taining the X-ray crystallographic results. We also thank the Niels Clauson-Kaas Laboratory for a generous sample of aminomalononitrile tosylate (AMNT, 1).

Supplementary Material Available: ^{13}C NMR (75.5 MHz) and ^1H NMR (300 or 500 MHz) spectra of 2-aza-1,3-butadienes **3a–c,e,g–i**, piperazines **4a** and **4f**, 3-pyrrolines **9a** and **10a**, and pyrroles **9b**, **10b**, and **11b** and the X-ray crystallographic results for (*E,E*)-4-methoxy-2-aza-1,3-butadiene (**3a**) (52 pages). Ordering information is given on any current masthead page.

Addition, Substitution, and Deoxygenation Reactions of α-Phenyl-β-nitrostyrenes with the Anions of Thiols and Diethyl Phosphite: Formation of Indoles by Reaction with Ethyl Phosphites

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Reactions of excess RS^- (R = Ph, *t*-Bu) with $Ph_2C{=}C(SPh)NO_2$ in Me_2SO form $Ph_2C{=}CHSR$ via conversion of the initial Michael-type adducts into $Ph_2C(SR)CH{=}NO_2^-$ and $Ph_2C{=}CHNO_2$. In a similar fashion, reaction of $(EtO)_2PO^-$ with $Ph_2C{=}C(SPh)NO_2$ forms initially mainly $PhSP(O)(OEt)_2$ and $PH_2C[P(O)(OEt)_2]CH{=}NO_2^-$, which upon acidic workup will yield the nitroalkane or the Nef reaction product, $Ph_2C[P(O)(OEt)_2]CHO$. The reaction of $(EtO)_2PO^-$ with $Ph_2C{=}C(SPh)NO_2$ also produces $Ph_2C[P(O)(OEt)_2]C{\equiv}N$ via a Perkow-type reaction of the Michael adduct to yield $Ph_2C[P(O)(OEt)_2]CH{=}N(O)OP(O)(OEt)_2$ as an intermediate. The nitrile is also formed from $Ph_2C[P(O)(OEt)_2]CH(NO_2)_2$ with $(EtO)_2PO^-$ in $(EtO)_2P(O)H$ or Me_2SO at 30 °C and in >95% yield by the reaction of $(EtO)_3P$ with $Ph_2C[P(O)(OEt)_2CH(NO_2)_2$ at 150 °C. Reaction of $Ph_2C{=}CHNO_2$ or Ph_2C-$[P(O)(OEt)_2]CH_2NO_2$ with excess $(EtO)_2PO^-$ in Me_2SO or $(EtO)_2P(O)H$ forms 3-(diethoxyphosphinyl)-2,2-diphenylaziridine by a process postulated to involve $Ph_2C{=}CHN(O^-)OP(O)(OEt)_2$, $Ph_2C{=}CHNOP(O)(OEt)_2^-$, and 2,2-diphenyl-2*H*-azirine. Similarly, $Ph_2C{=}C(SBu\text{-}t)NO_2$ and $(EtO)_2PO^-$ give 3-(*tert*-butylthio)-2,2-diphenyl-2*H*-azirine in Me_2SO or 2-(*tert*-butylthio)-3-phenylindole in $(EtO)_2P(O)H$ solution. Deoxygenation of $Ph_2C{=}C(X)NO_2$ to form the 2-X-3-phenylindoles occurs in high yield at 150 °C in $(EtO)_3P$ with X = H, PhS, or *t*-BuS while 2-nitro-3-phenylindole is formed from $Ph_2C{=}C(NO_2)_2$ in $(EtO)_2P(O)H$ at 150 °C.

Introduction

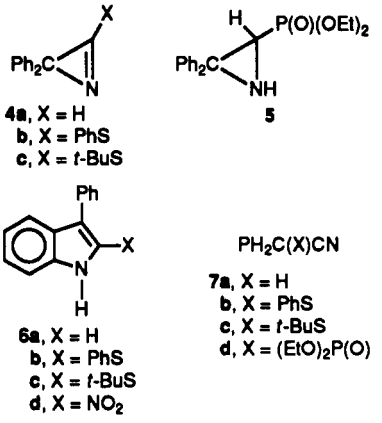
Reaction of 1,1-dinitro-2,2-diphenylethylene (**1d**) with 1 equiv of $(EtO)_2PO^-$ (P^-) in Me_2SO gives upon acidification a quantitative yield of the adduct **2d**.[1] The adduct **2a** is also formed from 2-nitro-1,1-diphenylethylene with P^- in the presence of $(EtO)_2P(O)H$ (PH). However, reactions of 1 equiv of PhS^- or *t*-BuS^- with **1d** in Me_2SO lead to the displacement of a nitro group forming **1b** or **1c** in high yield[1] while **1a** is converted to $Ph_2C{=}CHSR$.

$Ph_2C{=}C(X)NO_2$
1a, X = H
b, X = PhS
c, X = *t*-BuS
d, X = NO_2

$Ph_2C[P(O)(OEt)_2]CH(X)NO_2$
2a, X = H
b, X = PhS
c, X = *t*-BuS
d, X = NO_2

$Ph_2C(SR)CH(SPh)NO_2$
3a, R = Ph
b, R = *t*-Bu

We were initially drawn to a further study of these systems by the observation that excess PhS^- reacted slowly but essentially quantitatively with **1b** to form $Ph_2C{=}$ CHSPh and PhSSPh. Further work supported the premise that this denitrofication proceeded by the formation of the adduct **3a** followed by nucleophilic attack at the thiophenyl substituent to form the nitronate anion (Scheme I).[2,3] In a similar fashion the reaction of P^- with **1b** initially forms mainly **2a** and $PhSP(O)(OEt)_2$ via nucleophilic attack upon the sulfur atom in the adduct **2b**. However, we found that the reactions of excess P^- with the β-nitro-α-phenylstyrene derivatives **1** were complex and could yield heterocyclic products such as **4–6** or the nitriles **7**. This prompted us to examine the deoxygenations of



1 with $(EtO)_3P$ under conditions where nitroaromatics are converted to nitrenes.[4] At 150 °C the indoles **6a–c** are formed in high yield from **1a–c**, possibly via the azirines

Scheme I

$$3 + RS^- \rightarrow RSSPh + Ph_2C(SR)CH{=}NO_2^- \rightleftharpoons$$
$$RS^- + \mathbf{1a} \rightarrow Ph_2C{=}CHSR + NO_2^-$$

† Present address: Department of Chemistry, Yarmouk University, Irbid, Jordan.

(1) Russell, G. A.; Dedolph, D. F. *J. Org. Chem.* **1985**, *50*, 3878.
(2) Thiolate anions are known to attack 2-halo-2-nitropropanes to generate the nitronate anion and the sulfenyl halide: Bowman, W. R.; Rakshit, D.; Valmas, M. D. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2327; Bowman, W. R.; Richardson, G. D. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1407.
(3) The possibility exists that $Ph_2C(SR)CH{=}NO_2^-$ might be converted into $Ph_2C{=}CHSR + NO_2^-$ in an intramolecular process.[1]
(4) Cadogen, J. I. G. *Q. Rev. Chem. Soc.* **1968**, *22*, 222.

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Table I. Reaction of $Ph_2C{=}C(SPh)NO_2$ (1b) with $(EtO)_2POK$ in Me_2SO at 25–30 °C

reactants, M			products,[a] %				
1b	P^-	time, h	2a	7d	5	$PhSP(O)(OEt)_2$	others
0.006	0.03	0.5	37	7	tr	41	*b*
0.006	0.03	1.0	37	10	tr	43	*c*
0.006	0.03	24	17	11	+	37	*d*
0.072	0.36	2.0	15[e]	9[e]	30[e]	60	6a (tr)
0.054	0.27	17	+	+	50	+	

[a] By GC using biphenyl as an internal standard. [b] 7a (tr), 6b (tr), Ph_2S_2 (7%), $Ph_2C{=}CHSPh$ (6%), 1a (2%). [c] 7a (tr), 6b (tr), Ph_2S_2 (4%), $Ph_2C{=}CHSPh$ (6%), 1a (3%). [d] 7a (tr), 6b (tr), Ph_2S_2 (4%), $Ph_2C{=}CHSPh$ (8%), 1a (3%). [e] Isolated by column chromatography.

4a–c,[5–9] while 6d is formed from 1d in $(EtO)_2P(O)H$. β-Nitrostyrene does not lead to significant amounts of indole under these conditions[10–12] and at ambient temperatures yields products derived from the addition of $(EtO)_3P$ at the α-carbon atom,[13] a process apparently hindered by an α-phenyl substituent.

Results and Discussion

Reactions of Nucleophiles with 1-Nitro-2,2-diphenyl-1-(phenylthio)ethylene. Compound 1b reacted slowly with 5 equiv of PhS^- in Me_2SO to form $Ph_2C{=}CHSPh$ (94% isolated yield) and PhSSPh or with excess *t*-BuS^- to form $Ph_2C{=}CHSBu$-*t* (88% isolated yield). The reactions are neither stimulated by sunlamp irradiation nor retarded by 5–10 mol % of $(t\text{-}Bu)_2NO^\bullet$ or $p\text{-}O_2NC_6H_4NO_2$. The only effect of exposure to air is an increased yield of PhSSPh. It thus appears that the reaction of 1b with RS^- in Me_2SO is an ionic process.[14] Furthermore, in the early stages of the reaction, $Ph_2C{=}CHNO_2$ can be detected as an intermediate (Figure 1). This supports the process of Scheme I (R = Ph or *t*-Bu). The nitro-substitution product $[Ph_2C{=}C(SPh)_2]$ was not observed in the reaction of PhS^- with 1b although it was independently shown to persist under the reaction conditions.

No reaction was observed between PhS^- and 1c. In this case, the intermediate adduct $[Ph_2C(SPh)CH(SBu\text{-}t)NO_2]$ may not be formed, of if formed at a low equilibrium concentration, the adduct may be sterically hindered to nucleophilic attack by PhS^-. The adduct 3a could not be detected by GCMS in the CH_2Cl_2 extracts of the hydrolysis products from the reaction of 1b with a deficiency of PhSK or PhSK/PhSH in Me_2SO, THF, DMF, or EtOH. In Me_2SO apparently 3a is formed slowly but reacts rapidly with PhS^- according to Scheme I.

The reaction of 5 equiv of P^- with 1b in Me_2SO gave as major products $PhSP(O)(OEt)_2$, 2a, 7d, and 5 (Table I) with 5 increasing at the expense of 2a at higher concentrations of the reactants or longer reactions times. Reaction of 2a with excess P^- in Me_2SO formed 5 but not 7d. Thus, the major initial products from 1b are 2a and 7d, both of which can be reasonably formulated by further reactions of the initially formed adduct 2b. Initially 2a greatly predominates over 7d, consistent with preferred nucleophilic attack upon 2b to form the nitronate anion. In PH solution the reaction of excess P^- with 1b occurs more rapidly. Hydrolysis with brine after a 2-min reaction period gave a 50% yield of the Nef reaction product $Ph_2C[P(O)(OEt)_2]CHO$ expected from $Ph_2C[P(O)(OEt)_2]CH{=}NO_2H$.

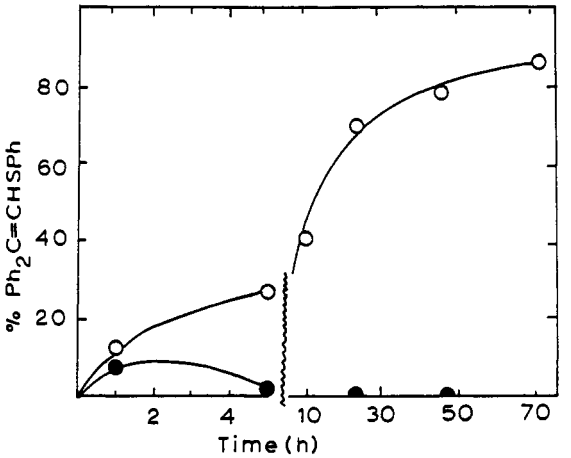


Figure 1. Reaction of 1b (initially 0.02 M) with PhSK (0.10 M) in Me_2SO at 25 °C; ○, % $Ph_2C{=}CHSPh$; ●, % $Ph_2C{=}CHNO_2$.

Table II. Reaction Products from $Ph_2C[P(O)(OEt)_2]CH_2NO_2$ (2a) or $Ph_2C[P(O)(OEt)_2]CH(NO_2)_2$ (2d) in Ethyl Phosphite Solution at 150 °C

substrate[a]	solvent	time, h	product,[b] % 7d	$Ph_2CHP(O)(OEt)_2$	5
2d	$(EtO)_3P$	1	>95	*c*	*c*
2d	$(EtO)_3P$/$(EtO)_2P(O)H$[d]	1	>95	*c*	*c*
2d	$(EtO)_2P(O)H$	1	14	3	*c*
2a	$(EtO)_3P$	1	23	26	7
2a	$(EtO)_3P$/$(EtO)_2P(O)H$[d]	1	22	76	tr
2a	$(EtO)_2P(O)H$	1	32	8	*c*
2a	$(EtO)_2P(O)H$	13	14	19	*c*

[a] 0.3 mmol of substrate in 1 mL of the phosphite. [b] By GC using biphenyl as an internal standard. [c] Not observed. [d] 1:1 volume ratio (3.9 mmol of $(EtO)_2P(O)H$ and 2.9 mmol of $(EtO)_3P$).

Minor products observed in the reaction of 1b with P^- in Me_2SO include 1a, 7a, Ph_2S_2, the indole 6b, and at longer reaction times the indole 6a. In moist Me_2SO, $Ph_2C{=}O$ is formed from the hydrolysis of 1b with traces of $Ph_2C(NH_2)CO_2Et$ observed. These products suggest minor reaction pathways leading to 7b (converted to 7a by P^-) and the azirine 4b (converted to the indole 6b or to $Ph_2C(NH_2)CO_2Et$).

Reactions Leading to $Ph_2C[P(O)(OEt)_2]C{\equiv}N$. The formation of the nitrile 7d as a minor product in the reaction of 1b with P^- can be rationalized as arising from a

(5) The thermal conversion of 2*H*-azirines to indoles is usually formulated to involve the nitrene as an intermediate.[6,7] In general, thermal processes leading to vinylnitrenes proceed by initial formation of 2*H*-azirines.[8,9]

(6) Isomura, K.; Kobayashi, S.; Taniguchi, H. *Tetrahedron Lett.* **1968**, 3497.

(7) Hemetsberger, H.; Knittle, D.; Weidmann, H. *Monatsch. Chem.* **1970**, *101*, 161. Hemetsberger, H.; Knittle, D. *Monatsch. Chem.* **1972**, *103*, 144. Hickey, D. M.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1419.

(8) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 231.

(9) L'abbé, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 775.

(10) Abramovich, R. A.; Davis, B. A. *Chem. Rev.* **1964**, *64*, 149.

(11) Pyrolysis of 2-phenyl-2*H*-azirine forms $PhCH_2CN$ and indole in approximately equal amounts.[6,12]

(12) Boyer, J. H.; Kreuger, W. E.; Mikol, G. J. *J. Am. Chem. Soc.* **1967**, *89*, 5504.

(13) Kreuger, W. E.; McLean, M. B.; Rizwaniuk, A.; Maloney, J. R.; Behelfer, G. L.; Boland, B. E. *J. Org. Chem.* **1978**, *43*, 2877.

(14) The conversion of 1a to $Ph_2C{=}CH_2$ and of $PhCH{=}C(R)NO_2$ to $PhCH{=}CHR$ (R = Ph, CO_2Et) by treatment with Na_2S/PhS in DMF has been suggested to involve $>C(SPh)CH(NO_2^{\cdot-})$: Ono, N.; Kawai, S.; Tanaka, K.; Kaji, A. *Tetrahedron Lett.* **1979**, 1733.

Perkow-type reaction[15,16] of the adduct **2b** to form 8 followed by deoxygenation and elimination of $(EtO)_2PO_2H$ (Scheme II, X = PhS). There are several literature pre-

Scheme II

2b or **2d** + P^- →
$Ph_2C[P(O)(OEt)_2]CH(X)N(O^-)OP(O)(OEt)_2$ →
X^- + $Ph_2C[P(O)(OEt)_2]CH{=}N(O)OP(O)(OEt)_2$
8

8 $\xrightarrow[-(EtO)_2PO_2H]{-[O]}$ **7d**

cedents for such reactions of α-substituted nitroalkanes with phosphorus nucleophiles. Thus, reaction 1 occurs

$Me_2C(NO_2)_2 + P^- \xrightarrow{Me_2SO}$
$[Me_2C{=}N(O)OP(OEt)_2] \xrightarrow{-[O]} Me_2C{=}NOP(O)(OEt)_2$ (1)

readily,[17] and the same product is formed from the Perkow/Arbuzov reaction of $(EtO)_3P$ with $Me_2C(Cl)NO_2$.[18] In these reactions the intermediate nitronic phosphate is deoxygenated to the oximino phosphate by oxygen atom transfer to $(EtO)_3P$ or P^-. However, in the case of 8 the timing of the deoxygenation and elimination steps is not clear since an E2 elimination from 8 would produce a nitrile oxide $[Ph_2C[P(O)(OEt)_2]C{\equiv}NO]$ which would be readily deoxygenated to the nitrile.[19-21]

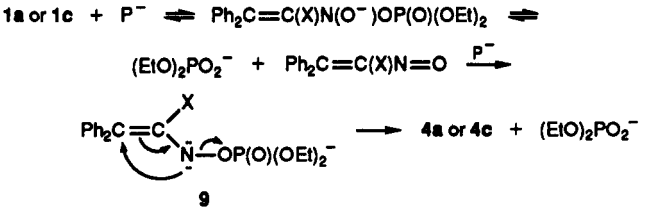
The reaction of **2d** with 5–10 equiv of P^- also forms the nitrile **7d** in Me_2SO or PH solution. However, the nitrile is now accompanied by an approximately equal amount of $Ph_2CHP(O)(OEt)_2$. Both products can be explained by Scheme II (with X = NO_2) if elimination of NO_2^- and $Ph_2CP(O)(OEt)_2^-$ are competitive. (With the better leaving group PhS the elimination of $Ph_2CP(O)(OEt)_2^-$ was not detected.) In the reaction of **2d** (0.3 M) with 5 equiv of P^- in PH an intermediate could be detected by GCMS at short reaction times. This intermediate gave m/z = 345 (3%) and 208 (100%) and is consistent with the nitrile oxide, $Ph_2C[P(O)(OEt)_2]C{\equiv}NO$ (fragmentation forms $Ph_2CC{\equiv}NO^+$ as the base peak).

In hopes of improving the yield of **7d**, the reactions of **2d** with $(EtO)_3P$ and PH at 150 °C were examined (Table II). The reaction with $(EtO)_3P$ was particularly clean leading to **7d** in >95% yield in 1 h. Presumably the reaction follows Scheme II with X = NO_2 and $(EtO)_3P$ in place of P^-. If this is so, only NO_2^- is eliminated from the intermediate $Ph_2C[P(O)(OEt)_2]CH(NO_2)N(O^-)OP(OEt)_3^+$, possibly because of an interaction between nitro oxygen atoms and the positively charged phosphorus atom.

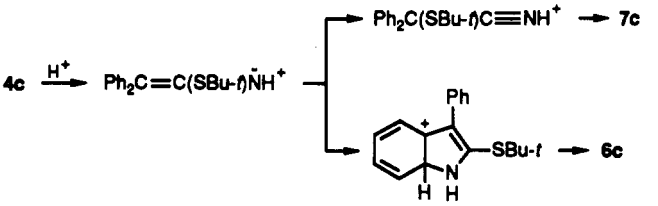
Nitroalkanes such as $PhCH_2CH_2NO_2$ are known to undergo deoxygenation/dehydration with $(EtO)_3P$ at elevated temperatures to yield the nitrile.[22] However, **2a** with $(EtO)_3P$ or PH at 150 °C formed considerable amounts of $Ph_2CHP(O)(OEt)_2$ in addition to **7d**, presumably from the elimination of $Ph_2CP(O)(OEt)_2^-$ from the intermediate $Ph_2C[P(O)(OEt)_2]CH_2N(O^-)OP(OEt)_3^+$. Table II also presents evidence that suggests that **7d** can be slowly converted to $Ph_2CHP(O)(OEt)_2$ by reaction with PH at 150 °C (compare entries 6 and 7).

Conversion of $Ph_2C{=}C(X)NO_2$ into 2*H*-Arirines and 2-X-3-phenylindoles. The reaction of 1 equiv of P^- with $Ph_2C{=}CHNO_2$ establishes an equilibrium with the anion of the adduct **2a**. With **1a** = 0.5 M, hydrolysis gave **2a** in 7% yield after 144 h in Me_2SO or in 37% after 1 h in PH. In PH solution **2a** was accompanied by significant amounts of the aziridine **5**. With excess P^- in Me_2SO or PH, the aziridine is the major product from either $Ph_2C{=}CHNO_2$ or the adduct **2a**. Thus, in 5 h with 10 equiv of P^- in PH, a 90% yield of **5** was isolated from a reaction initially 0.14 M in **2a** while in Me_2SO **2a** gave a 50% yield of **5** in 168 h. Formation of the nitrile **7d** was not observed in either solvent. The formation of **5** seems most reasonably formulated by attack of P^- upon the nitro group of **1a** (Scheme III with X = H) to yield the azirine **4a** which is trapped by P^- to give the aziridine **5**.

Scheme III

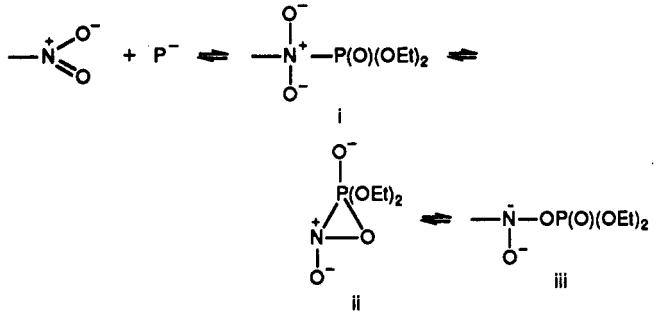


Scheme IV



(15) Lichtenthaler, F. W. *Chem. Rev.* **1961**, *61*, 607.

(16) For brevity intermediates are shown in which phosphorus is bonded only to the oxygen atom of a nitro or nitroso group. Initial attack by P^- may well occur at nitrogen followed by rearrangement of i to ii and iii.



Similar structures can be written for attack of $(EtO)_3P$. Although the conversion of a nitro group to a nitroso group can be readily rationalized from ii or iii, the Perkow reaction of **2b** or **2d** and azirine formation from **1**, is much better accommodated by iii and the analogous deoxygenated $NOP(O)(OEt)_2^-$.

(17) Russell, G. A.; Ros, F.; Hershberger, J.; Tashtoush, H. *J. Org. Chem.* **1982**, *47*, 1480.

(18) Allen, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 3071.

(19) Grundman, C.; Frommeld, H.-D. *J. Org. Chem.* **1965**, *30*, 2077. Jager, V. V.; Viehe, H. G. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 795.

(20) The reaction of $PhCH{=}NO_2K$ with $(EtO)_2PCl$ in ether yields PhCN by a process not involving the nitrile oxide. The initially formed $PhCH{=}CN(O)OP(OEt)_2$ rearranges to $PhCH{=}CNOP(O)(OEt)_2$ which eliminates $(EtO)_2PO_2H$: Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 812. Reaction of $Me_2C{=}NO_2^-$ with $(EtO)_2PCl$ yields $Me_2C{=}NOP(O)(OEt)_2$: Mukaiyama, T.; Nambu, H. *J. Org. Chem.* **1962**, *27*, 2201.

(21) Reactions of Ph_3P with α-substituted secndary nitroalkanes also occurs by a Perkow-type processes: Ohno, M.; Kawabe, N. *Tetrahedron Lett.* **1966**, 3935. The reaction of $RCH(Br)NO_2$ (R = Me, Et) with Ph_3P in PhH at 0–5 °C yields the isolable $HON{=}C(R)PPh_3^+Br^-$, which is hydrolyzed to the nitrile: Trippett, S.; Walker, D. M. *J. Chem. Soc.* **1960**, 2976. Trippett, S.; Walker, D. M.; Hoffmann, H. *J. Chem. Soc.* **1965**, 7140. A Perkow-type process has been postulated in the reaction of Ph_3P with $ArCH{=}C(Br)NO_2$ (Ar = Ph, *p*-MeC_6H_4) in MeOH to yield $ArCH{=}C{=}N(O)OPPh_3^+$, which after deoxygenation reacts with Ph_3P to form $Ph_3P{=}C(Ar)CN$ and a 2*H*-azirine which can be methanolized to $PhC(OMe){=}NCH_2PPh_3^+Br^-$: Devlin, D. J.; Walker, B. J. *J. Chem. Soc., Perkin Trans. 1*, **1973**, 1428; **1974**, 453.

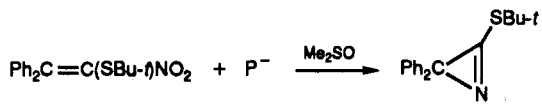
(22) Smolinsky, G.; Feuer, B. I. *J. Org. Chem.* **1966**, *31*, 3882 found that $PhCH_2CH_2NO_2$ or $PhCH_2CH{=}NOH$ form mainly $PhCH_2CN$ with $(EtO)_3P$ at 140–150 °C.

Table III. Reactions of $Ph_2C{=}C(X)NO_2$ with Ethyl Phosphites at 150 °C

X[a]	phosphite[b]	time, h	products[c]
H	$(EtO)_3P$	1	**6a** (73%), **5** (12%)
H	$(EtO)_3P$	24	**6a** (69%), **5** (14%)
H	$(EtO)_3P/(EtO)_2P(O)H$ (4:1)	24	**6a** (96%)
H	$(EtO)_3P$	24[d]	**6a** (90%)[e]
H	$(EtO)_3P$/EtOH (1:9)	5 h (95 °C)	**6a** (57%), **2a** (25%), **5** (5%), **1a** (10%)
PhS	$(EtO)_3P$	0.5	**6b** (99%)[e]
t-BuS	$(EtO)_3P$	1	**6c** (95%)[e]
t-BuS	$(EtO)_2P(O)H$	44	**6c** (25%),[e] 2-(ethylthio)-3-phenylindole (16%),[e] $Ph_2CHP(O)(OEt)_2$ (10%), $Ph_2CHC(O)SBu$-*t* (6%)[e]
NO_2	$(EtO)_2P(O)H$	0.5	**6d** (52%), **6a** (3%), **1a** (2%), **1d** (12%)
NO_2	$(EtO)_2P(O)H$	3	**6d** (19%),[e] **6a** (6%),[e] $Ph_2CHP(O)(OEt)_2$ (15%)[e]

[a] 0.3–1 mmol of $Ph_2C{=}C(X)NO_2$ per milliliter of phosphite. [b] Volume ratio for mixed solvents. [c] By GC with biphenyl as an internal standard. [d] 30 mol % of MeI added after 18 h. [e] Isolated yields.

Support for the mechanism of Scheme III was provided by the observation that in Me_2SO the major product formed from **1c** and excess P^- was the aziridine **4c** (reaction 2). Compound **4c** was isolated in 49% yield (plus 9% of

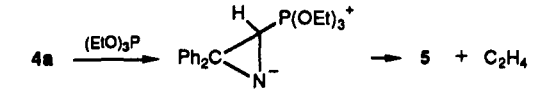


(2)

the hydrolysis product $Ph_2C(OH)C(SBu\text{-}t){=}NH$) after a 2-h reaction period in Me_2SO following the dropwise addition of **1c** to 10 equiv of 0.25 M P^-. Also observed were traces of Ph_2CHCN (**7a**) and *t*-$BuSP(O)(OEt)_2$. In PH as solvent **4c** appeared to be the major initial product (by GC), but it was rapidly converted to a 7:1 mixture of the indole **6c** and the nitrile **7c** (Scheme IV). The indole was isolated in 53% yield from a 30-min reaction of **1c** with 5 equiv of P^- in PH. In this reaction after 2 min, GC analysis indicated a ratio of **4c**:**6c** of ~5:1, but after 30 min **4c** was not detected. The nitrile **7a** and a trace of *t*-$BuSP(O)(OEt)_2$ were also observed, but the yield of **7a** did not increase after the initial 30-min reaction period. In this case, **7a** is not formed by nucleophilic attack upon **7c**.[23]

The contrasting behavior of **1b** and **1c** in reactions with P^- is easily understood in terms of the adduct **2**. With **1b** the adduct is formed and undergoes competing reactions with P^- by Schemes I and II with only a minor contribution from Scheme III. With **1c** either the adduct **2c** is not formed, or if it is present in equilibrium with **1c**, the adduct fails to react with P^- by Scheme I (steric) or by Scheme II (*t*-BuS^- is a poorer leaving group than PhS^-). The predominant reaction of **1c** thus follows Scheme III.

In view of the results obtained in the reactions of P^- with **1a–c**, it seemed reasonable that azirines would also be formed from reactions with $(EtO)_3P$ (i.e. via Scheme III with $(EtO)_3P$ in place of P^-). We thus examined the reaction of **1** with $(EtO)_3P$ at temperatures where 2-phenyl-2*H*-azirines are known to isomerize to indoles (Table III). With **1b** or **1c** the yields of the indoles **6b** and **6c** were essentially quantitative in a 1-h reaction at 150 °C. Reaction of **1a** led mainly to the indole **6a**, but significant amounts of the aziridine **5** were also formed, possibly via reaction 3. We therefore added PH as an



(3)

acidic catalyst in hopes of converting **4a** to **6a** (via Scheme IV). An excellent yield of **6a** (96%) was thus achieved. We also observed that **5** could be converted to **6a** at 150 °C by refluxing with MeI in $(EtO)_3P$ solution. Perhaps alkylation of **5** at oxygen followed by elimination of HI and $MeOP(OEt)_2$ occurs to regenerate the labile **4a**.

Reaction of **1d** with $(EtO)_3P$ gave a complex set of reaction products. However, with 4 equiv of PH for 30 min at 150 °C, **6d** was formed in 52% yield (12% of recovered **1d**). Also observed were **7d** (3%), **6a** (3%), and **1a** (2%). Reaction for 3 h gave **6a** and **6d** in about equal amounts, suggesting a denitrofication of **6d**. The low yield of **7d** indicated that addition of PH to **1d** was not important since under the reaction conditions the adduct **2d** forms **7d** in significant amounts (Table II). Reactions of **1b** or **1c** with PH at 150 °C yielded a complex set of reaction products including products formed from further reactions of Ph_2CHCN (e.g. $Ph_2CHC(O)SBu$-*t*, $Ph_2CHC(OEt){=}NH$).[24] With **1c** 2-(ethylthiyl)-3-phenylindole was also formed, presumably by dealkylation/alkylation of **6c**.

Reactions of Ethyl Phosphites with β-Nitrostyrene. Formation of the 2*H*-azirine from β-nitrostyrene should lead to $PhCH_2CN$ and indole.[11] In a previous study of the reactions of $(RO)_3P$ (neat, DME, *t*-BuOH) with $PhCH{=}CHNO_2$ at room temperature, $PhC[P(O)(OR)_2]{=}CH_2$, $PhCH[P(O)(OR)_2]CH_2NO_2$, and $PhC(OR)[P(O)(OR)_2]$-$CH{=}NOH$ were the major products.[13] In view of our success in forming azirine-derived products from α-phenyl-β-nitrostyrenes, we have examined reactions of $PhCH{=}CHNO_2$ with P^- at 25–30 °C and with $(EtO)_3P$ or $(EtO)_2P(O)H$ at 150 °C. However, indole or $PhCH_2CN$ were not observed.

With 1 equiv of P^- in PH, $PhCH[P(O)(OEt)_2]CH_2NO_2$ was formed slowly at room temperature (10% in 12 h) while with excess P^- the major product was $PhCH[P$-$(O)(OEt)_2]CH_2P(O)(OEt)_2$. Reaction of $PhCH{=}CHNO_2$ for 2 h at 150 °C with 3.2 equiv of $(EtO)_3P$ formed the diphosphonate (15%), $PhC[P(O)(OEt)_2](OEt)C{\equiv}N$ (23%) with traces of $PhC[O(O)(OEt)_2](OEt)CH{=}NOEt$ and $PhC[P(O)(OEt)_2]{=}NOEt$ while reaction with 5 equiv of PH yielded $PhC[P(O)(OEt)_2]{=}CH_2$ (23%), $PhCH[P$-$(O)(OEt)_2]C{\equiv}N$ (52%), and the diphosphonate (7%).

The formation of $PhC[P(O)(OEt)_2]{=}CH_2$ and the diphosphonate undoubtedly involves the elimination of HNO_2 from $PhCH[P(O)(OEt)_2]CH_2NO_2$. A similar process forming the diphosphonate via $PhCH[P(O)(OEt)_2]{=}CH_2$ from $PhCH{=}CHSO_2Ph$ and P^- in Me_2SO has been recently described.[25] The reaction of $PhCH{=}CHNO_2$ with

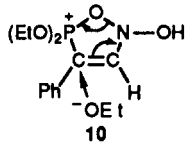
(23) Alternatively, Scheme III, with X = H could be entered by rearrangement of $Ph_2C[P(O)(OEt)_2]CH{=}NO_2^-$ to $Ph_2C{=}CHN(O^-)OP$-$(O)(OEt)_2$. Reactions which form **2a** in low yield, e.g. $[P^-] = [\mathbf{1a}] = 0.05$ Me_2SO, give very little of **5**.

(24) The source of **7a** in the reactions of **1b** or **1c** with P^- in Me_2SO or PH is unclear. Rearrangement with elimination of $(EtO)_2PO_2^-$ from **9** (X = PhS) to form **7b**, which could be precursor to **7a**, is a possibility, but this process seems to be excluded with X = *t*-BuS. Significant amounts of **7a** were only observed in PH solution. This suggests a sequence involving the protonation of **9** followed by the loss of the elements RS and $(EtO)_2PO_2$.

(25) Russell, G. A.; Ngoviwatchai, P. *J. Org. Chem.* **1989**, *54*, 1836.

PH at 150 °C apparently involves the initial formation of $PhCH[P(O)(OEt)_2]CH_2NO_2$ which can undergo either the loss of HNO_2 or deoxygenation–dehydration to form the nitrile.

In $(EtO)_3P$ solution the ethoxy derivatives $PhC[P(O)(OEt)_2](OEt)C{\equiv}N$ and $PhC[P(O)(OEt)_2](OEt)CH{=}NOEt$ are presumably formed from the previously reported $PhC[P(O)(OEt)_2](OEt)CH{=}NOH$ whose formation has been suggested to involve the cyclic intermediate **10**, de-



rivable from $PhCH[P(OEt)_3^+]CH{=}NO_2^-$ or $PhCH{=}CHN(O^-)OP(OEt)_3^+$.[13] The contrasting behaviors of $PhCH{=}CHNO_2$ and $Ph_2C{=}CHNO_2$ with P(III) reagents are a consequence of the presence of the ionizable α-hydrogen atom in the adducts formed from $PhCH{=}CHNO_2$.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were obtained with Nicolet NT300 or Varian Unity 500 spectrometers with tetramethylsilane as the internal standard. ^{31}P NMR spectra were obtained with a Brucker WM-200 spectrometer and reported in ppm relative to external 85% phosphoric acid. Mass spectra were obtained in the GC mode (EI or CI) or with a solids inlet probe (CI) by a Finnigan 4000 (INCOS data system). High-resolution spectra were obtained by a Kratos MS-50 spectrometer. Infrared spectra were obtained in the FT mode by an IBM IR 98 spectrometer. Neat spectra were recorded between NaCl plates. Elemental analyses were performed by Galbraith Laboratories, Inc. All melting points were determined on a Thomas-Hoover capillary melting point appartus and are uncorrected. Most products were isolated by flash column chromatography on silica gel (230–400-mesh ASTM). Analytical gas chromatography was performed with a Varian 3700 chromatography with a Hewlett-Packard 3390A integrator employing biphenyl as the internal standard and 7% OV-3 as the stationary phase. The purity of all title compounds was judged to be >95% since significant impurities could not be detected by GC or by ^1H NMR.

Materials. Dimethyl sulfoxide was vacuum distilled and stored over molecular sieves or CaH_2. The $(EtO)_3P$, $(EtO)_2P(O)H$, PhSH, *t*-BuSH, $PhCH{=}CHNO_2$, *t*-BuOK, and $Ph_2C{=}CH_2$ used were obtained from Aldrich Chemical Co. The anions PhS^-, *t*-BuS^-, $(EtO)_2PO^-$ were prepared in situ by reaction of 1 equiv of *t*-BuOK with the conjugate acids under N_2.

Reactants prepared according to literature procedures were **1a**,[26] **1b**,[1] **1c**,[1] **1d**,[27] and **2d**.[1] The following reaction products were either prepared according to literature procedures or had physical and spectroscopic properties in agreement with literature values: $Ph_2C{=}CH(SPh)$,[28] $Ph_2CH[P(O)(OEt)_2]$,[29] $PhSP(O)(OEt)_2$,[30] $PhCH[P(O)(OEt)_2]CH_2NO_2$,[13] $PhC[P(O)(OEt)_2]{=}CH_2$,[13,25] $PhC[P(O)(OEt)_2]CH_2P(O)(OEt)_2$,[25] 3-phenylindole,[31] and 1,1-diphenyl-2,2-bis(phenylthiyl)ethylene.[32]

Potassium Salt of Diethyl (2,2-Dinitro-1,1-diphenylethyl)phosphonate (2d). 1,1-Dinitro-2,2-diphenylethylene (5 mmol) in THF (20 mL) was added dropwise to a mixture of $(EtO)_2P(O)H$ (5.5 mmol) and *t*-BuOK (5.5 mmol) in 30 mL of THF at 35–40 °C. The solution turned from a deep brown to yellow. After stirring for 2 h, the THF was evaporated to give a yellow solid which was recrystallized from ethanol to give a 49% yield of $C_{18}H_{20}N_2O_7PK$ (elemental anal. C, H, N): mp 133–135 °C; ^1H NMR (Me_2SO-d_6) δ 7.20–7.06 (m, 10 H), 3.76–3.66 (m, 2 H), 3.45–3.33 (m, 2 H), 0.79 (t, J = 7.2 Hz, 6 H). The potassium salt (5 mmol) in 50 mL of EtOH was titrated with alcoholic HCl until the yellow solution became colorless. Upon cooling to 0 °C a 60% yield of **2d**, mp 131–133 °C (lit.[1] mp 128–129 °C) was obtained: ^1H NMR ($CDCl_3$) δ 7.68 (d, J_{PH} = 9.6 Hz, 1 H), 7.49–7.30 (m, 10 H), 4.07–3.96 (m, 4 H), 1.15 (td, J = 7.5, 0.6 Hz, 6 H); MS [solids probe, CI (isobutane)], m/z (relative intensity) 409 (m + 1, 100), 364 (28), 346 (10), 319 (9), 305 (3), 250 (3), 226 (2), 167 (5), 165 (1), 139 (9).

Diethyl (2-Nitro-1,1-diphenylethyl)phosphonate (2a). Solid $Ph_2C{=}CHNO_2$ (0.49 mmol) was added to a mixture of $(EtO)_2P(O)H$ (1 mL, 7.7 mmol) and *t*-BuOK (0.49 mmol). After stirring for 1 h the solution was poured into 5 mL of brine and extracted twice with 5 mL of CH_2Cl_2. The extract was washed, dried, filtered, and concentrated to give an oil, which was purified by flash column chromatography with hexane (75%)–ethyl acetate (25%) to give 37% of **2a**: mp 74–75 °C; ^1H NMR ($CDCl_3$) δ 7.55–7.32 (m, 10 H), 5.46 (d, J_{PH} = 9.0 Hz, 2 H), 3.94–3.84 (m, 2 H), 3.78–3.68 (m, 2 H), 1.16 (t, J = 7.2 Hz, 6 H); ^{13}C ($CDCl_3$) δ 136.1 (d, J_{PC} = 7.2 Hz), 129.7 (J_{PC} = 1.6 Hz), 127.9, 127.7, 78.7, 63.9 (d, J_{PC} = 7.0), 55.6 (d, $^1J_{PC}$ = 132 Hz), 16.1 (d, J_{PC} = 5.0 Hz); GC and HRMS, m/z (relative intensity) 363.1246 (M^+, 2, calcd for $C_{18}H_{22}NO_5P$ 363.1236), 317.1304 ($M^+ - NO_2$, 27, calcd for $C_{18}H_{20}O_3P$ 317.1302), 261 (8), 226 (14), 180 (100), 165 (26), 109 (28), 77 (6).

1,1-Diphenyl-2-(phenylthio)ethylene from 1-Nitro-2,2-diphenylethylene (1a). The nitroalkene (0.94 mmol) in 10 mL of Me_2SO was added dropwise to a solution of 4.75 mmol each of PhSH and *t*-BuOK in 10 mL of Me_2SO. After stirring for 30 h under N_2 the solution was hydrolyzed with 20 mL of brine and extracted three times with 20 mL of ether. The ether extract was washed, dried, and concentrated to give an oil that was purified by flash column chromatography (hexane) to give a 94% isolated yield of $Ph_2C{=}CHSPh$ whose spectra and GC retention time agreed with an independently prepared sample.[28]

Reaction of PhSK with 1-Nitro-2,2-diphenyl-1-(phenylthio)ethylene (1b). Reaction of **1b** (1 mmol) with 5 mmol each of PhSH and *t*-BuOK in 50 mL of Me_2SO containing biphenyl (1 mmol) as an internal standard was followed by GC after hydrolysis with brine and ether extraction (Figure 1). After 72 h there was an 87% yield of $Ph_2C{=}CHSPh$, 0.3% of $Ph_2C{=}CHNO_2$, and 1.3 mmol of PhSSPh. In Me_2SO, which had not been thoroughly dried, appreciable quantities of $Ph_2C{=}O$ were also formed.

On one occasion a product was isolated after column and thin-layer chromatography which GCMS did not indicate to be present in the original extract from the 1-h reaction. This material was unstable but gave a GCMS suggestive of **3a**, m/z (relative intensity) 336 (9), 335 (18), 334 (M^+ – PhS, 75), 225 ($M^+ - Ph_2S_2$, 100), 210 (94), 192 (27), 178 (52), 165 (48), 121 (38), 109 (2), 91 (41), 77 (10). A similar MS was initially observed in a MS solids inlet probe but with time the MS changed to give the spectrum of $Ph_2C{=}C(SPh)_2$, m/z 398 (2), 397 (4), 396 (M^+, 13), 287 (36), 254 (16), 231 (100), 153 (33), 121 (90).

2-(*tert*-Butylthio)-1,1-diphenylethylene. Solid **1b** (0.5 mmol) was added to 2.5 mmol of *t*-BuSK in 20 mL of Me_2SO and stirred for 23 h under N_2. The product was hydrolyzed with brine and extracted by CH_2Cl_2, and the filtrate was dried over Na_2SO_4. Using toluene as an internal standard the ^1H NMR yield of $Ph_2C{=}CHSBu$-*t* was 88%. Material isolated by column chromatography with hexane had the following properties: mp 56–58 °C; ^1H NMR ($CDCl_3$) δ 7.40–7.18 (m, 10 H), 6.77 (s, 1 H), 1.43 (s, 9 H); GC and HRMS, m/z (relative intensity) 270 (2.7), 268.12846 (M^+, 42; calcd for $C_{18}H_{20}S$ 268.12858), 212 (100), 178 (20), 165 (12), 77 (6), 57 (28).

α-(Diethoxyphosphinyl)diphenylacetaldehyde. Solid **1b** (1 mmol) was added to a mixture of $(EtO)_2P(O)H$ (3 mL) and *t*-BuOK (2 mmol). The green solution was stirred for 2 min, poured into 10 mL of brine, and extracted twice with 10 mL of CH_2Cl_2. The extract was washed, dried, filtered, and concentrated to give an oil which was purified by flash column chromatography using hexane (95%)–ethyl acetate (5%) to give a 50% yield of

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the aldehyde: mp 127–132 °C; ^{1}H NMR ($CDCl_3$) δ 9.93 (d, J_{PH} = 3.0 Hz, 1 H), 7.60–7.20 (m, 10 H), 4.12–3.87 (m, 4 H), 1.21 (t, J = 6.9 Hz, 6 H); IR (neat) 1730 cm^{-1}; GC and HRMS, m/z (relative intensity) 332.1170 (M^+, 0.5; calcd for $C_{18}H_{21}O_4P$ 332.1174), 304 (40), 276 (7), 248 (19), 207 (10), 178 (19), 165 (100), 105 (70), 77 (11); CI (solids probe, methane) 333 (MH^+, 100), 305 (20), 304 (13), 287 (1), 183 (3), 165 (1), 121 (2), 111 (2), 105 (1).

α-(Diethoxyphosphinyl)diphenylacetonitrile (7d). Addition of **2d** (0.217 mmol) to $(EtO)_3P$ (1 mL, 5.8 mmol) following by heating at 150 °C for 1 h gave after vacuum distillation of the unreacted $(EtO)_3P$ and $(EtO)_3PO$ which had been formed, an oily residue of **7d** (>95% yield by GC). Pure **7d** was obtained by TLC using hexane (90%)–ethyl acetate (10%) to give material with the following properties: mp 83–84 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 7.68–7.25 (m, 10 H), 4.01–3.95 (m, 2 H), 3.92–3.78 (m, 2 H), 1.14 (t, J = 7.2 Hz, 6 H); ^{13}C ($CDCl_3$) δ 134.2 (d, J_{PC} = 4.4 Hz), 128.8, 128.6, 128.5, 118.8 (d, J_{PC} = 12.6 Hz), 65.1 (d, J_{PC} = 7.1 Hz), 52.9 (d, $^1J_{PC}$ = 137 Hz), 16.2 (d, J_{PC} = 4.1 Hz); IR 2250 cm^{-1}; GC and HRMS, m/z (relative intensity) 329.1179 (M^+, 70; calcd for $C_{18}H_{20}NO_3P$, 329.1181), 304 (4), 273 (6), 193 (100), 165 (69), 109 (59), 91 (3), 77 (4).

Reaction of 0.27 mmol of **2a** with 1 mL of $(EtO)_3P$ at 150 °C for 1 h gave by GC **7d** (23%), $Ph_2CHP(O)(OEt)_2$ (26%), and **5** (7%). After reaction with a 1:1 mixture of $(EtO)_3P$ (2.9 mmol) and $(EtO)_2P(O)H$ (3.9 mmol) for 1 h at 150 °C, the GC yield of **7d** was 22% and of $Ph_2CHP(O)(OEt)_2$ was 76% with only a trace of **5** detected. Reaction of **2a** (0.16 mmol) with 1 mL of $(EtO)_2P(O)H$ for 1 h at 150 °C produced **7d** (32%) and $Ph_2CHP(O)(OEt)_2$ (8%) while a 13-h reaction period gave only 14% of **7d** and 19% of $Ph_2CHP(O)(OEt)_2$. Reaction of **2d** (0.19 mmol) with $(EtO)_2P(O)H$ (1 mL) at 150 °C for 1 h gave low yields of **7d** (14%) and $Ph_2CHP(O)(OEt)_2$ (3%).

3-(Diethoxyphosphinyl)-2,2-diphenylaziridine (5). Compound **2a** (0.14 mmol) was added to 1 mL of $(EtO)_2P(O)H$ and 0.14 mmol of *t*-BuOK. After stirring 5 h at room temperature, the solution was poured into 5 mL of brine and extracted twice with 5 mL of CH_2Cl_2. The extract was washed, dried, filtered, and concentrated to give by GC 90% of **5**. The material was chromatographed with hexane (90%)–ethyl acetate (10%) but remained upon the column from which it was eluted with ethyl acetate to give an oil having the following characteristics: IR (neat) 3238 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 7.60–7.20 (m, 10 H), 4.00 (p, J = 7.2 Hz, 2 H), 3.85–3.70 (m, 1 H), 3.60–3.40 (m, 1 H), 2.70 (d, J = 16.5 Hz, 1 H), 2.00 (br s), 1.24 (t, J = 7.2 Hz, 3 H) 1.05 (t, J = 7.2 Hz, 3 H); ^{13}C ($CDCl_3$) δ 143.6 (d, J_{PC} = 0.9 Hz), 138.4 (d, J_{PC} = 2.0 Hz), 132.2, 129.9, 128.8, 128.3, 128.1, 127.9, 127.5, 127.3, 126.9, 126.8, 62.0 (d, J_{POC} = 7.1 Hz), 61.9 (d, J_{POC} = 6.0 Hz), 49.4 (d, J_{PC} = 2.6 Hz), 38.5 (d, $^1J_{PC}$ = 199 Hz), 16.1 (d, J_{PC} = 6.6 Hz), 16.0 (d, J_{PC} = 6.0 Hz). The assignment of J_{PC} and δ for the diastereotopic carbons of the ethoxy groups was established by comparison of the 75- and 125-MHz proton-decoupled ^{13}C spectra. In **5** there is restricted rotation of the phenyl groups, and 12 different aromatic carbon atoms are observed. The ethoxy groups in **5** are diastereotopic as are the individual methylene hydrogen atoms. A 2D COSY spectrum showed that the δ 1.05 methyl is coupled to the methylene hydrogens at δ 3.78 and 3.50 while the methyl at δ 1.24 is coupled to the methylene group at δ 4.0 (the methylene hydrogens are also coupled to P with $^3J_{PH}$ = 7.2 Hz). The methine hydrogen at δ 2.70 is not coupled to any other hydrogen atom and therefore is coupled to phosphorous, $^2J_{PH}$ = 16.5 Hz (coupling to the methine ^{13}C is 164 Hz). The ^{31}P NMR spectrum is at δ 20.94 (d of pentets, J_{HP} = 16, 8 Hz). The GCMS and direct inlet HRMS spectra showed significant differences: GCMS (EI) m/z (relative intensity) 331 (0.5), 330 (1), 275 (1), 207 (1), 247 (1), 221 (1), 208 (7), 194 (34), 165 (9), 91 (100), 77 (4); GCMS (CI, isobutane), 332 (MH^+, 100), 208 (1), 194 (3), 165 (0.4); HRMS 331.13304 (M^+, 6; calcd for $C_{18}H_{22}NO_3P$ 331.13374), 330.12547 ($M - 1^+$, 6; calcd for $C_{18}H_{21}NO_3P$ 330.12591), 304 (11), 274 (4), 248 (3), 195 (9), 194 (37), 193 (100), 178 (4), 167 (10), 166 (18), 165 (39), 91.05467 (8; calcd for $C_7H_7^+$ 91.05478).

Reaction of 1b with $(EtO)_2PO^-$. With excess P^- (10 equiv) in dry Me_2SO the reaction leads mainly to $PhSP(O)(OEt)_2$, **2a**, **5**, and **7d**. The products listed in Table I were observed after workup with brine, extraction by CH_2Cl_2, and analysis by GC and GCMS. At lower P^-/**1a** ratios or in the presence of $(EtO)_2P(O)H$, the yield of the indole **6a** increased. In moist Me_2SO, $Ph_2C{=}O$ (and products derived from $Ph_2C{=}O$) is formed from the hydrolysis of **1b**. In one experiment with 2 equiv of P^- in moist Me_2SO the ethyl ester of α-aminodiphenylacetic acid [$Ph_2C(NH_2)CO_2Et$] was isolated by column chromatography: ^{1}H NMR (Me_2SO-d_6) δ 7.5–7.2 (m), 4.0 (q, J = 7.2 Hz, 2 H), 1.157 (t, J = 7.2 Hz, 3 H), 1.185 (s, 2 H); IR (neat) 3287, 1711, 1688 cm^{-1}; HRMS, m/z (relative intensity) 255.12565 (M^+, 73; calcd for $C_{16}H_{17}NO_2$ 255.12593), 226.0868 ($C_{14}H_{12}NO_2^+$, 97), 182.0968 ($C_{13}H_{12}N^+$, 100), 180.0815 ($C_{13}H_{10}N^+$, 20), 178.0863 ($C_{10}H_{12}NO_2^+$, 12), 167.0857 ($C_{13}H_{11}^+$, 37), 165.0707 ($C_{13}H_9^+$, 36), 152.0628 ($C_{12}H_8^+$, 13), 106.0657 ($C_7H_8N^+$, 20), 104.0501 ($C_7H_6N^+$, 62). All fragments were within 1.5 ppm of the assigned atomic composition.

Reaction of 2d with $(EtO)_2PO^-$. The solid potassium salt of **2d** (0.27 mmol) was added to $(EtO)_2P(O)H$ (1 mL) containing *t*-BuOK (1.35 mmol). Workup after stirring for 30 min showed the presence of **7d**, $Ph_2CHP(O)(OEt)_2$, and an intermediate with the following properties: GCMS, m/z (relative intensity) 345 (3), 317 (1), 284 (1), 292 (1), 208 (100), 165 (8), 105 (2), 77 (17). After being stirred for 26 h before workup, the above reaction mixture did not show the intermediate of m/z 345 by GCMS and gave by GC 15% of **7d** and 20% of $Ph_2CHP(O)(OEt)_2$.

3-(*tert*-Butylthio)-2,2-diphenyl-2*H*-azirine (4c). The nitroalkene **1c** (1.2 mmol) in 25 mL of Me_2SO was added dropwise to a mixture of $(EtO)_2P(O)H$ (12 mmol) and *t*-BuOK (12 mmol) in 25 mL of Me_2SO, and the resulting solution was stirred for 2 h before hydrolysis with 50 mL of brine. The product was extracted with two portions of 50 mL of CH_2Cl_2, and the extract was washed, dried over Na_2SO_4, and concentrated to an oily residue. Flash column chromatography using hexane (99%)–ethyl acetate (1%) gave a product which was separated by TLC into **4c** (49%) and 9% of a hydrolysis product. The azirine **4c** had the following properties: mp 69–72 °C; ^{1}H NMR ($CDCl_3$) δ 7.70–7.20 (m, 10 H), 1.67 (s, 9 H); IR (CH_2Cl_2) 1654 cm^{-1}; GC and HRMS, m/z (relative intensity) 283 (M^+, 0.2), 281.12349 (M^+, 3; calcd for $C_{18}H_{19}NS$ 281.122383), 225 (6), 193 (20), 192 (100), 177 (28), 165 (45), 77 (4), 57 (21).

The isolated hydrolysis product, mp 101–102.5 °C, was not detected by GCMS before column chromatography. The product in CCl_4 had IR absorption at 3207 (s, NH), 3000 (br, OH), and 1583 (s, C=N) cm^{-1}. The ^{1}H NMR ($CDCl_3$) contained a broad singlet at δ 9.63 with other absorptions at δ 7.50–7.30 (m, 11 H) and 1.49 (s, 9 H): HRMS, m/z (relative intensity) 299.1350 (calcd for $C_{18}H_{21}NOS$ 299.1344); CI (solids probe, methane) m/z (relative intensity) 300 (MH^+, 10), 284 (4), 254 (18), 244 (17), 227 (16), 226 (100), 184 (24), 183 (59), 166 (8), 105 (10). The MS data seems to favor the thioimidate structure, $Ph_2C(OH)C(SBu\text{-}t){=}NH$, rather than the oxime $Ph_2C(SBu\text{-}t)CH{=}NOH$. The HRMS is dominated by m/z 184.0881 (70%), 183.0810 (89%), and 105.0342 (100%). These fragments are within 2 ppm of the calculated masses for $C_{13}H_{12}O^+$ ($Ph_2CHOH^{\bullet+}$), $C_{13}H_{11}O^+$ (Ph_2COH^+) and $C_7H_5O^+$ ($PhCO^+$), respectively, and no fragments containing sulfur and/or nitrogen come close to the observed values of m/z (e.g. $PhCH{=}NH^{\bullet+}$ is 160 ppm lower than the mass measured for the 105 peak). The structure thus requires the unit Ph_2CO as in $Ph_2C(OH)C(SBu\text{-}t){=}NH$. Finally, the product can be easily rationalized by attack of H_2O upon $Ph_2C{=}C(SBu\text{-}t)NH^+$ derived by protonation of the azirine **4c**.

α-(*tert*-Butylthio)diphenylacetonitrile (7c). Reaction of **1c** with P^- in $(EtO)_2P(OH)$ produced mainly the indole **6c**. Column chromatography after a 24-h reaction period also yields the nitrile **7c**, mp 78–79 °C, which gives an IR spectrum without C=N absorption at ~1650 cm^{-1} and with a C≡N absorption at 2233 cm^{-1}: ^{1}H NMR ($CDCl_3$) δ 7.30–7.16 (m, 10 H), 1.59 (s, 9 H); the MS was identical with that observed for **4c**.

3-Phenylindole (6a). Material synthesized according to the literature but using $ZnCl_2$ as the catalyst had the following properties: mp 85.5–86 °C (lit.[31] 86–87 °C); ^{1}H NMR ($CDCl_3$) δ 8.24 (br s, 1 H, NH), 8.10–7.10 (m, 10 H); ^{13}C NMR ($CDCl_3$) 133.6, 135.5, 128.7, 127.4, 125.9, 125.7, 122.4, 121.7, 120.3, 129.8, 118.3, 111.4; IR (CCl_4) 3412 cm^{-1}; GC and HRMS, m/z (relative intensity) 194 (15), 193.08917 (M^+, 100, calcd for $C_{14}H_{11}N$ 193.08915), 177 (1), 165 (30), 115 (2), 97 (11), 82 (14), 77 (2).

3-Phenyl-2-(phenylthio)indole (6b). Compound **1b** (0.33 mmol) in 1 mL of $(EtO)_3P$ at 150 °C for 30 min followed by vacuum distillation of the volatiles gave a red oil as a residue which upon flash column chromatography with hexane (95%)–ethyl

acetate (5%) gave a 99% yield of the indole: mp 199–203 °C; ^{1}H NMR ($CDCl_3$) δ 8.16 (br s, 1 H), 7.80–7.0 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 138.9, 138.8, 133.7, 129.6, 129.1, 128.3, 127.1, 127.0, 126.8, 125.9, 124.4, 123.9, 121.7, 120.5, 120.1, 111.0; IR (neat) 3402 cm^{-1}; GC and HRMS, *m/z* (relative intensity) 301.0930 (M^+, 100; calcd for $C_{20}H_{15}NS$, 301.0925), 267 (10), 233 (26), 165 (7), 151 (4), 134 (5), 77 (5).

2-(*tert*-Butylthio)-3-phenylindole (6c). Reaction of **1c** (0.56 mmol) in 1 mL of $(EtO)_3P$ at 150 °C for 30 min gave a 95% isolated yield of the indole after flash column purification: mp 137–139 °C; ^{1}H NMR ($CDCl_3$) δ 8.16 (br s, <1 H), 7.82–7.10 (m, 9 H), 1.13 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 136.1, 134.7, 130.4, 128.0, 127.4, 126.3, 124.9, 124.0, 123.3, 120.1, 120.0, 110.9, 49.5, 31.1; IR (CCl_4) 3412 cm^{-1}; GC and HRMS, *m/z* (relative intensity) 283 (0.7), 281.1233 (M^+, 11; calcd for $C_{18}H_{19}NS$ 281.1238), 225 (100), 193 (7), 180 (1), 165 (6), 77 (2), 57 (14). Freshly prepared material does not contain a C=N IR absorption. However, absorption develops with time at 1620 cm^{-1}, suggesting the formation of the isoindole.

2-(Ethylthio)-3-phenylindole from the Reaction of 1c with $(EtO)_2P(O)H$. Material isolated by column chromatography had the following properties: mp 133–135 °C; IR (CCl_4) 3406, 1603 cm^{-1}; ^{1}H NMR δ 8.11 (br s, <1 H), 7.70–7.69 (m, 9 H), 2.66 (q, *J* = 7.2 Hz, 1.6 H), 2.83 (q, *J* = 7.2 Hz, 0.4 H), 1.09 (t, *J* = 7.2 Hz, 2.4 H), 1.04 (t, *J* = 7.2 Hz, 0.6 H). The NMR spectrum is consistent with a mixture of 4.3 parts of the indole to 1 part of the isoindole. The mixture has a MS *m/z* (relative intensity) GC, 255 (6), 253 (100), 234 (96), 193 (3), 178 (2), 165 (7), 77 (3); CI (solids probe, isobutane) 310 (M + 57$^+$, 5), 254 (M + 1$^+$, 100); HR 253.09222 (calcd for $C_{16}H_{15}NS$ 253.09253).

***S*-*tert*-Butyl Diphenylthioacetate.** Material isolated by column chromatography from the reactions of **1c** with $(EtO)_2P(O)H$ at 150 °C had the following properties: ^{1}H NMR ($CDCl_3$) δ 7.32–7.25 (m, 10 H), 5.10 (s, 1 H), 1.45 (s, 9 H); IR (neat) 1686 cm^{-1}; HRMS *m/z* 284.1231 (calcd for $C_{18}H_{20}OS$ 284.1235); CI (solids probe, isobutane) *m/z* (relative intensity) 285 (M + 1$^+$, 58), 271 (6), 229 (64), 209 (9), 167 (100), 152 (5), 123 (6).

***O*-Ethyl Diphenylacetimidate ($Ph_2CHC(OEt)$=NH).** Material isolated by column chromatography from the reaction of **1c** with $(EtO)_2P(O)H$ at 150 °C had the following properties: ^{1}H NMR ($CDCl_3$) δ 7.4–7.2 (m, 10 H), 5.65 (br s, 1 H), 4.90 (s, 1 H), 3.30 (m, 2 H), 1.09 (t, *J* = 7.2 Hz, 3 H); IR (neat) 3288, 1639 cm^{-1}; HRMS *m/z* (relative intensity) 239.13061 (M^+, 1; calcd for $C_{16}H_{17}NO$ 239.13102), 168.0936 ($C_{13}H_{12}^+$, 100), 167.0861 ($C_{13}H_{11}^+$, 75) 165.0709 ($C_{13}H_9^+$, 42), 152.0627 ($C_{12}H_8^+$, 20).

2-Nitro-3-phenylindole (6d). Reaction of 8 mmol of **1d** in 8 mL of $(EtO)_2P(O)H$ for 25 min at 150 °C gives by GC a 52% yield of **6d**. A 33% yield of **6d**, mp 157–159 °C (from hexane), was isolated after vacuum distillation of the volatiles and flash column purification of the residue using hexane (99%)–ethyl acetate (1%); IR (CCl_4) 3273 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.29 (1 H), 7.70–7.20 (9 H); ^{13}C ($CDCl_3$) δ 133.4, 139.4, 139.2, 127.5, 127.3, 127.2, 125.6, 122.8, 122.3, 118.5, 112.0; GC and HRMS, *m/z* (relative intensity) 238.07461 (M^+, 100; calcd for $C_{14}H_{10}N_2O_2$ 238.07423), 221 (5), 208 (16), 190 (41), 180 (15), 165 (36), 152 (11), 77 (19).

Diethyl *S*-Phenyl and *S*-*tert*-Butyl Thiophosphate. The *S*-phenyl thiophosphate prepared from the reaction of $(EtO)_3P$ with Ph_2S_2 by a literature procedure[30] has the following properties: ^{1}H NMR ($CDCl_3$) δ 7.62–7.26 (m, 5 H), 4.27–4.10 (m, 4 H), 1.31 (t, *J* = 6.9 Hz, 6 H); HRMS, *m/z* 246.0484 (calcd for $C_{10}H_{15}O_3PS$ 256.0480). The *S*-*tert*-butyl ester was identified by GCMS only, *m/z* (relative intensity) 226 (M^+, 1), 170 (100), 142 (30), 126 (48), 114 (43), 93 (23), 57 (60).

α-(Diethoxyphosphinyl)phenylacetonitrile. Reaction of 5 mmol of $PhCH$=$CHNO_2$ in 3 mL of $(EtO)_2P(O)H$ at 150 °C for 2 h gave an isolated yield of $PhCH[P(O)(OEt)_2]CN$ of 52% as a liquid after vacuum distillation of the volatiles and chromatography with hexane (90%)–ethyl acetate (10%). Also isolated were $PhCH[P(O)(OEt)_2]$=CH_2 (23%) and $PhCH[P(O)(OEt)_2]$-CH_2NO_2 (9%). The cyanophosphonate had the following properties: IR (neat) 2247 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45–7.20 (m, 5 H), 4.20 (d, *J* = 26.4 Hz, 1 H), 4.14–3.90 (m, 1 H), 1.24 (t, *J* = 7.5 Hz, 3 H), 1.18 (t, *J* = 7.5 Hz, 3 H); GC and HRMS, *m/z* (relative intensity) 253.0872 (M^+, 41; calcd for $C_{12}H_{16}NO_3P$ 253.08679), 225 (4), 197 (3), 137 (16), 117 (90), 109 (100), 89 (24), 81 (40), 77 (3); GCCI (ammonia) 271 (M + 18$^+$, 100), 254 (M + 1$^+$, 6).

α-Ethoxy-α-(diethoxyphosphinyl)phenylacetonitrile. Reaction of 10 mmol of $PhCH$=$CHNO_2$ with 5 mL of $(EtO)_3P$ for 2 H at 150 °C followed by distillation of the volatiles and column chromatography with hexane (80%)–ethyl acetate (20%) gave the ethoxy nitrile in 23% yield as a liquid. Also isolated were traces of $PhC[P(O)(OEt)_2]$=NOEt and $PhC(OEt)[P(O)$-$(OEt)_2]CH$=NOEt. A 15% yield of $PhC[P(O)(OEt)_2]CH_2P$-$(O)(OEt)_2$ was eluted from the column with pure ethyl acetate. $PhC(OEt)[P(O)(OEt)_2]CN$ has the following properties: IR (neat) 2235 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.70–7.40 (m, 5 H), 4.29 (p, *J* = 7.2 Hz, 2 H), 4.13–3.99 (m, 1 H), 3.97–3.82 (m, 1 H), 3.77–3.60 (m, 1 H), 3.53–3.40 (m, 1 H), 1.37 (dd, *J* = 5.9, 7.5 Hz, 3 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.16 (td, *J* = 7.2, 0.6 Hz, 3 H); GC and HRMS, *m/z* (relative intensity) 297.1134 (M^+, 7; calcd for $C_{14}H_{20}NO_4P$ 297.11300), 252 (1), 213 (1), 160 (13), 132 (20), 105 (100), 77 (11).

Ethyl Imino Ethers of α-Ethoxy-α-(diethoxyphosphinyl)phenylacetaldehyde Oxime and of Diethyl [α-(Hydroxyimino)benzyl]phosphonate. Traces of the imino ethers were isolated from the above reaction by column chromatography. $PhC(OEt)[P(O)(OEt)_2CH$=NOEt isolated as a liquid had the following properties: ^{1}H NMR ($CDCl_3$) δ 7.71 (d, *J* = 11.1 Hz, 1 H), 7.65–7.28 (m, 5 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 4.15–3.99 (m, 4 H), 3.80–3.68 (m, 1 H), 3.58–3.46 (m, 1 H), 1.33–1.20 (m, 12 H); GC and HRMS, *m/z* (relative intensity) 343.1549 (M^+, 1; calcd for $C_{16}H_{26}NO_5P$ 343.1549), 314 (1), 298 (2), 270 (1), 241 (1), 207 (13), 206 (100), 178 (28), 105 (30), 100 (19), 77 (16).

The $PhC[P(O)(OEt)_2]$=NOEt isolated as a liquid had the following properties: IR (neat) 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.92–7.30 (m, 5 H), 4.88 (q, *J* = 7.2 Hz, 2 H), 4.09 (p, *J* = 7.2 Hz, 4 H), 1.40 (t, *J* = 7.2 Hz, 3 H), 1.18 (t, *J* = 7.2 Hz, 6 H); MS, *m/z* (relative intensity) GC 285 (13), 284 (21), 267 (8), 240 (8), 197 (7), 168 (11), 152 (13), 138 (49), 105 (31), 104 (100), 91 (18), 77 (33); CI (solids probe, ammonia) 303 (M + 18$^+$, 29), 286 (M + 1$^+$, 100); HRMS 285.11244 (calcd for $C_{13}H_{20}NO_4P$ 285.11300).

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