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Further Characterization of Mitsunobu-Type Intermediates in the Reaction of Dialkyl Azodicarboxylates with P(III) Compounds

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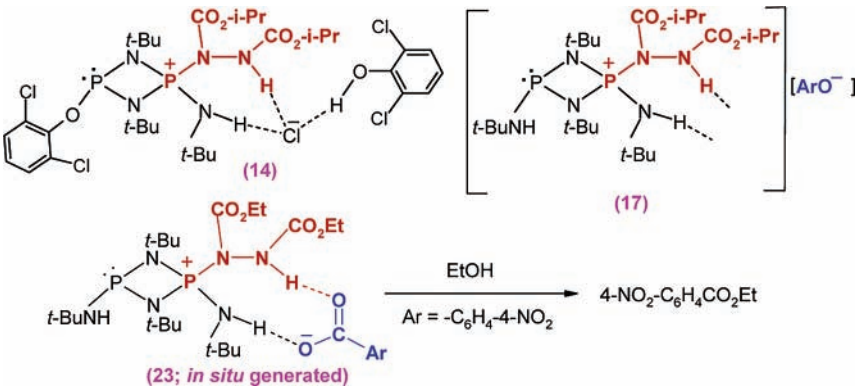
Received September 23, 2005



Structural characterization of compounds analogous to the proposed intermediates in the Mitsunobu esterification process is achieved by the combined use of NMR spectroscopy and X-ray diffractometric studies. The results show that compounds (*t*-BuNH)P(μ-N-*t*-Bu)$_2$P[(N-*t*-Bu)(N-(CO_2R)-N(H)(CO_2R))] [R = Et (**11**), *i*-Pr (**12**)], obtained by treating [(*t*-Bu-NH)P-μ-N-*t*-Bu]$_2$ (**10**) with diethylazodicarboxylate (DEAD) or diisopropylazodicarboxylate (DIAD), respectively, have a structure with the N*H* proton residing between the two nitrogen atoms ((P)*N*(*t*-Bu) and (P)N-*N*(CO_2Et)); this is the tautomeric form of the expected betaine (*t*-BuNH)P(μ-N-*t*-Bu)$_2$P$^+$[(NH-*t*-Bu)(N-(CO_2R)-N$^-$(CO_2R)]. Treatment of ClP(μ-N-*t*-Bu)$_2$P[(N-*t*-Bu){N-(CO_2-*i*-Pr)-N(H)(CO_2-*i*-Pr)] (**6**) with 2,6-dicholorophenol affords (2,6-Cl_2-C_6H_3-O)P-(μ-N-*t*-Bu)$_2$P$^+$[(NH-*t*-Bu){N[(CO_2*i*-Pr)($HNCO_2$*i*-Pr)]}](Cl$^-$)(2,6-Cl_2-C_6H_3-OH) (**14**) that has a structure similar to that of (CF_3CH_2O)P(μ-N-*t*-Bu)$_2$P$^+$[(NH-*t*-Bu){N[(CO_2*i*-Pr)($HNCO_2$*i*-Pr)]}](Cl$^-$) (**13**), but with an additional hydrogen bonded phenol. Both of these have the protonated betaine structure analogous to that of $Ph_3P^+N(CO_2R)NH(CO_2R)(R'CO_2)^-$ (**2**) proposed in the Mitsunobu esterification. Two other compounds, (ArO)P(μ-N-*t*-Bu)$_2$P$^+$(NH-*t*-Bu){N(CO_2*i*-Pr)($HNCO_2$*i*-Pr)}(Cl$^-$) [Ar = 2,6-$Me_2C_6H_3$O- (**15**) and 2-Me-6-*t*-Bu-C_6H_3-O- (**16**)], are also prepared by the same route. Although NMR tube reactions of **11** or **12** with tetrachlorocatechol, catechol, 2,2′-biphenol, and phenol revealed significant changes in the ^{31}P NMR spectra, attempted isolation of these products was not successful. On the basis of ^{31}P NMR spectra, the phosphonium salt structure (*t*-BuNH)P(μ-N-*t*-Bu)$_2$P$^+$[(HN-*t*-Bu){N-(CO_2R)-N(H)(CO_2R)]-(ArO$^-$) is proposed for these. The weakly acidic propan-2-ol or water did not react with **11** or **12**. Treatment of **12** with carboxylic acids/ *p*-toluenesulfonic acid gave the products (*t*-BuNH)P(μ-N-*t*-Bu)$_2$P$^+$[(HN-*t*-Bu){N-(CO_2-*i*-Pr)-N(H)(CO_2-*i*-Pr)](ArCO$_2^-$) [Ar = Ph (**18**), 4-Cl-$C_6H_4CH_2$ (**19**), 4-Br-C_6H_4 (**20**), 4-NO_2-C_6H_4 (**21**)] and (*t*-BuNH)P(μ-N-*t*-Bu)$_2$P$^+$[(HN-*t*-Bu){N-(CO_2-*i*-Pr)-N(H)(CO_2-*i*-Pr)](4-CH_3-$C_6H_4SO_3^-$) (**22**) that have essentially the same structure as **2**. Compound **18** has additional stabilization by hydrogen bonding, as revealed by X-ray structure determination. Finally it is shown that the in situ generated (*t*-BuNH)P(μ-N-*t*-Bu)$_2$P$^+$[(HN-*t*-Bu){N-(CO_2Et)-N(H)(CO_2Et)](4-NO_2-$C_6H_4CO_2^-$) can also effect Mitsunobu esterification. A comparison of the Ph_3P-DIAD system with the analogous synthetically useful Ph_3P-dimethyl acetylenedicarboxylate (DMAD) system is made.

Introduction

The triphenylphosphine/diethyl azodicarboxylate (DEAD)- or diisopropyl azodicarboxylate (DIAD)-mediated esterification of an acid (with inversion of configuration for asymmetric alcohols), known as the Mitsunobu reaction, has proven useful in a

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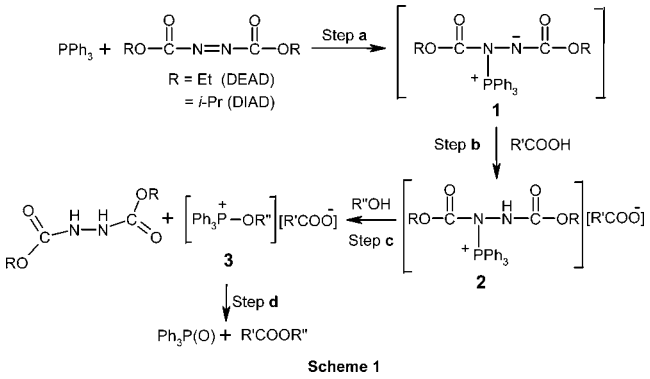
10.1021/jo051997x CCC: $33.50 © 2006 American Chemical Society
Published on Web 01/06/2006

wide variety of synthetic applications.[1] Mechanistic discernment of this reaction with respect to the initial redox chemistry has received substantial documentation.[2] Several other key features of this important reaction have been investigated by various groups.[2−5] An elegant DFT study in which different pathways are analyzed was recently conducted by Anders and co-workers.[6] The reaction is thought to proceed through the following steps (Scheme 1):[1a] (a) addition of phosphorus(III) compound to DEAD/ DIAD to lead to the Morrison−Brunn−Huisgen intermediate **1**, (b) protonation of **1** to lead to **2**, (c) formation of the alkoxy phosphonium salt **3**, and (d) S_N2 displacement of the phosphonium carboxylate **3** to give R′COOR″.

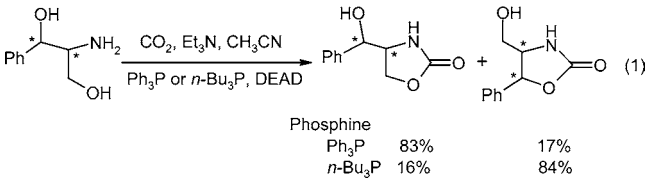
The Morrison−Brunn−Huisgen (MBH) betaine **1** is the intermediate in the first step of this reaction, and its involvement

SCHEME 1

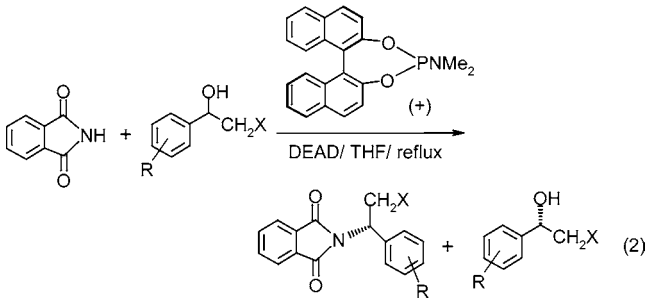


Scheme 1

has been previously substantiated by multinuclear NMR and FT-IR but not by X-ray diffraction.[2] Formation of **1** occurs through radical cations, and it was noted that the intensity of the EPR signal in the reaction of DIAD with P(III) compounds varies depending upon the substituents.[2d] Thus the nature of the intermediates and hence the product distribution could also vary depending upon the P(III) precursor.[2,7−9] In the formation of 2-oxazolidones from CO_2 and ethanolamine using a Mitsunobu protocol, the use of triphenylphosphine vs tributylphosphine did indeed afford different isomers (eq 1).[7]



Direct reaction of phosphoramidite $(Me_2N)P(2,2'\text{-}(OC_{10}H_6)_2)$ with DIAD/ DEAD led to the pentacoordinate phosphoranes $(Me_2N)P[2,2'\text{-}(OC_{10}H_6)_2][N(CO_2R)NC(OR)O]$ that could be utilized for the kinetic resolution of alcohols in an asymmetric Mitsunobu reaction (cf. eq 2).[8] Thus, even when the initial reaction of the P(III) compound with DEAD/ DIAD gives a product other than a betaine of type **1**, the esterification takes place smoothly.[8,9]



The betaine **1** formed in the first step can react with either carboxylic acids or alcohols to give phosphonium carboxylate salts (**2**) or phosphoranes (**4** and **5**, Scheme 2), respectively.[2] Thus the order of addition of the acid and the alcohol to betaine

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(3) (a) Michalski, J.; Skowronska, A.; Bodalski, R. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, Florida, 1987; Chapter 8, pp 255−296. (b) Pautard-Cooper A.; Evans, S. A., Jr. *J. Org. Chem.* **1989**, *54*, 2485.

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(6) Schenk, S.; Weston, J.; Anders, E. *J. Am. Chem. Soc.* **2005**, *127*, 12566. Alternate pathways involving phosphoranes of type $Ph_3P(OR)_2$ are shown in Scheme 1 of this article.

(7) Kodaka, M.; Tomohiro, T.; Okuno, H. (Y). *J. Chem. Soc., Chem. Commun.* **1993**, 81.

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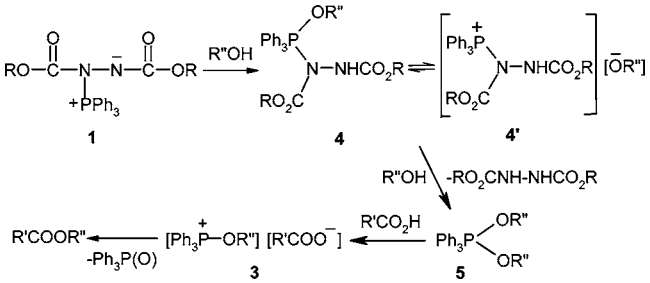
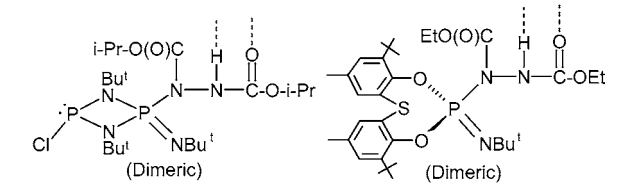
SCHEME 2

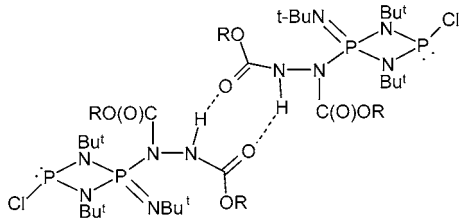


1 is important and implies a potential duality of the mechanism in that the alkoxyphosphonium salt $[Ph_3P^+(OR")](R'CO_2^-)$ (**3**) can be formed via either **2** or phosphorane **5**. Furthermore, the stability of intermediate **2** formed by the reaction of acid R′COOH and the betaine **1** can be enhanced by hydrogen bonding.[2] In the next step, the reaction of **2** with 1 molar equiv of R"OH leads to **3** (Scheme 1); the latter can also be formed from **5** and $R'CO_2H$ (cf. Scheme 2). It is possible that some of these various intermediates can be stabilized by a suitable choice of the P(III) precursor.

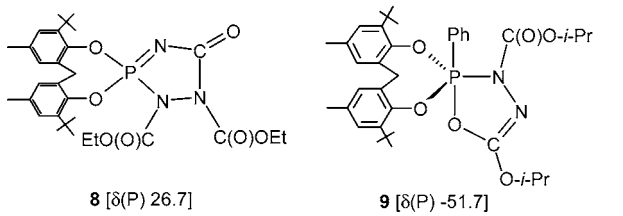
The above observations prompted us to look into the behavior of DIAD/ DEAD toward P(III) compounds other than Ph_3P.[10] Thus, we have previously characterized the first stage products **6**−**9** by starting with the precursors ClP(N-*t*-Bu)$_2$PNH-*t*-Bu, S(6-*t*-Bu-4-Me-$C_6H_2O)_2$P-NH-*t*-Bu, CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P−NCO, and CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$]PPh, respectively.[10b,11] Compounds **6** and **7** are the tautomeric forms of the corresponding betaines, with N(CO_2R)-H and C═O forming a hydrogen-bonded dimer (cf. **6′**). Compound **8**, despite having a structure different from the betaine **1**, *does participate in the Mitsunobu coupling* between ethanol and benzoic acid, suggesting that the five-membered heterocycle is in equilibrium with its betaine form.



6 [^{31}P NMR: broad signals] **7** [δ(P) -56.3 (298K)]



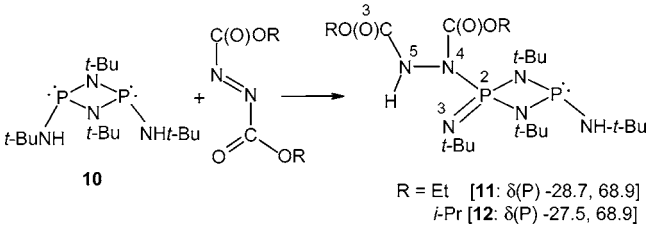
6′



8 [δ(P) 26.7] **9** [δ(P) -51.7]

In continuation of our previous studies, we present herein further data, including X-ray structures, pertaining to species

SCHEME 3



R = Et [**11**: δ(P) -28.7, 68.9]
i-Pr [**12**: δ(P) -27.5, 68.9]

whose structures are close to those of **1**, **2**, and **4′** by using cyclodiphosphazane precursors. These results shed light on some of the intricacies in the mechanism of Mitsunobu reaction. Some common features among Ph_3P-DIAD, Ph_3P-DMAD, and related systems are highlighted at the end. We also show that the compounds (of type **2**) thus obtained with our precursors can effect esterification.

Results and Discussion

(A) Compounds 11 and 12. The reaction of the cyclodiphosphazane [*t*-BuNHP-μ-N-*t*-Bu]$_2$ (**10**) with DEAD or DIAD readily affords the respective addition compounds **11** and **12** (Scheme 3).[10] A naive extrapolation of the previously published structure **6** to the amino compounds **11** and **12** (cf. Scheme 3) suggested a hydrogen-bonded dimer through the *syn*-oriented N−H and C═O groups (cf. **6′** above).[10b] However, the X-ray structure (Figure S1) of **11** is not consistent with the dimer structure due to the following observations:

(a) The P(2)−N(3) (numbering is shown on the structural drawing in Scheme 3) distance of 1.533(1) Å is much longer than the corresponding distance of 1.488(3) Å in **6**.[10b]

(b) The N(5)−H and C═O(3) are *transoidal* in **11**, whereas they are *cisoidal* in **6**. The structure of **11** is well refined, and the N(5)−H could be readily located by a difference Fourier map. In this structure, the N(5)−H proton is closer to N(3) (N(5)−H(N5) 0.83(2), H(N5)···N(3) 2.22(2), N5···N(3) 2.670(1), N(5)−H(N5)···N(3) 114.7°). Thus, unlike **6**, compound **11** does not form a hydrogen-bonded dimer. This feature suggests the hydrogen bonding is not the controlling factor for tautomeric phosphinimine structure (of the betaine form) observed in these compounds (**6** or **11**).

(c) The sum (Σ) of the bond angles at N(5) is 336.7°, and hence this nitrogen is quite far from planarity (i.e., more pyramidal); the corresponding nitrogen in **6** is essentially planar (ΣN = 357.8°).

All of these observations point to a greater contribution from the phosphonium structure **11′**.

(B) Reaction of 6, 11, and 12 with Phenols/Alcohols. In a previous paper, we briefly alluded to compound **13**, obtained by the reaction of **6** with trifluoroethanol (better X-ray data is now available; see Figure S2 in Supporting Information).[10b] Further work using 2,6-dichlorophenol has revealed that in such

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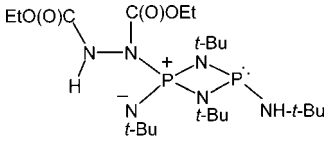
(11) Compounds of type **9** are interesting examples of pentacoordinate phosphoranes with "reversed apicophilicity". This aspect has been discussed by us as well others elsewhere. See ref 9 and (a) Timosheva, N. V.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 6552. (b) Kojima, S.; Sugino, M.; Matsukawa, S.; Nakamoto, M.; Akiba, K.-y. *J. Am. Chem. Soc.* **2002**, *124*, 7674. (c) Kommana, P.; Satish Kumar, N.; Vittal, J. J.; Jayasree, E. G.; Jemmis, E. D.; Kumara Swamy, K. C. *Org. Lett.* **2004**, *6*, 145.

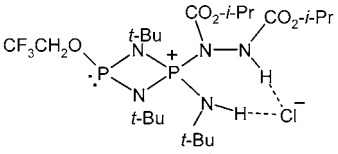


11'

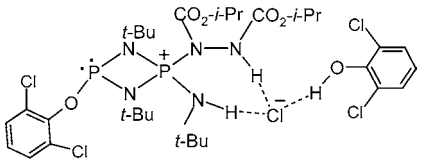
reactions more complex species such as **14** can also be formed. Figure S3 shows the structure of **14** with the hydrogen bond parameters. Considering the chloride ion as the equivalent of the carboxylate anion, this structure suggests that prior to the formation of phosphonium salts **3** from **2** (Scheme 1), the alcohol is perhaps held by hydrogen bonding with the carboxylate (RCO_2^-) ion. In the 2,2,2-trifluoroethoxy compound **13**, the chloride ion is hydrogen bonded only to the cyclophosphazane N*H* atoms.[12] While it is true that in the Mitsunobu reaction a carboxylate ion (in place of the chloride present here) is involved, the structures of **13** and **14**, obtained essentially from the same type of reaction, point toward an additional feature not explicit in Scheme 1. That is, hydrogen bonding between the carboxylate anion and the alcohol, and not just the substituents on phosphorus, is involved in bringing about the esterification. Both **13** and **14** are phosphonium salts with the hydrazine residue connected to phosphorus and are comparable to intermediates of type **2**. The chloride anion engages itself in hydrogen bonding as does a carboxylate (see below for discussion on the structure of a compound with a carboxylate anion). The anion in **13** and **14** has at least two hydrogen bonded partners: (a) -N*H* proton of hydrazine end and (b) N*H*(*t*-Bu) proton or/and the phenolic O*H* proton. The second partner in our structure is likely to be replaced by the alcoholic -O*H* in the normal Mitsunobu reaction.[13]

Use of the less acidic 2,6-dimethyl-phenol and 2-methyl-6-*tert*-butyl-phenol resulted in the isolation of compounds **15** and **16** for which we assign a structure analogous to that for **13**.

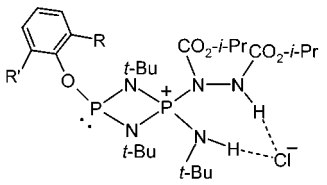
Our initial attempts to isolate a product from the corresponding reaction of **11** and **12** with trifluoroethanol or catechol were unsuccessful, and the starting compounds **11** and **12** crystallized out. However, ^{31}P NMR monitoring of the reaction revealed that there was a significant interaction ($\Delta\delta$ in the range 20−25



[13: δ(P) 11.7, 114.4; ^2J = 14.1 Hz]



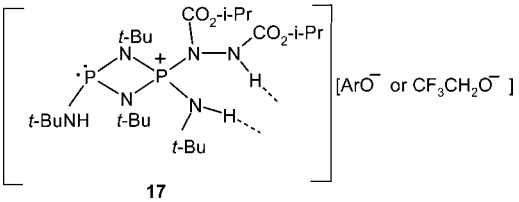
[14: δ(P) 10.9 (br), 115.9 (br)]



15 [R = R' = Me; δ(P) 10.7 (d), 119.5 (d), ^2J = 11.0 Hz]

16 [R = Me, R' = *t*-Bu; δ(P) 9.4 (d), 114.6 (d), ^2J = 10.4 Hz]

ppm for each of the phosphorus atoms) in solution between trifluoroethanol and phenols with **11** and **12** (cf. Figure 1). Based on the chemical shifts observed, it is unlikely that these species have pentacoordinate phosphorane structures of the type of **4** and **5**.[14] The structure **17** is proposed for these new compounds.

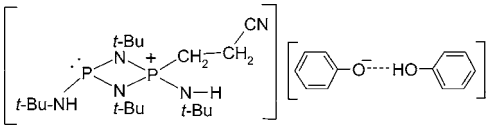


17

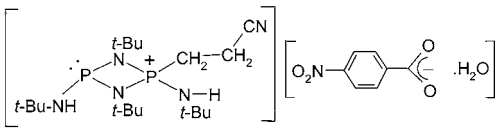
It is possible that the hydrogen bonding pattern could vary depending upon the alcohol/ phenol, but the local environment close to the tetracoordinate phosphorus is the same.[15] These structures are close to the ionic forms **4′** of the phosphoranes **4** displayed in Scheme 2. The less acidic propan-2-ol (or water), by contrast, showed little or no interaction (cf. Table 1; entries

(12) An interesting point related to the two structures, as regards phosphorus chemistry, is that the P-NH-*t*-Bu group and the P-OR (Ar) groups are *cis* in **10**, whereas they are *trans* in **11**. This has some relevance to cyclodiphosphazane chemistry but is not elaborated here. For *cis-trans* isomerization in cyclodiphosph(III)azanes, see: (a) Reddy, V. S.; Krishnamurthy, S. S.; Nethaji, M. *J. Organomet. Chem.* **1992**, *438*, 99. (b) Reddy, V. S.; Krishnamurthy, S. S.; Nethaji, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2661.

(13) This statement is corroborated by the observation of additional partners for hydrogen bonding in the structures of following compounds (phenol in **B** and water in **C**) (Bhuvan Kumar, N. N.; Manab Chakravarty; Kumara Swamy K. C., submitted for publication).



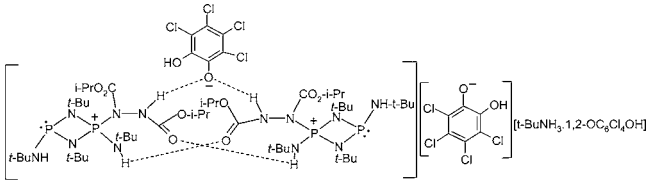
B



C

(14) Compounds of type **5** were isolated by several workers. See ref 3e and (a) Bone, S. A.; Trippett, S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 156. (b) von Itzstein, M.; Jenkins, I. D. *J. Chem. Soc.Perkin Trans. 1* **1986**, 437.

(15) Repeated attempts to crystallize the product, by cooling to 5 °C gave small amount of a crystalline material with the composition, [*t*-BuHNP(*μ*-N-*t*-Bu)$_2$P(NH-*t*-Bu){N-(CO$_2$*i*-Pr)-N(H)(CO$_2$*i*-Pr)}]$_2$(1,2-OC$_6$Cl$_4$-OH) [(1,2-OC$_6$Cl$_4$-OH) (*t*-BuNH$_3$·1,2-OC$_6$Cl$_4$OH)] (**A**), probably by partial decomposition. At room temperature, there appeared to be extensive deformation of the crystallinity. The data quality was not good, but by comparison of the bond parameters to structure of **18**, it does support the formulation **17** for these products. An ORTEP picture (Figure S5) with bond parameters around phosphorus is available as Supporting Information.



(**A**)

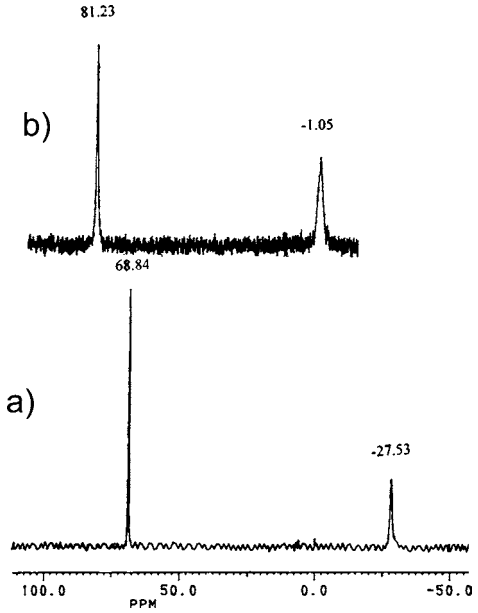


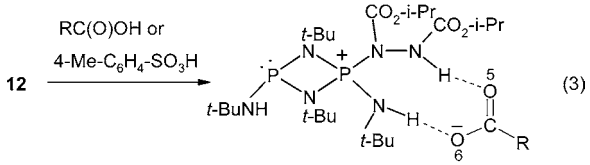
FIGURE 1. ^{31}P NMR spectra of (a) **12** and (b) immediately after the addition of 1,2-tetrachlorocatechol to **12**.

TABLE 1. NMR Data for the Products from the Addition of Alcohols/Phenols to 11 or 12

entry	phenol/alcohol/water	product ^{31}P NMR (δ)
1	none	-28.0 ± 0.5, 68.9 ± 0.5
2	tetrachlorocatechol	-1.0 ± 0.5, 81.2 ± 0.5
3	catechol	-2.9 ± 0.5, 80.2 ± 0.5
4	2,2′-biphenol	-2.7 ± 0.5, 80.6 ± 0.5
5	phenol	-9.7 ± 0.5, 76.1 ± 0.5
6	2,2,2-trifluoroethanol	0.5 ± 0.5, 81.2 ± 0.5
7	propan-2-ol	-25.9 ± 0.5, 69.4 ± 0.5
8	water	-26.6 ± 0.5, 69.2 ± 0.5

7 and 8). This observation shows that the alternative pathway shown in Scheme 2 may not occur when acid is present.

(C) Reaction of 12 with Carboxylic Acids. The reaction of **12** with acids straightforwardly leads to compounds **18**−**22** (eq 3), which are essentially intermediates of type **2**. After repeated

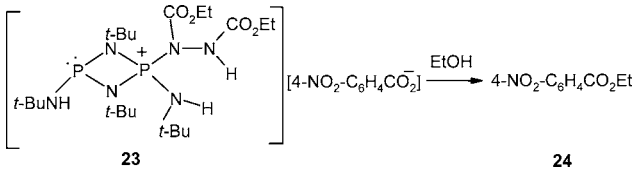


(3)

R = Ph [**18**: δ(P) 1.1, 81.0]
4-Cl-$C_6H_4CH_2$ [**19**: δ(P) 0.1 (br), 80.4 (br)]
4-Br-C_6H_4 [**20**: δ(P) 2.1, 81.5]
4-NO_2-C_6H_4 [**21**: δ(P) 2.9, 82.0]
4-Me-$C_6H_4SO_3^-$ instead of RCO_2^- [**22**: δ(P) 2.3, 82.2]

attempts, we were successful in crystallizing **18** whose X-ray structure (Figure S4) clearly shows stabilization by hydrogen bonding that was alluded to before. This interaction holds the carboxylate with the phosphorus substrate: one of the carboxylate oxygen atoms (O(6), see the drawing in eq 3 for numbering) is connected to the N*H*-*t*-Bu proton, whereas the other [O(5)] is connected to N-N*H*(COOR) proton. Hydrogen bonding had been invoked earlier by (a) Evans and co-workers in the reaction of phosphoranes of type **5** with alcohols to give

SCHEME 4



alkoxyphosphonium ions of type **3**[3b] and (b) Hughes and co-workers in connection with alcohol activation.[2b] The latter, in which hydrogen bonded HCOO−···HCOOH was considered responsible for the rate diminution in esterification when the amount of acid is higher, is relevant to the present study. However, as mentioned above, it is possible that one oxygen of the carboxylate anion is hydrogen bonded to hydrazine residue and the other to alcohol during the formation of the alkoxyphosphonium ion. More structural studies are required to ascertain whether this happens or not. One factor responsible for the isolation of the stable acid-addition product using our substrates is likely to be the additional hydrogen bonding possibility as shown by the X-ray structure, but nevertheless these compounds clearly demonstrate the existence of the second stage intermediates of type **2** (cf. Scheme 1) proposed in the Mitsunobu reaction. It is also noted that the ^{31}P NMR chemical shifts of **18**−**22** are in the same region as those for **17** (Table 1), lending credence to the structure assigned to **17**.

Although a different P(III) substrate in our reaction was used in these experiments, it is noteworthy that the esterification can be conducted, albeit at higher temperatures, by the addition of alcohol to the in situ generated **23** (δ(P) 3.8 and 82.9; DEAD analogue of **21**) to lead to the ester **24** (40% isolated yield) (Scheme 4). This leaves room for further expansion of Mitsunobu chemistry.

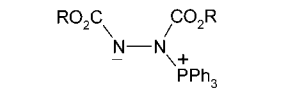
Summary and Outlook

This paper reports the isolation and structural characterization of compounds analogous to some of the proposed intermediates in the Mitsunobu esterification reaction. The X-ray structure of **11** shows that subtle changes in the substituents on the phosphine affect the nature of the first stage intermediate (betaines of type **1**). It is shown that the alcohol-added intermediates (**4**) are much less stable than the acid-added intermediates (**2**). Whereas the more acidic phenols (or trifluoroethanol) interact with the betaine **1** (or its tautomer in our case) more strongly, the less acidic propan-2-ol (or water) shows little or no interaction. We have also provided the first structural precedent for the acid-addition intermediate of type **2** through the isolation and characterization of product **18**. Although the present work is directed toward structural aspects of Mitsunobu-type intermediates, one can note the similarity of this Ph_3P-DIAD system to the Ph_3P-DMAD system. In the latter combination, Ph_3P is used as a catalyst to activate the electron-deficient alkyne and very interesting applications have emerged in the past few years.[16] An analogous intermediate (e.g., **25**) is proposed in these systems.[17] The cyclodiphosphazanes also react

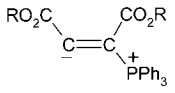
(16) (a) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535. (b) Nair, V.; Rajesh, C.; Vinod, A. U.; Bindu, S.; Sreekanth, A. R.; Mathen, J. S.; Balagopal, L. *Acc. Chem. Res.* **2003**, *36*, 899.

(17) For other types of products from the reaction of P(III) compounds with electron deficient alkynes, see: Kumaraswamy, S.; Kommana, P.; Satish Kumar, N.; Kumara Swamy, K C. *Chem. Commun.* **2002**, 40.

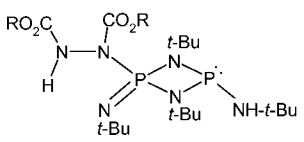
with DMAD (cf. species **26**).[18] It is interesting to note that in the synthetically useful reactions of pyridines or disulfides with DMAD also similar structures are proposed but characterization of such species is still to be undertaken.[19]



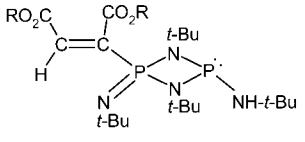
1 [δ(P) 44.8]



25



11 [δ(P) -28.7, 68.9]



26

[δ(P): -35.2 (br), -24.9 (br) and 72.0 (br)] (major peaks)

Experimental Section

The precursor [(*t*-Bu-NH)P-(*μ*-N-*t*-Bu]$_2$ (**10**)[20] was prepared by literature procedures and was crystallized prior to use. Compounds ClP(*μ*-N-*t*-Bu)$_2$P[(N-*t*-Bu){N-(CO$_2$-*i*-Pr)-N(H)(CO$_2$-*i*-Pr)] (**6**), (*t*-BuNH)P(*μ*-N-*t*-Bu)$_2$P[(N-*t*-Bu){N(CO$_2$R)-N(H)(CO$_2$R] [R = Et (**11**), *i*-Pr (**12**)], and (CF$_3$CH$_2$O)P(*μ*-N-*t*-Bu)$_2$P$^+$[(NH-*t*-Bu){N[(CO$_2$*i*-Pr)(HNCO$_2$*i*-Pr)]}](Cl$^-$) (**13**) were prepared as described before.[10b,21] Details of X-ray structure determination[22] and crystal data are available in Supporting Information.

Compounds (2,6-Cl$_2$-C$_6$H$_3$-O)P(*μ*-N-*t*-Bu)$_2$P$^+$[(NH-*t*-Bu)-{N[(CO$_2$-*i*-Pr)(HNCO$_2$*i*-Pr)]}](Cl$^-$)(2,6-Cl$_2$-C$_6$H$_3$-OH) (14), (ArO)P(*μ*-N-*t*-Bu)$_2$P$^+$(NH-*t*-Bu){N(CO$_2$-*i*-Pr)(HNCO$_2$*i*-Pr)}-(Cl$^-$) [Ar = 2,6-Me$_2$C$_6$H$_3$O$^-$ (15); 2-Me-6-*t*-Bu-C$_6$H$_3$O$^-$ (16)]. **Compound 14.** 2,6-Dichlorophenol (0.54 g, 3.31 mmol) in toluene (10 mL) was added dropwise to a stirred solution of **6** (1.70 g, 3.31 mmol) in toluene (20 mL), the mixture was stirred for 24 h and concentrated to 2 mL, and heptane (2 mL) was added to the residue. Crystals of **14** were obtained at 5 °C after 2 d. Yield: 1.08 g (50% based on phosphazane). Mp: 140−142 °C. IR (cm^{-1}): 3428 (vw), 3083, 1742, 1229, 1190, 1092. ^{1}H NMR: δ 1.23 (br d, J = 6.1 Hz, 6 H), 1.30−1.55 (3 lines, 15 H), 1.68 (br s, 18 H), 4.75−5.10 (m, 2 H), 6.92−7.60 (m, ∼8 H), 11.26 (s, 1 H). ^{13}C NMR: δ 21.3, 21.5, 21.8, 21.9, 30.4, 30.9, 31.5 and 31.6 (merged d and t), 56.6 (d, J = 9.0 Hz), 57.4, 70.4, 73.3, 120.7, 125.2, 126.3, 128.1, 130.0, 152.6 (d, J = 20.2 Hz), 155.6. ^{31}P NMR: δ 10.9, 115.9. The J value is < 5.0 Hz and hence slightly broadened signals instead of well-separated doublets are observed. Anal. Calcd for C$_{32}$H$_{50}$-Cl$_5$N$_5$O$_6$P$_2$: C, 45.75, H, 5.96; N, 8.34. Found: C, 45.89; H, 6.01; N, 8.42.

Compound 15. This compound was prepared in a manner similar to that for **14** using 2,6-dimethylphenol (0.30 g, 2.30 mmol) and **6** (1.18 g, 2.30 mmol). Yield: 1.11 g (75%). Mp: 138−140 °C. IR (cm^{-1}): 3090, 1750, 1235, 1182, 1065. ^{1}H NMR: δ 1.23−2.64 (many lines, 39 H), 2.43 (s, 6 H), 4.78−5.09 (m, 2 H), 6.92−7.60 (m, 3 H), 7.60 (d, J ≈ 9.0 Hz, 1 H), 9.95 (s, 1 H). ^{13}C NMR: δ 21.5, 21.8, 21.9, 22.0, 30.7 (d, J ≈ 4.5 Hz), 31.0 (∼t, J ≈ 4.5 Hz), 56.2, 57.0, 70.3, 73.5, 119.8, 124.1, 128.4, 130.0, 152.6 (d, J = 20.2 Hz), 156.3. ^{31}P NMR: δ 10.7, 119.5 (d each J ≈ 11 Hz). Anal. Calcd for C$_{28}$H$_{52}$ClN$_5$O$_5$P$_2$: C, 52.86; H, 8.20; N, 11.00. Found: C, 52.82; H, 8.25; N, 11.04.

Compound 16. This compound was prepared in a manner similar to that for **14** using 2-methyl-6-*tert*-butyl-phenol (0.48 g, 2.92 mmol) and **6** (1.50 g, 2.92 mmol). Yield: 1.60 g (81%). Mp: 156−158 °C. IR (cm^{-1}): 3138, 1757, 1305, 1229, 1186, 1074. ^{1}H NMR: δ 1.25−1.55 (many lines, 48 H), 2.23 (s, 3 H), 4.78−5.09 (br, 2 H), 6.72−7.60 (many lines, ca. 4 H). 10.4 (br, 1 H). ^{13}C NMR: δ 20.8, 21.5, 21.7, 21.8, 22.0, 29.6, 30.5, 30.8, 31.0, 31.1, 31.2, 34.4, 34.9, 56.3, 56.4, 57.3, 70.4, 73.3, 115.8, 116.6, 116.8, 127.0, 127.2, 129.3, 132.8, 135.5, 140.0, 150.5 (d, J = 19.2 Hz), 155.3. ^{31}P NMR: δ 9.4, 114.6 (d each, J = 10.4 Hz). Anal. Calcd for C$_{31}$H$_{58}$ClN$_5$O$_5$P$_2$: C, 54.90; H, 8.62; N, 10.33. Found: C, 54.92; H, 8.75; N, 10.39. The sample was not very stable; two additional doublets at δ −9.3 and 6.8 with a ^2J value of 40.0 Hz, probably due to the oxidation of the P(III) moiety, were observed in the reaction mixture.

Reaction of 11 or 12 with Phenols, Alcohols, or Water. These reactions were conducted in an NMR tube by adding an equimolar quantity of tetrachlorocatechol, catechol, 2,2′-biphenol, phenol, 2,2,2-trifluoroethanol, propan-2-ol or water to **11** or **12** in an NMR tube in CDCl$_3$ solution. Although there was significant shift in the phosphorus resonances except in the case of propan-2-ol (even when two mole equivalents were used), we were unable to isolate the products; the starting material (**11** or **12**) could be recovered in the reaction with biphenol/ trifluoroethanol. Details of the spectral changes are given in Table 1. Repeated attempts in the reaction of **11** using tetrachlorocatechol gave a crystalline material (A) with the structure at the phosphorus analogous to those proposed here (X-ray evidence, see Supporting Material), but with additional tetrachlorocatechol residues.[15]

Synthesis of (*t*-BuNH)P(*μ*-N-*t*-Bu)$_2$P$^+$[(HN-*t*-Bu){N-(CO$_2$-*i*-Pr)-N(H)(CO$_2$-*i*-Pr)](ArCO$_2^-$)[Ar = Ph (18), 4-Cl-C$_6$H$_4$CH$_2$ (19), 4-Br-C$_6$H$_4$ (20), 4-NO$_2$-C$_6$H$_4$ (21)] and (*t*-BuNH)P(*μ*-N-*t*-Bu)$_2$P$^+$[(HN-*t*-Bu){N-(CO$_2$-*i*-Pr)-N(H)(CO$_2$-*i*-Pr)](4-CH$_3$-C$_6$H$_4$SO$_3^-$) (22). Compound 18. Benzoic acid (0.25 g, 2.04 mmol) was added all at once to a stirred solution of **12** (1.12 g, 2.04 mmol) (preparation in situ also works well) in toluene (20 mL), the mixture was stirred for 2 h and concentrated to ∼2 mL, and heptane (2 mL) was added to the residue. Crystals of **18** were obtained at 5 °C after 2 d. Yield: 1.23 g (90%). Mp: 86−88 °C. IR (cm^{-1}): 3382, 1728, 1372, 1248, 1080. ^{1}H NMR: δ 1.14, 1.20, 1.25, 1.30 (4 d, J = 6.2 Hz, 12 H), 1.34 (d, 9 H, J ≈ 3 Hz), 1.41, 1.50 and 1.62 (s each, 27 H), 3.19 (d, J = 4.3 Hz, 1 H), 4.84 and 4.99 (2 m, 2 H), 7.10−7.44 (m, 3 H), 8.09 (m 2 H), 9.50 (br, 2 H). ^{13}C NMR: δ 21.7, 21.9, 22.0, 30.9, 31.2, 32.5, 32.6, 52.6 (d, J = 9.0 Hz), 54.8, 55.4, 55.8, 69.4, 72.3, 125.3, 127.3, 128.2, 129.6, 129.9, 137.4, 153.1 (d, J = 20.2 Hz), 155.9, 171.6. ^{31}P NMR: δ 1.1, 81.0 (J < 5.0 Hz). Anal. Calcd for C$_{31}$H$_{58}$N$_6$O$_6$P$_2$: C, 55.36; H, 8.63; N, 12.50. Found: C, 55.42; H, 8.72; N, 12.61.

Compound 19. DIAD (0.52 g, 2.56 mmol) was added dropwise to a stirred solution of **10** (0.90 g, 2.56 mmol) in toluene (20 mL), and the mixture was stirred for 30 min at room temperature. To this, (4-Cl-C$_6$H$_4$CH$_2$COOH) was added all at once, the mixture was stirred for 24 h at room temperature and concentrated to 2 mL, and heptane (2 mL) was added. Crystals of **19** were obtained at 5 °C after ca. 24 h. Yield: 1.70 g (92%). Mp: 80−82 °C. IR (cm^{-1}): 3382, 1726, 1379, 1246, 1084. ^{1}H NMR: δ 1.17−1.28 (merged 4 d, J ≈ 6.2 Hz, 12 H), 1.29, 1.32, 1.42 and 1.47 (s each, 36 H), 3.15 (br, 1 H), 3.47 (s, 2 H), 4.78−5.13 (m, 2 H), 7.10−7.30 (m, 4 H), 9.98 (br, 2 H). ^{13}C NMR: δ 21.6, 21.8, 22.0, 30.8, 30.9, 31.4, 32.4, 32.5, 44.6, 52.3 (d, J = 15.0 Hz), 55.2, 55.4, 69.1, 71.9, 125.9, 127.7, 128.1, 128.9, 130.8, 131.0, 137.2, 153.1 (d, J = 20.2

(18) In this reaction, apart from the broad peaks at δ(P) 72.0, −24.9, and −35.2 (major, combined intensity ca. 80%), sharp signals at δ(P) 90.1, 31.8, and 30.1 (combined intensity ca. 15%) were also observed in the ^{31}P NMR. The major peaks are close to (*t*-BuNH)P(*μ*-N-*t*-Bu)$_2$P(=N-*t*-Bu)-CH=CH(CO$_2$Me)] (δ(P) −25.7, 70.0) (X-ray) from the reaction of **10** with methyl propiolate. The results are discussed in connection with the utility of Ph$_3$P-DMAD system in another paper quoted in ref 13 above.

(19) (a) Nair, V.; Sreekanth, A.; Vinod, A. U. *Org Lett.* **2001**, *3*, 3495. (b) Li, C.-Qun; Shi, M. *Org. Lett.* **2003**, *5*, 4273. (c) Islamia, M. R.; Mollazehia, F.; Badieib, A.; Sheibania H. *ARKIVOC* **2005**, *XV*, 25.

(20) Bulloch, G.; Keat, R.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1977**, 99.

(21) Praveen Kumar, K.; Chakravarty, M.; Kumara Swamy, K. C. *Z. Anorg. Allg. Chem*. **2004**, *630*, 2063.

(22) Programs used: (a) Sheldrick, G. M. *SADABS*, Siemens Area Detector Absorption Correction; University of Göttingen: Germany, 1996. (b) Sheldrick, G. M. *SHELX-97*, A package for structure solution and refinement; University of Göttingen: Germany, 1997. (c) Sheldrick, G. M. SHELXLTL+, 1991.

Hz), 155.6, 176.3. ^{31}P NMR: δ 0.1 (br), 80.4 (br). Anal. Calcd for $C_{32}H_{59}ClN_6O_6P_2$: C, 53.29; H, 8.24; N, 11.66. Found: C, 53.39; H, 8.14; N, 11.37.

Compound 20. Procedure was the same as that for **19** using similar molar quantities. Yield: 90%. Mp: 84−86 °C. IR (cm^{-1}): 3383, 1725, 1368, 1304, 1219, 1080. ^{1}H NMR: δ 1.14, 1.21, 1.26 and 1.31 (4 d, J = 6.0 Hz, 12 H), 1.34, 1.43, 1.51 and 1.64 (4 s, 36 H), 3.05 (d, J = 6.0 Hz, 1 H), 4.82 and 4.98 (2 m, 2 H), 7.35 and 7.98 (2 d, $J \approx$ 12.0 Hz, 4 H). The NH proton signals were too broad. ^{13}C NMR: δ 21.6, 21.8, 21.9, 22.0, 30.9, 31.5, 32.4, 32.6, 52.5 (d, J = 17.0 Hz), 55.7 (d, J = 7.0 Hz), 55.2, 55.4, 55.6, 69.4, 72.2, 123.9, 130.3, 131.2, 137.7, 153.2 (d, J = 20.5 Hz), 155.7, 171.1. ^{31}P NMR: δ 2.1, 81.5. Anal. Calcd for $C_{31}H_{57}BrN_6O_6P_2$: C, 49.53; H, 7.59; N, 11.18. Found: C, 49.46; H, 7.76; N, 11.09.

Compound 21. Procedure was the same as that for **19** using the similar molar quantities. Yield: 90%. Mp: 118−120 °C. IR (cm^{-1}): 3370, 1734, 1227, 1082, 1030. ^{1}H NMR: δ 1.14, 1.21, 1.28 and 1.34 (4 d, J = 6.0 Hz, 12 H), 1.45, 1.49, 1.53 and 1.68 (4 s, 36 H), 3.20 (d, J = 6.0 Hz, 1 H), 4.78 and 4.90 (2 m, 2 H), 8.20 (AB qrt, 4 H). The NH proton signals were broad. ^{13}C NMR: δ 21.6, 21.7, 21.8, 22.0, 30.9 (t, J = 4.5 Hz), 31.3 (d, J = 3.7 Hz), 32.5 (d, J = 10.2 Hz), 52.6 (d, J = 18.0 Hz), 55.8 (d, J = 7.3 Hz), 55.7, 69.5, 72.3, 124.1, 128.2, 129.0, 130.4, 131.3, 137.2, 153.1 (d, J = 20.2 Hz), 155.7, 171.0. ^{31}P NMR: δ 2.9, 82.0. Anal. Calcd for $C_{31}H_{57}N_7O_8P_2$: C, 51.87; H, 8.00; N, 13.66. Found: C, 52.01; H, 7.94; N, 13.89.

Compound 22. Procedure was the same as that for **19** using similar molar quantities. Yield: 91%. Mp: 176−178 °C. IR (cm^{-1}): 3372, 3152, 1740, 1302, 1167, 1080. ^{1}H NMR: δ 1.08−1.21 (many lines, 48 H), 2.32 (s, 3 H), 3.21 (d, J = 4.0 Hz, 1 H), 4.00−5.10 (m, 2 H), 6.66 (d, $J \approx$ 13.2 Hz, 1 H), 7.10 and 7.85 (d each, 4 H, J = 7.0 Hz), 10.71 (br, 1 H). ^{13}C NMR: δ 21.2, 21.5, 21.7, 21.9, 30.8, 30.9, 31.1, 31.2, 32.3, 32.5, 52.8 (d, J = 17.0 Hz), 55.3 (d, J = 7.0 Hz), 55.6 (d, J = 7.0 Hz), 56.2, 69.5, 72.3, 126.4, 128.1, 138.1, 144.0, 152.6 (d, J = 20.2 Hz), 156.5. ^{31}P NMR ($CDCl_3$): δ 2.3, 82.2. Anal. Calcd for $C_{31}H_{60}N_6O_7P_2S$: C, 51.52; H, 8.31; N, 11.63. Found: C, 51.45; H, 8.25; N, 11.46.

Esterification Reaction Using in Situ Formed 23 and Ethanol Leading to Ester 24. DEAD (0.58 g, 3.44 mmol) was added dropwise to a stirred solution of **10** (1.20 g, 3.44 mmol) in toluene (20 mL) and the mixture stirred for 30 min at room temperature. To this 4-NO_2-C_6H_4COOH was added all at once, and the mixture stirred for 2 h at room temperature. To this mixture was added ethanol (0.24 g, 5.16 mmol), and the contents were heated at 80 °C (no reaction at room temperature; ^{31}P NMR δ 3.8 and 82.9 (90%; ascribed to **23** by comparing with the data for compound **21**)) for 12 h. Solvent was removed, dichloromethane (20 mL) added to the residue and insoluble material was filtered off. Evaporation of the solvent gave a gummy material that was chromatographed over silica gel (hexane followed by ethyl acetate/hexane 1:10) to afford the ester (4-NO_2-$C_6H_4CO_2$Et) (**24**). Yield: 0.26 g (40%). Mp: 54−58 °C; lit. mp 55−59 °C[23]. We also attempted the reaction utilizing **21**, but side reactions appear to occur, inhibiting the esterification at the high temperatures used.

Acknowledgment. This work was supported by the Department of Science and Technology (DST), New Delhi. We also thank (i) the Council of Scientific and Industrial Research, New Delhi for fellowships to N.N.B.K., (ii) UGC (New Delhi) UPE program for equipment, and (iii) DST (New Delhi) for Single Crystal Diffractometer facilities.

Supporting Information Available: Further X-ray structural information including plots for **11**, **13** (improved bond parameters), **14**, **18**, and **A**; ^{13}C NMR spectrum of **19**; and CIF files for **11**, **13**, **14**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO051997X

(23) This compound is available from Aldrich (cat. no. 15, 595-0).