Synthesis of *N*-Acyl-, *N*-Sulfonyl-, and *N*-Phosphinylphospha-λ^5-azenes by a Redox-Condensation Reaction Using Amides, Triphenylphosphine, and Diethyl Azodicarboxylate

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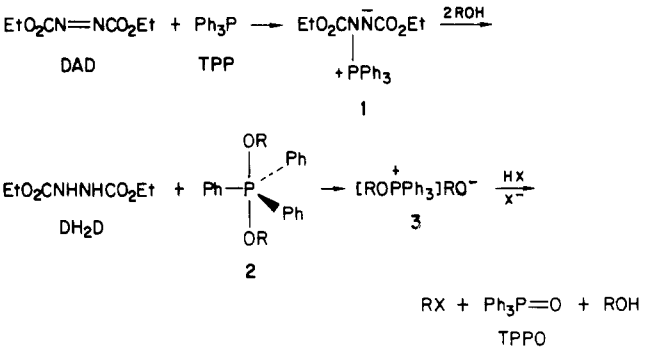
The reaction of phosphines and amides with diethyl azodicarboxylate (DAD) produced phospha-λ^5-azenes. Thus aromatic amides and those aliphatic amides with electron-withdrawing substituents gave *N*-acyl-*P*,*P*,*P*-triphenylphospha-λ^5-azenes (**5**) when triphenylphosphine (TPP) was employed. Both aryl- and alkylsulfonamides reacted with TPP and DAD to produce the *N*-sulfonylphospha-λ^5-azenes (**9**). Diphenylphosphinamide (**10**) and ethyl carbamate (**12**) also produced the respective phosphazenes (**11** and **13**) with TPP and DAD. Secondary carboxamides and sulfonamides did not react with TPP and DAD. The reaction of triethyl phosphite with sulfonamides in the presence of DAD produced the phosphorimidates (**20**) in an analogous reaction, along with the corresponding *N*,*N*-diethylsulfonamides and the deethylated adduct of triethyl phosphite and DAD (**23**). Triethyl phosphite–DAD failed, however, to give a phosphorimidate with carboxamides but gave, instead, the rearranged adduct of DAD and triethyl phosphite (**19**). Tris(dimethylamino)phosphine reacted with sulfonamides and DAD but the products were the corresponding ethyl *N*-sulfonylcarbamates (**26**) rather than the phosphazenes. Tris(dimethylamino)phosphine reacted with azodicarbonamide (a molecule which contains both the azo and carboxamide groups) with the production of *N*,*N*-dimethylurea, again without formation of the phosphazene. Finally, the reaction of triphenylarsine with benzenesulfonamide and DAD produced *N*-(phenylsulfonyl)triphenylarsa-λ^5-azene (**30**) but triphenylstibene with DAD and benzenesulfonamide only gave triphenylstibene oxide. Mechanistic possibilities for these reactions are also discussed.

The use of the redox–condensation system diethyl azodicarboxylate (DAD)–triphenylphosphine (TPP) is well-established.[2,3] Elimination of the elements of water is brought about by the combination of a reducing agent (TPP) and an oxidant (DAD). The betaine, **1**, is the first formed intermediate in all cases and, when an alcohol is a reactant, **1** reacts with the alcohol to produce the quasi-phosphonium salt, **3**, by way of a pentacoordinate phosphorane.[4-6] An S_N2 reaction, where triphenylphosphine oxide (TPPO) is the leaving group then follows. Scheme I shows what has been postulated as the mechanism[5] and includes the dialkoxyphosphorane (**2**) which has been shown to be produced from betaine **1** and 2 equiv of the alcohol, ROH.[4,5] TPP is oxidized to TPPO while DAD is reduced to diethyl hydrazinedicarboxylate (DH_2D). The term "condensation" is somewhat misleading as the redox system catalyzes nucleophilic substitution which is, in this case, the alkylation by alcohols of centers carrying an acidic hydrogen. This reaction has found general use and has been applied to various acidic substrates (e.g., carboxylic acids, phenols, carboximides, active methylene compounds) with pK_a values to about 11.[7] As carboxamides are not acidic enough, it was claimed[7] that no alkylation of such amides is possible by this method. However, it was demonstrated several years ago,[8,9] that a redox–condensation process *does* take place and the phosphorus(III) compound

Scheme I



is indeed oxidized to a phosphorus(V) compound. Instead of dehydration, however, the reaction takes a rather different course, and a condensation occurs between the amide and the phosphine (TPP) to produce *N*-acylphospha-λ^5-azenes. This new phospha-λ^5-azene synthesis is quite a remarkable one in that a phosphaazene is formed directly from the two partners (TPP and RNH_2, R = acyl, sulfonyl and phosphinyl) without the need for activated derivatives as in the classical methods.[10-12] The more common phospha-λ^5-azene preparations involve using either sensitive polyhalophosphorus(V) compounds[13,14] or unstable, and sometimes explosive, organic azides.[10,15] The current procedure offers the advantage of easier handling of the reactants and of occurring at lower temperatures and under neutral, nonpolar conditions. The purpose of the present work was to evaluate the reaction and to study the scope

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(2) Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 94.

(3) Mitsunobu, O. *Synthesis* **1981**, 1 and references cited therein.

(4) Grochowski, E.; Hilton, B. D.; Kupper, R. J.; Michejda, C. J. *J. Am. Chem. Soc.* **1982**, *104*, 6876.

(5) von Itzstein, M.; Jenkins, I. D. *Aust. J. Chem.* **1983**, *36*, 557.

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(7) Wada, M.; Mitsunobu, O. *Tetrahedron Lett.* **1972**, 1279.

(8) Assaf, Y., unpublished results, 1978; Ph.D. Dissertation, Ben-Gurion University, Beer Sheva, Israel, 1983.

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(11) Singh, G.; Zimmer, H. *Organomet. Chem. Rev.* **1967**, *2*, 279.

(12) Bestmann, H. J.; Zimmermann, R. In "Organic Phosphorus Compounds"; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 3, p 1.

(13) Kirsanov, A. V. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1950**, 426; *Chem. Abstr.* **1951**, *45*, 1503.

(14) Horner, L.; Oeidiger, H. *Liebigs Ann. Chem.* **1959**, *627*, 142.

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Table I. Some Properties of the *N*-Acylphospha-λ⁵-azenes (5)

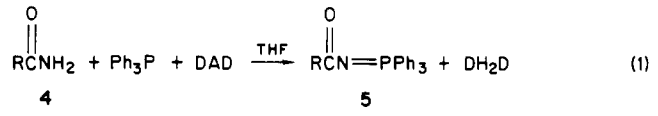
phospha-λ⁵-azene	R	recryst solvent	mp, °C	yield, %	IR, cm⁻¹ [f]
5a	Ph	methanol–water	195–196 [a]	78	1590 (C=O), 1330 (P=N)
5b	p-$NO_2C_6H_4$	methanol	206–207 [b]	69	1605 (C=O), 1520 (NO_2), 1320 (P=N)
5c	o-$CH_3C_6H_4$	methanol–water	155–156	97	1600 (C=O), 1322 (P=N)
5d	p-$CH_3C_6H_4$	methanol–water	152–153 [c]	61	1600 (C=O), 1330 (P=N)
5e	p-ClC_6H_4	methanol–water	180–181 [d]	58	1590 (C=O), 1320 (P=N)
5f	3-C_5H_4N	methanol–water	167–168	60	1595 (C=O), 1335 (P=N)
5g	Cl_3C	ethanol–water	182–183 [e]	62	1640 (C=O), 1310 (P=N)
5h	$ClCH_2$	ethanol–water	159–160	79	1605 (C=O), 1340 (P=N)
5i	CH_2=CH	hexane–ethyl acetate (3:10)	113–114	31	1760 (C=O), 1660 (C=C), 1342 (P=N)

[a] Lit. mp 192–193 °C. Derkach, G. I.; Gubnitskaya, E. S.; Shokol, V. A.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1962**, *32*, 1874; *Chem. Abstr.* **1963**, *58*, 6897. [b] Lit. mp 200–201 °C. Derkach, G. I.; Fedorova, G. K.; Gubnitskaya, E. S. *Zh. Obshch. Khim.* **1963**, *33*, 1017; *Chem. Abstr.* **1963**, *59*, 8783. [c] Lit. mp 153 °C. Lutskii, A. E. Shevchenka, Z. A.; Samara, L. I.; Pinchuk, A. H. *Zh. Obshch. Khim.* **1967**, *37*, 2034; *Chem. Abstr.* **1968**, *68*, 34386. [d] Lit. mp 152–154 °C. Krichedorf, M. R. *Synthesis* **1972**, 695. [e] Lit. mp 180–182 °C. Krichedorf, M. R. *Synthesis* **1972**, 695. [f] All IR spectra were taken in nujol mulls except **5f** which was as a CCl_4 solution.

and limitations of this new, mild method.

Results and Discussion

Reaction of Carboxamides with TPP and DAD. The reaction of aromatic carboxamides (**4a–e**) with equimolar quantities of TPP and DAD in THF at room temperature, under dry N_2, resulted in the formation of *N*-acylphospha-λ⁵-azenes, **5a–e** (eq 1). The products were



(1)

a, R = C_6H_5 f, R = 3-C_5H_4N
b, R = p-$NO_2C_6H_4$ g, R = Cl_3C
c, R = o-$CH_3C_6H_4$ h, R = $ClCH_2$
d, R = p-$CH_3C_6H_4$ i, R = CH_2=CH
e, R = p-ClC_6H_4

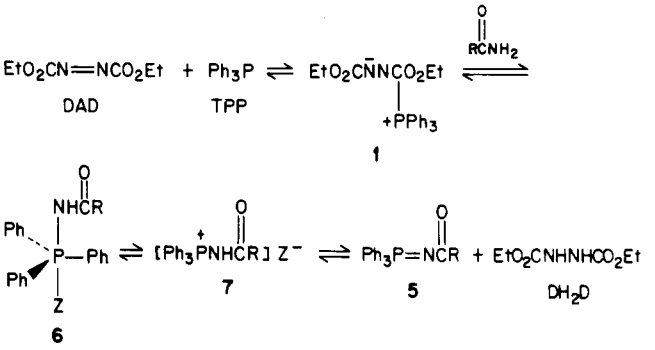
isolated and purified either by crystallization or by chromatographic methods. Table I summarizes some of the physical and spectroscopic data for the *N*-acylphosphaazenes (**5**). These phosphaazenes are stable compounds which melt at fairly high temperatures and decompose only above 150–200 °C to the triphenylphosphine oxide and the aryl cyanide.[15] They are also reasonably stable toward acidic and basic hydrolysis. In their infrared spectra they show two characteristic absorptions, first a C=O absorption at relatively low frequencies (~1600 cm^{-1}) due to the conjugation with the P=N bond and lone pair delocalization. The second, near 1330 cm^{-1}, is the P=N absorption.[16]

Although aromatic amides incorporate TPP oxidatively, simple aliphatic carboxylic amides fail to react under the same experimental conditions. However, aliphatic amides with an electronegative group bonded to the α-carbon atom do react. Thus, while acetamide, propanamide, butanamide, and decanamide failed to react, trichloroacetamide (**4g**), chloroacetamide (**4h**), and even acrylamide (**4i**) produced the corresponding *N*-acylphospha-λ⁵-azenes (**5g–i**). Electron-donating groups or electron-withdrawing groups on the aromatic ring do not seem to influence the reaction when substituted benzamides are used.

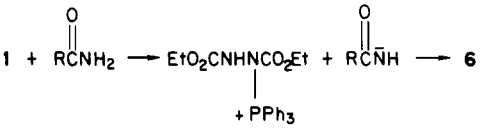
Similar behavior was reported[17] in the formation of trichlorophospha-λ⁵-azenes from amides and PCl_5 (eq 2). In this case aromatic amides and only aliphatic amides bearing electron-withdrawing α-substituents reacted.

$$PCl_5 + RC(=O)NH_2 \rightarrow RC(=O)N=PCl_3 + 2HCl \quad (2)$$

Scheme II



Scheme III



Lower reactivity of aliphatic amides compared to aromatic amides is observed in other transformations as well. Thus, dehydration to nitriles caused by heating with PCl_5 also goes only with aromatic amides or with aliphatic amides containing an α-electron-withdrawing group.[18] With P_2O_5 the dehydration of chloroacetamide proceeds at 100 °C while with isobutyramide it occurs only at 220 °C. It seems that in all of these reactions the electron-withdrawing inductive effect serves to either stabilize an intermediate or to aid in its collapse to products.

Based upon recent studies[4–6,19] the mechanism of formation of **5** shown in Scheme II can be postulated. There is good proof for the formation of betaine **1**[4–6] and, since there is good evidence that a pentacoordinated phosphorane is involved in the Mitsunobu reaction,[4–6] intermediate **6** can be postulated here. In the absence of any data, the nature of the group Z, whether derived from the DAD or another molecule of the amide, must remain unspecified. There is one suggestion that Z is derived from the DAD[19] but there is no compelling evidence although the evidence does suggest a pentacoordinate phosphorane intermediate.[19] Amidophosphonium salts such as **7** have been postulated as intermediates[3] but without any real evidence.

(16) Wiegräbe, W.; Bock, M. *Chem. Ber.* **1968**, *101*, 1414.
(17) Fluck, E.; Haubold, W. In "Organic Phosphorus Compounds"; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1973; Vol. 6.
(18) There are numerous examples in "Organic Syntheses"; Wiley: New York. The following are the collective colume and page numbers: Vol. 2, p 379; Vol. 3, p 493, 535, 584, 464, 646; Vol 4, p 62, 144, 166, 172, 436, 486, 706.
(19) Heesing, A.; Steinkamp, H. *Chem. Ber.* **1982**, *115*, 2854. See also: Penz, G.; Zbiral, E. *Monatsh. Chem.* **1981**, *112*, 1045.

Table II. Some Properties of the *N*-Sulfonylphospha-λ^5-azenes (9)

phosphaazene	R	recryst solvent	mp, °C	yield, %	IR, cm^{-1} [f]
9a	Ph	ethanol	157–158 [a]	95	1265 (SO_2), 1140 (P=N), 805 (SN)
9b	p-$CH_3C_6H_4$	ethanol	190 [b]	98	1270 (SO_2), 1150 (P=N), 780 (SN)
9c	m-$NO_2C_6H_4$	ethanol	168	95	1260 (SO_2), 1148 (P=N), 805 (SN), 1530 (NO_2)
9d	p-$H_2NC_6H_4$	methanol–$CHCl_3$	179–180	98	3430, 3350, 3240 (NH), 1240 (SO_2), 1155 (P=N), 800 (SN)
9e	CH_3	methanol	192–193 [c]	96	1255 (SO_2), 1150 (P=N), 805 SN)
9f	p-$NO_2C_6H_4$	methylene chloride–pentane	230–234 [d]	80	1265 (SO_2), 1144 (P=N), 792 (SN), 1348, 1522 (NO_2)
9g	p-ClC_6H_4	chloroform	212–215 [e]	66	1267 (SO_2), 1151 (P=N), 800 (SN)

[a] Lit. mp 156–157 °C. Shevchenko, V. I.; Stratienko, V. T.; Pinchuk, A. H. *Zh. Obshch. Khim.* **1964**, *34*, 3954; *Chem. Abstr.* **1965**, *62*, 9167d. 9167d. [b] Lit. mp 186–187 °C. Shevchenko, V. I.; Stratienko, V. T.; Pinchuk, A. H. *Zh. Obshch. Khim.* **1964**, *34*, 3954; *Chem. Abstr.* **1965**, *62*, 9167d. [c] Lit. mp 192 °C. Horner, L.; Christmann, A. *Chem. Ber.* **1963**, *96*, 388. [d] Lit. mp 229–231 °C. Garwood, D. G.; Jones, M. P.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 1925. [e] Lit. mp 215–216 °C. Sokol, V. A.; Molyavko, L. I.; Derkach, G. I. *Zh. Obshch. Khim.* **1966**, *36*, 930; *Chem. Abstr.* **1966**, *65*, 12229. [f] All IR spectra were taken as nujol mulls except **9f** and **9g** which were as CCl_4 solutions.

The observation that electron-withdrawing groups favor the reaction might be interpreted in several ways. Thus, for example, it is possible that such groups promote the decomposition of **6** to **7** or, perhaps more likely, favor the reaction of the amide with betaine **1**. Since, in the case of the Mitsunobu reaction, acidity seems important,[7] it could also be that simple aliphatic amides are not acidic enough to react with **1** by the mechanism shown in Scheme III. Unfortunately, to adequately test this hypothesis requires knowing the pK_a's of all (or most) of the amides and, except for a very few, these have not been determined. As a possible speculative probe we reasoned that if the order of acidity of amides follows the order of acidity of carboxylic acids, we might use an aromatic amide whose carboxylic acid pK_a is similar to those of the simple aliphatic acids. If this amide failed to react, it would support the idea that simple aliphatic amides are not sufficiently acidic. The pK_a of nicotinic acid (3-pyridinecarboxylic acid) is 4.85[20] and is close to those of the aliphatic acids (4.7–4.9) in water.[20] When nicotinamide (**4f**) was employed, however, a good yield of the phospha-λ^5-azene, **5f**, was obtained. Unfortunately no definite conclusion can be drawn since this result can be interpreted in two ways. First it is possible that the acidity is not the important factor or second, and perhaps more likely, the pK_a's of carboxylic acids measured in water are poor models for the pK_a's of amides in THF, the solvent for the reactions. Until pK_a values for the amides in THF become available the reasons for the better reaction of amides bearing electron-withdrawing groups must remain speculative.

Reaction of Sulfonamides with TPP and DAD. Sulfonamides with greater acidity than carboxamides were expected to react faster with TPP and DAD (assuming acidity is important) and to yield the corresponding *N*-sulfonylphospha-λ^5-azenes.[11,12,21,22] When sulfonamides **8a–e** were reacted with equimolar quantities of TPP and DAD in dry THF at 0 °C a fast reaction took place and high yields of the sulfonylphospha-λ^5-azenes (**9a–e**) were obtained (Table II; eq 3).

$$\underset{\mathbf{8}}{RSO_2NH_2} + Ph_3P + DAD \xrightarrow[0\ °C]{THF} \underset{\mathbf{9}}{RSO_2N{=}PPh_3} + DH_2D \qquad (3)$$

a, R = Ph; b, R = p-$CH_3C_6H_4$; c, R = m-$NO_2C_6H_4$; d, R = p-$H_2NC_6H_4$; e, R = CH_3; f, R = p-$NO_2C_6H_4$; g, R = p-ClC_6H_4

When comparing the reactions of sulfonamides with those of carboxamides, the following facts are worth mentioning: (a) The reactions with the sulfonamides are very fast even at 0 °C. TLC shows almost immediate formation of products, and the reaction is complete within 40–60 min. (b) The yields of *N*-sulfonylphospha-λ^5-azenes are generally close to quantitative. (c) The reaction proceeds both with aromatic and aliphatic sulfonamides. (d) Products are easy to isolate and in most cases they precipitate directly from the reaction mixture in almost pure form. Of further interest is the observation that *p*-aminobenzenesulfonamide afforded in nearly quantitative yield the [(*p*-aminophenyl)sulfonyl]phospha-λ^5-azene with no observable reaction at the free amino group. None of the known methods[13,14,23,24] for synthesizing phospha-λ^5-azenes is specific in this way. The sulfonylphosphaazenes (**9**) show characteristic infrared absorptions at ca. 1150 (P=N), 800 (SN), and 1250 cm^{-1} (conjugated SO_2).[16]

Scheme IV

$$Ph_3P + Me_3SiN_3 \xrightarrow{-N_2} \underset{\mathbf{14}}{Ph_3P{=}NSiMe_3}$$

$$\mathbf{14} + EtOC(=O)Cl \xrightarrow{Pyridine} \underset{\mathbf{13}}{Ph_3P{=}NC(=O)OEt}$$

The simplicity of this reaction, its mild conditions, the high yields, and the ease of product isolation all make this reaction the method of choice for the synthesis of *N*-sulfonyltriphenylphospha-λ^5-azenes.

Reaction of Other Amides with TPP and DAD. To gain a better understanding of the reaction, it was run with two other types of primary amides and with secondary amides. Diphenylphosphinamide (**10**) reacted with TPP in the same way as the sulfonamides and carboxamides and yielded the (triphenylphosphinyl)phospha-λ^5-azene, **11**, in 76% yield (eq 4). The P=N absorption in the IR (1280 cm^{-1}) and the UV maximum at 265.5 nm (log ϵ = 3.48) are in good agreement with the data in the literature.[25]

$$\underset{\mathbf{10}}{Ph_2P(=O)NH_2} + TPP + DAD \rightarrow \underset{\mathbf{11}}{Ph_2P(=O)N{=}PPh_3} \qquad (4)$$

Ethyl carbamate (**12**) similarly produced the carbethoxyphospha-λ^5-azene, **13**, in 48% yield when reacted with TPP and DAD (eq 5). **13** also showed its phosphaazene

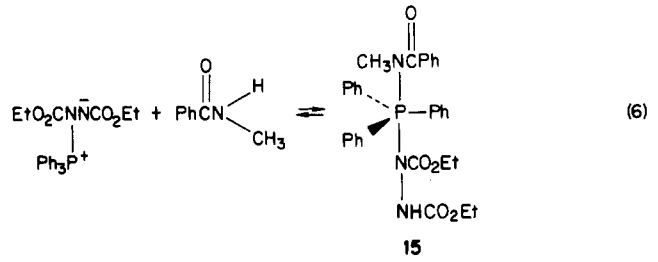
$$\underset{\mathbf{12}}{EtOC(=O)NH_2} + TPP + DAD \rightarrow \underset{\mathbf{13}}{EtOC(=O)N{=}PPh_3} \qquad (5)$$

(P=N) absorption at 1280 cm^{-1}.[16] This method comple-

(20) "Handbook of Chemistry and Physics", 50th ed.; Weast, R. C., Ed.; Chemical Rubber Co.: Cleveland, OH, 1969; p D118.
(21) Johnson, A. W. "Ylid Chemistry"; Academic Press: New York, 1966; p 217.
(22) Abel, G. W.; Mucklejohn, S. A. *Phosphorus Sulfur* **1982**, *9*, 235.
(23) Mann, P. G.; Chaplin, E. J. *J. Chem. Soc.* **1937**, 527.
(24) Senning, A. *Agew. Chem., Int. Ed. Engl.* **1965**, *4*, 357.
(25) Baldwin, R. A.; Washburn, R. M. *J. Org. Chem.* **1965**, *30*, 2093, 3860.

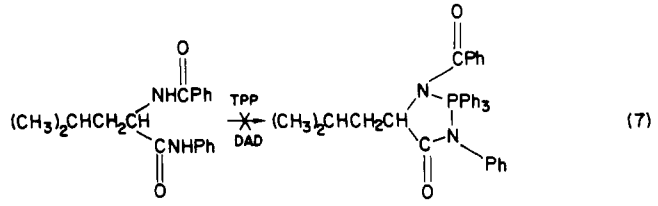
ments existing methods for the synthesis of phosphaazenes of type **13** and avoids the use of potentially explosive azidoformates.[16] It is also shorter than the two step process previously employed as shown in Scheme IV.[26]

Since secondary amides cannot form stable phosphaazenes, it was anticipated that their reaction with TPP and DAD would either take a totally different course or would not occur at all. In fact, no reaction is observed under a variety of experimental conditions when *N*-methylbenzamide is treated with TPP and DAD. The amide can be recovered quantitatively. This lack of reactivity can either be the result of the reduced acidity of the amide hydrogen or of the reversal of the potential phosphorane intermediate (e.g., **15**) back to reactants (eq 6). Such diaminophosphoranes are known to be rather



15 (6)

unstable.[27,28] An attempt to trap the potential phosphorane intermediate as a cyclic phosphorane, which would be expected to be somewhat more stable than **15**, by using a diamide derived from leucine also failed. This is shown in eq 7. In addition, N-monosubstituted sulfonamides were similarly inert to TPP and DAD, however, in the presence of an alcohol N-alkylation occurred.



(7)

We should also point out that aromatic amines, including those with electron-withdrawing groups, such as *p*-Cl-, NO_2-, and CH_3O_2C-, do not react with TPP and DAD under our experimental conditions (THF, 0 °C). This is to be contrasted with the results of Niclas and Martin[9] who observe reaction with nitroanilines, but their conditions are considerably more vigorous than those used here.

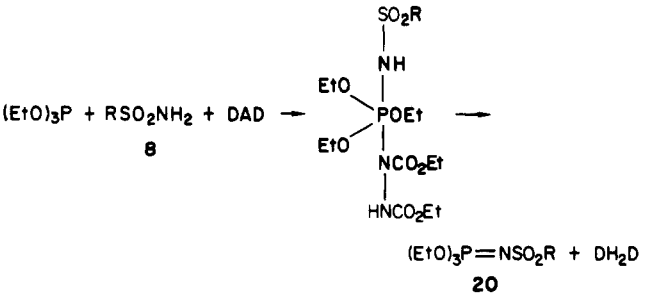
Reaction of Primary Amides with Trialkyl Phosphites and Tris(dialkylamino)phosphines. We next examined the reaction of trialkyl phosphites with primary amides again to see if reactions analogous to those described here might occur to produce trialkylphosphorimidates, **16** (eq 8).

$$RNH_2 + (EtO)_3P + DAD \rightarrow \underset{\mathbf{16}}{(EtO)_3P{=}NR} + DH_2D \quad (8)$$

R = acyl, sulfonyl

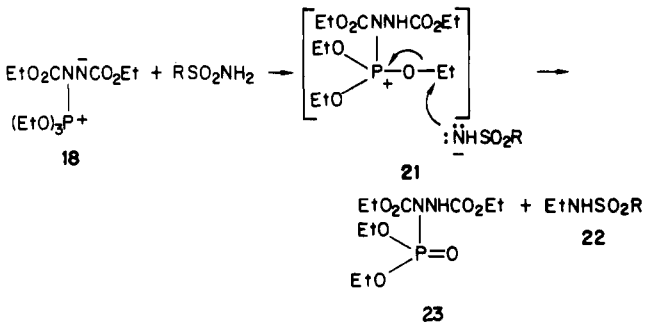
It is known that compounds of the type **16** are quite reactive compared to the phosphaazenes prepared from phosphines. They hydrolyze easily[22] and tend to undergo

Scheme V



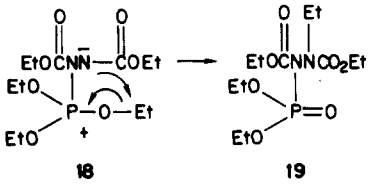
a, R = C_6H_5; b, R = *p*-$CH_3C_6H_4$

Scheme VI



the imidate–amidate rearrangement[29] with transfer of an alkyl group from oxygen to nitrogen forming the more stable isomer, $R_2NP(=O)(OR)_2$ (**17**). The acylphosphorimidates (**16**) also react with nucleophiles forming both N- and O-alkylated products.[10]

It has also been shown that the reaction of triethyl phosphite with DAD yields an adduct (**18**) which, in the absence of an external nucleophile, reacts internally to form diethyl *N*-ethyl-*N'*-(diethylphosphinyl)hydrazinedicarboxylate (**19**).[30] If this internal reaction (**18** → **19**) is faster than the phosphorimidate (**16**) formation, then only the former will occur and not the latter. Indeed reacting benzamide or *p*-chlorobenzamide with equimolar quantities of triethylphosphite and DAD at 0 °C under anhydrous conditions did not yield any phosphorimidate. The carboxamide was quantitatively recovered together with the phosphinylhydrazine **19**.[30]



Different results, however, were obtained in the reaction of DAD and phosphites with the much more acidic arylsulfonamides. The mixture of products obtained suggested several competing reactions. One of these was indeed the desired reaction as evidenced by isolation of the known trialkylphosphorimidates **20a,b**[31] from the reaction mixture (Scheme V). The IR spectrum showed both P=N (1148 cm^{-1}) and POC (1030 cm^{-1}) but P=O or NH absorptions. Another product isolated was the corresponding *N,N*-di-

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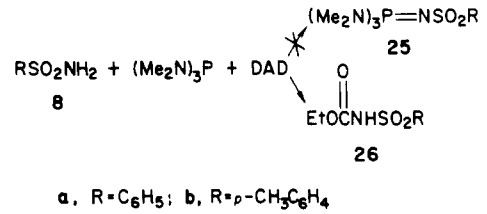
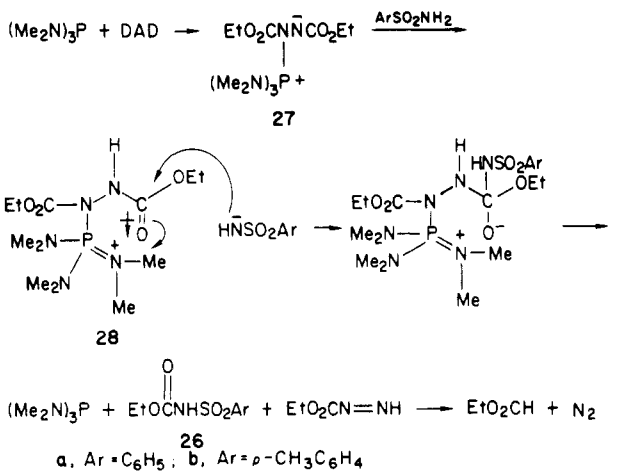
Scheme VII



Scheme VIII



ethylsulfonamide. This product must be the result of a competing alkylation which can be described as follows (Scheme VI). The high acidity of the sulfonamide readily leads to the formation of salt **21** from **18**. An alkylation reaction as shown, will then give the products, **22** and **23**. The same reaction repeats itself with the monosubstituted sulfonamide, and the end product is then the *N,N*-diethylsulfonamide **24a,b**. The phosphinylhydrazine **23** was also isolated and characterized.[32]

$$\mathbf{18}\text{ and }\mathbf{22} \rightarrow \underset{\mathbf{24}}{Et_2NSO_2R}$$

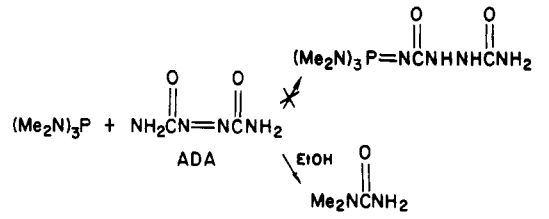
a, R = C_6H_5

b, R = *p*-$CH_3C_6H_4$

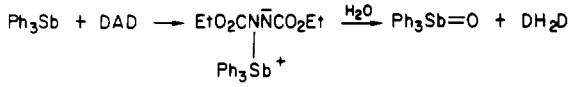
To summarize, trialkylphosphorimidates are *not* obtained from the reaction of trialkyl phosphites with carboxamides. The competing reaction between the phosphite and DAD prevails and produces a rearranged product (**19**). Trialkoxyphosphorimidates of the type $(RO)_3P{=}NSO_2R$ are obtained by reacting trialkyl phosphites with sulfonamides in the presence of DAD. The yields are low due to the competing dialkylation of the sulfonamide.

Phosphaazenes (**25**) derived from tris(dimethylamino)phosphine are labile[10] compounds that tend to undergo tautomerism, rearrangement,[33] or interaction with other functional groups in the molecule.[34] In order to see if these compounds could be prepared by the new method, we reacted tris(dimethylamino)phosphine with aromatic sulfonamides as above. The reaction did not yield any phosphaazene derivatives but instead produced ethyl

Scheme IX

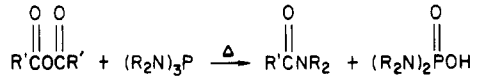


Scheme X



N-sulfonylcarbamate[35] (**26a,b**, Scheme VII). Compound **26** can be considered to come about by the mechanism shown in Scheme VIII. Tris(dimethylamino)phosphine and DAD react to form an adduct, **27**, analogous to that formed with TPP and DAD. Proton transfer from the acidic sulfonamide gives cation **28** and the sulfonamide anion. The positive charge on the phosphorus and nitrogen atoms in **28** could serve to activate the carbonyl toward nucleophilic attack thus ultimately producing **26**. A similar explanation has been suggested for the formation of mixed carbonates from tris(dimethylamino)phosphine, DAD and alcohols.[36]

We have also observed another reaction of tris(dimethylamino)phosphine but similar to that between **18** and **8** and **22** to give **24**. We recently reported on the reaction of trialkyl- and triarylphosphines with azodicarbonamide (ADA) which produces *N*-semicarbazidophosphaazenes.[37] This reaction is a variant of those reactions discussed here. When we attempted the reaction of tris(dimethylamino)phosphine with ADA the expected phosphaazene was not produced. Instead, dimethylamidation of the amidic carbonyl occurred, yielding 97% of *N,N*-dimethylurea (Scheme IX). Tris(dialkylamino)phosphines are known to cause aminations, usually producing dialkylamides of carboxylic acids.[38-42] For example, heating of carboxylic anhydrides with tris(dialkylamino)phosphines yields dialkylamides.[38] Similarly, *N,N,N',N'*-tetramethylterephthaldiamide was formed from terephthaloyl chloride and tris(dimethylamino)phosphine.[39] Without additional information mechanistic speculation is premature.



Reaction of Amides with Triphenylarsine and Triphenylstibine. Finally, we attempted to react triphenylarsine and triphenylstibine with aromatic amides and sulfonamides. The possibility of synthesizing arsa-λ^5-azenes[43] and stiba-λ^5-azenes[44] was rather intriguing.

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Equimolar quantities of triphenylarsine, DAD, and benzenesulfonamide were reacted in THF under anhydrous conditions; within 1 h a precipitate formed which was identified as the known[45] sulfonylarsaazene, **30** (eq 9). A

$$Ph_3As + H_2NSO_2Ph + DAD \xrightarrow[0\ °C]{THF} Ph_3As{=}NSO_2Ph + DH_2D \quad (9)$$
30

similar reaction with triphenylstibine did not yield a stibaazene product but instead $Ph_3Sb{=}O$ was isolated. It is possible that the adduct between Ph_3Sb is formed but is quite unstable relative to hydrolysis, even in the presence of minute quantities of water, and thus produces the oxide and DH_2D (Scheme X).

Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 377 or 599B spectrophotometer and NMR spectra on a Varian XL-100, T-60, or Nicolet NT-200 WB instrument as solutions in $CDCl_3$ (except where noted) with tetramethylsilane as an internal standard. Elemental analyses were determined by the Microanalytical Labs at the Hebrew University in Jerusalem or Galbraith Laboratories, Knoxville, TN. Some of the amides and sulfonamides were obtained from commercial suppliers and were used without further purification while others were made by standard methods. THF was distilled from $LiAlH_4$ immediately prior to use. All reactions involving phosphines, phosphites, or diethyl azodicarboxylate, were carried out under dry nitrogen or argon with oven-dried glassware.

***N*-Acyl- and *N*-Sulfonylphospha-λ⁵-azenes. General Procedure.** To a well-stirred solution of triphenylphosphine (1.31 g, 5 mmol) in dry tetrahydrofuran (10 mL), under an atmosphere of dry nitrogen, was added the amide (5 mmol). The mixture was cooled to 0 °C and diethyl azodicarboxylate (0.87 g, 5 mmol) in tetrahydrofuran (5 mL) was injected dropwise through a rubber septum (5 min). The mixture was allowed to warm and left at room temperature for 12 h. The tetrahydrofuran was evaporated under vacuum and the phosphaazene was washed with cold ether and recrystallized from the solvent shown in Tables I and II. In some cases column chromatography (silica gel) was used for purification.

***N*-Benzoyltriphenylphospha-λ⁵-azene (5a)**: NMR δ 7.4 (m, ArH); ^{31}P NMR ($CDCl_3$, with 85% H_3PO_4 as external standard) δ 21.07.[46] Anal. Calcd for $C_{25}H_{20}NOP$: C, 78.72; H, 5.28; N, 3.67; P, 8.12. Found: C, 78.73; H, 5.25; N, 3.54; P, 8.20.

***N*-(*p*-Nitrobenzoyl)triphenylphospha-λ⁵-azene (5b)**: NMR δ 7.5 (m, 15 H, ArH), 8.29 (m, 4 H, ArH). Anal. Calcd for $C_{25}H_{19}N_2O_3P$: C, 70.42; H, 4.49; N, 6.57; P, 7.26. Found: C, 70.62; H, 4.62; N, 6.47; P, 7.40.

***N*-*o*-Toluoyltriphenylphospha-λ⁵-azene (5c)**: NMR δ 2.6 (s, 3 H, CH_3), 7.6 (m, 19 H, ArH). Anal. Calcd for $C_{26}H_{22}NOP$: C, 78.97; H, 5.60; N, 3.54; P, 7.83. Found: C, 78.86; H, 5.56; N, 3.70; P, 7.76.

***N*-*p*-Toluoyltriphenylphospha-λ⁵-azene (5d)**: NMR δ 2.3 (s, 3 H, CH_3), 7.6 (m, 19 H, ArH). Anal. Calcd for $C_{26}H_{22}NOP$: C, 78.97; H, 5.60; N, 3.54; P, 7.83. Found: C, 78.72; H, 5.45; N, 3.40; P, 7.68.

***N*-(*p*-Chlorobenzoyl)triphenylphospha-λ⁵-azene (5e)**: NMR δ 7.6 (m, 15 H, ArH), 8.05 (m, 4 H, ArH); ^{31}P NMR (85% H_3PO_4 external standard) δ 21.42.[46a] Anal. Calcd for $C_{25}H_{19}ClNOP$: C, 72.20; H, 4.60; Cl, 8.52; N, 3.37; P, 7.45. Found: C, 72.10; H, 4.53; Cl, 8.27; N, 3.26; P, 7.39.

***N*-(3-Pyridylcarbonyl)triphenylphospha-λ⁵-azene (5f)**: NMR δ 7.30 (dd, 1 H, J = 5 and 8 Hz, H-5 on pyr), 7.52 (m, 9 H, ArH), 7.82 (m, 6 H, ArH), 8.50 (dt, 1 H, J = 2 and 8 Hz, H-4 on pyr), 8.65 (dd, 1 H, J = 2 and 5 Hz, H-6 on pyr), 9.56 (d, 1 H, J = 2 Hz, H-2 on pyr); ^{31}P NMR δ 21.62.[47] Anal. Calcd for $C_{24}H_{19}N_2OP$: C, 75.38; H, 5.01; N, 7.33. Found: C, 75.59; H, 4.94; N, 7.24.

***N*-(Trichloroacetyl)triphenylphospha-λ⁵-azene (5g)**: NMR δ 7.6 (m, ArH). Anal. Calcd for $C_{20}H_{15}Cl_3NOP$: C, 56.83; H, 3.58; N, 3.31; P, 7.33. Found: C, 56.82; H, 3.51; N, 3.19; P, 7.50.

***N*-(Chloroacetyl)triphenylphospha-λ²-azene (5h)**: NMR δ 4.2 (s, 2 H, CH_2), 7.5 (m, 15 H, ArH). Anal. Calcd for $C_{20}H_{17}ClNOP$: C, 68.90; H, 4.84; Cl, 10.02; N, 3.71; P, 8.75. Found: C, 68.72; H, 4.69; Cl, 9.93; N, 3.75; P, 8.90.

***N*-Acrylyltriphenylphospha-λ⁵-azene (5i)**: NMR δ 5.5 (m, 1 H, C=CH), 6.3 (d, 1 H, C=CH), 6.4 (d, 1 H, C=CH), 7.5 (m, 15 H, ArH). Anal. Calcd for $C_{21}H_{18}NOP$: C, 76.12; H, 5.47; N, 4.23; P, 9.35. Found: C, 76.03; H, 5.47; N, 4.16; P, 9.19.

***N*-(Phenylsulfonyl)triphenylphospha-λ⁵-azene (9a)**: NMR δ 7.2 (m, ArH). Anal. Calcd for $C_{24}H_{20}NO_2PS$: C, 69.05; H, 4.83; N, 3.35; P, 7.42. Found: C, 68.91; H, 5.01; N, 3.33; P, 7.60.

***N*-(*p*-Tolylsulfonyl)triphenylphospha-λ⁵-azene (9b)**: NMR δ 2.24 (s, 3 H, CH_3), 7.3 (m, 19 H, ArH). Anal. Calcd for $C_{25}H_{22}NOPS$: C, 69.60; H, 5.14; N, 3.25; P, 7.18. Found: C, 69.58; H, 5.23; N, 3.22; P, 7.21.

***N*-[(*m*-Nitrophenyl)sulfonyl]triphenylphospha-λ⁵-azene (9c)**: NMR δ 7.15–8.2 (m, ArH). Anal. Calcd for $C_{24}H_{19}O_4N_2PS$: C, 62.60; H, 4.13; N, 6.08; P, 6.74. Found: C, 62.58; H, 4.20; N, 6.15; P, 6.69.

***N*-[(*p*-Aminophenyl)sulfonyl]triphenylphospha-λ⁵-azene (9d)**: NMR (CD_3COCD_3) δ 3.0 (br s, 2 H, NH_2), 6.8 (dd, 4 H, ArH), 7.5 (m, 15 H, ArH); ^{31}P NMR δ 14.23.[47] Anal. Calcd for $C_{24}H_{21}N_2OPS$: C, 66.65; H, 4.89; N, 6.48; P, 7.16. Found: C, 66.77; H, 4.88; N, 6.35; P, 6.97.

***N*-(Methylsulfonyl)triphenylphospha-λ⁵-azene (9e)**: NMR δ 2.7 (s, 3 H, CH_3), 7.6 (m, 15 H, ArH). Anal. Calcd for $C_{19}H_{18}NO_2PS$: C, 64.21; H, 5.10; N, 3.94; S, 8.46; P, 8.71. Found: C, 63.99; H, 5.28; N, 4.04; S, 8.77; P, 8.59.

***N*-[(*p*-Nitrophenyl)sulfonyl]triphenylphospha-λ⁵-azene (9f)**: NMR δ 7.4–7.8 (m, 17 H, ArH), 8.03 (m, 2 H, ArH); ^{31}P NMR δ 16.89.[47]

***N*-[(*p*-Chlorophenyl)sulfonyl]triphenylphospha-λ⁵-azene (9g)**: NMR δ 7.16 (m, 2 H, ArH), 7.4–7.8 (m, 17 H, ArH); ^{31}P NMR δ 15.62.[47]

***N*-(Diphenylphosphinyl)triphenylphospha-λ⁵-azene (11).** Diphenylphosphinamide[48] (0.54 g, 2.5 mmol) was added to a mixture of triphenylphosphine (0.66 g, 2.5 mmol) in dry THF (5 mL) under an atmosphere of dry N_2. The suspension was stirred at 0 °C and diethyl azodicarboxylate (0.44 g, 2.5 mmol) in dry THF (5 mL) was added dropwise. During the addition, the suspension cleared and attained an orange color. The mixture was warmed to ambient temperature and stirred for an additional 24 h (TLC showed no starting material). The solvent was removed by a stream of nitrogen and the product was isolated by column chromatography by using silica gel and eluting with ethyl acetate–petroleum ether (1:1). The crude phosphinylphosphaazene was recrystallized from isopropyl alcohol–water: yield 0.90 g (76%); mp 171–172 °C (lit.[25] mp 170–171 °C); IR (nujol) 1280 (P=N), 1175 cm^{-1} (P=O); NMR (Me_2SO-d_6) δ 7.2–7.6 (m, ArH). Anal. Calcd for $C_{30}H_{25}NOP_2$: C, 75.46; H, 5.28; N, 2.93; P, 12.97. Found: C, 75.30; H, 5.26; N, 3.05; P, 12.77.

***N*-(Ethoxycarbonyl)triphenylphospha-λ⁵-azene (13).** To a well stirred and cooled solution of triphenylphosphine (1.31 g, 5 mmol) and ethyl urethane (0.44 g, 5 mmol) in dry THF (10 mL), diethyl azodicarboxylate (0.87 g, 5 mmol) in THF (5 mL) was added dropwise. The mixture was warmed to room temperature (1 h) and the solvent evaporated in vacuo. Treatment with ethyl acetate–petroleum ether precipitated diethyl hydrazinedicarboxylate and the product was isolated by column chromatography by using silica gel and eluting with ethyl acetate. The crude phosphaazene was recrystallized from ether: yield 0.83 g (48%); mp 134–136 °C (lit.[16] mp 136–137 °C); IR (nujol) 1630 (C=O), 1280 (P=N), 1100 cm^{-1} (CO); NMR δ 1.0 (t, 3 H, CH_3), 3.75 (q, 2 H, CH_2), 7.1–7.5 (m, 15 H, ArH). Anal. Calcd for $C_{21}H_{20}NOP$: C, 72.20; H, 5.73; N, 4.01; P, 8.88. Found: C, 72.37; H, 5.91; N, 3.89; P, 8.72.

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(46) (a) Recorded on a Bruker CXP-300 instrument at 121.5 MHz. (b) Lit. δ 20.6. Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Org. Chem.* **1976**, *41*, 2716.

(47) Taken on a Nicolet NT-200 WB spectrometer at 80.99 MHz.

(48) Kreutzkamp, N.; Schindler, H. *Arch. Pharm. (Athens)* **1960**, *293*, 296.

Reaction of *p*-Chlorobenzamide with Triethyl Phosphite. To a cold solution of *p*-chlorobenzamide (155 mg, 1 mmol) and triethyl phosphite (166 mg, 1 mmol) in anhydrous THF (5 mL) was added a solution of diethyl azodicarboxylate (174 mg, 1 mmol) in 5 mL of anhydrous THF. The solution was allowed to warm to room temperature and stirred for another 12 h. The solvent was removed in vacuo and the oily mixture was separated on preparative TLC plates. The *p*-chlorobenzamide was quantitatively isolated (153 mg) and a second substance isolated as an oil (98 mg) was identified as the diethyl *N*-ethyl-*N'*-(diethylphosphoryl)hydrazodicarboxylate (**19**):[30] IR (nujol) 1730 (C=O), 1260 (P=O), 1055 cm^{-1} (POC); NMR δ 1.0 (t, 3 H, CH_3CH_2N), 1.15 (m, 12 H, CH_3CH_2OP, $CH_3CH_2OC{=}O$), 3.2 (q, 2 H, CH_3CH_2N), 4.0–4.5 (m, 8 H, CH_3CH_2OP, CH_3CH_2OCO).

Reaction of Benzenesulfonamide with Triethyl Phosphite. When the procedure described above was used, 157 mg (1 mmol) of benzenesulfonamide was reacted with 249 mg (1.5 mmol) of triethyl phosphite and 358 mg (2 mmol) of diethyl azodicarboxylate. The mixture of products was separated by silica gel chromatography and further purified with preparative silica gel plates. In addition to diethyl hydrazinedicarboxylate and 18% of starting materials, three products were obtained. The first was triethyl *N*-(phenylsulfonyl)phosphorimidate (**20a**):[31] oil; 37% yield; IR (neat) 1270 (SO_2), 1150 (P=N), 1030 (POC), 805 cm^{-1} (SN); NMR δ 1.28 (t, 9 H, CH_3CH_2O), 4.2 (quintet, 6 H, CH_3CH_2O), 7.25–7.4 (m, 3 H, ArH), 7.78–7.92 (m, 2 H, ArH); mass spectrum (70 eV), *m/z* 321 (M^+).[49] The second was *N,N*-diethylbenzenesulfonamide (**24a**): mp 40 °C (lit.[50] mp 42 °C); 12% yield; IR (nujol) 1310 (SO_2), 1152 cm^{-1} (SO_2); NMR δ 1.0 (t, 6 H, CH_3CH_2N), 3.5 (q, 4 H, CH_3CH_2N), 7.4 (m, 3 H, ArH), 7.9 (m, 2 H, ArH). The third compound was diethyl *N*-(diethylphosphoryl)hydrazinedicarboxylate (**23**):[32] oil; 16% yield; IR (neat), 3250 (NH), 1740 (C=O),[32b,c] 1270, 1220 (P=O),[32b,c] 1030 cm^{-1} (POC); NMR δ 1.15 (m, 12 H, CH_3CH_2OP, CH_3CH_2OCO), 4.0–4.5 (m, 8 H, CH_3CH_2OP, CH_3CH_2OCO); mass spectrum (70 eV), *m/z* 312 (M^+).[49]

Reaction of *p*-Toluenesulfonamide with Triethyl Phosphite. When the same procedure described above was used, 0.43 g (2.5 mmol) of *p*-toluenesulfonamide was reacted with triphenylphosphine (0.66 g, 2.5 mmol) and diethyl azodicarboxylate (0.44 g, 2.5 mmol). The compounds isolated from the reaction mixture were first triethyl *N*-(*p*-tolylsulfonyl)phosorimidate (**20b**):[31] oil; 44% yield; IR (neat) 1272 (SO_2), 1150 (P=N), 1025 (POC), 800 cm^{-1} (SN); NMR δ 1.2 (t, 9 H, CH_3CH_2O), 2.25 (s, 3 H, CH_3Ar), 4.05 (quintet, 6 H, CH_3CH_2O) 7.3–7.6 (dd, 4 H, ArH). Second was *N,N*-diethyl-*p*-toluenesulfonamide (**24b**): mp 65 °C (lit.[51] mp 64 °C); IR (nujol) 1308 (SO_2), 1155 cm^{-1} (SO_2); NMR δ 1.1 (t, 6 H, CH_3CH_2N), 2.3 (s, 3 H, CH_3Ar), 3.5 (q, 4 H, CH_3CH_2N), 7.1, 7.8 (dd, 4 H, ArH). Third was diethyl *N*-(diethylphosphoryl)hydrazinedicarboxylate (**23**). It showed the same properties as described above.

Reaction of Benzenesulfonamide with Tris(dimethylamino)phosphine. To a solution of 0.78 g (5 mmol) of benzenesulfonamide and 0.82 g (5 mmol) of tris(dimethylamino)-phosphine in 5 mL of anhydrous THF under N_2 at 0 °C was added 0.87 g (5 mmol) of diethyl azodicarboxylate dissolved in 5 mL of THF. The solution turned pink and some gas evolution could be seen. After stirring at room temperature for another 2 h the solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 and run through a silica gel column. The product, ethyl *N*-(phenylsulfonyl)carbamate (**26a**) was obtained as a yellow oil (0.41 g, 35%):[41] IR (neat) 3220 (NH), 1700 (C=O), 1440, 1350 (SO_2), 1160 cm^{-1} (SO_2); NMR δ 1.12 (t, 3 H, CH_3CH_2O), 4.03 (q, 2 H, CH_3CH_2O), 7.26–7.52 (m, 3 H, ArH), 7.77–7.93 (m, 2 H, ArH).

Ethyl *N*-(*p*-tolylsulfonyl)carbamate (26b) was obtained by using the same procedure as above but with *p*-toluenesulfonamide: yield 0.39 g (33%); oil;[41] IR (neat) 3200 (NH), 1695 (C=O), 1440, 1340 (SO_2), 1160 cm^{-1} (SO_2); NMR δ 1.20 (t, 3 H, CH_3CH_2O), 2.4 (s, 3 H, CH_3Ar), 4.10 (q, 2 H, CH_3CH_2O), 7.22, 7.81 (dd, 4 H, ArH).

Reaction of Azodicarbonamide with Tris(dimethylamino)phosphine. *N,N*-Dimethylurea. A mixture of azodicarbonamide (0.53 g, 5.5 mmol) and tris(dimethylamino)phosphine (0.89 g, 5.5 nmol) in ethanol (10 mL) was refluxed for 2 h. During the reaction the evolution of a gas (N_2) was observed. The solvent was removed under vacuum and the residue was warmed with methylene chloride (10 mL) and allowed to cool. Crystallization of *N,N*-dimethylurea started almost immediately and was complete after 12 h at 0 °C: yield 0.47 g (97%); mp 182 °C (lit.[52] mp 182 °C); IR (nujol) 3380, 3200 (NH), 1610 (C=O), 1520, 1310, 1130, 1100, 1060 cm^{-1}; NMR δ 2.87 (s, 6 H, CH_3N), 4.3–4.8 (broad s, 2 H, NH_2). Anal. Calcd for $C_3H_8N_2O$: C, 40.90; H, 9.09; N, 31.81. Found: C, 41.04; H, 9.21; N, 31.59.

***N*-(Phenylsulfonyl)triphenylarsa-λ^5-azene (30).** To a solution of triphenylarsine (1.53 g, 5 mmol) and benzenesulfonamide (0.78 g, 5 mmol) in anhydrous THF (10 mL) at 0 °C was added diethyl azodicarboxylate (0.87 g, 5 mmol). The mixture was allowed to warm to room temperature and stirred for another 90 min. The precipitate which formed was filtered and recrystallized from THF: yield 0.75 g, 32%; mp 148–150 °C (lit.[45] mp 152–55 °C); IR (nujol) 1300, 1260 (SO_2), 1130, 1080, 1030, 1015, 990 (As=N), 770 (SN), 735, 690, 590, 560 cm^{-1} (AsC); NMR δ 7.1–7.6 (m, ArH). Anal. Calcd for $C_{24}H_{20}AsNO_2S$: C, 62.24; H, 4.36; N, 3.03; S, 6.94. Found: C, 62.14; H, 4.25; N, 3.21; S, 6.66.

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Registry No. **4a**, 55-21-0; **4b**, 619-80-7; **4c**, 527-85-5; **4d**, 619-55-6; **4e**, 619-56-7; **4f**, 98-92-0; **4g**, 594-65-0; **4h**, 79-07-2; **4i**, 79-06-1; **5a**, 17436-52-1; **5b**, 17437-54-6; **5c**, 95978-80-6; **5d**, 95978-81-7; **5e**, 39814-89-6; **5f**, 95978-82-8; **5g**, 17437-50-2; **5h**, 76908-68-4; **5i**, 95978-83-9; **8a**, 98-10-2; **8b**, 70-55-3; **8c**, 121-52-8; **8d**, 63-74-1; **8e**, 60-35-5; **8f**, 6325-93-5; **8g**, 98-64-6; **9a**, 1056-25-3; **9b**, 1058-14-6; **9c**, 13904-34-2; **9d**, 95978-84-0; **9e**, 1497-64-9; **9f**, 19871-19-3; **9g**, 7301-73-7; **10**, 5994-87-6; **11**, 2156-69-6; **12**, 51-79-6; **13**, 17437-51-3; **19**, 95978-85-1; **20a**, 7109-07-1; **20b**, 4779-09-3; **23**, 18370-70-2; **24a**, 1709-50-8; **24b**, 649-15-0; **26a**, 32111-09-4; **26b**, 5577-13-9; **30**, 22007-82-5; DH_2D, 4114-28-7; TPP, 603-35-0; DAD, 1972-28-7; ADA, 123-77-3; $Me_2NC(O)NH_2$, 598-94-7; $Ph_3Sb{=}O$, 4756-75-6; $(EtO)_3P$, 122-52-1; $(Me_2N)_3P$, 1608-26-0; Ph_3AS, 603-32-7; Ph_3Sb, 603-36-1.

(49) The mass spectrum was obtained on a Varian-MAT 112 GC–mass spectrometer.

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