaldehyde at room temperature to give **7** which was purified by vacuum distillation or by column chromatography to give a colorless liquid in 62% yield (Scheme 2). The structure was established by the NMR spectral data and confirmed by the high-resolution mass spectroscopy. The hydrogen atom originating from phthalic dicarboxaldehyde gave rise to two signals (i) a sharp singlet at 8.27 ppm (CH=N) and (ii) a doublet at 6.65 ppm (CH=C). The three protons which originated from **3** appeared as (i) a 2 H doublet at 3.67 ppm for CH_2 and (ii) a 1 H multiplet at 5.95 for the CH= proton. In the high-resolution mass spectrum, the molecular ion (*m/z* 143.0731) formed the base peak with another strong peak (*m/z* 115.0521) formed by loss of the CH_2N fragment.

Benzazepine (**7**) was not synthesized until recently: our preparation from **3** and phthalic dicarboxaldehyde[3] and Corriu's preparation from (*Z*)-3-(tributylstannyl)-allylamine/$Pd(PPh_3)_3$/2-bromobenzaldehyde[5] were reported almost simultaneously. Our method has the advantage of more readily available starting materials.

Wittig/aza-Wittig reactions of **3** with 1,2-diketones afforded 2,3-disubstituted pyrroles **8** in good yields (Scheme 2). These reactions also proceeded at 20 °C; the change of the yellow suspension to a deep brown solution indicated that the reaction was complete. The 2,3-disubstituted pyrroles **8** thus prepared were characterized by their NMR spectra and the new compounds **8b** and **8c** confirmed by elemental analyses. The two pyrrole ring protons appeared at 6.20−6.40 ppm and 6.50−6.80 ppm in the ^1H NMR spectra. The NH protons of **8a** and **8b** appeared at 8.10−8.15 ppm and that of **8c** was shifted to 11.10 ppm, probably because of a hydrogen bond with the nitrogen atom of the 2-pyridine ring.

(5) Corriu, R. J. P.; Geng, B.; Moreau, J. J. E. *J. Org. Chem.* **1993**, *58*, 1443.

Scheme 3



When 1-phenyl-1,2-propanedione was used, a mixture of the two isomeric 2,3-disubstituted pyrroles **9** and **10** was obtained, in approximately equal amounts as based on the NMR spectra (Scheme 2). Their structures were confirmed by GC−MS analysis.

Several publications have previously described the preparation of 3,4-disubstituted furans and thiophenes from bis(alkylidenetriphenylphosphoranes) **1** (Y = O and S, respectively) and 1,2-diketones (see the review[1]). However, we could locate no literature report of the construction of the pyrrole ring by bis-Wittig reactions. The compound **3** thus provides a new [3 + 2] construction of the pyrrole ring involving the formation of the N−C(5)−C(4) and C(2)−(3) bonds.

Reactions of 1-Aza-1,3-bis(triphenylphosphoranylidene)propane (3) with Aldehydes: Preparations of *N*-(Arylidene)allylamines 11 and Primary Allylamines 12 and 13. As already discussed, the Ph_3P=C and Ph_3P=N functionalities in **3** should independently undergo Wittig and aza-Wittig reactions, respectively. Treatment of the suspension of **3** with 2 equiv of *p*-tolualdehyde gave the expected imine **11** in 78% yield (Scheme 3); its structure was characterized by the NMR spectra and elemental analysis. Two singlets at 2.30 ppm and 2.35 ppm for two CH_3 groups, a doublet at 4.35 ppm for the CH_2 proton, and a sharp singlet at 8.10 ppm for the CH=N proton all indicated a single isomer with the C=C bond in the *E* configuration as shown by the coupling constant of 16.0 Hz at 6.52 ppm (for the ArCH: CH protons).

The different reactivity of the two functionalities in **3** with aldehydes allowed the development of an efficient new synthetic method for primary allylamines **12** (Scheme 3). Reaction of **3** with 1 equiv of an aldehyde at −78 °C and subsequent warming of the reaction mixture to room temperature gave primary allylamines **12a−h** in yields of 45% to 75% after aqueous workup. The primary allylamines **12** were easily separated by distillation from the byproducts, lithium benzotriazolate, and triphenylphosphine oxide. Use of an excess of the aldehyde lowered the yields of the primary allylamines **12** presumably due to the formation of the Wittig/aza-Wittig reaction product such as **11** from 2 equiv of aldehyde. Aliphatic, α,β-unsaturated, and heteroaromatic aldehydes all gave yields in about the same range. The

Table 1. Preparation of Compounds 7, 8, and 11, Primary Allylamines 12 and 13, and Compound 14

compd	yield (%)	E/Z of newly formed C=C	mp (°C) or bp (°C/mmHg)	molec formula	CHN analysis or HRMS found (calcd) C, H, N	(C, H, N)
7	62		89–92/0.5	$C_{10}H_9N$	143.0731	(143.0735)
8a	67		128–129[a]	$C_{16}H_{13}N$		
8b	75		124–125	$C_{18}H_{17}N$	87.39, 7.10, 5.34	(87.41, 6.93, 5.66)
8c	58		oil	$C_{14}H_{11}N_3$	76.01, 5.16, 18.85	(76.00, 5.01, 18.99)
11	62	100:0	80–81	$C_{18}H_{19}N$	86.43, 7.69, 5.54	(86.69, 7.69, 5.62)
12a	65	75:25	74–76/0.5	$C_{10}H_{13}N$	81.86, 9.13, 9.33	(81.59, 8.90, 9.51)
12b	72	75:25	89–93/1	$C_{10}H_{21}N$	77.29, 13.86, 9.01	(77.34, 13.64, 9.02)
12c	61	95:5	50–53/1	$C_8H_{15}N$	76.94, 12.36, 11.15	(76.74, 12.07, 11.19)
12d	58	75:25	80–85/1[b]	C_7H_9NO		
12e	45	70:30	75–79/0.5	$C_9H_{14}NCl$	63.15, 8.22, 7.88	(62.97, 8.22, 8.16)
12f	62	63:37	83–88/1	$C_{10}H_{13}NO$	73.33, 7.99, 8.43	(73.59, 8.03, 8.58)
12g	60	90:10	92–97/1	$C_{10}H_{13}NO$	73.90, 8.03, 8.31	(73.59, 8.03, 8.58)
12h	70	50:50	40–44/1	$C_8H_{15}N$	76.74, 12.07, 11.19	(76.50, 12.36, 10.79)
13	38		160–165/0.4[c]	$C_{15}H_{15}N$		
14	65		183–184[d]	$C_{25}H_{21}N_2O$		

[a] Lit.[13] mp 130–131 °C. [b] Lit.[6] bp 110–120 °C/20 mmHg. [c] Lit.[14] bp 150 °C/0.1 mmHg. [d] Lit.[11] mp 178–179 °C.

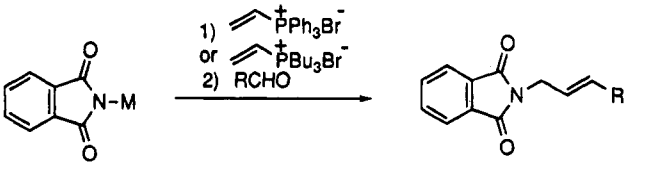
primary amine group of **12** derives from the unreacted iminophosphorane and demonstrates that when a limited amount of aldehyde is used, only the more nucleophilic C=PPh_3 of **3** reacts. The iminophosphorane acts as a protecting group for the primary amine functionality which is released during the aqueous workup. Classically, primary alkylamine groups have been protected as phthalimides;[6] the deprotection of an iminophosphorane is considerably more facile.

The higher reactivity of the C=PPh_3, as compared to the N=PPh_3 of **3**, was also reflected in the reaction with benzophenone from which primary allylamine **13** was isolated in 38% yield (Scheme 3). Unlike the corresponding reactions with aldehydes, no product analogous to **11** was detected even when 3 mol of benzophenone was used. Attempted preparations of primary allylamines from enolizable ketones (cyclohexanone and α-tetralone) gave only traces of the desired products as evidenced by NMR spectra. Evidently, enolizable ketones are deprotonated by the strong basic iminophosphorane of **3**. Less electrophilic 4,4′-dimethoxybenzophenone also failed to form an isolable amount of the corresponding primary allylamine probably because of the low reactivity of **3** toward the ketone carbonyl component at low temperature and the instability at ambient and higher temperature.

The structures of the primary allylamines produced were established by their NMR spectral data, and the new compounds were confirmed by CHN analyses. The characteristic signals of the CH_2, originating from **3**, appear as two doublets in the ^1H NMR, representing the *E* and *Z* isomers. Identification of the *E* and *Z* isomers and estimates of the *E*/*Z* ratios for the primary allylamines were based on the coupling constants and integrations of this CH_2 group and the newly formed CH=CH group.

We examined the effect of the structure of the aldehydes on the reaction stereoselectively. All primary allylamines were obtained as mixtures of *E* and *Z* isomers with the *E* configuration of the newly formed C=C bond predominating (Table 1). Reaction of the bulky 2-ethylheptanal gave predominantly (*E*)-allylamine **12b** (*E*/*Z* = 75/25). Steric effects of this type leading to dominant *E*-rich olefination were still more pronounced when an α-substituted α,β-unsaturated aldehyde was used. Thus, reaction of **3** with 2-methyl-2-pentenal showed *E*/*Z* = 95/5 for the newly formed C=C bond of **12c** *vs* E/Z = 50:50 from the reaction with 2-hexenal (**12h**). However, in

Scheme 4



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contrast to the high *E*-olefination selectivity of *p*-methoxybenzaldehyde (**12g**, *E*/*Z* = 90/10) and 2-methyl-2-pentenal (**12c**, *E*/*Z* = 95/5), less *E*-biased predominant ratios were observed in the reactions with β-heteroatom-substituted aldehydes such as *o*-methoxybenzaldehyde and 2-chloro-1-cyclohexanecarbaldehyde which gave primary allylamines **12f** with *E*/*Z* = 63/37 and **12e** with *E*/*Z* = 70/30, respectively. This enhancement of *Z*-olefination could be explained by a betaine intermediate stabilized through chelation of the charged group by the neighboring heteroatom in a supramolecular ensemble.[7] It was previously reported that Wittig reactions of the α-alkoxy-substituted aldehydes or ketones gave *Z*-rich alkene mixtures.[8] Finally, aromatic aldehydes with a strong electron-donating group at the para position apparently gave higher *E*-stereoselectivity, for example, *p*-methoxybenzaldehyde (for **12g**, *E*/*Z* = 90/10) as compared with *p*-tolualdehyde (for **12a**, *E*/*Z* = 75/25).

Primary allylamines have attracted increasing attention as enzyme inhibitors and natural products. Synthetic methods for them have been reviewed.[9] Most literature preparations introduce an amino group into allylic derivatives. Recently, Corriu *et al.* have reported the preparation of primary allylamines by connection of the H_2NCH_2CH=CH fragment to an aromatic ring via *N*,*N*-bis(silyl) enamines.[5] To our knowledge, the synthesis of protected primary allylamines by connection of the H_2NCH_2CH fragment to a functionalized carbon with the formation of a carbon–carbon double bond was reported only for reactions of vinyltriphenylphosphonium or vinyltri-*n*-butylphosphonium bromide with sodiophthalimide and aldehydes (Scheme 4).[6] The stereoselectivity (*E*/*Z* ratio) ranged from 15:85 to 74:26 with vinyltriphenylphosphonium bromide and from 71:29 to 91:9 with vinyltri-*n*-butylphosphonium bromide. 1-Aza-1,3-bis(triphenylphosphoranylidene)propane (**3**) thus provides a new route

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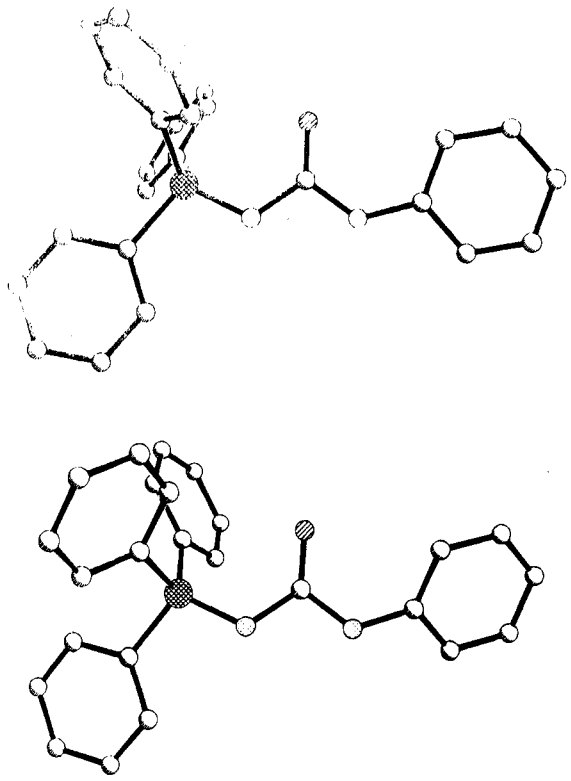

Figure 1. Perspective view of the two independent molecules of the iminophosphorane.

for the introduction of the H_2NCH_2CH: group. The stereoselectivity is higher than the literature preparation from vinyltriphenylphosphonium bromide and is comparable to that from vinyltri-*n*-butylphosphonium bromide. The present preparation is accomplished in one pot; the primary allylamines are released during workup and can be easily isolated by distillation.

Reactions of 1-Aza-1,3-bis(triphenylphosphoranylidene)propane (3) with Phenyl Isocyanates: Formation of [[(*N*-Phenylamino)carbonyl]methylene]-triphenylphosphorane (14). The reaction of **3** with 2 molar equiv of phenyl isocyanate gave [[(*N*-phenylamino)-carbonyl]methylene]triphenylphosphorane **(14)** (65%), instead of the anticipated double Wittig reaction products. Compound **14**, presumably formed by addition of the iminophosphorane of **3** followed by elimination of vinyltriphenylphosphonium benzotriazolate, was previously obtained by the reaction of (i) triphenylphosphine imide with phenyl isocyanate[10] and (ii) 1-[(mesitylene-sulfonyl)oxy]-3-phenylurea with triphenylphosphine.[11] The structure of **14** prepared by the present method was confirmed by X-ray analysis. Figure 1 shows a perspective view of the two independent molecules of the iminophosphorane. The P—N bond distances (1.590(2) and 1.594(2) Å) clearly indicate that this is a double bond, these bond lengths being similar to those found in related structures. The bond angles at the phosphorus atoms deviate significantly from tetrahedral (104.9(1)–115.8-(1)°) as has also been observed in the structures of other triphenylphosphazenes.[12] The two independent molecules differ significantly in the orientations of the phenyl rings. In particular, the torsional orientations of the triphenylphosphine groups differ in the two molecules by a rotation of approximately 18° about the P=N bond. Furthermore, the *N*-phenyl ring is inclined to the plane of the urea moiety at angles of 21.6(2) and 27.7(2)° in the two molecules. These differences are probably due to the minimization of intermolecular interaction associated with molecular packing.

Conclusion. In summary, a new 1,3-monoazabisylide, 1-aza-1,3-bis(triphenylphosphoranylidene)propane (**3**), has been developed. It undergoes Wittig/aza-Wittig reactions (analogous to the bis-Wittig[1]) with phthalic dicarboxaldehyde and 1,2-diketones to give 3*H*-2-benzazepine (**7**) and pyrroles, respectively. Compared with bis(alkylidenetriphenylphosphoranes) **1** and bis(iminophosphoranes) **2**. The compound **3** can react selectively with a single molar equivalent of an aldehyde to give the primary allylamine. The present method for the preparations of 3*H*-2-benzazepine (**7**), 2,3-diarylpyrroles (**8**), imine **11**, and primary allylamines **12** and **13** commences with the easily available betmip.

Experimental Section

THF was freshly distilled from sodium benzophenone ketyl immediately before use. Elemental analyses were performed in house.

Procedure for the Preparation of 1-Aza-1,3-bis(triphenylphosphoranylidene)propane (3) and Use *in Situ* for the Preparation of 3*H*-2-Benzazepine (7) and 2,3-Diarylpyrroles 8. Butyllithium (3.5 mL, 8.75 mmol, 2.5 M solution in hexane) was added to a suspension of methyltriphenylphosphonium bromide (3.0 g, 8.4 mmol) in THF (40 mL) under argon at −78 °C and the mixture stirred for 2 h at the same temperature. The yellow solution was stirred with betmip (3.5 g, 8.75 mmol) overnight at rt. Butyllithium (3.5 mL, 8.75 mmol, 2.5 M solution in hexane) was added to the suspension at −78 °C, and the mixture was stirred for 2 h followed by 0.5 h at *ca.* −30 °C. This was stirred with the appropriate dicarbonyl compound (7.5 mmol) overnight at rt, quenched with water (40 mL), and extracted with ether (3 × 40 mL). The organic layer was washed with 3 N NaOH (2 × 30 mL) and dried ($MgSO_4$) and the solvent removed.

3*H*-2-Benzazepine (7) was prepared from phthalic dicarboxaldehyde (1.1 g, 7.5 mmol) and isolated by column chromatography (silica gel/Et_2O). The analytical sample was distilled: ^{1}H NMR ($CDCl_3$) δ 3.67 (d, J = 6 Hz, 2 H), 5.95 (m, 1 H), 6.65 (d, J = 10 Hz, 1 H), 7.20–7.40 (m, 4 H), 8.27 (s, 1 H), ^{13}C NMR ($CDCl_3$) δ 48.4, 126.2, 129.0, 129.2, 129.2, 130.1, 131.9, 135.0, 137.4, 162.1.

2,3-Diphenylpyrrole (8a) was prepared from benzil and isolated by column chromatography (silica gel/Et_2O–hexane). The analytical sample was recrystallized from ethyl acetate: ^{1}H NMR ($CDCl_3$) δ 6.40 (m, 1 H), 6.82 (m, 1 H), 7.20–7.40 (m, 10 H), 8.15 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 111.0, 118.1, 121.9, 125.7, 126.8, 127.5, 128.2, 128.3, 128.4, 128.6, 133.3, 136.6.

2,3-Bis(4-methylphenyl)pyrrole (8b) was prepared from 4,4′-dimethylbenzil and isolated by column chromatography (silica gel/Et_2O–hexane). The analytical sample was recrystallized from hexane: ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 6 H), 6.37 (m, 1 H), 7.30 (m, 1 H), 7.05–7.35 (m, 8 H), 8.10 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.1, 21.2, 110.8, 117.7, 121.4, 127.4, 128.1, 128.4, 128.9, 129.2, 130.6, 133.7, 135.1, 136.4.

2,3-Di(pyridin-2-yl)pyrrole (8c) was prepared from 4,4′-pyridil and isolated by column chromatography (silica gel/Et_2O–hexane). The analytical sample was purified by acid extraction: the product from column chromatography was

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dissolved in CH_2Cl_2 (15 mL) and extracted with 2 N HCl (2 × 40 mL). The aqueous solution was washed with CH_2Cl_2 (2 × 10 mL), made basic with 3 N NaOH, and extracted with ether (2 × 60 mL). The organic layer was dried ($MgSO_4$) and the solvent removed to give the desired product: ^{1}H NMR ($CDCl_3$) δ 6.25 (m, 1 H), 6.50 (m, 1 H), 6.85 (m, 1 H), 6.95 (m, 1 H), 7.15 (m, 1 H), 7.45 (m, 2 H), 7.62 (m, 2 H), 8.45 (m, 1 H), 8.65 (m, 1 H), 11.10 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 112.0, 119.4, 120.8, 120.9 (two signals overlap), 123.4, 124.0, 128.1, 136.0, 136.1, 148.3, 149.1, 150.5, 156.1.

The mixture of 2-methyl-3-phenylpyrrole (9) and 2-phenyl-3-methylpyrrole (10) was prepared from 1-phenyl-1,2-propanedione and isolated by column chromatography (silica gel/Et_2O–hexane): ^{1}H NMR ($CDCl_3$) δ 2.45, 2.31 (two singlets, 3 H), 6.11, 6.33 (two multiples, 1 H), 6.57, 6.66 (two multiples, 1 H), 7.15–7.45 (m, 10 H), 7.95, 8.18 (two br, s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.5, 108.7, 112.1, 116.0, 117.7, 120.8, 124.1, 124.9, 125.8, 126.1, 127.7, 128.4, 128.5, 128.6, 133.0, 133.7, 137.4. The structures of the mixture components were confirmed by GC–MS analysis. MS of **9**: 156, 127, 104, 77, 51, 28 (base peak). MS of **10**: 156 (base peak), 128, 89, 78, 51.

***N*-(Methylbenzylidene)-3-(*p*-methylphenyl)-2-propenylamine (11).** A suspension of 1-aza-1,3-bis(triphenylphosphoranylidene)propane **(3)** (8.4 mmol), prepared *in situ* as above (see preparation of **7**), was stirred with 4-methylbenzaldehyde (1.70 g, 15 mmol) in THF for 2 h at −78 °C and overnight at 20 °C. The reaction mixture was quenched with water (40 mL) and extracted with ether (2 × 50 mL). The combined organic layer was washed with 3 N NaOH (2 × 30 mL) and dried ($MgSO_4$), and the solvent was removed. The product was purified by column chromatography (silica gel/Et_2O). The analytical sample was recrystallized from hexane: ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 2.35 (s, 3 H), 4.35 (d, J = 6 Hz, 2 H), 6.35 (m, 1 H), 6.52 (d, J = 16 Hz, 1 H), 7.10 (d, J = 8.0 Hz, 2 H), 7.22 (d, J = 9.5 Hz, 2 H), 7.28 (d, J = 9.5 Hz, 2 H), 7.62 (d, J = 8.0 Hz, 2 H), 8.30 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.1, 21.5, 63.0, 126.2, 126.2, 126.5, 128.1, 129.2, 129.3, 131.1, 133.6, 134.4, 137.0, 141.0, 161.9.

Procedure for the Preparation of Primary Allylamines 12. A suspension of 1-aza-1,3-bis(triphenylphosphoranylidene)propane **(3)** (16.8 mmol), prepared *in situ* as described above (see preparation of **7**), was stirred with the appropriate aldehyde (15 mmol) overnight at rt, quenched with water (40 mL), and extracted with ether (3 × 50 mL). The organic layer was washed with 3 N NaOH (2 × 30 mL) and dried ($MgSO_4$) and the solvent removed. The residue was extracted with 4 N HCl (2 × 60 mL). The aqueous solution was washed with methylene dichloride (2 × 20 mL), made basic with 20% NaOH, and extracted with ether (3 × 60 mL). The solvent was removed, and the product was purified by distillation.

3-(*p*-Methylphenyl)-2-propenylamine (12a) was prepared from *p*-tolualdehyde and purified by distillation: ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 2 H), 2.28 (s, (*E*)-CH_3), 2.29 (s, (*Z*)-CH_3), 3.35 (d, J = 6 Hz, (*E*)-CH_2), 3.50 (d, J = 6 Hz, (*Z*)-CH_2), 5.6 (m, (*E*)-CH=), 6.18 (m, (*E*)-CH=), 6.4 (d, J = 16 Hz, (*E*)-CH=), 6.38 (d, (*Z*)-CH=, overlap with (*E*)-CH=), 7.05 (d, J = 9.1 Hz, 2 H), 7.21 (d, J = 9.1, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.2, 39.7, 125.5 (overlap with the signal of the *Z*-isomer), 128.1, 128.3, 132.8, 133.6, 135.9 (*E*); 20.6, 43.8, 125.5, 128.5, 128.6, 129.8, 133.9, 136.3 (*Z*).

4-Ethyl-2-octenylamine (12b) was prepared from 2-ethylhexanal and purified by distillation: ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J = 7.2 Hz, 3 H), 0.88 (t, J = 7.2 Hz, 3 H), 1.10–1.50 (m, 11 H), 1.82 (m, (*Z*)-CH), 2.18 (m, (*E*)-CH), 3.25 (d, J = 5.2 Hz, (*Z*)-CH_2N), 3.29 (d, J = 7.1 Hz, (*E*)-CH_2N), 5.07 (t, J = 15.0 Hz, (*E*)-CH=), 5.27 (d, J = 8.3 Hz, (*Z*)-CH=), 5.50 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.5, 11.6, 22.5, 28.2, 29.4, 35.0, 38.9, 43.9, 130.7, 135.2 (*E*); 11.3, 11.4, 13.8, 27.7, 29.2, 29.4, 34.4, 39.0, 131.0, 138.6 (*Z*).

4-Methyl-2,4-heptadienylamine (12c) was prepared from 2-methylpentenal and purified by distillation: ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.5 Hz, 3 H), 1.53 (s, 2 H), 1.72 (s, 3 H), 2.13 (m, 2 H), 3.43 (d, J = 5.5 Hz, 2 H), 5.42 (t, J = 5.5 Hz, 1 H), 5.67 (td, J_1 = 16 Hz, J_2 = 5.5 Hz, 1 H, CH=), 6.15 (d, J = 16.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.1, 13.9, 13.9, 21.2, 44.1, 127.7, 132.4, 133.8, 134.5.

3-(2-Furanyl)-2-propenylamine (12d) was prepared from 2-furaldehyde and purified by distillation: ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 2 H), 3.41 (d, J = 5.4 Hz, (*E*)-CH_2N), 3.69 (d, J = 5.4 Hz, (*Z*)-CH_2N), 5.60 (td, J_1 = 11.2 Hz, J_2 = 5.0 Hz, (*Z*)-CH=), 6.25 (m, 4 H), 7.32 (s, (*E*)-CH=), 7.38 (s, (*Z*)-CH=); ^{13}C NMR ($CDCl_3$) δ 40.6, 107.0, 109.7, 117.0, 131.6, 141.8, 152.7 (*Z*); 43.8, 107.0, 111.1, 117.9, 130.0, 141.6, 152.7 (*E*).

3-(2-Chloro-1-cyclohexenyl)-2-propenylamine (12e) was prepared from 2-chloro-1-cyclohexenecarbaldehyde and purified by distillation: ^{1}H NMR ($CDCl_3$) δ 1.65 (m, 4 H), 1.86 (s, 2 H), 2.18 (m, (*Z*)-CH_2), 2.25 (m, (*E*)-CH_2), 2.41 (m, 2 H), 3.31 (d, J = 6.5 Hz, (*E*)-CH_2N), 3.40 (d, J = 6.0 Hz, (*Z*)-CH_2N), 5.52 (td, J_1 = 10.5 Hz, J_2 = 6.5 Hz, (*Z*)-CH=), 5.81 (td, J_1 = 16.0 Hz, J_2 = 6.0 Hz, (*E*)-CH=), 5.95 (d, J = 10.5 Hz, (*Z*)-CH=), 6.78 (d, J = 16 Hz, (*E*)-CH=); ^{13}C NMR ($CDCl_3$) δ 21.5, 29.1, 26.0, 34.0, 43.7, 126.6, 128.5, 130.0, 130.4 (*E*); 21.7, 23.2, 30.4, 33.3, 40.0, 127.4, 128.6, 129.7, 132.29 (*Z*).

3-(2-Methoxyphenyl)-2-propenylamine (12f) was prepared from *o*-anisaldehyde and purified by distillation: ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 2 H), 3.38 (d, J = 5.5 Hz, 2 H), 3.73 (s, 3 H), 5.70 (td, J_1 = 11.5 Hz, J_2 = 5.5 Hz, (*Z*)-CH=), 6.21 (td, J_1 = 16.0 Hz, J_2 = 5.5 Hz), 6.49 (d, J = 11.5 Hz, (*Z*)-CH=), 6.71 (d, J = 16 Hz, (*E*)-CH=), 6.80 (m, 2 H), 7.12 (m, 2 H), 7.32 (d, J = 7.6 Hz); ^{13}C NMR($CDCl_3$) δ 44.7, 55.3, 110.6, 120.5, 124.0, 126.1, 126.6, 128.2, 132.0, 156.4 (*E*); 40.2, 42.2, 110.2, 119.5, 124.6, 123.5, 128.3, 130.0, 133.6, 156.4 (*Z*).

3-(4-Methoxyphenyl)-2-propenylamine (12g) was prepared from *p*-anisaldehyde and purified by distillation: ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 2 H), 3.35 (d, J = 5.5 Hz, (*E*)-CH_2N), 3.47 (d, J = 6.0 Hz, (*Z*)-CH_2N), 3.67 (s, 3 H), 5.55 (m, (*Z*)-CH=), 6.08 (td, J_1 = 16.0 Hz, J_2 = 5.5 Hz, (*E*)-CH=), 6.35 (d, J = 16 Hz, (*E*)-CH=), 6.75 (d, J = 7.5 Hz, 2 H), 7.20 (d, J = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 44.2, 55.1, 113.8, 127.1, 128.7, 129.0, 129.8, 158.8 (*E*).

2,4-Octadienylamine (12h) was prepared from 2-hexenal and purified by distillation: ^{1}H NMR ($CDCl_3$) δ 0.92 (two triplets, J = 7.0 Hz, 3 H), 1.37 (s, 2 H), 1.40 (m, 2 H), 2.07 (m, 2 H), 3.31 (d, J = 5.5 Hz, (*E*)-CH_2N), 3.45 (d, J = 7.0 Hz, (*Z*)-CH_2N), 5.37, 5.76, 6.05, 6.29 (four multiples, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 13.7, 22.4, 22.4, 34.6, 34.9, 39.1, 43.9, 125.1, 129.1, 129.8, 130.0, 130.2, 132.3, 134.0, 136.0 (*E* and *Z* signals could not be assigned).

3,3-Diphenyl-2-propenylamine (13). A suspension of 1-aza-1,3-bis(triphenylphosphoranylidene)propane **(3)** (8.4 mmol), prepared *in situ* as above (see preparation of **7**), was stirred with benzophenone (4.5 g, 25 mmol) in THF for 2 h at −78 °C and overnight at 20 °C. The reaction mixture was quenched with water (40 mL) and extracted with ether (2 × 50 mL). The combined organic layer washed with 3 N NaOH (2 × 30 mL) and dried ($MgSO_4$) and the solvent removed. The residue was column chromatographed (silica gel) with ethyl acetate to remove triphenylphosphine oxide and the excess benzophenone. The product was eluted from the column with methanol (0.60 g, 38%): ^{1}H NMR δ 1.35 (s, 2 H), 3.32 (d, J = 7.5 Hz, 2 H), 6.15 (t, J = 7.5 Hz, 1 H), 7.12–7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 41.0, 127.1, 127.3, 127.9, 128.0, 128.1, 129.6, 130.1, 139.4, 142.0, 142.1.

[[(*N*-Phenylamino)carbonyl]methylene]triphenylphosphorane (14). A suspension of **3** (8.4 mmol), prepared *in situ* as above, was stirred with phenyl isocyanate (2.0 g, 17 mmol) in THF for 2 h at −78 °C and overnight at 20 °C. The reaction mixture was refluxed for 4 h and then quenched with water (40 mL) and extracted with ether (2 × 50 mL). The combined organic layer was washed with 3 N NaOH (2 × 30 mL) and dried ($MgSO_4$) and the solvent removed. The product was purified by column chromatography (silica gel/Et_2O): ^{1}H NMR ($CDCl_3$) δ 6.30–6.40 (m, 1 H), 7.10–7.20 (m, 1 H), 7.35–7.55 (m, 12 H), 7.72–7.85 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 118.1, 121.7, 128.0, 128.4, 128.6, 129.3, 132.1, 132.0, 132.8, 133.0, 140.9, 140.9, 161.6.