NEW APPROACHES TO SYNTHESIS OF FUNCTIONALLY SUBSTITUTED AZOLES (REVIEW)

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The literature on reactants suitable for the preparation of functionally substituted azoles which has appeared in the 1980's is reviewed.

The chemistry of azoles has undergone a period of rapid development during the last decade. Advantages in methods for the synthesis of a variety of functionally substituted azoles have been discussed in detail in recent basic monographs [1-6] and new reviews on oxazoles [7, 8], thiazoles [9], imidazoles [10-12], pyrazoles [13, 14], isoxazoles [15], 1,2,3-thiadiazoles [16], 1,2,4-thiadiazoles [17], and tetrazoles [18]. Important information on the preparation of azoles has also appeared in discussions of the heterocyclization of nitrogen compounds of various types [19-27].

In spite of these reviews, many methods for the introduction of functional substituents into azoles have not yet been systematized, and are scattered throughout many journal publications of the 1980's. It has not been possible to cover this work in detail within the limits of the present review, and it has been necessary to restrict it to those reports which describe relatively simple but nevertheless general methods for the preparation of difficultly accessible or previously unknown types of functionally substituted azoles. The interest in the development of preparative methods for these compounds arises partly from the fact that they are often useful subjects for the investigation of structure-reactivity relationships in unique aromatic systems, and partly that they are required for the creation of effective drugs, pesticides, dyes, and other compounds with practical applications.

The methods available for the preparation of these compounds may be divided into three basic groups:

a) synthesis of azoles from acyclic compounds,

b) conversion of certain functionally-substituted azoles into others, and

c) recyclization of some heterocyclic compounds to azoles.

None of these approaches can be ignored, since the limits of their application overlap. The first approach is, however, especially important, since the use of efficient reagents has resulted in the greatest progress in the synthesis of azoles. It is therefore desirable to dwell at some length on acyclic compounds which are clearly of value in this respect, but which have not been widely reported.

PREPARATION OF 1,3-AZOLES FROM N-ALKYLAMIDES AND ENAMIDES

Diagram 1 shows the intramolecular condensation of the related compounds (I) and (II), which are convenient reagents for the preparation of substituted oxazoles and thiazoles with a range of nitrogen-, sulfur-, and phosphorus-containing groups in the 4-position. It is noteworthy that the heterocyclization of the chlorinated N-substituted amides (I) has been examined systematically only quite recently [28], although N-acylated simple α-aminocarbonyl compounds (II) have long been used for the preparation of 1,3-azoles [1, 4].

Comparison of the reactivities of structurally similar pairs of compounds (I) and (II) shows that they are not usually interchangeable in heterocyclization, and their areas of application are complementary rather than exclusive. In addition, the ease of access of these compounds is usually different. Of particular interest are the most readily available and also the simplest compounds (I), which contain a dichloromethyl group. As will be seen from Diagram 1, they are readily obtained from the condensation products of carboxamides with chloral or dichloroacetaldehyde. Treatment of these compounds with bases frequently affords

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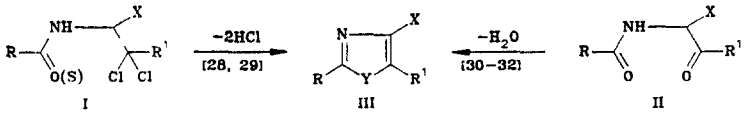
2,4-disubstituted azoles which cannot usually be obtained from the compounds (II), since the synthesis of methylene group functionalized acylaminoacetaldehydes is a far from simple task.

Important intermediates for the preparation of the compounds (I) are the highly reactive N-(1,2,2-trichloroethyl)amides (IV) and the N-(2,2-dichlorovinyl)amides (V). The use of the latter is well illustrated by two examples, namely the preparation of 4-aminooxazoles (VI) and the 4-mercaptothiazoles (VII), although this does not of course exhaust the possibilities of the use of the enamides (V) for the synthesis of 4-functionalized 1,3-azoles.

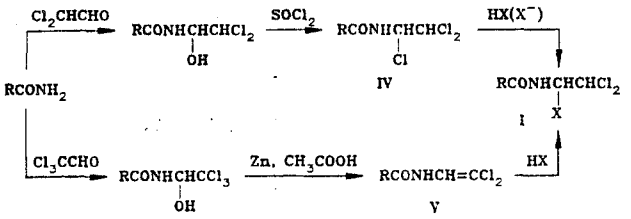
Diagram I



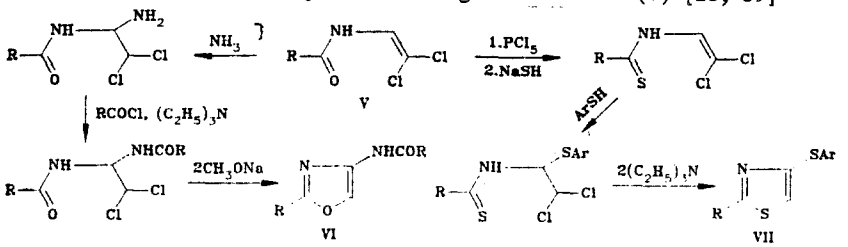
I III II

X = N-, S-, and P-containing R¹ = H, AlkHal, Ar; Y = O, S

Preparation of the simplest representatives of I [33—38]



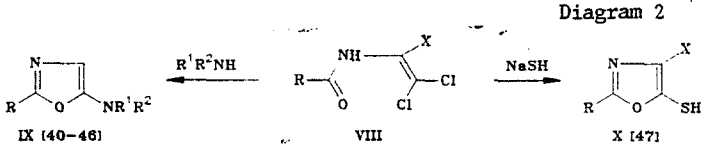
Examples of syntheses using the enamides (V) [28, 39]



Still more valuable reactants for heterocyclization are the enamides (V) containing electron-acceptor groups in the α-position of the alkenyl residue. A large group of compounds of this type of general formula (VIII) are shown in Diagram 2. Treatment of these compounds with an excess of highly basic primary or secondary amines frequently gives high yields of the 5-aminooxazoles (IX). The compounds (VIII) react similarly with sodium hydrosulfide, to give the previously unknown 5-mercaptooxazoles (X).

The driving force in these condensations is the orbitally-controlled addition of the nucleophile to the soft electrophilic C=C bond in (VIII). The intermediates in this addition apparently usually contain the reactive $>NCCl_2-$ and $-SCl_2-$ groupings, which readily condense with the adjacent acylamino-residues with the closure of the oxazole [40-47].

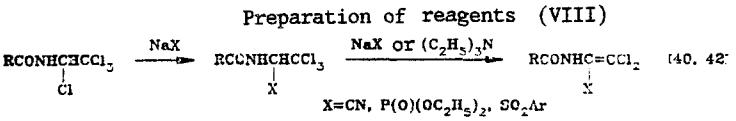
Diagram 2



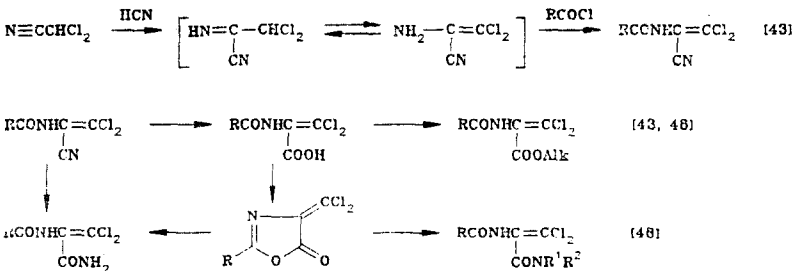
IX [40-46] VIII X [47]

X = CN, COOAlk, $CONH_2$, CONHAlk, $P(O)(OAlk)_2$, SO_2Ar и др.

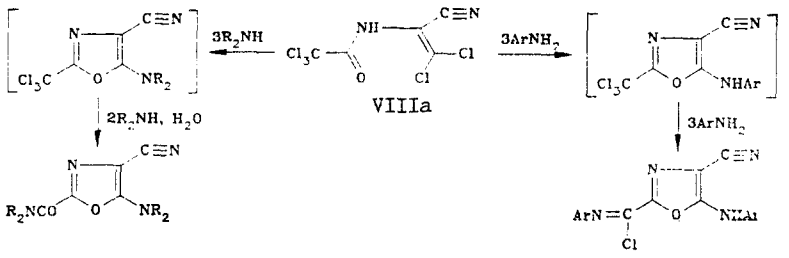
Preparation of reagents (VIII)



X = CN, $P(O)(OC_2H_5)_2$, SO_2Ar



Heterocyclization with shared reagent (VIIIa) [49]



The course of the reaction of the enamides (VIII) with nucleophiles is highly dependent on the electronic nature of the substituent X and the rigidity of the nucleophile [46]. In addition to substituted oxazoles, acyclic compounds are also often formed [44, 46], but even with these limitations the area of use of the compounds (VIII) remains quite extensive.

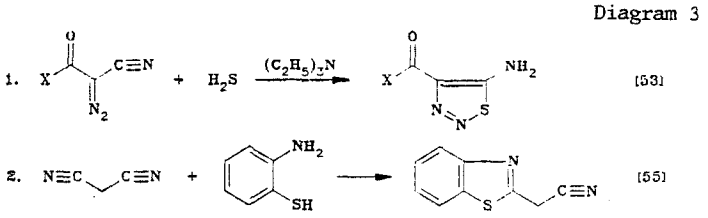
An important representative of the compounds (VIII) is 2-trichloroacetylamino-3,3-dichloroacrylonitrile (VIIIa), which has been used by G. N. Mis'kevich to introduce three different functional groups into the oxazole ring (Diagram 2). It is noteworthy that many other nitriles have been used to obtain 1,2- and 1,3-azoles, and these are discussed in the following section.

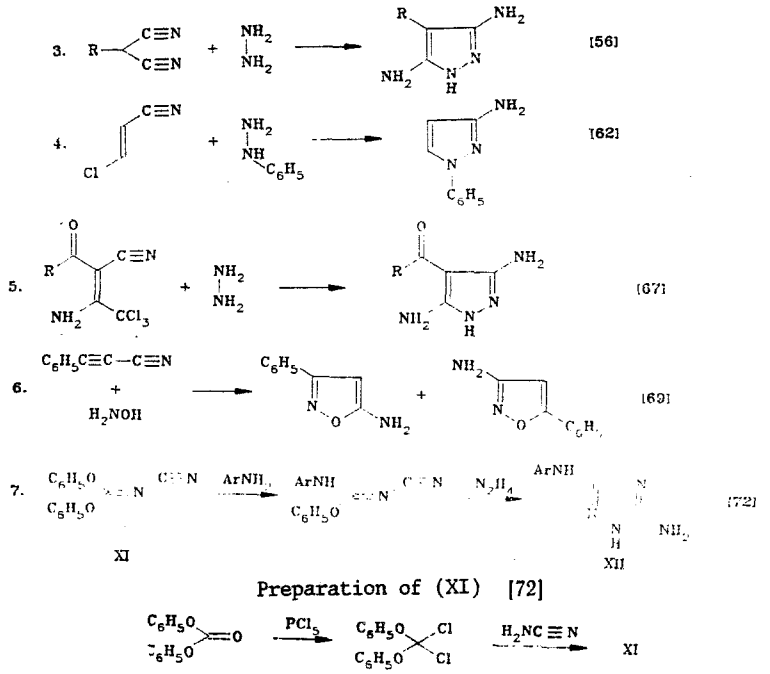
FUNCTIONALLY SUBSTITUTED AZOLES FROM NITRILES AND ISONITRILES

The value of nitriles for the synthesis of azoles cannot be overstressed. This conclusion follows from an examination of several new reviews of the heterocyclization with malononitrile [19], cyanoacetamide [24], its thio-analog [24, 26], and many other substituted nitriles [27]. In recent times acylacetonitriles and their derivatives [50-54], malononitrile and its analogs [55-58], aminonitriles [59-61], substituted acrylonitriles [62-67], nitriles of acetylenic and allenecarboxylic acids [68-71], and other N-cyanoimidocarbonic acid derivatives [72-81] have been used to prepare azoles.

Normally, condensations with multicentered reactants containing other electrophilic groups in addition to the nitrile group are carried out with hydrazine and its homologs, hydroxylamine, primary amines, and hydrogen sulfide and its organic derivatives. Seven examples of such heterocyclizations are shown in Diagram 3. Of particular interest are: the reaction of o-aminothiophenol with malononitrile, a convenient route to the valuable intermediate 2-cyanomethylbenzothiazole (example 2), the condensation of hydrazine with 2,3-disubstituted-3-trichloromethylacrylonitriles, which involves haloform cleavage to give 3,5-diaminopyrazoles (example 5), and finally the reaction of diphenyl N-cyanoimidocarbonic acid (XI) with aromatic amines, followed by hydrazine (example 7), which has been used to obtain 5-amino-3-arylamino-1,2,4-triazoles (XII). As will be seen from diagram 3, the important reactant (XI), which can be used in many heterocyclizations, is obtained from the readily available compounds diphenyl carbonate and cyanamide.

Diagram 3

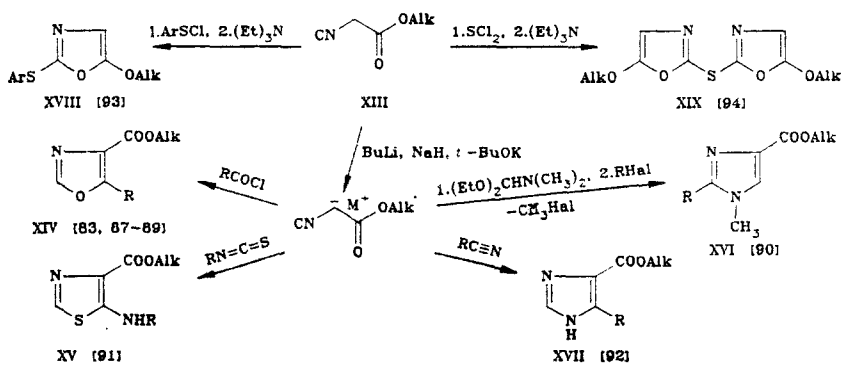




Preparation of (XI) [72]

In addition to numerous nitriles, isonitriles are also used to obtain azoles [82-95]. Of special interest are the alkyl isocyanoacetates (XIII), which are valuable reactants for the preparation of a variety of oxazoles (XIV), thiazoles (XV), and imidazoles (XVI) and (XVII) (Diagram 4). The compounds (XIII) are usually subjected to Schollkopf metallation [82], then reacted with various electrophiles. In the first step, the isonitrile group is retained, and in the second cyclization is effected under conditions appropriate to the electrophile used. This approach, a very productive one [82, 83, 85-92], has recently been augmented by Bossio et al [93, 94], who have added arenesulfenyl chlorides and sulfur dichloride to the isonitrile group in (XIII), followed by cyclization to the 2,5-disubstituted oxazoles (XVIII) and (XIX). It is as yet difficult to assess the value of this method, but it may well be that its range of uses will be extended.

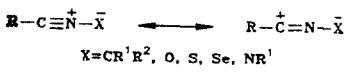
Diagram 4



In conclusion, it may be pointed out that 1,3-azoles have been obtained from analogs of (XIII) containing electron-acceptor groups other than the alkoxycarbonyl group, namely CONRR' [84], P(O)(OAlk)$_2$ [85, 86], and SO_2Ar [95].

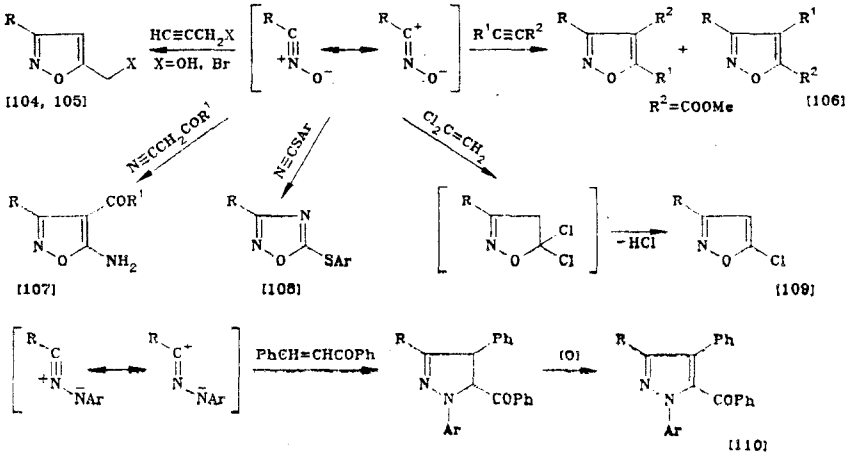
BIPOLAR NITROGEN COMPOUNDS IN THE SYNTHESIS OF AZOLES

At the present time, the chemistry of azoles cannot be significantly extended without the use of bipolar nitrogen compounds of the type



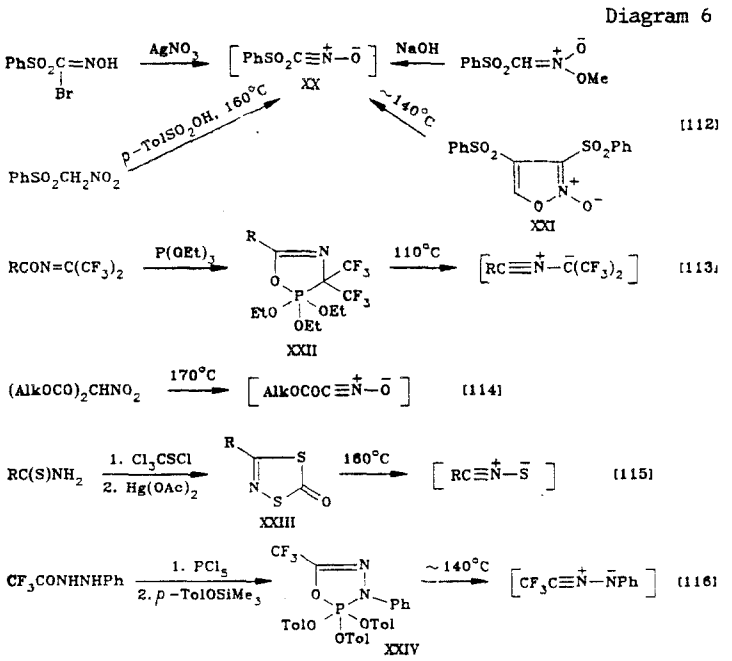
The use of nitrile ylids, nitrile oxides, and their analogs in heterocylizations has been discussed in detail in an excellent recent monograph [6], and it is therefore unnecessary to cite the numerous publications given therein. We mention only some recent articles describing the synthesis of various azoles using bipolar nitrogen compounds [96-110]. These compounds are usually reacted with electrophiles containing the C≡C, C≡N, or C=C bonds to give the 1,3-dipolar cycloaddition products. Some examples of cyclization with nitrile oxides and nitrileimines are shown in Diagram 5. This reaction is of particular value for the preparation of isoxazoles and 1,2,4-oxadiazoles with functional substituents in the 5-position.

Diagram 5



Nontrivial methods have been developed for the generation of bipolar reagents of low stability, in addition to standard methods. Some of these are shown in Diagram 6, from which it will be seen that compound (XX), for instance, may be obtained by four different methods. Nitrile ylids and their analogs are sometimes obtained from the cyclic intermediates (XXI-XXIV), which undergo thermal cleavage [111]. This cleavage is often carried out in the presence of unsaturated electrophiles, enabling the bipolar reagents to undergo immediate 1,3-dipolar cycloaddition [111-116].

Diagram 6

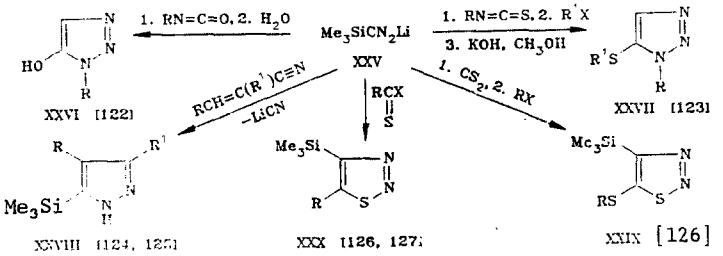


SYNTHESIS OF AZOLES FROM HETEROORGANIC COMPOUNDS

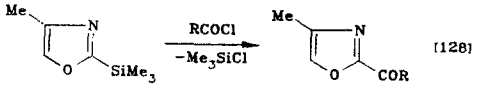
Simple organosilicon compounds (trimethylsilyl azide, trimethylsilylmethylazide, trimethylsilyldiazomethane and its derivatives) have recently been used extensively for the synthesis of functionally substituted pyrazoles, thiazoles, 1,2,3-triazoles, 1,2,3-thiadiazoles, 1,2,4-thiadiazoles, and tetrazoles (see review [117] and reports [118-127]).

Diagram 7 shows some condensations using lithium trimethylsilyldiazomethane (XXV), which reacts readily with a variety of electrophiles to give the substituted azoles (XXVI-XXX). These condensations always result in the formation of silylated azoles, which can sometimes be isolated (cf. (XXVIII-XXX)). The C—Si bond in these compounds is readily hydrolyzed, and this method is usually used to obtain the silicon-free azoles (e.g. (XXVI) and (XXVII)).

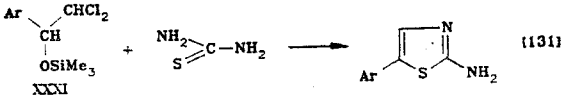
Diagram 7



The C—Si bond in (XXX) is cleaved not only by water, but also by acid chlorides, aldehydes, and other electrophiles, resulting in the introduction of simple and important functional groups into the azole systems. Numerous examples of these introductions have been discussed in a recent review by Dondoni on new methods for the functionalization of thiazole [9]. Similar reactions also occur with silylated oxazoles, for example:

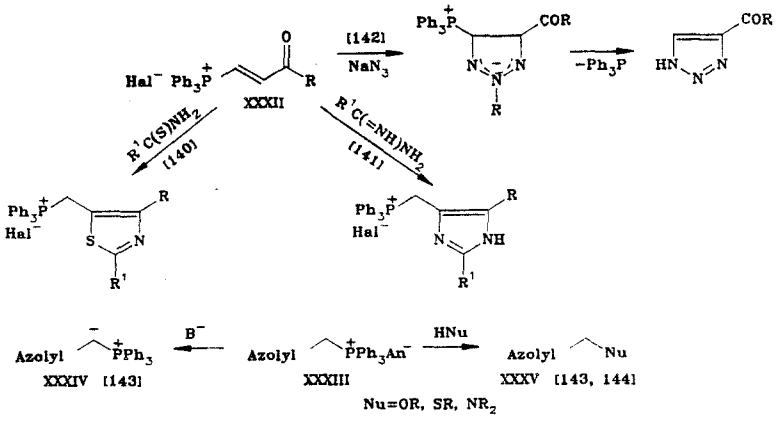


In addition to (XXV) (Diagram 7), many other organosilicon compounds have been used to obtain azoles [117, 128-130], of which we mention the accessible reactants (XXXI) used by Ya. G. Bal'on et al. [131] to obtain 2-amino-5-aryl-thiazoles:

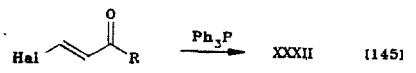


In addition to organosilicon compounds, phosphorus compounds (phosphonium ylids, iminophosphoryl compounds, substituted vinylphosphonium compounds, and many others) play an important part in azole synthesis. Heterocyclizations involving these compounds have been discussed in a special monograph [132] and recent reports [133-139]. Of special interest are Zbiral-Dombrovskii reagents (the 2-acylvinylphosphonium salts (XXXII), which condense with bifunctional nucleophiles (Diagram 8). The products from these reactions are usually azolylmethylphosphonium salts of general formula (XXXIII), which can be used to obtain the corresponding ylids (XXXIV) or the substituted phosphorus-free azoles (XXXV).

Diagram 8



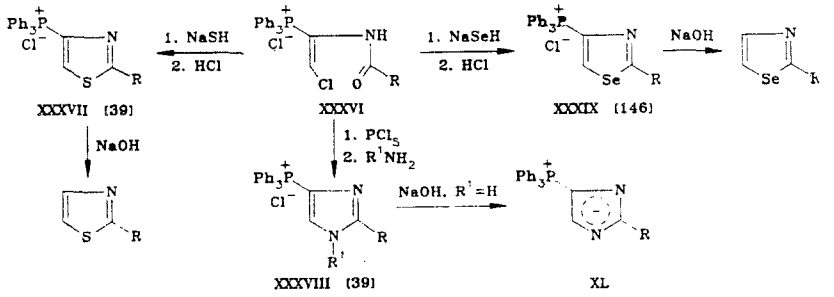
Preparation of reagent XXXI



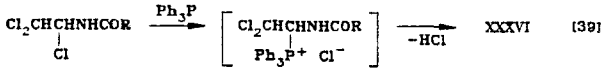
Substituted vinylphosphonium compounds include, in addition to (XXXII), the 1-acylamino-2-chlorovinylphosphonium salts (XXXVI), which have recently been used to introduce the phosphonium grouping into the 4-position of some 1,3-azoles (Diagram 9). The structure of the phosphorylated azoles (XXXVII-XXXIX) were reliably proved by chemical methods. For instance, compounds (XXXVII) and (XXXIX) are readily cleaved by alkali at the C—P bond to give the 2-substituted thiazoles and selenazoles, which were obtained by other methods for the purpose of identification.

It is interesting that the phosphorylated imidazoles (XXXVIII), which are unsubstituted at nitrogen, are not cleaved by alkali at the C—P bond, but are converted into the mesomeric betaines (XL), which are highly reactive towards electrophiles, and are of considerable value for the synthesis of novel types of substituted imidazoles.

Diagram 9



Preparation of reagents XXXVI



Close analogs of (XXXVI) containing two chlorine atoms in the vinyl residue are unique reactants for the preparation of oxazoles, thiazoles, and selenazoles with nitrogen-, sulfur-, and selenium-containing substituents in the 5-position (Diagram 10). The compounds (XLI) are similar in their reactivity to other N-2,2-dichlorovinylamides with electron-acceptor substituents in the 1-position of the alkenyl residue, which have been discussed above (Diagram 2).

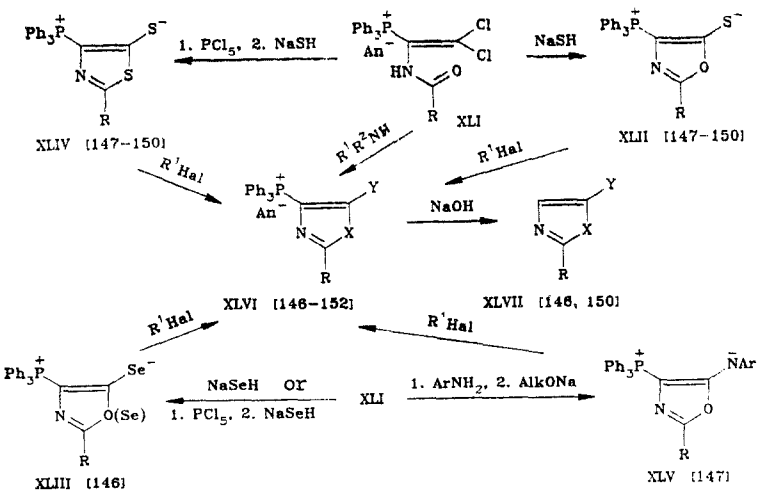
Unlike the latter compounds, however, (XLI) shows specific behavior, being reaadily converted into the mesomeric 1,3-azole phosphonium betaines (XLII-XLV), which are in turn closely related to 4-azolylphosphonium salts (XLVI). The triphenylphosphonium grouping in (XLI) activates the C=C bond towards soft or not very hard nucleophiles, resulting in directed addition to give intermediates which readily undergo heterocyclization.

Treatment of the final products in these reactions with alkali affords high yields of the 5-functionalized azoles (XLII), which are frequently difficult or impossible to obtain by other methods. Essentially, the sequence of reactions (XLI)→(XLVI)→(XLVII) is a fairly general method for the introduction of a variety of groups (for example Alk_2N, Alk(Ar)N, AlkS, ArS, HetS, AlkSe, etc.) into the 5-position in 1,3-azole systems.

As will be seen from Diagram 10 (following page), the range of applications of the accessible compounds (XLI) is already quite wide, and will doubtless be extended yet further in the future. The novel types of phosphonium betaines (XL) and (XLII-XLV) are unique additions to the general group of other mesomeric betaines, which have been reviewed in detail by Ollis and Stanforth in a fundamental review [153].

In conclusion, it may be remarked that in addition to cyclization of initially acyclic compounds, azoles are increasingly being obtained by recyclization of a variety of heterocyclic compounds. A detailed discussion of this route does not lie within the scope of this review, and the reader is merely directed towards two valuable reviews [154, 155] in which important information on recyclizations affording functionalized azoles is given.

Diagram 10



X=O, S, Se; Y = N-, S-, or Se-containing groups

Preparation of reagents XLI

$$Cl_3CCHClNHCOR \xrightarrow{Ph_3P} [Cl_3CCH(NHCOR)\overset{+}{P}Ph_3Cl^-] \xrightarrow[-HCl]{} XLI \quad [151, 152]$$

In recent years, therefore, the armamentarium of azole chemists has been extended substantially by the use of novel, effective acyclic and heterocyclic compounds, some of which have been discussed above. In consequence, functional derivatives of oxazoles, imidazoles, isoxazoles, isomeric triazoles, tetrazoles, and 1,2,3- and 1,2,4-triazoles have become accessible for which no convenient methods of synthesis were available.

LITERATURE CITED

1. J. V. Metzger (editor), The Chemistry of Heterocyclic Compounds. Thiazole and Its Derivatives. Wiley, New York (1979).
2. K. T. Finley, The Chemistry of Heterocyclic Compounds. Triazoles: 1-3. Wiley, New York (1980).
3. C. Temple, The Chemistry of Heterocyclic Compounds. Triazoles: 1,2,4. Wiley, New York (1981).
4. I. J. Turchi (editor), The Chemistry of Heterocyclic Compounds. Oxazoles. Wiley, New York (1986).
5. A. R. Katritzky, C. W. Rees, and K. T. Potts (editors), Comprehensive Heterocyclic Chemistry, Pergamon Press, Oxford (1984), Vols. 5, 6.
6. A. Padwa (editor), 1,3-Dipolar Cycloaddition Chemistry, Wiley, New York (1984), Vols. 1, 2.
7. L. S. Peshakova, V. B. Kalcheva, and S. A. Simov, Khim. Geterotsikl. Soedin., No. 8, 1011 (1981).
8. S. N. Ivanova, N. N. Mel'nikov, L. P. Klimkina, A. V. Massal'skaya, and N. L. Poznanskaya, Reactions and Methods of Study of Organic Compounds (I. L. Knunyants, N. N. Mel' nikov, and V. D. Simonov, editors), Khimiya, Moscow (1983), p. 72.
9. A. Dondoni, Phosph. Sulf., 24, 1 (1985).
10. M. R. Grimmett, Advances in Heterocyclic Chemistry (A. R. Katritzky and A. J. Boulton, editors), Acad. Press, New York (1980), Vol. 27, p. 241.
11. J. Suwinski, and E. Salvinska, Wiadom. Chem., 36, 721 (1982).
12. A. M. Smirnov, Khim. Geterotsikl. Soedin., No. 12, 1589 (1982).
13. G. Dorn, Khim. Geterotsikl. Soedin., No. 1, 3 (1981).
14. M. N. Elnagdi, Heterocycles, 23, 3121 (1985).
15. A. A. Akhrem, F. A. Lakhvich, and V. A. Khripach, Khim. Geterotsikl. Soedin., No. 8, 1155 (1981).
16. V. A. Bakulev and V. S. Mokrushin, Khim. Geterotsikl. Soedin., No. 8, 1011 (1986).
17. F. Kurzer, Advances in Heterocyclic Chemistry (A. R. Katritzky and A. J. Boulton, editors), Acad. Press, New York (1982), Vol. 32, p. 404.

18. G. I. Koldobskii, V. A. Ostrovskii, and V. S. Poplavskii, Khim. Geterotsikl. Soedin., No. 10, 1299 (1981).
19. F. Freeman, Synthesis, No. 12, 925 (1981).
20. V. G. Granik, Usp. Khimii, 52, 669 (1983).
21. N. De Kimpe and N. Shamp, Org. Prep. Proc. Int., 15, 71 (1983).
22. V. G. Granik, Usp. Khimii, 53, 651 (1984).
23. Y. Tominaga and Y. Matsuda, J. Heterocycl. Chem., 22, 937 (1985).
24. F. M. Abdel-Galil, S. M. Sherif, and M. H. Elnagdi, Heterocycles, 24, 2023 (1986).
25. J. M. Bobbitt and A. J. Bourque, Heterocycles, 25, 601 (1987).
26. B. Y. Riad, A. M. Negm, S. E. Abdou, and H. A. Daboun, Heterocycles, 26, 205 (1987).
27. M. H. Elnagdi, S. M. Sherif, and R. M. Mohareb, Heterocycles, 26, 497 (1987).
28. T. K. Vinogradova, A. P. Martynyuk, and B. S. Drach, Zh. Org. Khim., 16, 1783 (1980).
29. Ya. G. Bal'on and R. N. Moskaleva, Zh. Org. Khim., 19, 2456 (1983).
30. B. S. Drach, I. Yu. Dolgushina, and A. D. Sinitsa, Zh. Org. Khim., 9, 2368 (1973).
31. B. S. Drach, I. Yu. Dolgushina, and A. D. Sinitsa, Zh. Obshch. Khim., 45, 1251 (1975).
32 B. H. Lipshutz, R. W. Hungate, and K. E. McCarthy, J. Am. Chem. Soc., 105, 7703 (1983).
33. G. Zaugg and V. Martin, Organic Reactions [Russian translation], Mir, Moscow (1967), Vol. 14, p. 65.
34. B. S. Drach, G. N. Mis'kevich, and T. Ya. Lavrenyuk, Zh. Org. Khim., 12, 421 (1976).
35. A. N. Mirskova, É. F. Zorina, and A. S. Atavin, Zh. Org. Khim., 8, 1150 (1972).
36. B. S. Drach and É. P. Sviridov, Zh. Org. Khim., 9, 680 (1973).
37. H. E. Zaugg, Synthesis, No. 2, 85 (1984).
38. H. E. Zaugg, Synthesis, No. 3, 181 (1984).
39. V. S. Brovarets, O. P. Lobanov, T. K. Vinogradova, and B. S. Drach, Zh. Obshch. Khim., 54, 288 (1984).
40. B. S. Drach, É. P. Sviridov, A. A. Kisilenko, and A. V. Kirsanov, Zh. Org. Khim., 9, 1818 (1973).
41. B. S. Drach, É. P. Sviridov, and T. Ya. Lavrenyuk, Zh. Org. Khim., 10, 1271 (1974).
42. B. S. Drach, É. P. Sviridov, and Ya. P. Shaturskii, Zh. Obshch. Khim., 44, 1712 (1974).
43. K. Matsumura, T. Sarate, and N. Hashimoto, Chem. Pharm. Bull., 24, 912, 924 (1976).
44. K. Matsumura, J. Shimadzu, O. Miyashita, and N. Hashimoto, Chem. Pharm. Bull., 24, 941 (1976).
45. K. Matsumura, O. Miyashita, J. Shimadzu, and N. Hashimoto, Chem. Pharm. Bull., 24, 948 (1976).
46. B. S. Drach, G. N. Mis'kevich, and A. P. Martynyuk, Zh. Org. Khim., 14, 508 (1978).
47. T. K. Vinogradova, A. A. Kisilenko, and V. S. Drach, Zh. Org. Khim., 18, 1864 (1982).
48. B. S. Drach and G. N. Mis'kevich, Zh. Org. Khim., 10, 2315 (1974).
49. B. S. Drach and G. N. Mis'kevich, Zh. Org. Khim., 14, 501 (1978).
50. E. V. P. Tao and G. S. Staten, Org. Prep. Proc. Int., 17, 235 (1985).
51. C.-K. Kim, P. A. Zielinski, and C. A. Maggiulli, J. Org. Chem., 49, 5247 (1984).
52. Yu. M. Shafran, V. A. Bakulev, V. S. Mokrushin, and S. G. Alekseev, Khim. Geterotsikl. Soedin., No. 9, 1266 (1984).
53. Yu. M. Shafran, V. A. Bakulev, V. S. Mokrushin, and G. I. Validuda, Khim. Geterotsikl. Soedin., No. 5, 691 (1986).
54. Yu. M. Shafran, V. A. Bakulev, V. S. Mokrushin, S. G. Alekseev, A. T. Lebedev, and P. A. Sharbatyan, Khim. Geterotsikl. Soedin., No. 7, 926 (1986).
55. K. Saito, S. Kambe, and Y. Nakano, Synthesis, No. 3, 210 (1983).
56. G. Zvilichowsky and M. David, J. Chem. Soc., Perkin Trans. 1, No. 1, 11(1983).
57. F. M. Abdelrazek and A. W. Erian, Synthesis, No. 1, 74 (1986).
58. E. M. Zayed and S. A. S. Ghozlan, Z. Naturforsch., No. 40, 1727 (1985).
59. R. S. Hosmane, Annalen, No. 4, 831 (1984).
60. K. Takahashi, K. Shibasaki, K. Ogura, and H. Iida, Synthesis, No. 8, 794 (1985).
61. L. Koshy and C. P. Joshua, Indian J. Chem., 25B, 530 (1986).
62. G. Ege and H. Franz, J. Heterocycl. Chem., 19, 1265, 1267 (1982).
63. H. Hartmann and J. Liebsher, Synthesis, No. 3, 276 (1984).
64. J. N. Vishwakarma, B. K. Chowdhury, and R. Ila, Indian J. Chem., 24B, 472 (1985).
65. P. Giori, A. C. Veronese, C. B. Vicentini, and M. Guarneri, J. Heterocycl. Chem., 22, 1093 (1985).
66. N. P. Peet, J. Heterocycl. Chem., 23, 193 (1986).
67. B. B. Gavrilenko, V. V. Momot, and N. D. Bodnarchuk, Zh. Org. Khim., 10, 601 (1974).
68. L. I. Vereshchagin, T. M. Filippova, R. L. Bol'shedvorskaya, L. D. Gavrilov, and G. A. Pavlova, Zh. Org. Khim., 20, 142 (1984).
69. Z. T. Fomun and P. F. Asobo, J. Chem. Soc., Perkin Trans. 1, No. 5, 1079 (1984).

70. Z. T. Fomum and P. N. Ifeadike, J. Heterocycl. Chem., 22, 1611 (1985).
71. M. I. Komendantov, A. P. Zavgorodnyaya, I. N. Domnin, and R. R. Bekmukhametov, Zh. Org. Khim., 22, 1541 (1986).
72. R. L. Webb and C. S. Labaw, J. Heterocycl. Chem., 19, 1205 (1982).
73. H. Kristinsson and T. Winkler, Helv. Chim. Acta, 66, 1129 (1983).
74. T. Fuchigami and T. Nonaka, J. Org. Chem., 48, 3340 (1983).
75. T. Fuchigami, M.-Y. Yen, T. Nonaka, and H.-J. Tien, Bull. Chem. Soc. Japan, 56, 3851 (1983).
76. T. P. Selby and G. E. Lepone, J. Heterocycl. Chem., 21, 61 (1984).
77. G. D. Krapivin, A. Jurasek, J. Kovač, and V. G. Kul'nevich, Coll. Czech. Chem. Commun., 49, 2285 (1984).
78. I. Hayakawa and Y. Tanaka, Heterocycles, 22, 1697 (1984).
79. I. Kramer and W. Schunack, Arch. Pharm., 318, 888 (1985).
80. W. Ried and D. Kuhnt, Annalen, No. 4, 780 (1986).
81. J. Reiter and L. Pongo, J. Heterocycl. Chem., 23, 401 (1986).
82. U. Schöllkopf, Angew. Chem., 82, 795 (1970).
83. U. Schöllkopf and R. Schröder, Angew. Chem., 83, 358 (1971).
84. J. P. Chupp and K. L. Leschinsky, J. Heterocycl. Chem., 17, 705, 711 (1980).
85. J. Rachon and U. Schöllkopf, Annalen, No. 7, 1186 (1981).
86. J. Rachon and U. Schöllkopf, Annalen, No. 9, 1693 (1981).
87. Y. Ozaki, S. Maeda, T. Iwasaki, K. Matsumoto, A. Odawara, Y. Sasaki, and T. Morita, Chem. Pharm. Bull., 31, 4417 (1983).
88. S. Maeda, M. Suzuki, and T. Iwasaki, Chem. Pharm. Bull., 32, 2536 (1984).
89. T. Moriya et al., J. Med. Chem., 29, 333 (1986).
90. H.-H. Lau and U. Schöllkopf, Annalen, No. 11, 2093 (1982).
91. M. Suzuki, T. Moriya, K. Matsumoto, and M. Miyoshi, Synthesis, No. 10, 874 (1982).
92. T. Murakami, M. Otsuka, and M. Ohno, Tetrahedron Lett., 23, 4729 (1982).
93. R. Bossio, S. Marcaccini, and R. Pepino, Heterocycles, 24, 2003 (1986).
94. R. Bossio, S. Marcaccini, and R. Pepino, Heterocycles, 24, 2411 (1986).
95. A. Kreutzberger and K. Kolter, Chem. Ztg., 110, 256 (1986).
96. F. De Sarlo, A. Guarna, and A. Brandi, J. Heterocycl. Chem., 20, 1505 (1983).
97. L. Bruche and G. Zecchi, J. Heterocycl. Chem., 20, 1705 (1983).
98. K. Tanaka, H. Masuda, and K. Mitsuhashi, Bull. Chem. Soc. Jpn., 57, 2184 (1984).
99. R. S. Tewari, P. Parinar, and P. D. Dixit, J. Chem. Eng. Data, 28, 281 (1983).
100. A. O. Abdelhamid, C. Parkanyi, A. S. Shawali, and M. A. Abdalla, J. Heterocycl. Chem., 21, 1049 (1984).
101. K. Tanaka, S. Maeno, and K. Mitsuhashi, J. Heterocycl. Chem., 22, 565 (1985).
102. L. Bruche, M. I. Gelmi, and G. Zecchi, J. Org. Chem., 50, 3206 (1985).
103. D. Chiarino, M. Napoletano, and A. Sala, Tetrahedron Lett., 27, 3181 (1986).
104. C. De Micheli, M. De Amici, and M. Sclafi, Farmaco, Ed. Sci., 39, 487 (1984).
105. R. G. Micetich, C. C. Shaw, T. W. Hall, P. Spevak, R. A. Fortier, P. Wolfert, B. C. Foster, and B. K. Bains, Heterocycles, 23, 571 (1985).
106. Y. Shen, J. Zheng, and Y. Huang, Synthesis, No. 10, 970 (1985).
107. K. Tanaka, T. Suzuki, S. Maeno, and K. Mitsuhashi, J. Heterocycl. Chem., 23, 1535 (1986).
108. R. M. Paton and D. G. Hamilton, Tetrahedron Lett., 24, 5141 (1983).
109. R. V. Stevens and K. F. Albizati, Tetrahedron Lett., 25, 4587 (1984).
110. H. M. Hasaneen, R. H. Hilal, and N. M. Elvan, J. Heterocycl. Chem., 21, 1013 (1984).
111. G. Bianchi, C. De Micheli, and R. Gandolfi, Angew. Chem., 91, 781 (1979).
112. P. A. Wade, H.-K. Yen, S. A. Hardinger, M. K. Pillay, N. V. Amin, P. D. Vail, and S. D. Morrow, J. Org. Chem., 48, 1796 (1983).
113. K. Burger and S. Tremmel, Chem. Ztg., 106, 302 (1982).
114. T. Shimizu, Y. Hayashi, and K. Teramura, Bull. Chem. Soc. Jpn., 58, 2519 (1985).
115. D. J. Greig, R. M. Paton, J. G. Rankin, and J. F. Ross, Tetrahedron Lett., 23, 5453 (1982).
116. K. Tanaka, T. Igarashi, S. Maeno, and K. Mitsuhashi, Bull. Chem. Soc. Jpn., 57, 2689 (1984).
117. O. V. Drygina and A. D. Garnovskii, Usp. Khimii, 55, 1495 (1986).
118. R. M. Moriarty, K.-C. Hou, and R. S. Miller, Synthesis, No. 8, 683 (1984).
119. O. Tsuge, S. Kanemaza, and K. Matsuda, Chem. Lett., No. 7, 1131 (1983).
120. T. Aoyama and T. Shioiri, Chem. Pharm. Bull., 30, 3450 (1982).
121. T. Aoyama, K. Sudo, and T. Shioiri, Chem. Pharm. Bull., 30, 3910 (1982).
122. T. Aoyama, M. Kabeya, A. Fukushima, and T. Shioiri, Heterocycles, 23, 2363, 2367 (1985).
123. T. Aoyama, M. Kabeya, and T. Shioiri, Heterocycles, 23, 2371 (1985).
124. T. Aoyama, S. Inoue, and T. Shioiri, Tetrahedron Lett., 25, 433 (1984).

125. S. Inoue, K. Sudo, T. Aoyama, and T. Shioiri, Heterocycles, 21, 620 (1984).
126. T. Aoyama, Y. Iwamoto, and T. Shioiri, Heterocycles, 24, 589 (1986).
127. T. Shioiri, Y. Iwamoto, and T. Aoyama, Heterocycles, 26, 1467 (1987).
128. A. Dondoni, T. Dall'Occo, G. Fantin, M. Fogagnolo, A. Medici, and P. Pedrini, Chem. Commun., No. 4, 258 (1984).
129. T. A. Oster and T. M. Harris, J. Org. Chem., 48, 4307 (1983).
130. A. S. Kostyuk, K. A. Knyaz'kov, S. V. Ponomarev, and I. F. Lutsenko, Zh. Obshch. Khim., 55, 2088 (1985).
131. Ya. G. Bal'on, M. D. Shul'man, and V. E. Paranyuk, Current Topics in Experimental and Clinical Endocrinology. Abstr. Reps. 4th Confeence of Endocrinologists of the Ukrainian SSR [in Russian], Naukova Dumka, Kiev (1987), p. 23.
132. J. I. G. Cadogan (editor), Organophosphorus Reagents in Organic Synthesis, Acad. Press, London (1979), p. 608.
133. Y. Kobayashi, T. Yamashita, and I. Kumadaki, Heterocycles, 21, 492 (1984).
134. A. Alemagna, P. Del Buttero, and E. Ligandro, Tetrahedron, 40, 971 (1984).
135. L. Bruche, L. Garanti, and G. Zecchi, Synthesis, No. 3, 304 (1985).
136. P. B. Rasmussen, U. Pedersen, I. Thomsen, B. Yde, and S.-O. Lawesson, Bull. Soc. Chim. France, No. 1, 11 (1985).
137. B. Golankiewich and P. Januszczyk, Tetrahedron, 41, 5989 (1985).
138. U. Burger and D. Hubl, Chem. Ztg., 110, 89 (1986).
139. J. W. Lyga, Synth. Commun., 16, 163 (1986).
140. E. Zbiral, Tetrahedron Lett., No. 58, 5107 (1970).
141. E. Zbiral and E. Hugl, Phosphorus, 2, 29 (1972).
142. M. Rasberger and E. Zbiral, Monatsh. Chem., 100, 64 (1969).
143. R. L. Webb, B. L. Lam, J. J. Lewis, G. R. Wellman, and C. E. Berkoff, J. Heterocycl. Chem., 19, 639 (1982).
144. R. L. Webb and J. J. Lewis, J. Heterocycl. Chem., 18, 1301 (1981).
145. E. Zbiral and E. Werner, Liebigs Ann., 707, 130 (1967).
146. V. S. Brovarets and B. S. Drach, Zh. Obshch. Khim., 56, 321 (1986).
147. O. P. Lobanov, A. P. Martynyuk, and B. S. Drach, Zh. Obshch. Khim., 50, 2248 (1980).
148. V. S. Brovarets, O. P. Lobanov, and B. S. Drach, Zh. Obshch. Khim., 52, 1438 (1982).
149. V. S. Brovarets, O. P. Lobanov, and B. S. Drach, Zh. Obshch. Khim., 53, 660 (1983).
150. V. S. Brovarets, O. P. Lobanov, and B. S. Drach, Zh. Obshch. Khim., 53, 2015 (1983).
151. B. S. Drach, É. P. Sviridov, and A. V. Kirsanov, Zh. Obshch. Khim., 45, 12 (1975).
152. A. M. Martynyuk, V. S. Brovarets, O. P. Lobanov, and B. S. Drach, Zh. Obshch. Khim., 54, 2186 (1984).
153. W. D. Ollis and S. P. Stanforth, Tetrahedron, 41, 2239 (1985).
154. G. L'abbe, J. Heterocycl. Chem., 21, 627 (1984).
155. B. C. Lipshutz, Chem. Rev., 86, 795 (1986).