JOC Article

# Synthesis of Pyrroles from 1-Dialkylamino-3-phosphoryl(or phosphanyl)allenes through 1,5-Cyclization of Conjugated Azomethine Ylide Intermediates

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1-Dialkylamino-1,3-diaryl-3-diphenylphosphanylallenes **3a**−**e** are thermally converted into *a*-annulated 3,5-diarylpyrroles **6a**−**f** and [*a*]-annulated benzo[*c*]azepines **7a**,**b**,**d**. These transformations are likely to include conjugated azomethine ylide intermediates that can undergo either a 1,5- or a 1,7-electrocyclization. The periselectivity is markedly shifted toward 1,5-cyclization when the diphenylphosphanyl substituent is replaced by the diphenylphosphoryl group. Thus, 1-dialkylamino-3-(diphenylphosphoryl)allenes **4a**−**f** yield pyrroles **6** exclusively and with improved yields, unless the 3-aryl substituent in the allene is too electron-rich (e.g., benzodioxol-5-yl, **4f** → **7f**). The preparation and thermal transformation of aminoallenes **4** over three or four steps can be conducted as a one-pot procedure, thus providing a convenient synthesis of [*a*]-annulated 3,5-diarylpyrroles from enaminoketones.

## Introduction

The pyrrole ring is probably the most important of the five-membered heteroaromatic ring systems. Pyrrole moieties are not only found in the porphine-type molecules of life but also in many other natural products of plant or marine origin, and they form the backbone of several important pharmaceuticals and agrochemicals. Therefore, it is not surprising that the wide array of established and practical pyrrole syntheses[1] is continuously supplemented by novel methods to prepare substituted and functionalized pyrroles, in particular those that are not readily available by the classical approaches. Novel recent pyrrole syntheses include the reductive ring contraction of pyridazines,[2] the Cu(I)-assisted 1,5-cyclization of alkynyl imines,[3] the palladium-catalyzed cyclization of α-propargyl-*β*-iminophosphanoxides,[4] cyclization of 4-aminobut-2-en-1-ones[5] and 4-amino-3-hydroxyketones,[6] and cyclization of *δ*-enaminoesters with *N*-bromosuccinimide.[7]

A mechanistically interesting approach to the pyrrole ring system is the 1,5-electrocyclization of in-situ generated α,*β*-unsaturated nitrile ylides and azomethine ylides,[8] representative examples of which are shown in Scheme 1. While the nitrile ylide system[9] yields the pyrrole ring directly, the azomethine ylide[10] requires a subsequent *β*-elimination to establish the conjugated *π* system; to this end, vinamidinium[10a] and 3-chloropropene iminium salts[10b−f] are well-suited starting materials which yield the conjugated azomethine ylide after reaction with *N*-alkylglycinates and deprotonation.

We have previously reported that 1-amino-3-vinylallenes and 1-amino-3-(het)arylallenes undergo a thermal isomerization to form dihydroazepine derivatives.[11] The mechanistic proposal for this transformation includes an initial 1,4-H shift to form an α,*β*;*γ*,*δ*-conjugated azomethine ylide **1** which then undergoes an eight-electron 1,7-electrocyclic ring closure (Scheme 2). Numerous examples of 1,7-electrocyclizations of α,*β*;*γ*,*δ*-unsaturated 1,3-dipoles are known,[12] and the preferential 1,7- vs 1,5-

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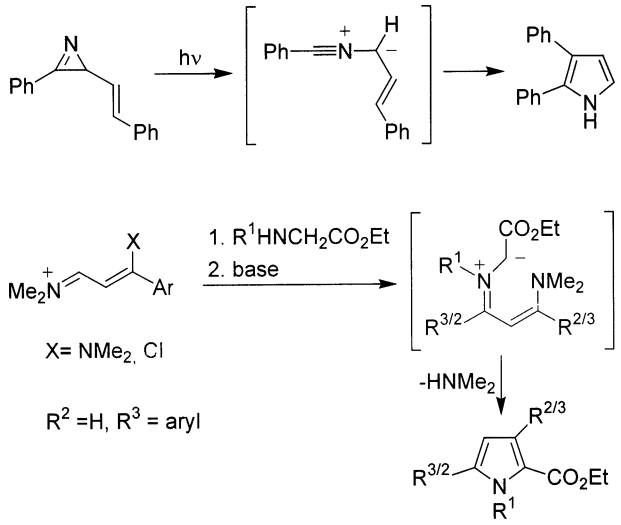
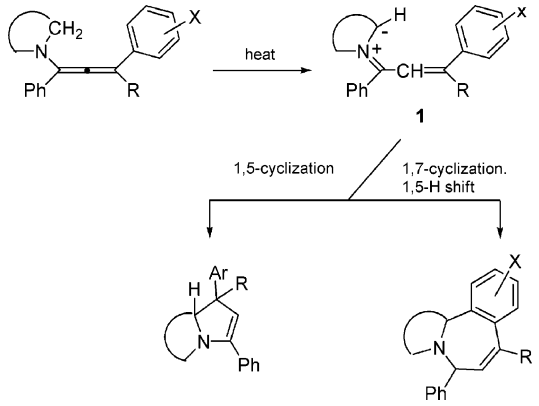
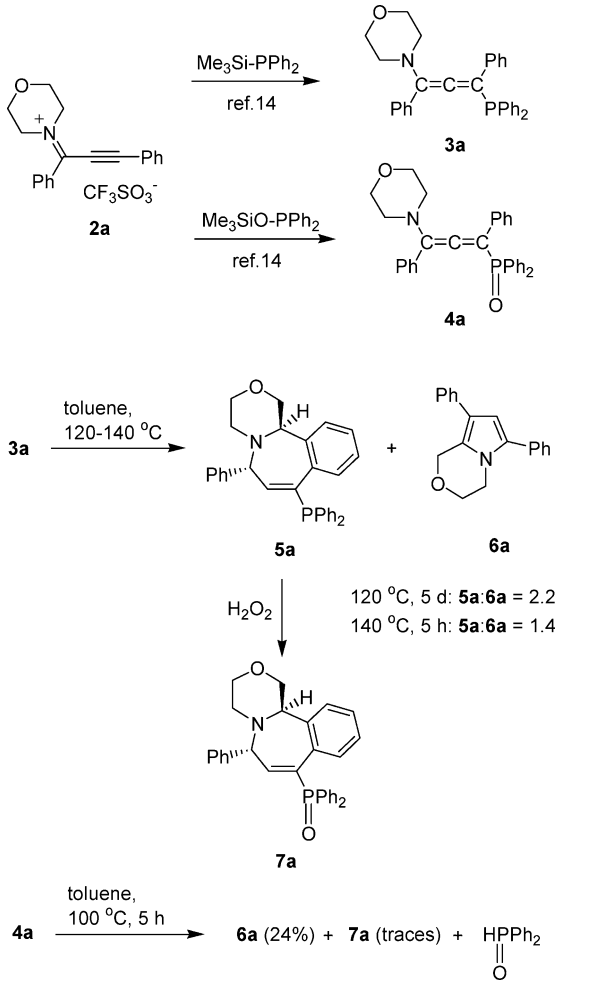
**SCHEME 1**




**SCHEME 2**




**SCHEME 3**




cyclization of these entities has been adressed by several authors.[13] Nevertheless, we wondered why we never observed products resulting from the 1,5-cyclization of azomethine ylides **1**, in particular in those cases where the 1,7-cyclization required the temporary loss of aromaticity of the involved (het)aryl ring.

We report now that the nature of substituent R in Scheme 2 has a decisive influence on the periselectivity of the electrocyclic ring closure of azomethine ylide intermediates **1**: while we had observed only 1,7-electrocyclization when R was a phenyl, 2-furyl, 2-thienyl, *t*-Bu, or $SiPh_2$-*t*-Bu substituent,[11] 1,5-electrocyclization becomes a competitive or the dominant pathway when R is a phosphanyl or phosphoryl group.

## Results and Discussion

We began our thermal isomerization studies with phosphorus-substituted aminoallenes **3a** and **4a**, which were prepared, as we have reported recently,[14] from propyne iminium triflate **2a** and diphenyl(trimethylsilyl)-phosphane or *O*-trimethylsilyl diphenylphosphinite, respectively (Scheme 3). When allene **3a** was heated in toluene at 120−140 °C in a closed Schlenk tube, a complex product mixture was obtained. The $^{31}P$ NMR spectrum showed the presence of three major phosphorus-containing products: while the signal at $\delta = -41$ ppm was attributed to $HPPh_2$ and the signal at $\delta$ 0.6 could later be assigned to the expected oxazino[4,3-*a*]azepine derivative **5a**, the origin of a peak at $\delta$ −13.9 remained unclear. The proton NMR spectrum of the crude mixture, after flash chromatography over silica gel, also indicated the formation of pyrrolo[2,1-*c*][1,4]oxazine **6a**.[15] Unfortunately, compounds **5a** and **6a** have very similar $R_f$ values so that a straightforward chromatographic separation was not possible and only a small amount of pure azepine derivative **5a** could be isolated by preparative thick-layer chromatography. On the other hand, treatment of the crude mixture of **5a** and **6a** with aqueous hydrogen peroxide converted **5a** into phosphanoxide **7a**, and the mixture of **6a** and **7a** was readily separated by column chromatography. However, the isolated yields (12% each of **6a** and **7a**) no longer agree with the initial product ratio where the azepine derivative dominated over the bicyclic pyrrole.

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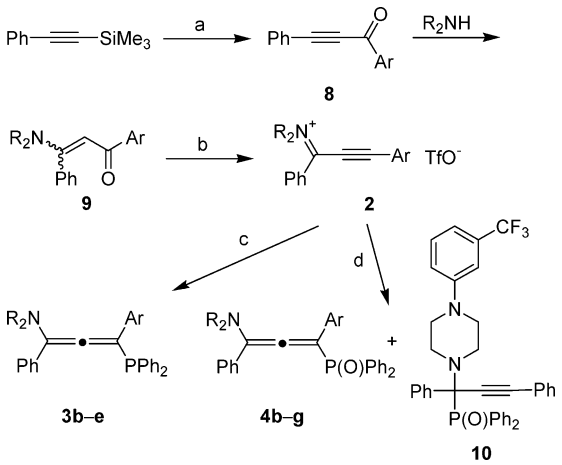
(15) A diagnostic test for the presence of this and all other pyrroles reported in this study was provided by the strong fluorescence on a TLC plate upon irradiation with 366 nm light.

**SCHEME 4** [a]




[a] Conditions: (a) ArCOCl, $AlCl_3$, $CH_2Cl_2$, 0 °C, 55−80%; (b) (1) $Tf_2O$, $CH_2Cl_2$, −78 → 0 °C, (2) remove solvent, then 180−200 °C/0.001 mbar/15 min (**2b**,**c**,**e**); or NEt-*i*-$Pr_2$, $CH_2Cl_2$, −78 → 0 °C (**2d**,**f**−**j**); (c) (1) $Me_3Si$−$PPh_2$, anhyd LiCl, THF, −78 → +20 °C, (2) remove volatiles, extract allene into toluene; (d) (1) $Me_3SiO$−$PPh_2$, LiCl, THF, −78 → +20 °C, (2) remove volatiles, add toluene. See Table 1 and Scheme 5 for substituents

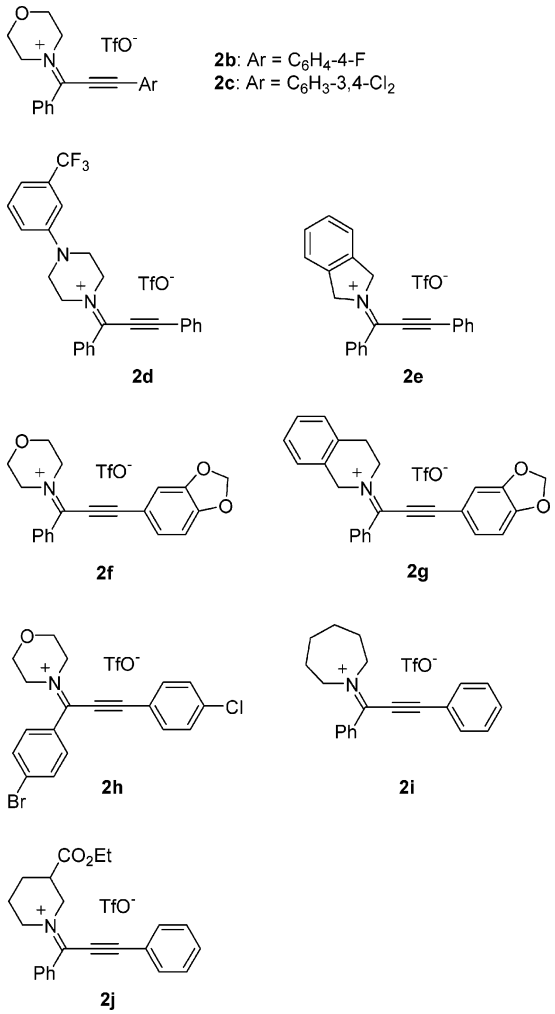
Diphenylphosphoryl-substituted morpholinoallene **4a** undergoes the thermal reaction much more readily than **3a**. The allene was almost completely consumed after 1 h when kept in toluene at 100 °C. The chromatographic workup furnished pyrrole **6a** (24% yield) and only trace amounts of oxazinoazepine derivative **7a**; the formation of diphenylphosphanoxide ($\delta(^{31}P)$ 22.9) and of several minor byproducts was indicated by the $^1H$ and $^{31}P$ NMR spectra. Among these products are the inevitable products of hydrolysis of the extremely moisture-sensitive allene **4a**.

To explore the substituent effects on the rate and periselectivity of the thermal transformations, several other 3-phosphorus-substituted aminoallenes were prepared. The synthetic plan followed our established procedure[16,17] by which enaminoketones **9**, readily obtained from propynones **8**, were O-sulfonylated with triflic anhydride and the resulting 3-trifloxypropene iminium triflates were converted into propyne iminium triflates **2** by thermal or NEt-*i*-$Pr_2$-assisted elimination of triflic acid (Scheme 4).

The thermal elimination (180−200 °C/0.001 mbar) was suited to prepare salts **2b**,**c**,**e** (Chart 1) but could not be used in other cases because of the acid sensitivity of substituents or nonselective reactions. In these cases, the generally applicable base-assisted elimination procedure was applied which gave an equimolar mixture of the corresponding propyne iminium triflate **2d**,**f**−**j** and diisopropylethylammonium triflate that could be used for the synthesis of allenes **3** and **4**.

Reaction of salts **2b**−**e** with diphenyl(trimethylsilyl)-phosphane provided the expected diphenylphosphanyl-substituted allenes **3b**−**e** in high yields. Allenes **3b**−**d** are thermally stable at 20 °C but are very moisture-sensitive so that purification, including the complete separation from lithium triflate formed as a byproduct,

**CHART 1. Propyne Iminium Salts Prepared in This Study**




was not possible. However, the crude allenes could be subjected to thermal reactions without complication. Allene **3e** is thermally labile even at 20 °C; in solution it was completely consumed within 1 day, yielding pyrrole **6e** as the only heterocyclic product. All allenes were unequivocally identified by their $^1H$ and $^{13}C$ NMR spectra; in particular, the $^{13}C$ resonance of the central allenic carbon atom ($\delta$ = 205.1−206.5 ppm) is diagnostic.

The 3-diphenylphosphoryl-substituted aminoallenes **4b**−**g** were prepared by reaction of propyne iminium salts **2f**−**g** with *O*-trimethylsilyl diphenylphosphinite (Scheme 4). In almost all cases, the attack of the phosphorus nucleophile at the conjugated iminium salt is regiospecific, except for salt **2d** which also gave a small amount of (1-piperazinopropargyl)diphenylphosphanoxide **10**. None of the allenes **4b**−**g** was isolated because of their anticipated[14] moisture sensitivity; rather, the crude product mixtures, after replacing THF by toluene as solvent, were directly subjected to the thermal transformations. The benzylamino-substituted allenes **4e**,**g** underwent further thermal reaction even faster than allene **2e** mentioned above: at ambient temperature, this transformation is so fast that these allenes could not be detected by NMR spectroscopy.

The thermally induced transformations of allenes **3b**−**e** and **4b**−**f** are summarized in Table 1. For **3b**−**d**,

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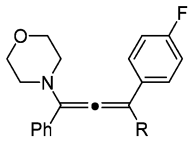
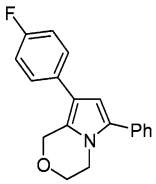
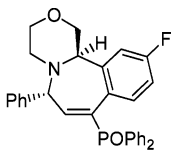
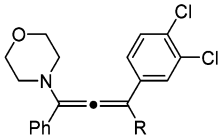
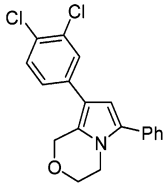
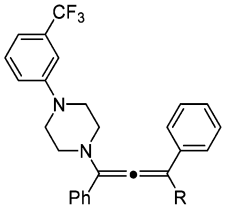
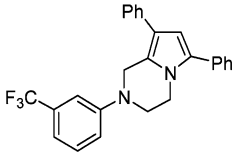
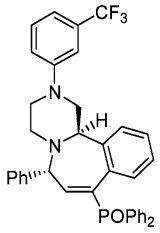
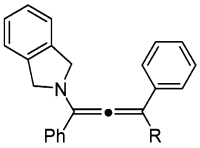
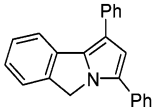
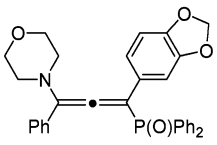
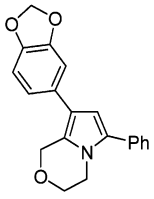
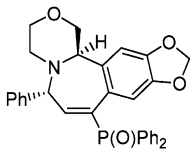
**TABLE 1. Thermally Induced Transformations of 1-Amino-3-(diphenylphosphanyl)allenes 3b−e and 1-Amino-3-(diphenylphosphoryl)allenes 4b−f**

| starting compound | conditions | products (isolated yield,[a] %) | |
|---|---|---|---|
|  | |  **6b** |  **7b** |
| **3b**: R = $PPh_2$ | DMF, 150 °C, 12 h [b] | 28% | 18% |
| **4b**: R = $P(O)Ph_2$ | toluene, 100 °C, 5 h [c] | 66% | – |
|  | |  **6c** | |
| **3c**: R = $PPh_2$ | DMF, 150 °C, 12 h | 2% | |
| **4c**: R = $P(O)Ph_2$ | toluene, 100 °C, 5 h [c] | 77% | |
|  | |  **6d** |  **7d** |
| **3d**: R = $PPh_2$ | DMF, 150 °C, 12 h [b] | 15% | 21% |
| **4d**: R = $P(O)Ph_2$ | toluene, 100 °C, 5 h [c,d] | 57% | 1.6% |
|  | |  **6e** | |
| **3e**: R = $PPh_2$ | toluene, 20 °C, 12 h [c] | 29% | |
| **4e**: R = $P(O)Ph_2$ | THF, 20 °C, 24 h [b] | 43% | |
|  | |  |  |
| **4f** | toluene, 100 °C, 5 h [c] | **6f** (11%) | **7f** (38%) |

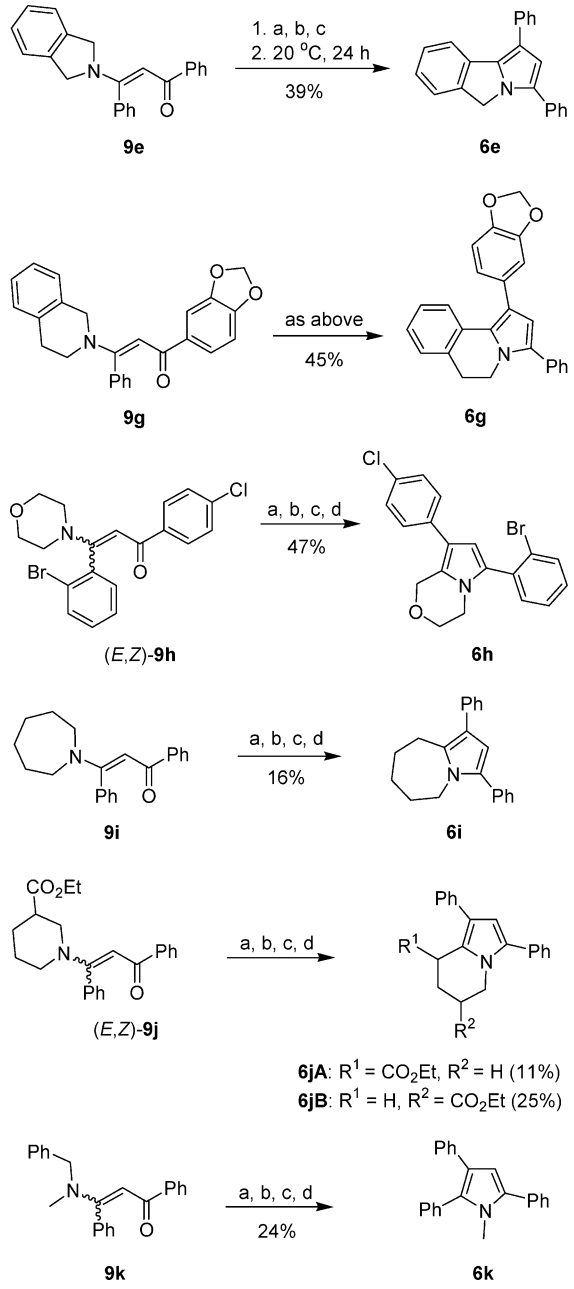
[a] Repeated recrystallization to remove impurities caused material loss in several cases, explaining some of the low yields reported here. [b] The crude product mixture was treated with 1% aqueous $H_2O_2$ before chromatographic workup. The following ratios of pyrrole **6** and $PPh_2$-substituted azepine derivative **5** were determined by $^1H$ NMR before oxidation and workup: **5b**/**6b** = 1.5; only **6c** from **3c**; only **6e** from **3e**; **5d**/**6d** = 0.48. [c] The allene was not isolated (see text); the yield of the product(s) refers to the corresponding iminium salt **2**. [d] Propargylamine **10** was also formed (8% based on iminium salt **2d**).

DMF was chosen as the reaction medium because this did not require conducting the reaction at a temperature far beyond its boiling point as would have been the case with toluene; it was tested, however, that the results in DMF or toluene solution were similar. It can be seen that in some cases mixtures of pyrroles **6** and azepine derivatives **7** were obtained while in other cases the pyrrole was the only product found. Starting with allenes **3b**,**d**, it was again necessary to oxidatively convert the $PPh_2$-substituted azepine derivatives into phosphanoxides **7b**,**d** in order to achieve the chromatographic separation of **6** and **7**. The isolated yields given in Table 1 do not always reflect the true yields, not even the original ratios of 1,5- vs 1,7-cyclization product, because of material loss during workup or purification. Nevertheless, including the results discussed above for **3a** and **4a**, the following general observations can be made: None of the $PPh_2$-substituted aminoallenes **3a**−**e** reacts cleanly, and the heterocyclic products are isolated only in low yields. In contrast, a $P(O)Ph_2$ substituent at the C-3 terminus of the allenes (**4a**−**g**) accelerates the reaction significantly and yields the corresponding pyrrole with much better selectivity and generally in markedly enhanced yield. The best pyrrole yields were obtained with those aminoallenes that in addition to the $P(O)Ph_2$ group bear an acceptor-substituted phenyl ring at the C-3 terminus (**4b**,**c**) while the benzodioxol-5-yl substituent in **4f** clearly favors formation of the seven-membered ring system **7f**. It is also worth being noted that the mildness of the thermal transformation, which is observed whenever the aminoallene contains a benzylamino moiety (reactions occur at ≤20 °C), does not guarantee a clean transformation into pyrroles **6** or azepine derivatives **7**. This suggests that the significant loss of material in the majority of these reactions, the reason of which remains unknown so far, is not a consequence of the elevated reaction temperatures.

It should be noted that *a*-annulated benzazepine derivatives **5** and **7** have two stereogenic centers but only one diastereomer was obtained. The trans configuration was derived from the similarity of the relevant $^1H$ NMR data with those of closely related systems the structure of which was established by X-ray structure determination.[11a,18,19] This configuration is in agreement with a conrotatory 8$\pi$ electrocyclization mode of azomethine ylide intermediates **1** (Scheme 2) followed by a suprafacial [1,5]-H shift.

Having established some directions for a selective pyrrole synthesis, we explored the possibility of making the four-step conversion of enaminoketones **9** into pyrroles **6** more convenient. In fact, we found that the four-step reaction sequence could be conducted as a one-pot procedure without isolation of any reaction intermediate. Thus, successive treatment of an enaminoketone with triflic anhydride, diisopropylethylamine, and $(Me_3SiO)$-$PPh_2$/LiCl at low temperature, followed by the thermal conversion of the allene, gave pyrroles **6e**,**g**−**k** (Scheme 5). The procedure becomes essentially a three-step process for *N*-benzyl enaminoketones **6e**,**g**,**k** because the allene-to-pyrrole conversion occurs already at 20 °C and does not require a change of solvent. The one-pot procedure also allows a reasonable scale-up; thus, the conversion (*E*,*Z*)-**9h** → **6h** was performed without a problem on a 0.12 M scale.

**SCHEME 5**[a]




[a] Conditions: (a) $Tf_2O$ (1 equiv), $CH_2Cl_2$, −78 → +20 °C, 45 min; (b) NEt-*i*-$Pr_2$ (1 equiv), −78 → 0 °C, 30 min; (c) $Me_3SiO-PPh_2$ (1 equiv), anhyd LiCl (1 equiv), −78 → +20 °C, 12 h; (d) toluene, 100 °C, 12 h.

The examples given in Scheme 5 provide further information on the scope of the novel pyrrole synthesis: (a) The exclusive formation of pyrrole **6g** from enaminoketone **9g** contrasts with the predominant dihydroazepine formation from allene **4f** (see Table 1). This suggests that the lower reaction temperature in the case of *N*-benzyl enaminoketones (or aminoallenes) is suf-

(18) Maas, G.; Manz, B.; Mayer, T.; Werz, U. *Tetrahedron* **1999**, *55*, 1309−1320.

(19) In particular, the H,H coupling constants indicate that the angular hydrogen 12b-H occupies an equatorial position at the chairlike morpholine or piperazine ring. In the NOESY spectrum, 12b-H shows a weak correlation peak with 7-H but not with 6-H.

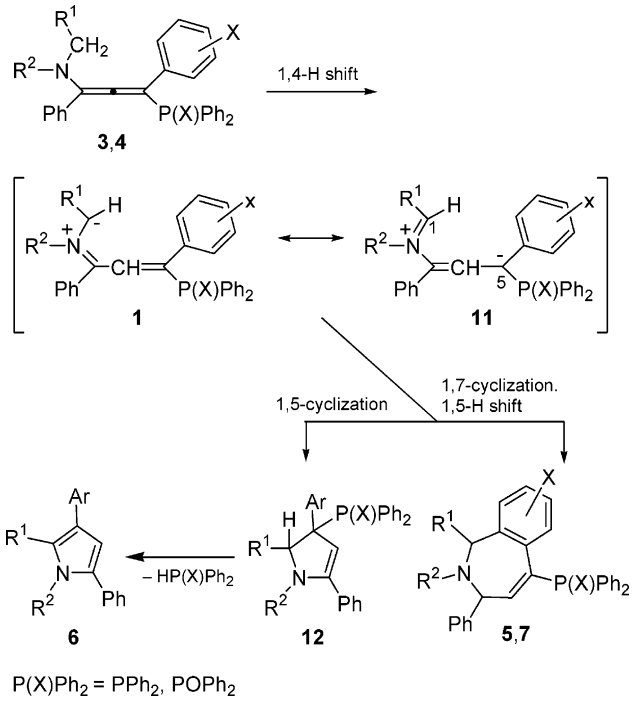
ficient to override the unfavorable influence of the electron-rich benzodioxolyl substituent on the 1,5-cyclization. (b) For enaminoketone **9j**, the ester group at C-3 of the piperidine ring controls the regioselectivity of the ring closure only to a limited extent. The preferential formation of **6jB** may be due to steric reasons, assuming an equilibrium between the two possible azomethine ylide intermediates. An electronic effect is also conceivable: if the initial [1,4]-H shift, which converts **9j** into an azomethine ylide, is hydridic in nature (vide infra), the developing positive charge on the carbon atom adjacent to N is slightly better stabilized at C-6 rather than C-2 of the piperidine-3-carboxylate. This example also shows that the presence of the ester group is compatible with the use of triflic anhydride as a reagent and the intermediate formation of a trifloxypropene iminium salt; in contrast, 3-trifloxypropene iminium salts derived from 2-dialkylamino-4-oxobutenoates underwent cylization to form iminium-substituted $\Delta^{2,3}$-butenolides.[20]

Further variations of the reaction conditions for the pyrrole synthesis provided the following results: The use of *O*-trimethylsilyl bis(4-fluorophenyl)phosphonite (A) or *O*-trimethylsilyl bis(4-chlorophenyl)phosphonite (B) instead of $Me_3SiO-PPh_2$ appears to improve the yield of pyrrole (one-pot procedure from enaminoketone: 33% of **6a** using A, 14% of **6f** with A, 76% of **6d** with B), but a systematic comparison was not made. On the other hand, $Me_3SiO-PPh_2$ cannot generally be replaced by the phosphite $Me_3SiO-P(OEt)_2$ which tends to react with propyne iminium salts to give propargylphosphonates rather than allenylphosphonates.[14] Because of the same regioselectivity problem, *N*-aryl-*N*-alkyl enaminoketones are less efficiently converted into pyrroles using the procedure shown in Scheme 5.

Under the aspect of synthetic methodology, it is evident that the conversion of enaminoketones **9** into pyrroles **6** is a simple intramolecular cyclocondensation reaction with elimination of a water molecule. The procedure developed here solves the problem that the $NCH_2$ protons of the enaminoketones are not mobile enough to get the cyclocondensation going. In this context, the following observation[21] deserves being mentioned: The reaction of dibenzoylmethane and pyrrolidine in benzene and in the presence of molecular sieves yields either the expected enaminoketone or 5,7-diphenyl-2,3-dihydro-1*H*-pyrrolizine, depending on the reaction conditions. It is not clear whether the latter product results from a cyclocondensation of the enaminoketone and if so, what the exact mechanism is. To our knowledge, a generalization of this finding has not been reported.

**Mechanistic Aspects.** A general outline of the mechanistic scenario has been given in the Introduction. As shown in Scheme 2, our previous investigations have suggested that the initial [1,4]-H shift, although probably a concerted process, corresponds to a proton migration to the electron-rich central allenic carbon atom. On the other hand, the rate-accelerating effects of the phosphoryl and *N*-benzyl substituents in aminoallenes **4** indicate that the [1,4]-H shift is more favorable if it has a hydridic character, similar to thermal isomerization reactions of

**SCHEME 6**




2-vinyl-*N*,*N*-dialkylanilines.[22] Thus, the $P(O)Ph_2$ substituent renders the central allenic carbon more electron-deficient, and the resulting conjugated azomethine ylide is stabilized in the 1,5-dipolar form **11**, relative to resonance structure **1**, by a phenyl substituent at the iminium carbon atom C-1 and the electron-accepting $P(O)Ph_2$ substituent at C-5 (Scheme 6). The observation that the *N*-benzyl-substituted aminoallenes **3e**, **4e** as well as those derived from **9e** and **9k** (Scheme 5, allenes not shown) undergo thermal conversion already at 20 °C, while all other aminoallenes investigated in this study require much more forcing conditions, indicates that at least in these latter cases the initial [1,4]-H shift is the rate-limiting step; furthermore, it is obvious that all subsequent steps of pyrrole formation (cyclization of the azomethine ylide intermediate, elimination of $HPPh_2$ or $HP(O)Ph_2$ from the dihydropyrrole) occur already at room temperature.[23]

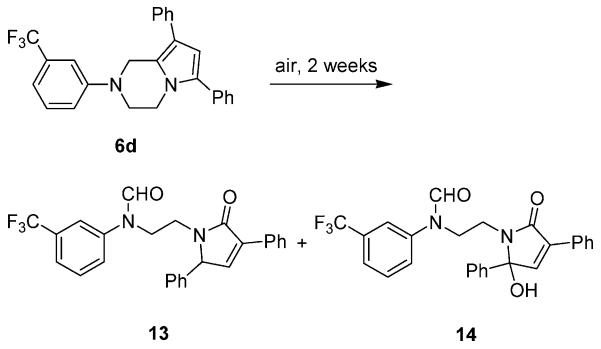
A discussion of the factors governing the periselectivity of the azomethine ylide cyclization (1,5- vs 1,7-cyclization) remains speculative at present, above all because the true yields (i.e., before workup) of pyrroles **6** and azepine derivatives **5** and **7** are not known. Inspection of literature studies on related conjugated dipoles (see the Introduction) leaves us with the impression that several different factors may be in operation the relative importance of which changes from one particular system to the

(20) Nikolai, J.; Maas, G. *Synthesis* **2003**, 2679−2688.
(21) Soeder, R. W.; Bowers, K.; Pegram, L. D.; Cartaya-Marin, C. P. *Synth. Commun.* **1992**, *33*, 2737−2740.

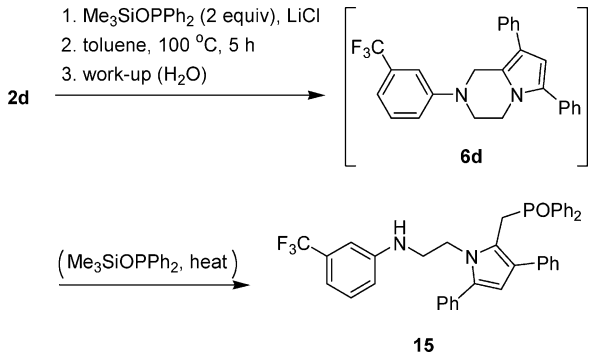
(22) (a) Reinhoudt, D. N.; Verboom, W.; Visser, G. W.; Trompenaars, W. P.; Harkema, S.; van Hummel, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 1341−1350. (b) Verboom, W.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 311−324.

(23) A reviewer has suggested a competitive pathway for the conversion of aminoallenes **3**,**4** into pyrroles **6,** which includes 3-$P(X)Ph_2$-substituted propene iminium salts being formed by C2-protonation of the aminoallenes. Preliminary experiments have shown that, e.g., the C2-protonated aminoallene **4a** is converted into pyrrole **6a** at much harsher conditions ($NEt_iPr_2$, $CH_3CN$, 140 °C, 12 h) and in lower yield than aminoallene **4a** itself. This suggests that the thermal conversion of aminoallenes **4** reported in this study does not proceed via their C-protonated form.

**SCHEME 7**




**SCHEME 8**




other. The cyclization step could be orbital- or charge-controlled (i.e., a "true" 6$\pi$ vs 8$\pi$ electrocyclization or a 1,5- vs 1,7-dipolar cyclization[8]). Calculations by Eberbach and Marx for butadienyl-substituted pyridinium ylides[13c] support the view that the orbital-controlled mode favors the 1,7-cyclization, because the helical transition-state geometry is particularly suited for a conrotatory 8$\pi$ cyclization. On the other hand, a 1,5-dipolar bond structure such as **11** may be stabilized by appropriate substituents, and we consider it likely that formation of pyrroles **6** from the 3-phosphanyl- and 3-phosphoryl-substituted aminoallenes is due to a charge-controlled pathway. Furthermore, it has occasionally been speculated that the absence of 1,5-cyclization products may also be due to the reversibility of dihydropyrrole (**12**) formation. If this was the case, one could argue that the fast $\beta$-elimination of $HPPh_2$ or $HP(O)Ph_2$ renders dihydropyrrole formation irreversible and therefore supports the 1,5-cyclization mode. However, the isolation of dihydropyrroles in cases where $P(O)Ph_2$ was replaced by $SiMe_3$[24] shows that the 1,5-cyclization can compete with the 1,7-cyclization mode also in cases where the 1,5-cyclization is not triggered by a subsequent elimination step.

**Further Transformations of Pyrroles 6d and 6h.** Pyrrole **6d** features the 1,2,3,4-tetrahydropyrrolo[1,2-*a*]-pyrazine skeleton which is found in several compounds of considerable pharmacological interest.[25] Notably, **6d** was found to be extremely sensitive to aerial oxidation, in contrast to all other pyrroles synthesized in this study. It was therefore necessary to perform the chromatographic separation of **6d** under an inert atmosphere. When solid **6d** was exposed to air for 2 weeks, it underwent complete oxidative degradation to a complex mixture of products. According to mass spectrometry, the major constituents of the mixture had molecular masses which were by 14, 32, and 48 units higher than that of **6d**. Complete chromatographic separation of the mixture was not possible due to similar $R_f$ values and the instability of some of the components. At least, a small amount of two compounds could be obtained to which structures **13** and **14** were assigned (Scheme 7) which correspond to the incorporation of two and three oxygen atoms, respectively. A product with 14 mass units higher than **6d**, which is presumably the 1-oxo derivative of **6d**, was not isolated. While **14** turned out to be stable and could be fully characterized by spectroscopy and elemental analysis, the air-sensitive desoxy analogue **13** could not be obtained in analytically pure form. The $^1H$ and $^{13}C$ NMR data of **14** fully agree with the proposed structure; among other things, the observation of an ABMN spin system for the $NCH_2CH_2$ protons indicates the presence of a neighboring stereogenic center. The NMR spectra of **13** are quite similar to those of **14**, except for the changes caused by the absence of the OH substituent. However, an unexpected difference was found for the chemical shifts of the $N_{formamide}-CH_2$ group (**13**: $\delta_H = 3.73, 4.14$, $\delta_C = 43.1$; **14**: $\delta_H = 3.32, 4.74$, $\delta_C = 46.3$), while the chemical shifts for the $N_{pyrrole}-CH_2$ group are very similar. This suggests that either the conformations at the NCCN bonds or the configuration at the N−CHO bond are different, perhaps due to the presence of an intramolecular O−H···O hydrogen bond in **14**. It should be mentioned that oxidation reactions of pyrroles are known to be complex;[26] a 5-hydroxypyrrolin-2-one similar to **14** was obtained by air oxidation of 2,4-dimethylpyrrole.[27]

Another transformation of pyrrole **6d** was found when the synthesis from propyne iminium salt **2d** was attempted in the presence of 2 equiv rather than 1 equiv of $Me_3SiO-PPh_2$ (Scheme 8). Formanilide **15** was isolated as the only product in 33% yield which obviously results from a nucleophilic attack at the pyrrolyl-$CH_2$ position of **6d** and ring-opening.

The pyrrole synthesis presented in this work yields 1,2,3,5-tetrasubstituted pyrroles with a low degree of functionalization. With a view to further synthetic elaboration, we show here as an example how additional functional groups can be introduced into **6h** (Scheme 9). First, position C-4 of the pyrrole ring should be amenable to electrophilic halogenation. In fact, bromination with $NBS/AlBr_3$ provided bromopyrrole **16** in acceptable yield. Notably, attempts to achieve bromination with $CuBr_2$ and iodination with $I_2/K_2CO_3$/MeOH or ICl met with failure, probably because of steric shielding of the C-4 position by the adjacent aryl rings. The acylation of the pyrrole ring using acetyl chloride, oxalyl chloride or acetic anhydride in the presence of $AlCl_3$ or pyridine was also unsuccessful, probably for the same reason. On the other hand, a polar functional group was readily introduced

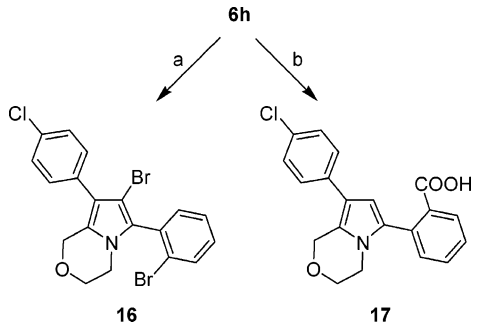
(24) J. Schlegel, Doctoral Thesis, University of Ulm, 1999.

(25) See, for example: (a) Branca, Q.; Jakob-Røtne, R.; Kettler, R.; Röver, S.; Scalone, M. *Chimia* **1995**, *49*, 381−385. (b) Katritzky, A. R.; Jain, R.; Xu, Y.-J.; Steel, P. J. *J. Org. Chem.* **2002**, *67*, 8220−8223. (c) Wyss, P. C.; Gerber, P.; Hartman, P. G.; Hubschwerlen, C.; Locher, H.; Marty, H.-P.; Stahl, M. *J. Med. Chem.* **2003**, *46*, 2304−2312 and references cited therein.

(26) Gardini, G. P. *Adv. Heterocycl. Chem.* **1973**, *15*, 67−98.

(27) Höft, E.; Katritzky, A. R.; Nesbit, M. R. *Tetrahedron Lett.* **1967**, 3041−3044; **1968**, 2028.

**SCHEME 9** [a]




[a] Conditions: (a) NBS, $AlBr_3$ (10 mol %), $CH_2Cl_2$, −78 → +20 °C, 57%; (b) (1) Mg, THF, 100 °C, 12 h, (2) $CO_2$, (3) 5% aq HCl; 63% yield.

by the conversion of the bromophenyl into a benzoic acid moiety (**6h** → **17**).

## Conclusion

The introduction of a $PPh_2$ or, even better, a $P(O)Ph_2$ substituent at the C-3 position of 1-dialkylamino-1,3-diarylallenes has allowed us, for the first time, to achieve the thermal conversion of these allenes into pyrroles. In mechanistic terms, these substituents favor the 1,5- over the 1,7-electrocyclization of α,*β*:*γ*,*δ*-unsaturated azomethine ylide intermediates which are generated by a thermal [1,4]-H shift from the aminoallenes. While the full scope of the new pyrrole synthesis remains to be explored, the present results indicate that it is particularly suited to prepare 3,5-diarylpyrroles that are [*a*]-annulated with five- or six-membered rings, e.g., of compounds with the pyrrolizidine, indolizidine, and pyrrolo[1,2-*a*]-pyrazine ring skeleton. Furthermore, the aminoallene-to-pyrrole transformation can be applied to convert *N*,*N*-dialkylenaminoketones into pyrroles through a formal 1,5-cyclocondensation of the $CH_2NC{=}CC{=}O$ unit. The required three- or four−step sequence can be performed conveniently without isolation of any intermediate product.

## Experimental Section

Diphenyl(trimethylsilyl)phosphane[28] ($Me_3SiPPh_2$) and *O*-trimethylsilyl diphenylphosphinite[29] ($Me_3SiOPPh_2$) were prepared by published procedures. Anhydrous lithium chloride was obtained by heating at 150 °C/0.04 mbar for 2 h.

**4-[3-(4-Fluorophenyl)-1-phenyl-2-propynylidene]morpholinium Trifluoromethanesulfonate (2b).** A solution of triflic anhydride (17.00 g, 0.060 mol) in $CH_2Cl_2$ (350 mL) was cooled at −78 °C, and solid enaminoketone **9b** (18.50 g, 0.059 mol) was added portionwise under an argon atmosphere. The solution was brought to 20 °C during 2 h and concentrated to half of its volume, and anhydrous ether was added in order to precipitate the formed product, [3-(4-fluorophenyl)-1-phenyl-3-(trifluoromethylsulfonyl)oxy-2-propenylidene]morpholinium triflate. The precipitate was isolated by filtration under an argon atmosphere and washed with anhydrous ether until the crystalline solid was almost colorless. It was then briefly kept at 0.01 mbar to remove residual solvent and was kept in a rotating Kugelrohr apparatus at 180 °C/0.001 mbar until evolution of triflic acid was over (15 min). The black residue was allowed to cool and then dissolved in a minimum amount of $CH_3CN$, and ether was added until the solution became turbid. After 24 h at −30 °C, some product had crystallized. An also separated black oil was removed with a pipet. Additional batches of product were obtained by addition of more ether and repeating this procedure. Analytically pure salt **2b** was obtained after at least two recrystallizations from acetonitrile−ether: yield 11.55 g (44%) of a light-brown microcrystalline powder; mp 128 °C; IR (KBr) 2191 (vs), 1592 (s), 1264 (vs), 1030 (s), 636 (s) $cm^{-1}$; $^1H$ NMR (500.14 MHz) *δ* 3.91 (pseudo-t, 2H), 4.17 (pseudo-t, 2H), 4.25 (pseudo-t, 2H), 4.67 (pseudo-t, 2H), 7.15 (mc, 2H), 7.54−7.86 (m, 7H); $^{13}C$ NMR (125.77 MHz) *δ* = 54.0, 56.5, 66.1, 66.3, 83.8, 114.3 (d, $J \sim 5$ Hz), 116.6 (d, $J_{C,F} = 22.6$ Hz), 120.6, 129.2, 129.5, 130.0, 133.7, 135.5 (d, $J_{C,F} = 9.5$ Hz), 162.0, 165.4 (d, $J_{C,F} = 258.4$ Hz). Anal. Calcd for $C_{20}H_{17}F_4NO_4S$ (443.41): C, 54.17; H, 3.86, N, 3.16. Found: C, 53.97; H, 3.64; N, 3.07.

**4-[3-(3,4-Dichlorophenyl)-1-phenyl-2-propynylidene]morpholinium Trifluoromethanesulfonate (2c).** Following the procedure described for **2b**, triflic anhydride (11.84 g, 0.042 mol) was combined with enaminoketone **9c** (14.50 g, 0.040 mol) in $CH_2Cl_2$ (300 mL). The formed salt, [3-(3,4-dichlorophenyl)-1-phenyl-3-(trifluoromethylsulfonyl)oxy-2-propenylidene]morpholinium triflate, was kept in a rotating Kugelrohr apparatus at 200 °C/0.001 mbar until evolution of triflic acid had ceased. The residual product was recrystallized twice from a mixture of $CH_3CN$ (30 mL) and ether (40 mL) to give a light-brown solid (9.55 g, 48%): mp 166 °C; IR (KBr) 2206 (s), 1603 (w), 1273 (s), 1255 (vs), 1028 (vs), 637 (s) $cm^{-1}$; $^1H$ NMR (400.13 MHz) *δ* 3.90 (pseudo-t, 2H), 4.13 (pseudo-t, 2H), 4.21 (pseudo-t, 2H), 4.64 (pseudo-t, 2H), 7.45−7.85 (m, 8H); $^{13}C$ NMR (100.61 MHz) *δ* 54.5, 57.2, 66.3, 66.5, 84.5, 118.1, 118.1, 129.3, 129.8, 130.2, 131.3, 132.7, 133.7, 133.9, 134.7, 138.3, 162.4. Anal. Calcd for $C_{20}H_{16}Cl_2F_3NO_4S$ (494.31): C, 48.60; H, 3.26; N, 2.83. Found: C, 48.53; H, 3.16; N, 2.84.

**2-(1,3-Diphenyl-2-propynylidene)-2,3-dihydro-1*H*-isoindolium Trifluoromethanesulfonate (2e).** Prepared as described for **2c**, from enaminoketone **9e** (11.50 g, 0.035 mol) and triflic anhydride (10.30 g, 0.036 mol): rose-colored solid; yield 8.82 g (55%); mp 192 °C; IR (KBr) 2200 (vs), 1556 (s), 1377 (s), 1268 (vs), 1150 (s), 1032 (vs), 638 (s) $cm^{-1}$; $^1H$ NMR (500.14 MHz) *δ* 5.45 (s, 2H), 5.79 (s, 2H), 7.10−8.05 (m, 14H); $^{13}C$ NMR (125.77 MHz) *δ* 60.5, 63.4, 84.6, 117.6, 120.1, 122.3, 122.6, 128.6, 129.0, 129.46, 129.53, 130.3, 131.5, 132.6, 133.4, 133.8, 134.5, 160.5. Anal. Calcd for $C_{24}H_{18}F_3NO_3S$ (457.47): C, 63.01; H, 3.96; N, 3.06. Found: C, 63.08; H, 4.22; N, 3.03.

**Synthesis of Propyne Iminium Triflates 2d,f−j in Solution (General Procedure).** Triflic anhydride (1.48 g, 5.25 mmol) was placed in a round-bottom flask that had been dried with a heat gun and flushed with argon. Anhydrous $CH_2Cl_2$ (20 mL) was added, and the solution was cooled at −78 °C in an acetone/dry ice bath. A solution of an enaminoketone **9** (5 mmol) in $CH_2Cl_2$ (20 mL) was added dropwise. The cooling bath was removed, and the solution was allowed to assume a temperature of 0 °C within 15 min (formation of a 3-trifloxypropene iminium salt). After cooling again at −78 °C, diisopropylethylamine (0.87 mL, 0.646 g, 5.0 mmol) was added, and the solution was brought to 0 °C within 15 min, thereby assuming an orange or light-brown color. This solution of propyne iminium triflate **3** and diisopropylethylammonium triflate was used for further reactions. According to $^1H$ NMR, the formation of **3** was virtually quantitative.

After removal of the solvent, salts **2b−j** were obtained in admixture with diisopropylethylammonium triflate and were characterized by the following spectroscopic data: IR *ν*(C≡C) 2179−2206 $cm^{-1}$; $^{13}C$ NMR *δ* 83.4−89.3 (C≡*CC*=$N^+$), *δ* 153.8−163.5 (C=$N^+$).

Salt **2d** was exemplarily separated from the ammonium salt byproduct as follows. Anhydrous ether was added to the $CH_2Cl_2$ solution until precipitation began. The precipitate was collected, and the colorless crystals of the ammonium salt were

(28) Appel, R.; Geisler, K. *J. Organomet. Chem.* **1978**, *112*, 61−64.
(29) (a) Issleib, K.; Walther, B. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 88. (b) Issleib, K.; Walther B. *J. Organomet. Chem.* **1970**, *22*, 375−386.

manually separated from the orange-colored crystals of **2d**, for which the purification procedure was repeated four times to furnish a batch of **2d** which still contained about 5−10% of the ammonium salt: IR (KBr) 2203 (s), 1608 (m), 1590 (m), 1266 (vs), 1153 (s), 1032 (s), 638 (s) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ 3.51 (pseudo-t, 2H), 3.78 (pseudo-t, 2H), 4.40 (pseudo-t, 2H), 4.80 (pseudo-t, 2H), 7.07−7.85 (m, 14H); $^{13}C$ NMR (125.77 MHz) $\delta$ 48.2, 48.7, 53.2, 56.0, 84.0, 112.5, 117.2, 117.9, 119.5 121.9, 122.6, 133.8, 129.0−133.8, 149.0, 162.6. $C_{27}H_{22}F_6N_2O_3S$ (568.53).

**Thermal Reactions of (Diphenylphosphanyl)allene 3a.** A solution of allene **3a**[14] (2.30 g, 5.0 mmol) in anhydrous toluene (10 mL) was placed in a thick-walled Schlenk tube and kept at 140 °C for 5 h. After cooling, the mixture was submitted to flash chromatography [(silica gel (100 g), cyclohexane/ethyl acetate = 3/1] to remove high-molecular byproducts as well as the polar diphenylphosphanoxide which was formed under these conditions from the reaction product diphenylphosphane. A $^1H$ NMR spectrum indicated the formation of **5a** and **6a** in a 1.4:1 ratio. Separation of the two products was not possible because of very similar $R_f$ values. The following workup procedures were chosen: (a) Preparative thick-layer chromatography (silica gel, cyclohexane/ethyl acetate = 9/1) gave a small amount of (rel-6*R*,12b*R*)-diphenyl-(6-phenyl-3,4,6,12b-tetrahydro-1*H*-benzo[*c*][1,4]oxazino[4,3-*a*]azepin-8-yl)phosphane (**5a**) which could not be obtained analytically pure, however. (b) The solvent was replaced by $CH_2Cl_2$ (150 mL), 1% aqueous $H_2O_2$ (100 mL) was added, and the mixture was shaken vigorously. The organic phase was concentrated and submitted to column chromatography (silica gel (200 g), cyclohexane/ethyl acetate = 3/1) to furnish 6,8-diphenyl-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine (**6a**) (0.165 g, 12%) and diphenyl(6-phenyl-3,4,6,12b-tetrahydro-1*H*-benzo[*c*][1,4]oxazino-[4,3-*a*]azepin-8-yl)phosphanoxide (**7a**) (0.285 g, 12%). The latter product was recrystallized from cyclohexane/ethyl acetate (1:2).

Data for **5a**: $^1H$ NMR ($CDCl_3$, 500.14 MHz) $\delta$ 2.15−2.39 (2 m, 2H), 3.25 (mc, 1H), 3.60 (ddd, $J$ = 10.9, 10.6, 3.4 Hz), 3.79 (d, $J$ = 11.0 Hz), 3.97 (mc), 4.13 (dd, $J$ = 11.8, 3.5 Hz, 1-$H^{ax}$), 4.41 (d, $J$ = 11.8 Hz), 5.80 (dd, $J$ = 6.0, 5.9 Hz), ca. 7.05−7.90 (m, 19H); $^{31}P$ $\delta$ −0.65. Data for **6a**: mp 154−155 °C; IR (KBr) 1601 (s), 1490 (m), 1449 (m), 1344 (m), 1096 (s), 753 (s), 694 (s) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ 4.03−4.06 (mc, 4H), 5.15 (s, 2H), 6.57 (s), 7.25 (t, $J$ = 7.0 Hz, 1H), 7.35−7.51 (m, 9H); $^{13}C$ NMR (125.77 MHz) $\delta$ 44.2, 64.4, 65.1, 107.7, 119.5, 123.5, 125.3, 126.7, 127.0, 128.4, 128.5, 128.6, 132.4, 135.8, 133.7; MS (EI, 70 eV) *m*/*z* (rel int) 275 ($M^+$, 100), 244 (52). Anal. Calcd for $C_{19}H_{17}NO$ (275.35): C, 82.88; H, 6.22; N, 5.08. Found: C, 82.95; H, 6.22; N, 5.04. Data for **7a**: mp 255 °C; IR (KBr) 2840 (w), 2812 (w), 1585 (m), 1435 (m), 1176 (m), 698 (m) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ 2.21−2.33 (m, 2H, 4-H), 3.31 (dd, $^3J_{H,H}$ = 5.9 Hz, $^4J_{H,P}$ = 3.3 Hz, 6-H), 3.56 (dt, $^2J$, $^3J_{Hax,Hax}$ =10.8, 10.6 Hz, $^3J_{Hax,Heq}$ = 3.5 Hz, 3-$H^{ax}$), 3.70−3.85 (m, 2H, 3-$H^{eq}$, 12b−H), 4.07 (dd, $^2J_{H,H}$ = 12.0 Hz, $^3J_{Hax,Heq}$ = 3.5 Hz, 1-$H^{ax}$), 4.38 (d, $^2J_{H,H}$ = 12.0 Hz, 1-$H^{eq}$), 6.57 (dd, $^3J_{H,H}$ = 5.9 Hz, $^3J_{H,P}$ = 18.0 Hz, 7-H), 6.85−8.00 (m, 19 $H_{aryl}$); $^{13}C$ NMR (50.32 MHz) $\delta$ 46.8 (C-4), 56.2 (C-12b), 64.9 (C-3), 67.0 (d, $^3J_{C.P}$ = 13.4 Hz, C-6), 68.9 (C-1), 125.1−146.3 ($C_{aryl}$, 1 $C_{olefin}$); $^{31}P$ NMR $\delta$ 28.2. Anal. Calcd for $C_{31}H_{28}NO_2P$ (477.54): C, 77.97; H, 5.91; N, 2.93. Found: C, 77.77; H, 6.02; N, 2.90.

**Preparation and Thermal Reactions of (Diphenylphosphanyl)allenes 3b−e. Allene 3b.** A solution of iminium salt **2b** (2.11 g, 4.76 mmol) and LiCl (0.40 g, 9.44 mmol) in anhydrous THF (50 mL) was cooled at −78 °C, and $Me_3SiPPh_2$ (1.24 g, 4.79 mmol) was added. The solution was allowed to warm to 20 °C during 12 h, and the solvent as well as formed $Me_3SiCl$ were removed at 0.01 mbar. The solid residue was extracted three times with toluene (30 mL each time) in an ultrasonic bath (5 min). The combined toluene extracts were evaporated to dryness at 0.01 mbar to furnish allene **3b** as a gray-greenish solid which was not purified further. It was dissolved in dry DMF (30 mL) and heated at 150 °C for 12 h. After cooling, the solvent was evaporated at 15 mbar and the residue was subjected to flash chromatography [silica gel (100 g), cyclohexane/ethyl acetate = 3:1]. The crude product mixture was then dissolved in $CH_2Cl_2$ (150 mL), and the solution was shaken vigorously for a few minutes with 1% aqueous $H_2O_2$. The organic phase was concentrated and submitted to column chromatography [silica gel (200 g), cyclohexane/ethyl acetate = 3/1] to furnish pyrrole **6b** (0.39 g, 28%) and 10-fluoro-6-phenyl-3,4,6,12b-tetrahydro-1*H*-benzo[*c*][1,4]oxazino[4,3-*a*]-azepin-8-yl(diphenyl)phosphanoxide (**7b**) (0.42 g, 18%). The latter product was recrystallized from cyclohexane/ethyl acetate (1:2).

Allene **3c** was prepared in the same manner from salt **2c** (2.41 g, 4.87 mmol) and was treated analogously to furnish pyrrole **6c** (0.035 g, 2%, after three recrystallizations from cyclohexane/ethyl acetate = 3/1).

Allene **3d** was prepared analogously from salt **2d** (4.76 mmol) which was contaminated with about 10 mol % of NEt-*i*-$Pr_2$·HCl. Thermolysis and workup as described above furnished pyrrole **6d** (0.30 g, 15%) and diphenyl{6-phenyl-2-[3-(trifluoromethyl)phenyl]-1,2,3,4,6,12b-hexahydrobenzo[*c*]-pyrazino[1,2-*a*]azepin-8-yl}phosphanoxide (**7d**) (0.62 g, 21%).

Allene **3e** was prepared analogously from salt **2e** (2.33 g, 5.10 mmol). The residue left after evaporation of the solvent was treated with pentane (30 mL) in an ultrasonic bath for 5 min, and after removal of the pentane it was extracted with toluene (3 × 30 mL). The combined toluene extracts, which contained **3e** ($^{13}C$ NMR $\delta$ 206.3 ppm), were left at 20 °C for 24 h, concentrated, and worked up by column chromatography (see above) to furnish pyrrole **6e** which was recrystallized from cyclohexane/ethyl acetate (3:1): yield 0.46 g (29%).

Data for **3b**: $^1H$ NMR (200.13 MHz) $\delta$ 2.30−2.45 (m, 4H), 3.50−3.60 (m, 4H), 7.1−7.8 (19H); $^{13}C$ NMR (50.32 MHz) $\delta$ 50.4, 66.7, 111.0 (d, $J_{C,P}$ = 19.5 Hz), 115.2 (d, $J_{C,F}$ = 21.6 Hz), 126.8−135.5, 163.0 (d, $J_{C,F}$ = 251 Hz), 205.1; $^{31}P$ NMR $\delta$ −3.0. Data for **3c**: $^1H$ NMR ($CDCl_3$, 500.14 MHz) $\delta$ 2.31−2.42 (m, 4H), 3.55−3.61 (m, 4H), 7.17−7.77 (m, 18H); $^{13}C$ NMR ($CDCl_3$, 125.77 MHz) $\delta$ 50.5, 66.7, 110.3 (d, $J_{C,P}$ = 20.1 Hz), 126.2−137.9, 206.5; $^{31}P$ NMR $\delta$ −6.9.

Data for **7b**: mp 204−5 °C; IR (KBr) 2850 (w), 2812 (w), 1586 (w), 1571 (w), 1487 (m), 1437 (m), 1172 (s), 1121 (s), 699 (s), 527 (s) $cm^{-1}$; $^1H$ NMR (200.13 MHz) $\delta$ = 2.23−2.37 (m, 2H, 4-H), 3.29 (dd, $^3J_{H,H}$ = 5.8 Hz, $^3J_{H,P}$ = 3.3 Hz, 6-H), 3.53 (dt, $^2J_{H,H}$ = $^3J_{Hax,Hax}$ = 10.9 Hz, $^3J_{Hax,Heq}$ = 4.1 Hz, 3-$H^{ax}$), 3.62−3.74 (m, 2H, 3-$H^{eq}$, 12b−H), 4.08 (dd, $^2J_{H,H}$ = 12.1 Hz, $^3J_{Hax,Heq}$ = 3.0 Hz, 1-$H^{ax}$), 4.35 (d, $^2J_{H,H}$ = 12.1 Hz, 1-$H^{eq}$), 6.51 (dd, $^3J_{H,H}$ = 5.9 Hz, $^3J_{H,P}$ = 17.8 Hz, 7-H), 6.83, (t, $J$ = 7.4 Hz, 1H), 7.20−7.80 (m, 17 $H_{aryl}$); $^{13}C$ NMR (50.32 MHz) $\delta$ 46.8 (C-4), 56.0 (C-12b), 66.9 (C-3), 67.4 (d, $^3J_{C,P}$ = 13.4 Hz, C-6), 68.7 (C-1), 114.4 (d, $^2J_{C,F}$ = 21.5 Hz, C-10), 116.3 (d, $^2J_{C,F}$ = 22.3 Hz, C-12), 127.6−132.4, 137.3, 138.1, 140.3, 140.9, 145.9 (d, $^2J_{C,P}$ = 8.8 Hz, C-7), 161.9 (d, $^1J_{C,F}$ = 249 Hz, C-11); $^{31}P$ NMR $\delta$ 28.3; MS (EI, 70 eV) *m*/*z* (rel int) 495 ($M^+$, 35), 294 ($M^+$ − P(O)$Ph_2$, 100). Anal. Calcd for $C_{31}H_{27}FNO_2P$ (495.53): C, 75.14; H, 5.49; N, 2.83. Found: C, 75.11; H, 5.55; N, 2.76. Data for **7d**: mp 240 °C; IR (KBr) $\nu$ 2816 (m), 1608 (m), 1586 (m), 1495 (s), 1443 (s), 1311 (s), 1197 (vs), 1164 (vs), 1123 (s) $cm^{-1}$; $^1H$ NMR (200.13 MHz) $\delta$ 2.44−2.54 (m, 2H), 2.89 (pseudo-t, 1H), 3.41−3.48 (m, 3H), 4.09 (d, $J$ = 12.3 Hz), 4.14 (s, 1H), 6.64 (dd, $J$ = 18.6, 5.9 Hz, 1H), 7.12−7.90 (m, 23H); $^{13}C$ NMR (50.32 MHz) $\delta$ 46.0, 48.3, 51.2, 55.8, 66.9 (d), 112.0, 116.1, 118.9, 127.3−138.0, 141.0, 146.6, 151.1; $^{31}P$ NMR $\delta$ 28.3; MS (EI, 70 eV) *m*/*z* (rel int) 620 ($M^+$, 34), 219 ($M^+$ − P(O)$Ph_2$, 100). Anal. Calcd for $C_{38}H_{32}F_3N_2OP$ (620.65): C, 73.54; H, 5.20; N, 4.51. Found: C, 73.55; H, 5.16; N, 4.43.

**Synthesis of Pyrroles 6a−g from Iminium Salts 2 via (Diphenylphosphoryl)allenes 4. Pyrrole 6a (Method A).** A solution of $Me_3SiOPPh_2$ (2.03 g, 7.4 mmol) and anhydrous LiCl (0.42 g, 10.0 mmol) in anhydrous THF (50 mL) was cooled at −78 °C, and powdered iminium salt **2a**[17] (3.16 g, 7.4 mmol) was added. The mixture was allowed to warm to 20 °C during 12 h. The solvent and $Me_3SiCl$ were evaporated at 0.1−0.001

mbar. Anhydrous toluene (30 mL) was added to the black residue, and the mixture was heated at 100 °C for 5 h. After cooling, water (150 mL) was added and the mixture was extracted with 3 × 50 mL of ether. The combined organic phases were washed with water (50 mL) and dried ($CaCl_2$), and the solvent was removed at 15 mbar. The dark-brown residue was separated by column chromatography (silica gel (200 g), cyclohexane/ethyl acetate = 3/1) to furnish subsequently pyrrole **6a** and a fraction that contained a trace of **7a** together with other phosphorus-containing products. The yield of **6a** after recrystallization from ether was 0.49 g (24%); see above for physical data.

**(rel-6*R*,12b*R*)-8-(4-Fluorophenyl)-6-phenyl-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine (6b).** Prepared from iminium salt **2b** (4.43 g, 10 mmol) by Method A: yield 1.95 g (66%), after recrystallization from cyclohexane/ethyl acetate (3:1); mp 145−146 °C; IR (KBr) 1525 (s), 1497 (s), 1222 (s), 1157 (s), 1089 (s), 987 (m), 842 (s), 756 (m) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ 4.01−4.06 (m, 4H), 5.08 (s, 2H), 6.49 (s, 1H), 7.08−7.50 (several m, 9H); $^{13}C$ NMR (125.77 MHz) $\delta$ 44.1, 64.2, 64.8, 107.6, 115.3 (d, $J_{C,F}$ = 21.3 Hz), 128.0 (d, $J_{C,F}$ = 7.7 Hz), 131.9 (d, $J_{C,F}$ = 3.1 Hz), 160.1 (d, $J_{C,F}$ = 244.3 Hz), 118.5, 123.2, 126.9, 128.3, 128.5, 132.3, 133.7; MS (EI, 70 eV) *m*/*z* (rel int) 294 (19), 293 ($M^+$, 100), 292 (48), 262 (64). Anal. Calcd for $C_{19}H_{16}FNO$ (293.34): C, 77.80; H, 5.50; N, 4.77. Found: C, 77.42; H, 5.29; N, 4.71.

**(rel-6*R*,12b*R*)-8-(3,4-Dichlorophenyl)-6-phenyl-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine (6c).** Prepared from iminium salt **2c** (2.47 g, 5.0 mmol) by Method A: yield 1.33 g (77%), after recrystallization from ether; pale yellow crystals; mp 130−131 °C; IR (KBr) 1591 (m), 1482 (s), 1136 (s), 1099 (s), 988 (m), 758 (s), 700 (s) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ 3.97 (s, 4H), 5.00 (s, 2H), 6.40 (s, 1H), 7.05 (dd, $J$ = 8.0, 2.0 Hz, 1H), 7.27−7.39 (m, 7H); $^{13}C$ NMR (125.77 MHz) 44.1, 64.2, 64.7, 107.4, 117.1, 124.1, 125.7, 127.2, 128.1, 128.4, 128.5, 128.7, 130.4, 132.0, 132.5, 134.0, 136.0. Anal. Calcd for $C_{19}H_{15}Cl_2NO$ (344.24): C, 66.29; H, 4.39; N, 4.07. Found: C, 66.40; H, 4.42; N, 4.02.

**6,8-Diphenyl-2-[3-(trifluoromethyl)phenyl]-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazine (6d).** Prepared from iminium salt **2d** (3.38 g, 5.94 mmol, contaminated with additional 0.09 g of NEt*i*$Pr_2$·HCl), $Me_3SiOPPh_2$ (1.63 g, 5.94 mmol), and LiCl (0.42 g, 10.0 mmol) according to method A. Because of the high oxidation semsitivity of the pyrrole, column chromatography was carried out under nitrogen atmosphere with silica gel that had been kept at 0.001 mbar for several days and had been purged with argon. Thus, the following products were obtained in the given order: pyrrole **6d** (1.43 g, 57%), 1,3-diphenyl-1-{4-[3-(trifluoromethyl)phenyl]piperazino}-2-propynyl(diphenyl)phosphanoxide (**10**) (0.30 g, 8%), and dihydrobenzazepine **7d** (0.06 g, 1.6%). Data for **6d**: obtained as a yellow glassy solid which did not crystallize; air-sensitive; IR (KBr) 1606 (m), 1494 (m), 1449 (m), 1315 (m), 1120 (s), 759 (m), 696 (s) $cm^{-1}$; $^1H$ NMR (200.13 MHz) $\delta$ 3.31 (pseudo-t, 2H), 3.97 (pseudo-t, 2H), 4.58 (s, 2H), 6.42 (s, 1H), 6.82−7.48 (m, 14H); $^{13}C$ NMR (50.32 MHz) $\delta$ 43.9, 45.9, 46.1, 108.0, 110.8, 115.3, 117.6, 120.2, 123.3, 125.4, 126.8, 126.9, 128.0, 128.5, 128.6, 129.7, 131.3, 132.2, 133.3, 135.8, 149.6. Anal. Calcd for $C_{26}H_{21}F_3N_2$ (418.46): C, 74.63, H, 5.06, N, 6.69. Found: C, 74.22, H, 4.80, N, 6.55. Data for **10**: mp 172 °C (recryst from cyclohexane/ethyl acetate (1:2)); IR (KBr) 1612 (m), 1448 (m), 1189 (s), 1116 (s), 693 (s) $cm^{-1}$; $^1H$ NMR (200.13 MHz) $\delta$ 2.72−2.85 (m, 2H, $NCH_2$), 3.08−3.30 (m, 6 H), 7.00−7.72 (m, 22H), 8.05−8.15 (m, 2H); $^{13}C$ NMR (50.32 MHz) $\delta$ 48.7 (2 C), 49.2 (d, $J_{C,P}$ = 5.0 Hz), 71.4 (d, $J_{C,P}$ = 81.7 Hz), 84.0, 94.3 (d, $J_{C,P}$ = 8.3 Hz), 111.7, 115.5, 118.4, 121.5, 122.0, 126.9−135.2, 151.1; $^{31}P$ NMR $\delta$ 30.2; MS (EI, 70 eV) *m*/*z* (rel int) 621 ($M^+$, 2.6), 620 ($M^+$, 7.4), 419 ($M^+ - P(O)Ph_2$, 100). Anal. Calcd for $C_{38}H_{32}N_2F_3OP$ (620.65): C, 73.54; H, 5.20; N, 4.51. Found: C, 73.55; H, 5.02; N, 4.42.

**1,3-Diphenyl-5*H*-pyrrolo[2,1-*a*]isoindole (6e).** Prepared from iminium salt **3e** (2.81 g, 6.14 mmol), $Me_3SiOPPh_2$ (1.68 g, 6.14 mmol), and LiCl (0.42 g, 10.0 mmol) in THF (50 mL) as described in method A. This reaction mixture was allowed to come from −78 to +20 °C within 12 h and then left at room temperature for an additional 24 h. The solvent was evaporated, and the residue was dissolved in ether, washed with water, and dried ($CaCl_2$). Column chromatography [silica gel (200 g), cyclohexane/ethyl acetate = 3:1] provided **6e** which was recrystallized from ether: yield 0.80 g (43%); mp 162 °C; IR (KBr) 1601 (vs), 1468 (s), 1453 (s), 1443 (s), 1174 (s), 753 (vs), 726 (vs), 702 (s) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ 5.13 (s, 2H), 6.76 (s, 1H), 7.17−7.79 (m, 14H); $^{13}C$ NMR (125.77 MHz) $\delta$ 51.1, 111.5, 118.8, 119.1, 122.8, 124.9, 125.2, 126.0, 126.4, 127.8, 127.9, 128.6, 128.8, 131.1, 132.6, 133.2, 135.6, 136.3, 140.0. Anal. Calcd for $C_{23}H_{17}N$ (307.39): C, 89.87; H, 5.57; N, 4.55. Found: C, 89.70; H, 5.68; N, 4.38.

**8-(1,3-Benzodioxol-5-yl)-6-phenyl-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine (6f) and (rel-6*R*,12b*R*)-Diphenyl-(6-phenyl-3,4,6,13b-tetrahydro-1*H*-[1,3]dioxolo[4',5':4,5]-benzo[*c*][1,4]oxazino[4,3-*a*]azepin-8-yl)phosphanoxide (7f) (Method B).** A solution of salt **2f** (5.10 mmol) in $CH_2Cl_2$ (40 mL), obtained by the general procedure, was cooled at −78 °C. $Me_3SiOPPh_2$ (1.40 g, 5.10 mmol) and LiCl (0.84 g, 10.0 mmol) were added, and the mixture was allowed to come to 20 °C during 12 h. Thermolysis in toluene and workup was done as described in method A. Column chromatography [silica gel (200 g), elution with cyclohexane/ethyl acetate mixture, first 3/1 (∼1 L), then 1/1] furnished successively pyrrole **6f**, dihydrobenzazepine **7f**, and several unidentified phosphorus-containing byproducts. Yield of **6f** after recrystallization from ether: 0.19 g (11%); yield of **7f** after recrystallization from cyclohexane/ethyl acetate (1:1): 1.00 g (38%). Data for **6f**: colorless tiny needle crystals; mp 151 °C; IR (KBr) 1598 (m), 1497 (s), 1485 (s), 1336 (m), 1228 (vs), 1093 (s), 1039 (s), 764 (s) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ 4.01 (s, 4H), 5.03 (s, 2H), 5.94 (s, 2H), 6.40 (s, 1H), 6.74 (d, $J$ = 8.0 Hz, 1H), 6.82 (d, $J$ = 8.0 Hz, 1H), 6.83 (s, 1H), 7.25−7.45 (m, 5H); $^{13}C$ NMR (125.77 MHz) $\delta$ 44.2, 64.3, 64.9, 100.8, 107.5, 107.7, 108.4, 119.3, 119.9, 123.0, 126.9, 128.4, 128.5, 129.9, 132.4, 133.5, 145.4, 147.8. Anal. Calcd for $C_{20}H_{17}NO_3$ (319.36): C, 75.22; H, 5.36; N, 4.38. Found: C, 74.94; H, 5.38; N, 4.29. Data for **7f**: yellowish crystalline solid; mp 221−222 °C; IR (KBr) 2887 (w), 2849 (w), 2810 (w), 1497 (m), 1481 (vs), 1247 (s), 1176 (s), 1122 (s), 1041 (s), 700 (vs), 565 (vs) $cm^{-1}$; $^1H$ NMR (200.13 MHz) $\delta$ 2.20−2.42 (m, 2 H) 3.28 (dd, $J_{H,H}$ = 5.9, 3.4 Hz, 1H), 3.57 (dt, $J$ = 10.9, 3.1 Hz, 1H), 3.72−3.78 (m, 2H), 4.07 (dd, $J$ = 11.9, 3.5 Hz, 1H), 4.32 (d, $J$ = 11.9 Hz, 1H), 5.93/5.96 (AB system, $^2J$ = 5.9 Hz, 2H), 6.46 (dd, $J$ = 18.2, 5.9 Hz, 1H), 7.03 (s, 1H), 7.20−7.80 (m, 16H); $^{13}C$ NMR (50.32 MHz) $\delta$ 46.8, 56.1, 66.9, 67.7 (d, $J_{C,P}$ = 13.3 Hz), 69.1, 101.2, 108.3, 109.6, 127.6−147.5; $^{31}P$ NMR $\delta$ 28.3; MS (EI, 70 eV) *m*/*z* (rel int) 521 ($M^+$, 3.8), 320 ($M^+ - P(O)Ph_2$, 25). Anal. Calcd for $C_{32}H_{28}NO_4P$ (521.55): C, 73.69; H, 5.41; N, 2.69. Found: C, 73.77; H, 5.39; N, 2.64.

**Synthesis of Pyrroles 6 from Enaminoketones 9 (Method C). 6-(2-Bromophenyl)-8-(4-chlorophenyl)-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine (6h).** A solution of triflic anhydride (34.68 g, 0.12 mol) in $CH_2Cl_2$ (350 mL) was cooled at −78 °C in an acetone/dry ice bath, and neat enaminoketone **9h** (50.00 g, 0.12 mol) was added. The cooling bath was removed, and the solution was allowed to assume 20 °C within 30 min, left at this temperature for 15 min, and cooled again to −78 °C. Diisopropylethylamine (15.88 g, 21.0 mL, 0.12 mol) was added, and the solution was allowed to come to 20 °C within 30 min, thereby developing a dark-red color. The solution of the so formed propyne iminium salt **2h** was cooled again at −78 °C, and $Me_3SiOPPh_2$ (33.72 g, 0.12 mol) and anhydrous LiCl (5.50 g, 0. 13 mol) were added. The mixture was then brought to room temperature within 12 h, and most of the solvent together with formed $Me_3SiCl$ was distilled off. The remaining volatiles were evaporated at 0.01 mbar. The residue was dissolved in anhydrous toluene (250 mL) and heated at 100 °C for 5 h. After cooling, the mixture

was poured into water (500 mL). The toluene was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic phases were washed with water (150 mL), dried ($CaCl_2$), and concentrated. The residue was separated by column chromatography [silica gel (1000 g), cyclohexane/ethyl acetate = 5:1]. After recrystallization from cyclohexane/ethyl acetate (1:1), pyrrole **6h** was obtained as yellow crystals: yield 22.43 g (47%); mp 115 °C; IR (KBr) 1594 (m), 1555 (m), 1484 (s), 1104 (s), 1091 (s), 834 (s), 750 (s) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ 3.76 (pseudo-t, 2H), 4.00 (pseudo-t, 2H), 5.02 (s, 2H), 6.37 (s, 1H), 7.20−7.45 (m, 7H), 7.63 (d, $J$ = 7.9 Hz, 1H); $^{13}C$ NMR (125.77 MHz) $\delta$ 43.3, 64.2, 64.8, 108.1, 117.7, 123.0, 125.3, 127.2, 127.7, 128.6, 129.8, 130.7, 131.8, 132.8, 132.9, 133.5, 134.3. Anal. Calcd for $C_{19}H_{15}BrClNO$ (388.69): C, 58.86; H, 3.90; N, 3.61. Found: C, 58.74, H, 3.95; N, 3.51.

**Pyrrole 6e.** Prepared according to method C from enaminoketone **9e** (1.63 g, 5.00 mmol). After the reaction with $Me_3SiOPPh_2$/LiCl, the $CH_2Cl_2$ solution was kept at 20 °C for 1 day. The solvent was evaporated and the residue was separated by column chromatography [silica gel (200 g), cyclohexane/ethyl acetate = 3/1] to furnish pyrrole **6e** which was recrystallized from ether: yield 0.60 g, 39%. See above for physical and spectroscopic data.

**1-(1,3-Benzodioxol-5-yl)-3-phenyl-5,6-dihydropyrrolo-[2,1-*a*]isoquinoline (6g).** Prepared according to method C from enaminoketone **9g** (3.62 g, 9.40 mmol). After the reaction with $Me_3SiOPPh_2$/LiCl, the $CH_2Cl_2$ solution was kept at 20 °C for 1 day. Workup as described above for **6e** furnished pyrrole **6g** as the only product: yield 1.54 g (45%); yellow solid; mp 155−156 °C; IR (KBr) 1600 (m), 1491 (s), 1479 (s), 1237 (s), 1229 (s), 1042 (s), 938 (m), 701 (m) $cm^{-1}$; $^1H$ NMR (200.13 MHz) $\delta$ 2.88 (t, $J$ = 6.1 Hz, 2H), 3.98 (t, $J$ = 6.1 Hz, 2H), 5.83 (s, 2H), 6.28 (s, 1H), 6.70−7.40 (m, 12H); $^{13}C$ NMR (50.32 MHz) $\delta$ 30.1, 42.2, 100.7, 108.3, 109.5, 111.0, 122.1, 122.4, 124.3, 125.4, 125.5 (2C), 126.8, 127.5, 128.3, 128.5, 129.8, 131.2, 132.2, 132.3, 133.2, 146.0, 147.5; MS (EI, 70 eV) $m/z$ 365 ($M^+$, 100). Anal. Calcd for $C_{25}H_{19}NO_2$ (365.43): C, 82.17; H, 5.24; N, 3.83. Found: C, 82.10; H, 5.33; N, 3.80.

**1,3-Diphenyl-6,7,8,9-tetrahydro-5*H*-pyrrolo[1,2-*a*]-azepine (6i).** Prepared according to method C from enaminoketone **9i** (2.98 g, 9.78 mmol). The product obtained after column chromatography was recrystallized three times from cyclohexane/ethyl acetate (1:1) to furnish 0.45 g (16%) of **6i** as a waxlike solid: mp 130−131 °C, in agreement with the literature;[30] IR (KBr) 1602 (s), 1487 (m), 1393 (m), 1345 (m), 756 (s), 707 (s), 698 (s) $cm^{-1}$; $^1H$ NMR (200.13 MHz) $\delta$ 1.68−1.92 (m, 6H), 2.90−2.95 (m, 2H), 3.98−4.02 (m, 2H), 6.23 (s, 1H), 7.15−7.42 (m, 10H); $^{13}C$ NMR (50.32 MHz) $\delta$ 25.8, 27.8, 29.5, 31.1, 46.4, 108.0, 121.5, 125.2, 126.6, 128.3, 128.4, 128.6, 129.1, 133.3, 133.4, 133.6, 137.5; MS (EI, 70 eV) $m/z$ 287 ($M^+$, 100). Anal. Calcd for $C_{21}H_{21}N$ (287.40): C, 87.76; H, 7.36; N, 4.87. Found: C, 87.50; H, 7.30; N, 4.72.

**Ethyl 1,3-Diphenyl-5,6,7,8-tetrahydroindolizine-8-carboxylate (6jA) and Ethyl 1,3-Diphenyl-5,6,7,8-tetrahydroindolizine-6-carboxylate (6jB).** Prepared according to method C from enaminoketone **9j** (1.90 g, 5.2 mmol). Column chromatography [silica gel (200 g), cyclohexane/ethyl acetate = 3/1] gave a mixture of pyrroles **6jA** and **6jB** (0.66 g, 39%) which could be separated chromatographically using cyclohexane/ethyl acetate (11:1) as the eluent: (a) **6jA** (0.19 g, 11%); (b) **6jB** (0.45 g, 25%). Data for **6jA**: yellow oil; $^1H$ NMR (500.14 MHz) $\delta$ 1.17 (t, $J$ = 7.1 Hz), 1.91 (mc, 1H), 2.21 (mc, 3H), 3.97−3.99 (m, 1H), 4.08 (q, $J$ = 7.1 Hz), 4.14−4.18 (m, 1H), 4.34−4.37 (m, 1H), 6.56 (s, 1H), 7.30−7.58 (m, 10H); $^{13}C$ NMR ($CDCl_3$, 125.77 MHz) $\delta$ 13.6, 20.9, 25.0, 40.1, 44.4, 60.4, 108.7, 122.2, 123.0, 125.1, 126.4, 127.4, 127.9, 128.0, 128.4, 132.8, 133.2, 136.4, 173.3. Anal. Calcd for $C_{23}H_{23}NO_2$ (345.44): C, 79.97; H, 6.71; N, 4.05. Found: C, 79.91; H, 6.74; N, 4.08. Data for **6jB**: mp 114 °C; IR (KBr) 1727 (vs), 1600 (s), 1309 (s), 1190 (vs), 1171 (vs), 766 (vs), 701 (vs) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ 1.18 (t, $J$ = 7.1 Hz), 1.84−1.92 (mc, 1H), 2.15−2.22 (mc, 1H), 2.74−2.80 (mc, 1H), 2.90−2.97 (mc, 1H), 3.07−3.13 (m, 1H), 4.03−4.14 (m, 4H), 6.43 (s, 1H), 7.12−7.43 (m, 10H); $^{13}C$ NMR (125.77 MHz) $\delta$ 13.9, 22.6, 24.0, 39.9, 45.6, 60.7, 108.3, 120.1, 124.8, 125.7, 126.6, 126.9, 128.2, 128.3, 128.5, 132.8, 133.1, 136.4, 172.5; MS (EI, 70 eV) $m/z$ 345 ($M^+$, 100). Anal. Calcd for $C_{23}H_{23}NO_2$ (345.44): C, 79.97; H, 6.71; N, 4.05. Found: C, 79.92; H, 6.59; N, 3.98.

**1-Methyl-2,3,5-triphenylpyrrole (6k).** Prepared according to method C from enaminoketone **9k** (1.70 g, 5.20 mmol). The product obtained after column chromatography [silica gel (200 g), cyclohexane/ethyl acetate = 3:1] was recrystallized from ether: yield 0.39 g (24%); mp 178 °C. Melting point and NMR data agree with reported data.[29] Anal. Calcd for $C_{23}H_{19}N$ (309.41): C, 89.28; H, 6.19; N, 4.53. Found: C, 89.18; H, 6.20; N, 4.55.

***N*-[2-(2-Oxo-3,5-diphenyl-2,5-dihydro-1*H*-pyrrolyl)ethyl]-*N*-[3-(trifluoromethyl)phenyl]formamide (13) and *N*-[2-(2-Hydroxy-5-oxo-2,4-diphenyl-2,5-dihydro-1*H*-pyrrolyl)-ethyl]-*N*-[3-(trifluoromethyl)phenyl]formamide (14).** A mixture of compounds was formed when pyrrole **6d** (1.00 g) was stored for 2 weeks under air. This mixture was subjected to column chromatography [silica gel (250 g), cyclohexane/ethyl acetate = 5:1] which furnished first **14** and then **13**. Similar $R_f$ values and continuing oxidative decomposition prevented the complete purification of the two products. However, after repeated column chromatography, a sample (~0.13 g) of sufficiently pure **14** was obtained and was fully characterized, while the air-sensitive compound **13** could only be characterized by NMR spectrroscopy. Data for **14**: IR (KBr) 3236 (br, m), 1686 (vs), 1649 (s), 1342 (s), 1326 (s), 1169 (s), 1121 (s), 693 (s) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ 2.86 (broadened d, $^2J$ = 14.8 Hz, 1H), 3.32 (broadened d, $^2J$ = 14.3 Hz, 1H), 3.98 (mc, 1H), 4.76 (mc 1H), 6.03 (s, 1H, OH), 7.06 (s, 1 H), 7.32−7.88 (m, 14H), 8.18 (s, 1H); $^{13}C$ NMR (125.77 MHz) $\delta$ 37.3, 46.3, 90.4, 122.3, 124.5, 125.9, 126.7, 127.4, 128.4, 128.7, 128.9, 129.4, 130.4, 130.7, 132.1 (q, $J_{C,F}$ = 32.9 Hz), 133.2, 137.2, 141.1, 144.5, 163.8, 169.7; MS (EI, 70 eV) $m/z$ (rel int) 466 ($M^+$, 80), 438 ($M^+$ − CO, 8), 277 (20), 235 (100). Anal. Calcd for $C_{26}H_{21}F_3N_2O_3$ (466.46): C, 66.95, H, 5.62, N, 6.00. Found: C, 66.88, H, 5.46, N, 5.57. Data for **13**: $^1H$ NMR (500.14 MHz) $\delta$ 2.98 (mc, 1H), 3.73 (m, $J$ = 14.0 Hz, 1H), 4.00 (m, 1H), 4.14 (m, 1H), 5.34 (d, $^3J$ = 1.9 Hz), 7.10−7.55 (m, 15H), 8.28 (s, 1H); $^{13}C$ NMR (125.77 MHz) $\delta$ 38.0, 43.1, 63.8, 120.5−134.6, 140.93, 140.95, 162.0, 170.3; MS (EI, 70 eV) $m/z$ 450 ($M^+$, 100); $C_{26}H_{21}F_3N_2O_2$ (450.46).

**Diphenyl[3,5-diphenyl-1-{2-[3-(trifluoromethyl)anilino]ethyl}-1*H*-pyrrol-2-yl]methylphosphanoxide (15).** The synthesis was carried out in complete analogy to that of **6d** according to method A, but with 2 equiv of $Me_3SiOPPh_2$, starting from 2.84 g (5.00 mmol) of salt **2d** (contaminated with additional 0.08 g of NEt*i*Pr$_2$·HCl), 2.74 g (10.0 mmol) of $Me_3SiOPPh_2$, 0.42 g (10.0 mmol) of LiCl. Column chromatography [silica gel (250 g), cyclohexane/ethyl acetate = 1:1] provided, after recrystallization from the same solvent mixture, 1.02 g (33%) of **15** as a colorless powder: mp 169−170 °C; IR (KBr) 3302 (s), 1614 (s), 1438 (s), 1341 (vs), 1315 (s), 1117 (vs), 741 (vs), 695 (vs) $cm^{-1}$; $^1H$ NMR (500.14 MHz) $\delta$ = 3.16 (t, $^3J_{H,H}$ = 6.0 Hz, 2H), 3.88 (d, $J_{P,H}$ = 12.8 Hz,), 4.49 (t, $J_{H,H}$ = 6.0 Hz, 2H), 6.14 (s, 1H), 6.35 (d, $J$ = 8.1 Hz), 6.50 (s, 1H), 6.81−7.45 (m, 22H); $^{13}C$ NMR (125.77 MHz) $\delta$ 28.5 (d, $J_{C,P}$ = 67.4 Hz), 43.7, 44.4, 108.7, 110.7, 113.4, 115.2, 120.1 (d, $J_{C,P}$ = 10.2 Hz), 125.6 (d), 129.5, 135.3, 147.8, 125.7−136.6; $^{31}P$ NMR $\delta$ 30.5; MS (EI, 70 eV) $m/z$ 620 ($M^+$, 22). Anal. Calcd for $C_{38}H_{32}F_3N_2OP$ (620.65): C, 73.54; H, 5.20; N, 4.51. Found: C, 73.44; H, 5.29; N, 4.40.

**7-Bromo-6-(2-bromophenyl)-8-(4-chlorophenyl)-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]oxazine (16).** A suspension of *N*-bromosuccinimide (0.89 g, 5.00 mmol) and $AlBr_3$ (0.13 g, 0.50

(30) (a) Gotthardt, H.; Huisgen, R. *Chem. Ber.* **1970**, *103*, 2625−2632. (b) Armesto, D.; Horspool, W. M.; Ortiz, M. J.; Romano, S. *J. Chem. Soc., Perkin Trans. 1* **1992**, 171−175.

mmol) in $CH_2Cl_2$ (40 mL) was cooled at −78 °C, pyrrole **6h** (1.94 g, 4.99 mmol) was added, and the mixture was allowed to come to 20 °C within 12 h. The precipitated succinimide was removed by filtration, and the filtered solution was extracted with water (3 × 50 mL). The organic phase was dried, the solvent was evaporated (15 mbar), and the residue was purified by column chromatography [silica gel (200 g), cyclohexane/ethyl acetate = 5:1]. The product was dissolved in the minimum amount of the same solvent mixture from which it crystallized after ∼3 weeks as a colorless powder: yield 1.33 g (57%); mp 143−144 °C; IR (KBr) 1484 (s), 1328 (s), 1185 (s), 1105 (vs), 1090 (vs), 835 (s), 754 (s) $cm^{-1}$; $^1H$ NMR (200.13 MHz) $\delta$ 3.52−3.64 and 3.74−3.85 (2 m, AA′ of AA′BB′), 3.92−3.12 (m, 2H), 4.80/4.89 (AB system, $^2J$ = 14.4 Hz, 2H), 7.22−7.45 (m, 7H), 7.68 (d, $J$ = 7.9 Hz, 1H); $^{13}C$ NMR (50.32 MHz) $\delta$ 43.4, 64.0, 64.4, 97.1, 117.2, 123.6, 126.0, 127.5, 128.4, 130.0, 130.5, 130.6, 131.9, 132.0, 132.2, 132.9, 133.7. Anal. Calcd for $C_{19}H_{14}Br_2ClNO$ (467.59): C, 48.81; H, 3.18; N, 2.99. Found: C, 48.98; H, 3.09; N, 2.87.

**2-[8-(4-Chlorophenyl)-3,4-dihydro-1*H*-pyrrolo[2,1-*c*][1,4]-oxazin-6-yl]benzoic Acid (17).** Magnesium turnings (0.12 g, 5.0 mmol) were placed in anhydrous THF (5 mL) and activated successively with 1,2-dibromoethane, $Me_3SiCl$, and treatment in an ultrasonic bath (15 min). Pyrrole **6h** (1.94 g, 5.0 mmol) was added, and the mixture was heated at 100 °C for 12 h. After the metal had been consumed completely, the solution was poured into THF (150 mL) and $CO_2$ gas was bubbled through the liquid. The precipitated salt was isolated by filtration, washed with ether (3 × 50 mL), and then added to 5% aq HCl (100 mL). The precipitated product was then isolated by filtration and recrystallized from ethyl acetate to furnish yellow crystals (1.11 g, 63%): mp 208 °C; IR (KBr) 3150−2646 (br, m), 1701 (vs), 1486 (s), 1301 (s), 1275 (s), 1084 (vs), 827 (m), 795 (m), 764 (m) $cm^{-1}$; $^1H$ NMR (pyridine-$d_5$, 200.13 MHz) $\delta$ 3.88 (s, 4H), 5.05 (s, 2H), 6.65 (s, 1H), 7.20−7.60 (m, 7H), 8.34 (d, $J$ = 6.6 Hz, 1H); $^{13}C$ NMR (pyridine-$d_5$, 125.77 MHz) $\delta$ 43.6, 64.3, 65.1, 107.7, 117.7, 127.9, 128.1, 128.3, 128.4, 129.0, 130.3, 130.5, 131.3, 132.9, 133.0, 133.1, 134.7, 170.3; MS (EI, 70 eV) $m/z$ 355 ($M^+$, 33), 354 ($M^+$, 32), 353 ($M^+$, 100). Anal. Calcd for $C_{20}H_{16}ClNO_3$ (353.80): C, 67.89; H, 4.56; N, 3.96. Found: C, 67.80, H, 4.74, N, 3.93.

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**Supporting Information Available:** Experimental details and physical/spectroscopic data for compounds **2b**−**e**, **5a**, **6a**−**k**, **7a**,**b**,**d**,**f**, and **13**−**17**; peak assignment of $^1H$ and $^{13}C$ NMR spectral data for compounds **5a**, **6a**−**k**, and **7a**,**b**,**d**,**f**; NMR spectra of compounds **2d**, **3b**,**c**, **5a**, **13**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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