at 532–535 mμ) and **2b** (peak at 460–464 mμ). Compounds with a rigid molecular structure are being prepared in order to test this point.

Since the electronic transitions occurring in **1** and **3** should not be significantly different from those in **2a** and **2b**, an equilibrium constant between the conformers can be calculated. Assuming our assignments of respective conformations and absorption maxima to be correct, form **2b** is favored over **2a** in the ground state by a ratio of 53:45. The slight destabilization of **2a** relative to **2b** in the ground state (assuming a negligible entropy differential) must then be entirely overcome by resonance stabilization amounting to at least 8.8 kcal in the excited state. Lack of a measurable solvent effect on the visible spectra suggests that the low-energy transition occurs without wide charge separation characteristic of normal charge-transfer complexes.[15]

(15) In response to a referee's comment it is perhaps worth noting here that the monoketones related to **1** and to **3** are colorless, having no absorption maxima above 330 mμ.[16]

(16) See J. R. S. Irelan, Ph.D. Thesis, University of Oklahoma, July 1968.

Jordan J. Bloomfield, Robert E. Moser
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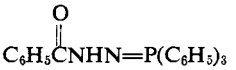
Received June 3, 1968

N-Acylamidotriphenylphosphinimines, Reactive Ylidic Reagents

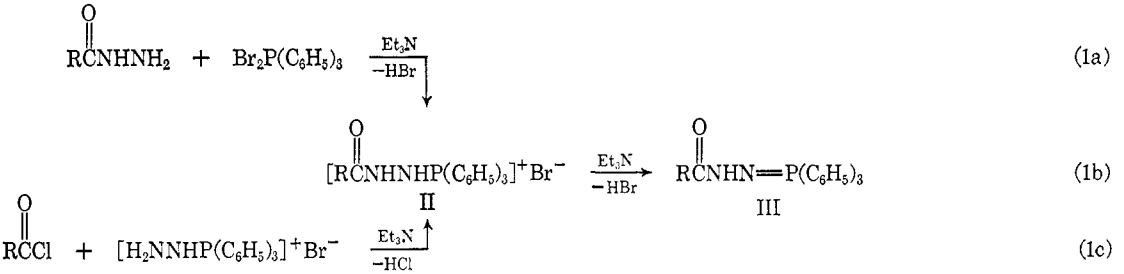
Sir:

Triphenylphosphine dibromide and benzhydrazide in the presence of triethylamine are reported to give N-benzamidotriphenylphosphinimine (I) in 18% yield.[1] The chemistry of the phosphinimine was not investigated however.



I

It has been found that N-acylamidotriphenylphosphinimines (III) can be prepared conveniently and essentially quantitatively from N-acylamidotriphenylphosphiniminium bromides (II, eq 1b) by reaction with bases. N-Acylamidotriphenylphosphiniminium bromides (II) are generated efficiently *in situ* or are isolable in high yields from either (1) acyl hydrazides, triphenylphosphine dibromide, and triethylamine (eq 1a) or (2) hydrazinotriphenylphosphinium bromide (as derived from triphenylphosphine dibromide and hydrazine),[2] acyl chlorides, and triethylamine (eq 1c). We now describe the advantageous properties and chemistry of typical N-acylamidotriphenylphosphinimines (III) and in particular the extraordinary intramolecular reactivity of their O-acylated intermediates, α-acyloxytriphenylphosphazines (see example IX below), as ylidic reagents to yield 1,3,4-oxadiazoles.



(1a)

(1b)

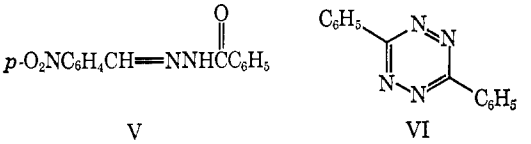
(1c)

II III

N-Benzamidotriphenylphosphinimine (I, white crystals, mp 202–203° from ethyl acetate, lit.[1] mp 177–180°)[3] is obtained immediately upon adding aqueous sodium hydroxide or excess triethylamine to N-benzamidotriphenylphosphiniminium bromide[3] (IV, white crystals, mp 180° from isopropyl alcohol; strong infrared absorption at 3.6, 5.9, 6.9, 9.0, and 13.7 μ) in chloroform. The structure of I as an ylidic hydrazide is indicated by its strong absorption at 5.8 (-CONH-) and 7.5 μ (-P=N-) and its near-transparency in the 3.0-μ (hydroxyl) region. The behavior of I as a phosphorus–nitrogen ylidic reagent is demonstrated by its exothermic reactions with *p*-nitrobenzaldehyde and with *m*-nitrobenzaldehyde in benzene to give, along with triphenylphosphine oxide, *p*-nitrobenzaldehyde benzoylhydrazone (V, >82% yield; mp, lit.[4] mp, and mmp 243°) and *m*-nitrobenzaldehyde benzoylhydrazone (79% yield, mp and lit.[4] mp 197°), respectively. It is also noteworthy that IV, upon heating, undergoes dehydrobromination, bimolecular condensation, and dehydrogenation to 3,6-diphenyl-1,2,4,5-tetrazine (VI, red crystals, mp 199–200°, lit.[5a] mp 195°, identical infrared absorption with that of authentic material[5a]) and triphenylphosphine oxide.[5b]

N-Acylamidotriphenylphosphinimines are acids and they exhibit enolic behavior. I gives a deep blue color with ferric chloride and is converted to its isolable lithium salt (VII, yellow, mp 205°) by butyllithium in hexane. Acidification of VII with hydrogen bromide results in generation of N-benzamidotriphenylphosphiniminium bromide (IV). Occasionally the enol, α-hydroxybenzylidenetriphenylphosphazine (VIII, infrared absorption at 3.1 and 7.4 μ (P=N); very weak C=O absorption at 5.8 μ) can be precipitated from chloroform; on heating or on storage it isomerizes essentially quantitatively to I.

What is presently of principal interest is that the lithium salt VII of I reacts rapidly with benzoyl chloride at 20–25° to give 2,5-diphenyl-1,3,4-oxadiazole (XI,



V VI

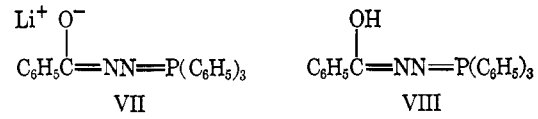
(1) L. Horner and H. Oediger, *Ann.*, **627**, 142 (1959).

(2) (a) H. Zimmer and G. Singh, *J. Org. Chem.*, **29**, 1579 (1964); (b) H. Appel and R. Schöllhorn, *Angew. Chem.*, **76**, 991 (1964); (c) C. C. Walker and H. Shechter, *Tetrahedron Letters*, 1447 (1965).

(3) All new compounds obtained in the present work gave satisfactory analyses.

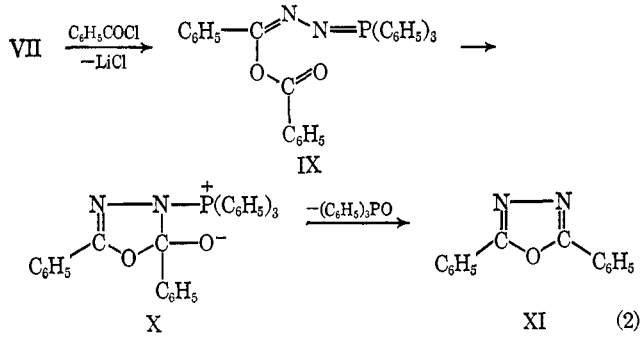
(4) P. Grammaticakis, *Bull. Soc. Chim. France*, 690 (1950).

(5) (a) E. Muller and L. Herrdegen, *J. Prakt. Chem.*, **102**, 136 (1921). (b) For a related reaction see C. E. Griffin and G. Witschard, *J. Org. Chem.*, **27**, 3334 (1962).



VII VIII

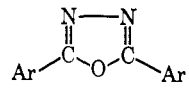
eq 2, 94% yield, mp 138°, lit.[6a] mp 138°) and triphenylphosphine oxide.[6b] Reaction of I with other acid chlorides yields unsymmetrical 2,5-disubstituted 1,3,4-



IX X XI (2)

oxadiazoles (Table I). The new oxadiazole synthesis is general, efficient, and the mildest yet reported. Formation of the 1,3,4-oxadiazoles must involve

Table I. 1,3,4-Oxadiazoles Derived from I and Aroyl Chlorides

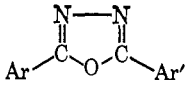


Ar	Ar′	Yield,[a] %
C_6H_5	C_6H_5	>64
C_6H_5	p-$O_2NC_6H_4$	94
C_6H_5	3,5-$(O_2N)_2C_6H_3$	79
C_6H_5	p-BrC_6H_4	70

[a] Procedure 1; no attempts were made to maximize yields.

intramolecular ring closure of intermediate α-acyloxybenzylidenetriphenylphosphazines such as IX. Such intermediates are producible by reaction of hydrazinotriphenylphosphonium bromide[1,2] with 2 equiv of an acyl halide in the presence of excess triethylamine. There results indeed therefrom (eq 1b, 1c, and 2) a rapid and effective method of generating symmetrical 2,5-disubstituted 1,3,4-oxadiazoles (Table II).

Table II. 1,3,4-Oxadiazoles Derived from Hydrazinotriphenylphosphiniminium Bromide and Aroyl Chlorides



Ar	Yield,[a] %
C_6H_5	93
p-BrC_6H_4	76
p-$O_2NC_6H_4$	69
m-$O_2NC_6H_4$	67

[a] Procedure 2, no attempts were made to maximize yields.

The cyclizations of the intermediate α-acyloxybenzylidenetriphenylphosphazines (eq 2) are the first examples of reaction of phosphorus–nitrogen ylides phosphazines) with carbonyl groups of esters with expulsion of triphenylphosphine oxide.[7] The rapid ring-closure processes are apparently related to favorable intramolecular probability factors and in particular to the delocalization in 1,3,4-oxadiazoles.

The following procedures are representative for preparing unsymmetrical (procedure 1) and symmetrical (procedure 2) 1,3,4-oxadiazoles.

(1) p-Nitrobenzoyl chloride (0.19 g, 1.0×10^{-3} mol) was added to N-benzoylamidotriphenylphosphinimine (I, 0.40 g, 1.0×10^{-3} mol) and triethylamine (0.20 g, 2.0×10^{-3} mol) in benzene (30 ml). After 24 hr the benzene was removed, and the residue was washed with water and ethanol to yield 2-p-nitrophenyl-5-phenyl-1,3,4-oxadiazole (0.25 g, 94% yield, mp 210–211°, lit.[8] mp 206.5–208°).

(2) m-Nitrobenzoyl chloride (0.74 g, 4.0×10^{-3} mol) and then triethylamine (1.0 g, 1.0×10^{-2} mol) were added to a stirred slurry of hydrazinotriphenylphosphinium bromide (0.75 g, 2.0×10^{-3} mol) in ether (30 ml). After 30 hr at 25° the solid was filtered, washed with water, and boiled with ethanol to give 2,5-bis(m-nitrophenyl)-1,3,4-oxadiazole as residue (0.45 g, 67% yield, mp 228–229°, no depression by an authentic sample[9]).

The utility of alkylation of salts of N-acylamidotriphenylphosphinimines and of base-catalyzed acylation of N-thioacylamidotriphenylphosphinimines and of N-acylamidinotriphenylphosphinimines will be reported subsequently.

Acknowledgment. This research was supported in part by the National Science Foundation.

(6) (a) R. Stolle, *J. Prakt. Chem.*, **69**, 157 (1904). (b) A related reaction is described by T. L. Bieber and E. H. Eisman, *J. Org. Chem.*, **27**, 678 (1962).

(7) (a) Phosphoranes do not react with esters other than formates (slowly) with expulsion of triphenylphosphine oxide (H. Pommer and G. Wittig, German Patent 1,047,763 (Dec 31, 1958): see *Chem. Abstr.*, **52**, 16411*h* (1958)). (b) Reactions of phosphoranes with azides to give 1,2,3-triazoles involve intermediates structurally related to X (G. R. Harvey, *J. Org. Chem.*, **31**, 1587 (1966)).

(8) R. Huisgen, J. Sauer, H. J. Sturm, and J. H. Markgraf, *Ber.*, **93**, 2112 (1960).

(9) A. Siegrist, E. Maeder, and M. Duennenberger, Swiss Patent 383,985 (Jan 29, 1965); *Chem. Abstr.*, **62**, 14867*b* (1965).

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A Variation of the Square-Pyramidal Copper(II) Surrounding. A Possible Copper Interaction with Tyrosine[1]

Sir:

In a series of investigations on the crystal structures of metal complexes of amino acids and peptides, we determined the structure of the copper chelate of glycyl-*l*-leucyl-*l*-tyrosine. The complex can be prepared by mixing equimolar amounts of $CuSO_4$, $Ba(OH)_2$, and the peptide. After separation of $BaSO_4$, large blue crystals of the complex can be obtained by equilibration with ether of the aqueous (pH 6–7) chelate solution. The crystals decompose very rapidly (within 1 min) on exposure to the atmosphere. The crystals are stable in solution when ether is added to the mother liquor.

(1) This research was supported by Grant GM 10514 from the National Institutes of Health.