IR ($CHCl_3$, solvent-subtracted spectrum) 3025, 2230 (C≡N), 1590, 1480, 1225 cm^{-1} (C-O-C); ^1H NMR (CD_2Cl_2) δ 6.80-7.80 (m); ^{13}C NMR ($CDCl_3$) δ 104.6 and 112.9 (C—C≡N), 118.1 and 118.3 (C≡N), 117.2, 118.5, 120.5, 125.5, 129.5, 130.4, 132.6, and 135.9 (aromatic C-H), 142.1 and 145.6 (biphenyl carbons), 154.5 and 161.8 (ethereal carbons). HRMS:[40] calcd for $C_{20}H_{12}N_2O$, 296.0951, obsd 296.0935; rel intensity calcd for M + 1 22.6, obsd 22.9. An isolated sample of **5** exhibits the following: mass spectrum[39] (GC-MS) m/z (rel intensity) 296 (M^+, 100), 297 (M + 1, 23), 295 (24), 268 (14), 267 (20), 164 (10), 77 (26), and 51 (12); IR (CCl_4) 2230 (C≡N), 1551, 1223 cm^{-1} (C-O-C); ^1H NMR (CD_2Cl_2) δ 7.02-7.85 (m); ^{13}C NMR ($CDCl_3$) δ 103.6 and 111.1 (C—C≡N), 115.6 and 117.0 (C≡N), 117.8, 120.3, 123.0, 125.4, 128.8, 129.7, 130.3, 133.0, 133.9, and 134.3 (aromatic C-H), 143.0 and 143.9 (biphenyl carbons), 154.4 and 159.7 (ethereal carbons). Isolated samples of **4** and **5** were employed for product quantitation of electrolysis solutions.

(40) HRMS data were provided by the Midwest Center for Mass Spectrometry, University of Nebraska.

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Registry No. **3**, 1591-30-6; **4**, 96807-04-4; **5**, 96807-05-5; 2-phenoxybenzamide, 72084-13-0; 4-bromobenzonitrile, 623-00-7; potassium phenoxide, 100-67-4; 4-cyanodiphenyl ether, 3096-81-9; 2-cyanodiphenyl ether, 6476-32-0; 2-phenoxybenzoic acid, 2243-42-7.

The Chemistry of Free and Complexed Phosphirenes: Reactivity toward Electrophiles, Nucleophiles, and Conjugated Dienes

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Abstract: The direct conversion of phosphole into phosphirene complexes has been achieved by reaction of the former with dimethyl acetylenedicarboxylate and alkynes. The cleavage of the phosphirene ring in some P-$W(CO)_5$ complexes has been observed with basic water, morpholine, and methanol under UV. In all cases, vinylphosphorus compounds are obtained. A [4 + 2] Diels-Alder cycloaddition of 2,3-dimethylbutadiene with the double bond of 2-ethoxycarbonyl-1,3-diphenylphosphirene P-$W(CO)_5$ complex has given the expected bicyclic phosphirane. 1,2,3-Triphenylphosphirene obtained from the corresponding P-$W(CO)_5$ complex by decomplexation with iodine and *N*-methylimidazole reacts sluggishly with Me_3O^+, BF_4^- to give the 1-methylphosphirenium salt, which is instantly opened by neutral water at room temperature to give the corresponding vinylphosphine oxide. The same phosphirene reacts readily with *n*-butyllithium at -70 °C in THF to give the open-chain butylphenylphosphino-substituted vinyl carbanion as a mixture of cis and trans species. The reactions of this carbanion with water, methyl iodide, and *p*-chlorobenzaldehyde have been studied and always give a mixture of *Z* and *E* vinyl compounds, the trans attack being favored in each case. Triphenylphosphirene is also cleaved by sodium-naphthalene at -70 °C in THF. According to protonation and methylation experiments, the P,C dianion thus obtained does not isomerize.

The chemistry of heterocyclopropenes $XC_2R'_2$ is a field of considerable current interest. Whereas 1*H*-azirines (X = NR), oxirenes (X = O), and thiirenes (X = S) are still elusive species, stable borirenes (X = BR),[1-3] silirenes (X = SiR_2),[4-6] germirenes (X = GeR_2),[7] and thiirenium salts (X = S^+R)[8,9] have been discovered recently. There are at least three reasons why such rings deserve a special interest. Firstly, drastic changes of the reactivity of both the heteroatoms and the X-C bonds are expected due to the very high strain of these heterocycles. Secondly, various two- and four-electron stabilizing and destabilizing interactions between the carbon-carbon double bond and the heteroatoms can be envisaged and experimentally probed in such systems. Thirdly, these species are expected to be very versatile synthons through ring openings and ring expansions.

With such a background, phosphirenes (X = PR) were an obvious target for phosphorus chemists. The first attempted synthesis of this ring was reported by Stille.[10] The suspected 1,2,3-triphenylphosphirene oxide was later shown to be an open-chain product.[11] Then, Russian[12] and Indian chemists[13] claimed to have prepared pentacoordinate phosphirenes, but the data provided were so limited that the phosphirene structure cannot be considered established. In 1982, we reported the first unambiguous synthesis of the phosphirene ring, the existence of which was proven by X-ray crystal structure analysis.[14] The ring was

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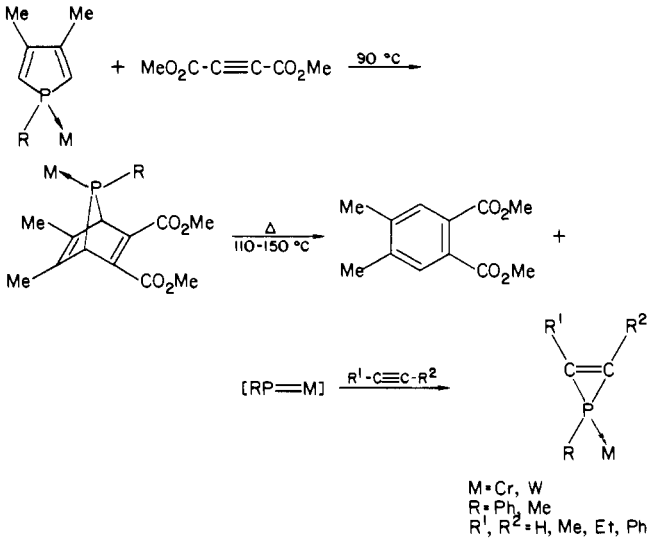
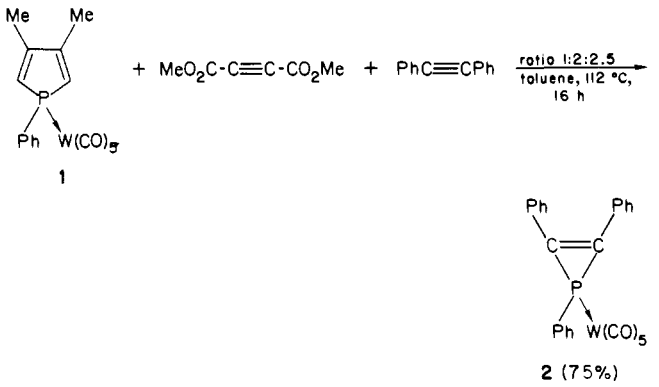
obtained as a series of very stable $P\rightarrow M(CO)_5$ complexes (M = Cr, W) through the reaction of transient terminal phosphinidene complexes $[RP{=}M(CO)_5]$ with alkynes. Subsequently, we showed that it was possible to decomplex such systems and we described 1,2,3-triphenylphosphirene, the first known stable tervalent phosphirene.[15] Quite independently, Hogeveen[16] described a direct synthesis of phosphirenium salts ($X = P^+(R)Cl$) by reaction of $RPCl_2{\cdot}AlCl_3$ with alkynes. The reaction was extended to monohalophosphines R_2PCl by Breslow.[17] The rings of these phosphirenium salts appear to be readily opened by reaction with water. In the meantime, we have studied in depth the properties of phosphirenes and we wish to report hereafter on a series of new results concerning the chemistry of this fundamental heterocycle.

Results and Discussion

Synthesis and Chemistry of Phosphirene Complexes. The initial synthesis of phosphirene complexes relied on a two-step scheme starting from phosphole complexes:

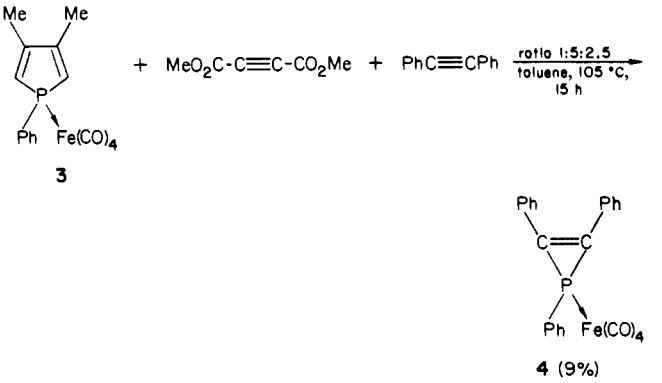


The crucial step was the obtention of the 7-phosphanorbornadiene complex, the stability of which depends critically on the nature of the complexing unit.[18] We have found now that it is possible to avoid the isolation of this intermediate and to perform a one-pot conversion of phosphole into phosphirene complexes:



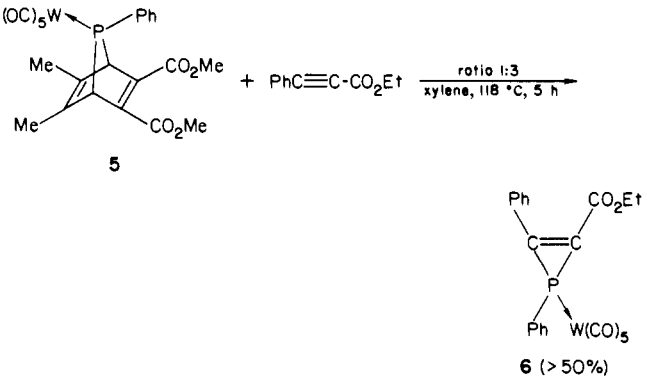
The initial two-step scheme gave only a 33% overall yield of **2** from **1**. The rationale behind this new synthesis is quite obvious.

In a first step, the dienic system of **1** is only able to react with the highly electrophilic acetylenedicarboxylate. The 7-phosphanorbornadiene complex thus formed decomposes in situ to give the terminal phosphinidene complex. According to experimental and theoretical[19] data, this species is highly electrophilic and discriminates easily between the two acetylenic compounds in favor of the electron-rich tolan. Apart from its higher yield and simplicity, this new method does not require stable 7-phosphanorbornadiene intermediates. Thus its generality is higher than that of the previous one. We have demonstrated this assumption in the case of an iron complex:

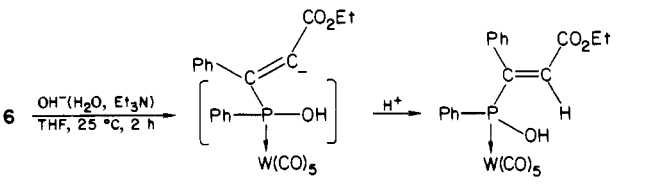


The low yield probably reflects the low stability of **4** at 105 °C over extended periods of time. Nevertheless, the obtention of **4** is significant since we have previously shown that 7-phosphanorbornadiene $P\rightarrow Fe(CO)_4$ complexes are unstable and cannot be isolated.[18]

Due to their high electrophilicity,[19] terminal phosphinidene complexes easily react with electron-rich alkynes. Conversely, they react much less efficiently with electron-poor alkynes. For example, we have checked that $[PhP{=}W(CO)_5]$ does not react with dimethyl acetylenedicarboxylate. It was thus interesting to study one intermediate case where the alkyne bears only one electron-withdrawing group. In fact, the synthesis of phosphirene complexes appears to be fairly general since terminal phosphinidene complexes are even able to react with phenylpropiolates:



Complex **6** is the first functional phosphirene described in the literature. It shows a varied and interesting reactivity toward nucleophiles. For example, the hydroxide ion attacks **6** at the phosphorus atom:



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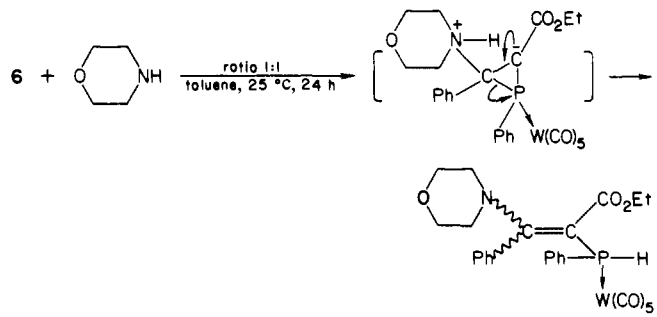
Mass spectrometry shows conclusively that **7** results from the addition of water to **6**: (EI, 70 eV, ^{184}W) *m/e* 624 (M, 50), 484 (M − 5CO, 100); (CI, CH_4) *m/e* 623 (M − H, 100), 606 (M − H_2O, 45). Similarly, ^{31}P NMR spectroscopy proves that the phosphirene ring of **6** has been opened: δ ^{31}P(**7**) 102.2 ($CDCl_3$) vs. −138 for **6**. This chemical shift is close to that recorded for various $(R_2POH)W(CO)_5$ complexes (i.e., δ ^{31}P([PhP-($CH_2CH{=}CH_2$)OH]$W(CO)_5$) 98 in C_6D_6[20]). The ^1H NMR spectrum in $CDCl_3$ shows the vinylic proton at 6.73 ppm (^3J(H–P) = 17.1 Hz). The ^{13}C NMR spectrum shows a very deshielded fully substituted olefinic Ph–*C*–P carbon at 158.2 ppm (^1J(C–P) = 23.2 Hz) in agreement with the expected polarization of the double bond. It is interesting to note that only one isomer of **7** is obtained according to all our spectroscopic results. We propose the *E* configuration on the basis of the similarities of the ^3J(H–P) vinylic couplings in **7**, **9a**, and **11** (vide infra).

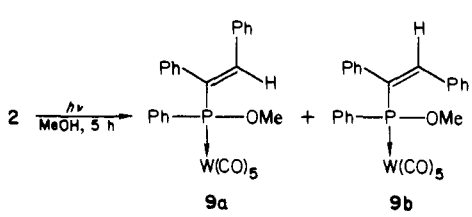
The preferential attack of phosphorus by hydroxide ion is probably partly driven by the high oxophilicity of phosphorus. Indeed, a nitrogen nucleophile such as morpholine attacks **6** not at phosphorus but at the positive carbon of the double bond:



8 (70%)

Mass spectrometry indicates that **8** results from the addition of one molecule of morpholine to **6**: (CI, NH_3, ^{184}W) *m/e* 693 (M, 80), 262 (100). The cleavage of the ring and the presence of a P–H bond in **8** are demonstrated by ^{31}P NMR spectroscopy: δ ^{31}P(**8**) −31.8 (toluene) (^1J(P–H) = 344.2 Hz). The chemical shifts of the two olefinic carbons indicate a high polarization of the double bond, as expected: δ(P–C=) 91.9 (^1J(C–P) = 53.7 Hz); δ(P–C=*C*) 165.4 (^2J(C–P) = 13.4 Hz) in $CDCl_3$. As for **7**, we observe the formation of only one isomer of **8**, but we are unable to assign a stereochemistry to the double bond.

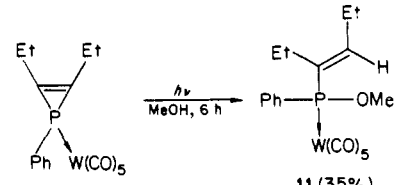
The ethoxycarbonyl substituent of **6** obviously sharply increases the sensitivity of the phosphirene ring toward nucleophilic attack since, under similar conditions, the 1,2,3-triphenylphosphirene complex **2** is completely insensitive toward both aqueous base and morpholine. Nevertheless, it is possible to cleave the ring of **2** by reaction with methanol under UV:



9a **9b**

(total yield 25%)

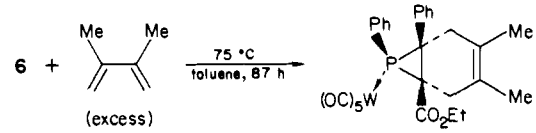
The two isomers **9a** and **9b** are formed in approximately similar quantities (ratio ~54:46). Only the major isomer has been obtained in the pure state. We have assigned the formula **9b** to the minor product which shows a more shielded vinylic proton on its ^1H NMR spectrum because we expected such an effect from the appropriately located vicinal phenyl group (a similar effect has been noted in other structures such as **21a** and **21b**, vide infra). Of course, such an assumption remains questionable. Similarly, the ^{31}P resonance appears at higher field for **9b** (δ ^{31}P 122.7 in C_6D_6) than for **9a** (δ ^{31}P 129.3). This observation can be correlated with steric compression (vide infra).[26] An analogous reaction has been carried out with the 1-phenyl-2,3-diethylphosphirene complex **10**:



10 **11** (35%)

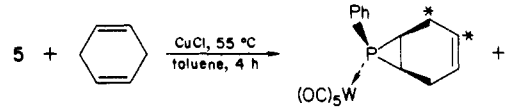
Here, the minor isomer is formed in very low quantity. Since **11** shows a more deshielded phosphorus atom than its minor counterpart, we assign it a formula similar to that of **9a**. The ^3J(H–P) vinylic couplings have the same magnitude for **9a** and **11** (^3J(H–P) = 22.5 Hz for **11**), confirming such an assignment.

Since X-ray crystal structure analysis suggests that there is no special conjugation between the C=C double bond and the phosphorus atom in phosphirene complexes,[14] we have also attempted a Diels–Alder reaction between an activated phosphirene complex such as **6** and 2,3-dimethylbutadiene:

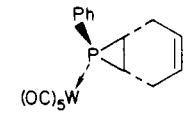


12 (44%)

^{31}P NMR spectroscopy indicates that **12** contains a three-membered ring and that only one isomer has been formed (δ ^{31}P(**12**) −115.5). The stereochemistry of **12** was established as follows. The reaction of the 7-phosphanorbornadiene complex **5** with 1,4-cyclohexadiene yields a mixture of two isomeric bicyclic phosphirane complexes **12a** (major isomer) and **12b** (minor isomer):



12a (major)

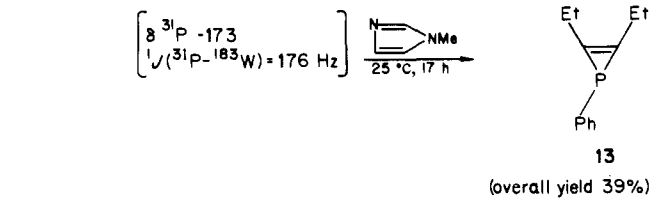


12b (minor)

This experiment will be detailed elsewhere. The less hindered **12a** shows relatively shielded CH_2* and =CH* protons and carbons on its ^1H and ^{13}C NMR spectra due to a through-space interaction with the *P*-phenyl group. The same CH_2 and =CH groups resonate at lower fields in **12b** since this interaction is suppressed. The ^2J(C–P) couplings of the CH_2 carbons of **12**, **12a**, and **12b** show a stereochemical dependence. We have recorded the following values: **12** ($^2J(CH_2{\cdots}P)$ = 0 Hz); **12a** ($^2J(CH_2{\cdots}P)$ = 4.9 Hz); **12b** ($^2J(CH_2{\cdots}P)$ = 0 Hz). Thus, **12** has the same stereochemistry as **12b**. This corresponds once again to the less hindered structure since the steric demand of the cyclohexene ring of **12** is obviously smaller than the steric demand of the phenyl and ethoxy carbonyl groups.

Synthesis and Chemistry of Tervalent Phosphirenes. The fact that it is possible to perform both ring cleavages and reactions at the C=C double bond demonstrates that a rich chemistry can already be built around phosphirene complexes. But, of course, we were eager to study the chemistry of the free phosphirenes themselves. In our preliminary communication,[15] we described the two-step decomplexation of **2** yielding 1,2,3-triphenylphosphirene through tungsten(0)→tungsten(2+) oxidation by iodine followed by displacement of phosphirene from its tungsten(2+) complex by *N*-methylimidazole. In order to check the generality of this procedure and also whether the 2,3-diphenyl

substitution played a significant role in the stability of tervalent phosphirenes or not, we attempted a similar decomplexation with the 2,3-diethyl-substituted complex **10**:

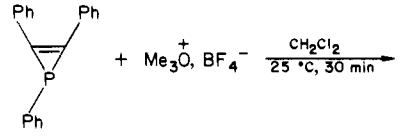


13

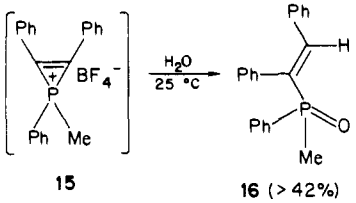
(overall yield 39%)

The intermediate complex was not isolated but directly treated in situ with *N*-methylimidazole. The tervalent phosphirene **13** is a colorless oil which was purified by chromatography on silica gel with hexane–ether (98:2). Its formula was unambiguously established by mass, ^1H, and ^{31}P NMR spectroscopies (δ ^{31}P(**13**) −188.2 in hexane).

Theoretical calculations indicate that the HOMO of a phosphirene has only a poor localization at phosphorus (ca. 50%).[21] From this and from classical ring strain arguments, we can expect a rather low nucleophilic reactivity of the phosphorus lone pair in phosphirenes unless some electronic cyclic delocalization stabilizes the phosphirenium salts. Such a possibility is not very likely since theoretical considerations suggest that, in such systems and in the isoelectronic silirenes,[22] (3d–2p)π interactions remain minimal and that the stabilization of the ring comes mainly from an electronic transfer from the heteroatomic subunit into the empty orbitals of the acetylenic subunit. If this is so, the phosphirenium salts must obviously be much less stable than the isoelectronic silirenes since the $^+PR_2$ unit is significantly more electronegative than the SiR_2 unit and thus less prone to transfer electrons. In line with this, we soon found that the quaternization of 1,2,3-triphenylphosphirene (**14**) was very difficult. In ether solution with an excess of methyl iodide, **14** reacts slowly (~24 h) at room temperature to give what is probably the corresponding phosphirenium salt (δ ^{31}P −125.8) but, simultaneously, a ring-opened product appears at 20.4 ppm. A similar but faster reaction is observed with trimethyloxonium tetrafluoroborate. The phos-

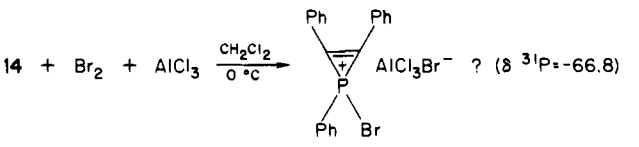


14



15 **16** (> 42%)

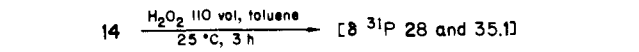
phirenium salt **15** gives a ^{31}P resonance at −109.9 ppm in dichloromethane. We have not attempted to isolate it, but we have directly reacted it with water. In such a way, we obtain the ring-opened phosphine oxide **16** which can be purified by chromatography on silica gel with ethyl acetate. The vinyl proton of **16** appears at 8.03 ppm in C_6D_6 with a ^3J(H–P) coupling of 20 Hz demonstrating the *E*-configuration.[11] In the same way, bromine and aluminum trichloride react with **14** to give a single product which is probably a halogenophosphirenium salt similar to those directly prepared by Hogeveen.[16] The ^{31}P chemical shift of **17** is very close to those recorded by Hogeveen. Its sensitivity



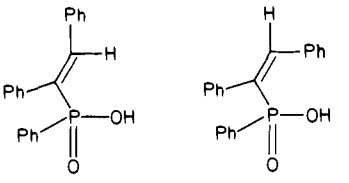
17

toward hydrolysis precluded its analysis.

The sensitivity of tetracoordinate phosphirenes toward ring opening is such that we have been unable to prepare the oxide of **14**. When reacting **14** with hydrogen peroxide, we always obtained two ring-opened products.

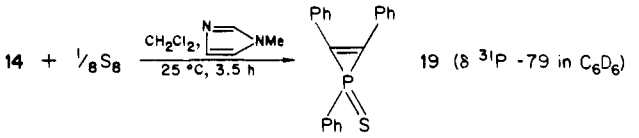


The purification of these products is difficult because they tend to polymerize. The mass spectrum of the mixture (EI at 70 eV or CI with NH_3) shows in all cases a huge peak at *m/e* 178 corresponding to tolan. The peaks at higher masses are less reproducible and more difficult to interpret. Chromatography on silica gel with ethyl acetate–methanol (90:10) allowed a partial purification of the mixture. The ^1H NMR spectrum of such a purified sample shows a characteristic vinylic proton at ca. 8.47 ppm with a ^3J(H–P) coupling of 21 Hz. On this limited basis, we suspect that these two ring-opened products are the two isomeric vinylphosphinic acids **18a,b**.



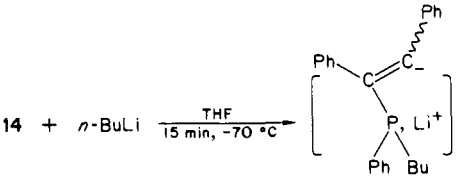
E **18a** *Z* **18b**

The synthesis of the sulfide **19** proved to be far easier. The sulfurization of **14** was carried out in the presence of *N*-methylimidazole as a catalyst (see ref 15 and the experimental part):



The stability of **19** remains low in solution, however.

The low nucleophilicity of phosphorus in **14** is paralleled by a rather high electrophilicity. Indeed, theoretical calculations indicate a significant localization of the LUMO at phosphorus (ca. 50%).[21] Thus, we were not surprised when we observed that *n*-butyllithium reacts easily with **14** to give the corresponding open-chain anion **20**:

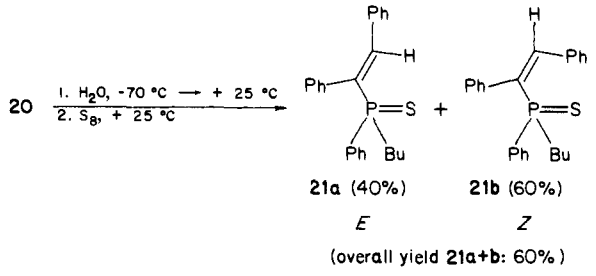


20

Such nucleophilic attacks of alkyllithiums onto tertiary phosphines have been known for a long time,[23,24] but they are generally far less easy than seen here except in the case of some special cyclic phosphines such as phospholes.[25] Protonation of **20** at low tem-

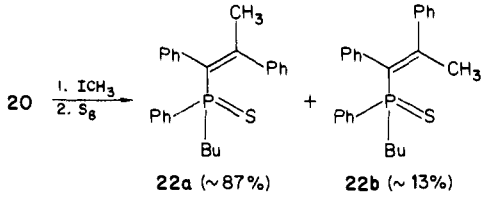
(21) Gonbeau, D.; Pfister-Guillouzo, G. *Nouv. J. Chim.* **1985**, *9*, 71.
(22) Barthelat, J. C.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1979**, *101*, 3785.
(23) Wittig, G.; Maercker, A. *J. Organomet. Chem.* **1967**, *8*, 491.
(24) Kyba, E. P. *J. Am. Chem. Soc.* **1975**, *97*, 2554.
(25) Mathey, F. *Tetrahedron* **1972**, *28*, 4171.

perature afforded the mixture of the *Z* and *E* phosphines isolated as their P sulfides:

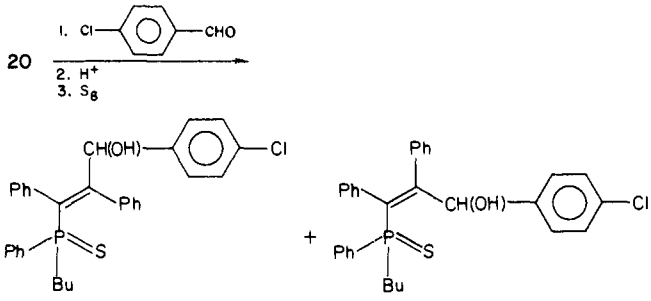


(overall yield **21a+b**: 60%)

The assignment of the *E* and *Z* configurations to the minor and major products, respectively, was based on the work of Gallagher comparing *E* and *Z* alkenylphosphorus compounds by ^1H, ^{13}C, and ^{31}P NMR spectroscopies.[26] As a first general rule, Gallagher has noted that *Z* compounds systematically show more shielded ^{31}P nuclei than the corresponding *E* compounds. This observation is correlated with the higher steric compression existing in the *Z* compounds. If we extend these results concerning vinylic phosphines, phosphine oxides, phosphine sulfides, and phosphonium salts to vinylic phosphine complexes, we note a satisfactory agreement between this rule and our proposals on the structures of complexes **9a** and **11**. Gallagher has also noted that the magnitude of the ^3J(H–P) vinylic couplings in vinylphosphine oxides and sulfides was far lower (ca. 20 Hz) for cis hydrogens than for trans hydrogens (ca. 40 Hz). On this basis, the assignments of structures **21a** and **21b** are straightforward. The minor isomer **21a** shows a ^{31}P resonance at 45.2 ppm and a ^3J(H–P) vinylic coupling of 23.9 Hz whereas the major isomer **21b** shows a ^{31}P resonance at 37.9 ppm (the vinylic proton is buried under the phenyl resonances). Recent work has demonstrated that vinyl anions with second-row substituents such as silyl groups isomerize rapidly above ca. −35 °C.[27] Our results seem to indicate that such an isomerization already takes place at −70 °C in the case of the phosphino-substituted vinyl anion **20**. This anion has also been allowed to react with methyl iodide and *p*-chlorobenzaldehyde:



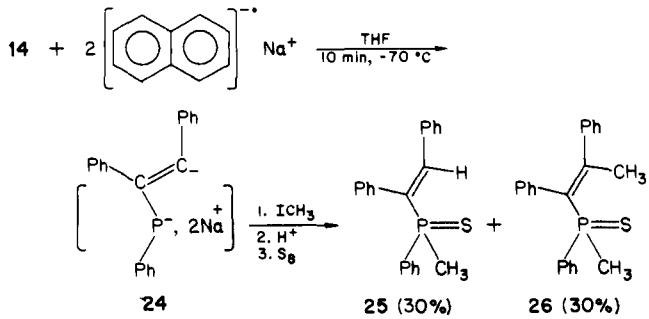
(overall yield **22a+b**: 81%)



(overall yield **23a+b**: 71%)

In both cases, we obtained two isomers and we were able to get the major one in the pure state. The ratio of major:minor isomers was calculated by using ^{31}P NMR spectra of the crude reaction mixtures after hydrolysis but before sulfurization. As can be noted, trans functionalization is more predominant than trans protonation. This observation is rather easy to rationalize. The bulky reagents react more easily with the less hindered trans anion and the equilibrium between cis and trans anions is displaced in favor of the latter. It is also interesting to note that **23a** shows a more deshielded phosphorus atom than **23b** in agreement with the steric compression argument: δ ^{31}P(**23a**) 43.4; δ ^{31}P(**23b**) 38.5 in THF.

The cleavage of **14** by alkali metals appeared to be more difficult than its reaction with *n*-butyllithium. Lithium in THF proved to be ineffective. The cleavage was only observed when using the naphthalene sodium radical anion. The resulting dianion was allowed to react with methyl iodide:



The structure of the protonation product **25** was easily established by comparison of its ^1H NMR spectrum with the corresponding spectrum of **21a**. The data for the vinylic protons are as follows in C_6D_6: **21a**, δ(=CH) 8.24 (^3J(H–P) 23.9 Hz); **25**, δ(=CH) 8.14 ppm (^3J(H–P) 24.2 Hz). Establishing the structure of the alkylation product **26** was less straightforward. Gallagher[26] has shown that in vinylic phosphine sulfides such as **22a**, **22b**, and **26**, the vinylic methyl was highly coupled to phosphorus when it was trans to P (^3J(C–P) ca. 20 Hz) and weakly coupled when it was cis (^3J(C–P) ca. 10 Hz). In line with this, we have noted a $^3J(CH_3{}^{\cdots}P)$ coupling of 17.1 Hz for **22a** and of 8.5 Hz for **26**. Thus it appears that contrary to anion **20**, dianion **24** does not isomerize at −70 °C, since no other products than **25** and **26** are formed upon alkylation, hydrolysis, and sulfurization according to the ^{31}P NMR spectrum of the crude reaction mixture. We have no obvious explanation for that, but anyhow, this result offers interesting synthetic opportunities.

Experimental Section

NMR spectra were recorded on a Bruker WP 80 instrument at 80.13 MHz for ^1H, 32.435 MHz for ^{31}P, and 20.15 MHz for ^{13}C. Chemical shifts are reported in parts per million from internal Me_4Si for ^1H and ^{13}C and from external 85% H_3PO_4 for ^{31}P. Downfield shifts are noted positive in all cases. IR spectra were recorded on a Perkin-Elmer Model 297 spectrometer. Mass spectra were recorded on a VG 30 F spectrometer by Service Central d'Analyse du CNRS (Lyon). All reactions were carried out under argon. Chromatographic separations were performed on silica gel columns (70–230 mesh Riedel de Haën) under argon.

(1,2,3-Triphenylphosphirene)pentacarbonyltungsten (2), (1-Phenyl-3,4-dimethylphosphole)pentacarbonyltungsten[18] (**1**) (11.6 g, 22.7 mmol), dimethyl acetylenedicarboxylate (5.6 mL, 45.6 mmol) and diphenylacetylene (10 g, 56.1 mmol) were heated at 112 °C in toluene (30 mL) for 16 h. The solvent was removed by evaporation. The residue was chromatographed first with hexane in order to remove the diphenylacetylene and then with hexane–toluene (90:10) to recover **2**: yield 10.4 g, 17 mmol (75%) (see ref 14).

(1,2,3-Triphenylphosphirene)tetracarbonyliron (4), (1-Phenyl-3,4-dimethylphosphole)tetracarbonyliron (**3**) was synthesized according to the literature.[28] Complex **3** (1.6 g, 4.5 mmol), dimethyl acetylenedicarboxylate (3 mL, 24.4 mmol), and diphenylacetylene (2.0 g, 11.2 mmol) were heated at 105 °C in toluene (9 mL) for 15 h. The solvent was removed by evaporation. The residue was chromatographed first with hexane in order to remove the diphenylacetylene and then with hexane–toluene (95:5) to recover **4**: yield 0.18 g, 0.4 mmol (9%); yellow solid; mp 97 °C (pentane); ^{31}P NMR (pentane) δ −90.4; IR (decalin) ν(CO) 2050 (m), 1982 (m), 1955 (vs), 1942 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 454 (M, 33), 398 (M − 2CO, 37), 370 (M − 3CO. 67); 342 (M − 4CO, 100), 178 (C_2Ph_2, 56), 164 (FePPh, 28). Anal. Calcd for $C_{24}H_{15}O_4PFe$: C, 63.47; H, 3.33; P, 6.82; Fe, 12.30.

(26) Duncan, M.; Gallagher, M. J. *Org. Magn. Reson.* **1981**, *15*, 37.
(27) Knorr, R.; von Roman, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 366.
(28) Mathey, F.; Muller, G. *J. Organomet. Chem.* **1977**, *136*, 241.

Found: C, 63.60; H, 3.24; P, 6.79; Fe, 12.32.

(1,3-Diphenyl-2-ethoxycarbonylphosphirene)pentacarbonyltungsten (6), Complex **5**[29] (5 g, 7.6 mmol) was heated at 118 °C for 5 h in xylene (30mL) with ethyl phenylpropiolate (3.8 mL, 23 mmol). The solvent was evaporated. After several chromatographic separations (eluant hexane–toluene 80:20), 2.3 g, 3.8 mmol (50%), of pure **6** were recovered: yellow solid; mp 63 °C (hexane); ^{31}P NMR (C_6D_6) δ −138.8 ($^1J(^{183}W-^{31}P)$ = 273 Hz); IR (decalin) ν(CO) 2075 (m), 1950 (vs) cm^{-1}; (KBr) ν(CO ester) 1700 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.94 (t, ^3J(H–H) = 7.08 Hz, 3 H, CH_3), 4.02 (ABX_3, ^2J(A–B) = 10.5 Hz, 2 H, CH_2), 6.8–8.1 (m, 10 H, Ph); mass spectrum (^{184}W) *m/e* (relative intensity) 606 (M, 33), 522 (M − 3CO, 28), 466 (M − 5CO, 27), 438 (100). Anal. Calcd for $C_{22}H_{15}O_7PW$: C, 43.59; H, 2.49; P, 5.11; W, 30.33. Found: C, 43.58; H, 2.42; P, 5.11; W, 31.14.

Hydrolysis of Complex 6. Complex **6** (1.1 g, 1.8 mmol) was hydrolyzed with basic water (H_2O/Et_3N) in THF (15 mL) at room temperature for 2 h. After evaporation, the residue was chromatographed with toluene–ethyl acetate (90:10) (R_f ~0.4): yield 0.74 g, 1.2 mmol (66%), of colorless solid **7**; mp 132 °C (toluene); ^{31}P NMR (CH_2Cl_2) δ 104.3 ($^1J(^{183}W-^{31}P)$ = 283 Hz); IR (decalin) ν(CO) 2075 (m), 1952 (vs), 1945 (sh) cm^{-1}; (KBr) ν(OH) 3300 cm^{-1}; ν(CO ester) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, ^3J(H–H) = 7.08 Hz, 3 H, CH_3), 3.97 (q, 2 H, CH_2), 6.73 (d, ^3J(H–P) = 17.1 Hz, C*H*Ph), 6.7–7.6 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 13.51 (s, CH_3), 61.13 (s, CH_2), 133.7 (d, J(C–P) = 8.5 Hz, C (phenyl)), 137.49 (d, J(C–P) = 42.8 Hz, *C* (phenyl)), 158.21 (d, ^1J(C–P) = 23.2 Hz, P–C–Ph), 165.48 (d, ^3J(C–P) = 18.3 Hz, CO_2), 195.87 (d, ^2J(C–P) = 7.3 Hz, cis CO). Complex **7** tenaciously retains some traces of solvent. A sample containing 6.3% of dichloromethane gave the following results. Anal. Calcd for $C_{22}H_{17}O_8PW$ + 6.3% CH_2Cl_2: C, 40.56; H, 2.73; P, 4.65. Found: C, 40.56; H, 2.67; P, 4.37.

Morpholine Addition to Complex 6. Morpholine (0.15 mL, 1.7 mmol) was added to a solution of **6** (1 g, 1.7 mmol) in toluene (10 mL). After 24 h at room temperature, the solvent was evaporated and the crude complex **8** purified by chromatography (eluant 95:5 toluene–ethyl acetate (R_f ~ 0.2)): yield 0.8 g, 1.2 mmol (70%) of colorless solid; mp 207 °C (toluene–hexane); IR (decalin) ν(CO) 2070 (m), 1935 (vs) cm^{-1}; (KBr) ν(CO ester) 1670 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.90 (t, ^3J(H–H) = 7.08 Hz, 3 H, CH_3), 2.81–3.25 (m, 8 H, morpholine), 4.1 (m, 2 H, CH_2CH_3), 6.01 (d, ^1J(H–P) = 345.2 Hz, 1 H, PH), 6.9–7.8 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.05 (s, CH_3), 52.10 (s, NCH_2), 60.16 (s, CH_2CH_3), 67.06 (s, OCH_2), 91.96 (d, ^1J(C–P) = 53.7 Hz, P–*C*–CO_2Et), 165.36 (d, ^2J(C–P) = 13.4 Hz, Ph–*C*–N), 166.27 (d, ^2J(P–C) = 6.1 Hz, CO_2), 197.14 (d, ^2J(C–P) = 7.3 Hz, cis CO). Anal. Calcd for $C_{26}H_{24}O_8NPW$: C, 45.04; H, 3.49; P, 4.47; W, 26.52. Found: C, 44.93; H, 3.39; P, 4.40; W, 27.07.

[*O*-Methyl (1,2-diphenylvinyl)phenylphosphinite]pentacarbonyltungsten (9a,b). Complex **2** (0.75 g, 1.2 mmol) and methanol (250 mL) were irradiated at room temperature for 5 h with a Pyrex-filtered light (Medium-pressure 125-W mercury lamp). The solvent was removed by evaporation. The residue was chromatographed with hexane–toluene (95:5). Some unreacted complex **2** was eluted first (R_f ~0.6) and then a mixture of **9a,b** was recovered (R_f ~0.5) to yield 0.20 g, 0.3 mmol (25%). Pure **9a** was obtained by crystallization from hexane. ^{31}P NMR (C_6D_6) δ 129.3 ($^1J(^{31}P-^{183}W)$ = 278 Hz); IR (decalin) ν(CO) 2070 (m), 1985 (vw), 1955 (s), 1943 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 3.26 (d, ^3J(H–P) = 13.4 Hz, 3 H, OMe), 6.7–7.2 (m, 15 H, Ph), 7.78 (d, ^3J(H–P) = 21.2 Hz, 1 H, C*H*Ph). Mass spectrum (^{184}W) *m/e* (relative intensity) 642 (M, 17), 558 (M − 3CO, 100), 502 (M − 5CO, 83). Anal. Calcd for $C_{26}H_{19}O_6PW$: C, 48.62; H, 2.98; P, 4.82. Found: C, 49.76; H, 3.22; P, 4.91.

9b: ^{31}P NMR (C_6D_6) δ 122.7; ^{1}H NMR (C_6D_6) δ 2.58 (d, ^3J(H–P) = 12.9 Hz, 3 H, OMe), 6.7–7.9 (m, 16 H, Ph + C*H*Ph).

[*O*-Methyl (1,2-diethylvinyl)phenylphosphinite]pentacarbonyltungsten (11a,b). The same procedure as for **9a,b** was used, with complex **10**[14] replacing complex **2**. Yield from 0.75 g of **10** (1.5 mmol) was 0.29 g, 0.53 mmol (35%), of a mixture of **11a,b**, colorless oil. **11a**: ^{31}P NMR (hexane) δ 133.2 ($^1J(^{31}P-^{183}W)$ = 276 Hz); ^{1}H NMR (C_6D_6) δ 0.57 (t, ^3J(H–H) = 7.3 Hz, 3 H, CH_3), 0.91 (t, ^3J(H–H) = 7.3 Hz, 3 H, CH_3), 2.0 (m, 4 H, CH_2), 3.15 (d, ^3J(H–P) = 13.4 Hz, 3 H, OCH_3), 6.50 (dt, ^3J(H–P) = 22.5 Hz, ^3J(H–H) = 7.08 Hz, 1 H, CH), 6.9–7.7 (m, 5 H, Ph). IR (decalin) ν(CO) 2070 (m), 1980 (vw), 1950 (s), 1940 (vs) cm^{-1}; mass spectrum (^{184}W) *m/e* (relative intensity) 546 (M, 46), 518 (M − CO, 39), 461 (M − 3CO − H, 100).

[1-(Ethoxycarbonyl)-3,4-dimethyl-6,7-diphenyl-7-phosphabicyclo-[4,1.0]-3-heptene]pentacarbonyltungsten (12), Complex **6** (1.7 g, 2.8 mmol), toluene (2 mL), and dimethylbutadiene (4 mL) were heated at 75 °C for 87 h in a sealed tube. After evaporation, the residue was chromatographed with hexane–toluene (80:20). The starting complex was eluted first (R_f ~0.5) and then **12** was recovered (R_f ~0.4): yield 0.84 g, 1.2 mmol (44%) of colorless solid; mp 145 °C (CH_2Cl_2–hexane); ^{31}P NMR (C_6D_6) δ −115.5 ($^1J(^{31}P-^{183}W)$ = 266 Hz); IR (decalin) ν(CO) 2070 (m), 1965 (vs), 1950 (vs); (KBr) ν(CO ester) 1710 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.78 (s, 3 H, C–CH_3), 0.96 (t, ^3J(H–H) = 7.08 Hz, 3 H, CH_2CH_3), 0.96 (s, 3 H, C–CH_3), 2.43 (br) (d, ^3J(H–P) ~ 12 Hz, 2 H, CH_2), 2.48 (br, dd, ^3J(H–P) ~ 7 Hz, ^2J(H–H) ~ 17 Hz, 1 H, CH_2), 3.44 (br, ps t, ^3J(H–P) ≃ ^2J(H–H) ~ 17 Hz, 1 H, CH_2), 4.0 (m, 2 H, CH_2CH_3), 6.7–7.4 (m, 10 H, Ph); ^{13}C NMR (C_6D_6) δ 14.5 (s, CH_2CH_3), 18.1 (s, C–CH_3), 18.4 (s, C–CH_3), 34.0 (s, CH_2), 41.0 (d, ^1J(C–P) = 17.1 Hz, P–*C*), 44.2 (s, CH_2), 47.5 (d, ^1J(P–C) = 18.3 Hz, P–*C*), 62.2 (s, CH_2CH_3), 123.6 (s, Me–*C*), 124.1 (s, Me–*C*), 136.7 (d, ^1J(C–P) = 23.2 Hz, P–C (phenyl)), 142.4 (d, ^2J(C–P) = 4.9 Hz, *C* (phenyl)), 170.2 (s, CO_2), 196.7 (d, ^2J(C–P) = 8.5 Hz, cis CO). Mass spectrum (^{184}W) *m/e* (relative intensity) 660 (M − CO, 18), 602 (M − 3CO, 8), 546 (M − 5CO, 6), 404 ($PhPW(CO)_4$, 32), 348 ($PhPW(CO)_2$, 24), 256 ($PhC_6H_4Me_2CO_2Et$, 33), 183 ($PhC_6H_4Me_2$, 100). Anal. Calcd for $C_{28}H_{25}O_7PW$: C, 48.86; H, 3.66; P, 4.50; W, 26.71. Found: C, 48.78; H, 3.64; P, 4.27; W, 26.79.

2,3-Diethyl-1-phenylphosphirene (13), Complex **10** (2.5 g, 4.9 mmol) was treated with iodine (1.3 g, 5.2 mmol) in dichloromethane at room temperature for 15 min. *N*-Methylimidazole (2.4 mL, 30.1 mmol) was then added and the mixture was stirred at room temperature for 17 h under argon. The brown oily residue was extracted with diethyl ether. The solvent was removed by evaporation; the crude product was purified by chromatography (eluant: hexane–ether 98:2) (R_f ~0.7). Yield 0.36 g, 1.9 mmol (39%), of colorless oil. ^{31}P NMR (hexane) δ −188.1; ^{1}H NMR (C_6D_6) δ 1.02 (t, ^3J(H–H) = 7.08 Hz, 6 H, CH_3), 2.44 (dq, ^3J(H–P) = 4.15 Hz, 4 H, CH_2), 7.0–7.5 (m, 5 H, Ph); mass spectrum *m/e* (relative intensity) 190 (M, 80), 161 (M − Et, 100). The low stability of the product precluded its elemental analysis.

Quaternization of 1,2,3-Triphenylphosphirene. 1,2,3-Triphenylphosphirene (0.6 g, 2.1 mmol) was treated with trimethyloxonium tetrafluoroborate (0.34 g, 2.3 mmol) in dichloromethane at room temperature for 30 min. The phosphirenium salt **15** (^{31}P NMR (CH_2Cl_2) δ −109.9) was then hydrolyzed at room temperature. After evaporation, the residue was purified by chromatography (eluant ethyl acetate). Pure **16** (0.27 g, 0.85 mmol) was recovered (R_f ~0.3). Yield 40%; colorless solid; ^{31}P NMR (CH_2Cl_2) δ 28.9; ^{1}H NMR (C_6D_6) δ 1.52 (d, ^2J(H–P) = 13.2 Hz, 3 H, PCH_3), 6.7–7.7 (m, 15 H, Ph), 8.03 (d, ^3J(H–H) = 20.0 Hz, 1 H, C*H*Ph); ^{13}C NMR ($CDCl_3$) δ 13.63 (d, ^1J(C–P) = 75.7 Hz, PCH_3), 140.9 (d, ^2J(C–P) = 7.3 Hz, *C*HPh); mass spectrum (chemical ionization) *m/e* (relative intensity) 319 (M + 1, 100).

1,2,3-Triphenylphosphirene Sulfide (19), 1,2,3-Triphenylphosphirene (**14**) (0.78 g, 2.7 mmol), sulfur (90 mg, 2.8 mmol), and *N*-methylimidazole (0.15 mL) were stirred in dichloromethane at room temperature for 3.5 h. Hexane was added to the mixture and the solvent partially evaporated. The sulfide **19** was obtained, after cooling of the mixture, as colorless crystals: yield 0.65 g (2.0 mmol, 76%); mp 95 °C (hexane–CH_2Cl_2); ^{31}P NMR (C_6D_6) δ −79. Anal. Calcd for $C_{20}H_{15}PS$: C, 75.45; H, 4.75; S, 10.07. Found: C, 73.48; H, 4.74; S, 10.11.

(1,2-Diphenylvinyl)phenyl-*n*-butylphosphine Sulfide (21a,b). 1,2,3-Triphenylphosphirene (**14**) (1 g, 3.5 mmol) in THF (40 mL) was cooled to −70 °C and treated with *n*-butyllithium (2.6 mL, 4.2 mmol, solution 1.6 M in hexane). After 15 min, the mixture was hydrolyzed with distilled water and warmed to room temperature. The two alkenylphosphines thus obtained (δ ^{31}P −2.7 and −27.5) were then reacted with sulfur (120 mg, 4.1 mmol) at room temperature for 15 min. The solvent was removed by evaporation. The residue was chromatographed with hexane–toluene (70:30). **21b** was eluted first (R_f ~0.6) and then sulfide **21a** was recovered (R_f ~0.5). Overall yield 0.78 g, 2.1 mmol (60%). Pure **21b** was obtained by crystallization from $CHCl_3$–pentane: mp 102 °C; ^{13}C NMR (C_6D_6) δ 13.81 (s, CH_3), 24.11 (d, ^2J(C–P) = 20.8 Hz, CH_2), 24.78 (d, ^3J(C–P) = 6.1 Hz, CH_2), 35.69 (d, ^1J(C–P) = 58.6 Hz, CH_2), 136.56 (d, J(C–P) = 4.9 Hz, C), 139.65 (d, ^1J(C–P) = 70.8 Hz, C), 142.31 (d, J(C–P) = 12.2 Hz, C), 144.98 (d, ^2J(C–P) = 4.9 Hz, *C*HPh). Mass spectrum (chemical ionization) *m/e* (relative intensity) 377 (M + 1, 100). Anal. Calcd for $C_{24}H_{25}PS$: C, 76.56; H, 6.69; P, 8.23; S, 8.52. Found: C, 76.29; H, 6.66; P, 8.21; S, 8.65. Pure **21a** was obtained by crystallization from hexane: mp 49 °C; mass spectrum (chemical ionization) *m/e* (relative intensity) 377 (M + 1, 100).

(2-Methyl-1,2-diphenylvinyl)-*n*-butylphenylphosphine Sulfide (22a,b). 1,2,3-Triphenylphosphirene (**14**) (0.75 g, 2.6 mmol) in THF (30 mL) was cooled to −70 °C and treated with *n*-butyllithium (2 mL, 3.2 mmol, 1.6 M in hexane). After 15 min, iodomethane (0.2 mL, 3.2 mmol) was added. The two alkenylphosphines thus obtained (δ ^{31}P −26.9 and −27.7) were then reacted with sulfur (88 mg, 2.7 mmol) at room temperature for 15 min. The solvent was removed by evaporation. The residue was chromatographed with hexane–toluene (70:30). Sulfide **22a** was eluted first (R_f ~0.3) and then sulfide **22b** was recovered (R_f ~0.25). Overall

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yield 0.82 g, 2.1 mmol (81%), of colorless solid.

22a: ^{31}P NMR (C_6D_6) δ 38.2; ^1H NMR (C_6D_6) δ 0.45 (t, 3 H, CH_3-CH_2-); 0.8 (m, 4 H, CH_2 (butyl)), 1.6 (m, 2 H, PCH_2), 1.73 (d, ^4J(H-P) = 2.3 Hz, 3 H, CH_3), 6.8-7.8 (m, 15 H, Ph); ^{13}C NMR (C_6D_6) δ 14.00 (s, CH_3), 24.36 (d, ^3J(C-P) = 17.1 Hz, C-CH_3), 24.78 (s, CH_2 (butyl)), 26.51 (d, ^2J(C-P) = 11.0 Hz, CH_2), 35.32 (d, ^1J(C-P) = 58.6 Hz, PCH_2), 136.65 (d, ^1J(C-P) = 76.9 Hz, *C*), 139.71 (d, J(C-P) = 9.8 Hz, *C*), 142.65 (d, J(C-P) = 6.1 Hz, *C*), 151.67 (d, J(C-P) = 6.1 Hz, *C*); mass spectrum (chemical ionization) m/e (relative intensity) 391 (M + 1, 100). Anal. Calcd for $C_{25}H_{27}PS$: C, 76.89; H, 6.97; P, 7.93; S, 8.21. Found: C, 76.67; H, 7.12; P, 7.71; S, 8.24.

(2-(*p*-Chlorophenylhydroxymethyl)-1,2-diphenylvinyl)-*n*-butylphenylphosphine Sulfide (23a,b). 1,2,3-Triphenylphosphirene (0.6 g, 2.4 mmol) in THF (30 mL) was cooled to -70 °C and treated with *n*-butyllithium (1.8 mL, 2.9 mmol). After 15 min, *p*-chlorobenzaldehyde (0.41 g, 2.9 mmol) was added. After 15 min at -70 °C, the mixture was hydrolyzed (δ ^{31}P -26.62 and -29.33) and then reacted with sulfur at room temperature. The solvent was evaporated and the products purified by chromatography with ethyl acetate. **23b** ($R_f \sim 0.5$) and **23a** ($R_f \sim 0.4$) were recovered. Yield 0.86 g, 1.7 mmol (71%). Pure **23a** was obtained by crystallization in THF: mp 221 °C; colorless solid; ^{31}P NMR (THF) δ 43.38; IR (KBr) ν(OH) 3380 cm^{-1}; mass spectrum (chemical ionization) (^{35}Cl) m/e (relative intensity) 517 (M + 1, 75), 199 (100). Anal. Calcd for $C_{31}H_{30}OPSCl$: C, 72.01; H, 5.85; S, 6.20; Cl, 6.86. Found: C, 71.36; H, 5.81; S, 6.07; Cl, 6.99.

Cleavage of 14 by Naphthalene-Sodium. 1,2,3-Triphenylphosphirene (**14**) (0.75 g, 2.6 mmol) was added to a solution of 1:1 naphthalene-sodium radical anion (5.8 mmol) in THF at -70 °C. After 10 min, iodomethane (0.33 mL, 5.3 mmol) was added. The mixture was hydrolyzed and reacted with sulfur at room temperature. The solvent was removed by evaporation. The residue was chromatographed with hexane-ether (93:7). Yield of **26** ($R_f \sim 0.3$) was 0.28 g, 0.8 mmol (31%); **25** ($R_f \sim 0.2$), yield 0.3 g, 0.9 mmol (34%).

25: colorless solid; mp 98 °C (THF-hexane); ^{31}P NMR (C_6D_6) δ 36.3; ^1H NMR (C_6D_6) δ 1.67 (d, ^2J(H-P) = 13.2 Hz, 3 H, PCH_3), 6.8-7.8 (m, 15 H, Ph), 8.14 (d, ^3J(H-P) = 24.2 Hz, 1 H, C*H*Ph); mass spectrum (chemical ionization) m/e (relative intensity) 335 (M + 1, 100). Anal. Calcd for $C_{21}H_{19}PS$: C, 75.42; H, 5.73; S, 9.59. Found: C, 75.67; H, 5.96; S, 9.60.

26: colorless solid; mp 111 °C (THF-hexane); ^{31}P NMR. (toluene) δ 32.8; ^1H NMR (C_6D_6) δ 1.25 (d, ^2J(H-P) = 12.7 Hz, 3 H, PCH_3), 1.71 (d, ^4J(H-P) = 2.4 Hz, 3 H, CH_3-C-Ph), 6.9-7.8 (m, 15 H, Ph); ^{13}C NMR. (C_6D_6) δ 24.93 (d, ^1J(C-P) = 62.3 Hz, PCH_3), 26.26 (d, ^3J(C-P) = 8.5 Hz, C-CH_3), 136.59 (d, J(C-P) = 76.9 Hz, *C*), 139.50 (d, J(C-P) = 11.0 Hz, *C*), 142.49 (d, J(C-P) = 7.3 Hz, *C*), 151.22 (d, J(C-P) = 7.3 Hz, *C*); mass spectrum (chemical ionization) m/e (relative intensity) 349 (M + 1, 100).

Registry No. **1**, 74363-95-4; **2**, 82265-68-7; **3**, 64439-05-0; **4**, 90635-58-8; **5**, 83603-06-9; **6**, 96826-84-5; **7**, 96826-85-6; **8**, 96826-86-7; **9a**, 96826-87-8; **9b**, 96894-22-3; **10**, 82265-69-8; **11a**, 96826-88-9; **11b**, 96894-23-4; **12**, 96826-89-0; **12a**, 96826-90-3; **12b**, 96894-24-5; **13**, 96845-00-0; **14**, 90633-10-6; **15**, 96845-02-2; **16**, 96845-03-3; **17**, 96826-92-5; **19**, 90633-11-7; **21a**, 96826-93-6; **21b**, 96845-04-4; **22a**, 96845-05-5; **22b**, 96845-06-6; **23a**, 96845-07-7; **23b**, 96845-08-8; **25**, 96845-09-9; **26**, 96845-10-2; dimethyl acetylenedicarboxylate, 762-42-5; diphenylacetylene, 501-65-5; ethyl phenylpropiolate, 2216-94-6; morpholine, 110-91-8; dimethylbutadiene, 513-81-5; trimethyloxonium tetrafluoroborate, 420-37-1; 1:1 naphthalene sodium radical anion, 3481-12-7; 1,3-cyclohexadiene, 592-57-4; copper chloride, 7758-89-6.

Proximity as a Component of Organic Reactivity

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Abstract: Neither the S_N2 reaction of methyl iodide in 100% pyridine, nor the S_N2 reaction of triethylamine in 100% ethyl iodide, nor the elimination reaction of 4-(4-nitrophenoxy)-2-butanone in 100% piperidine displays special reactivity ascribable to the continuous bimolecular contact. It is concluded that proximity, by itself, cannot explain the fast rates characteristic of many intramolecular reactions. Two parameters, time and distance, must be incorporated into the proximity concept to make it viable.

This article addresses a question that has not yet been experimentally answered: What is the kinetic effect on a bimolecular reaction A + B → C when A is totally surrounded by B (i.e., when reactant B serves as the solvent in which solute A cannot escape contact)? Obviously, the literature describes a multitude of solvolyses in water, acetic acid, etc., where the solvent participates as one of the reactants. But the role of "total contact" (if any) has not been determined because it is impossible to reduce the concentration of a protic solvent without concurrently changing the properties of the medium. For example, a comparison of reactions in pure water with those in 0.5 M water/acetonitrile would likely entail large solvent effects that obscure all other phenomena. We have now completed a series of experiments involving bimolecular substitutions and eliminations in which the reactant-solvent is *aprotic*. Dilution of this component was then carried out, with minimal perturbations to the medium, using inert aprotic solvents of almost identical polarity. Thus, bimolecular proximity could, for the first time, be rigorously assessed.

Results and Discussion

In all previously published articles on S_N2 kinetics, low levels of both nucleophile and electrophile were invariably added to a particular solvent. We, on the other hand, studied the S_N2 reactivity of methyl iodide (1.1×10^{-3} M) dissolved in pyridine. Since pyridine served as both the nucleophile and solvent, the methyl iodide is continually "bathed" in the second S_N2 component. Moreover, dipole-dipole interactions within the solvent shell of methyl iodide would tend to place a pyridine nitrogen backside of the carbon-iodine bond[1] (where it needs to be prior to bond formation).

Formation of the *N*-methylpyridinium iodide charge-transfer band was followed at 370 nm to obtain a $k_{obsd} = 3.6 \times 10^{-3}$ s^{-1} at 25.0 ± 0.1 °C in 100% pyridine. We then obtained rate constants with systems where the pyridine concentration had been reduced stepwise to less than 1% by adding either *o*-dichlorobenzene or ethylene dichloride. In this manner we could reduce the "proximity" of methyl iodide to the pyridine. Medium effects on the rate were not a concern for several reasons. (1) The cosolvents were selected because their dielectric constants and $E_T(30)$ values[2] resemble closely those of pyridine (i.e., *o*-dichlorobenzene, 9.9 and 38; ethylene dichloride, 10.4 and 42; pyridine, 12.4 and 40). (2) We used both an aromatic and ali-

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