## References and Notes

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# Coupling Reactions of Diorganophosphides with Organic Halides. Evidence for a One-Electron Path

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The reactions of diorganophosphides with organic halides have been examined by $^{31}P$ CIDNP and product analysis. These reactions are shown to proceed in part by a radical mechanism and in part by a competing nonradical path. The preference for one mechanism or the other is highly dependent on the nature of the organic group, halide, and substituents bound to phosphorus. Thus, alkyl, allyl, and benzyl iodides and bromides react, to some degree, by a radical mechanism; alkyl chlorides follow an apparent $S_N2$ path. There is no evidence for radical participation in the reactions of dialkylphosphides with aryl halides or of diarylphosphides with alkyl halides. For those examples proceeding by a radical mechanism, the CIDNP data are consistent with an electron-transfer step, followed by coupling of the dialkylphosphinyl and organic radicals.

Diorganophosphide anions are useful precursors for the synthesis of *tertiary*[1] and polydentate phosphines.[1a,b,d,2] Their utility arises, in part, from their ready availability and because coupling reactions with organic halides generally proceed in high yields and tolerate substantial variation of phosphide or substrate.[1,2] To the inorganic chemist the primary asset of procedures employing these reagents is the ability to design ligands with specific electronic and steric properties or containing a functionality as a probe for ligand–metal interactions. Organophosphide ions are generally regarded as potent nucleophiles[1-4] and coupling reactions have long been assumed to proceed by an $S_N2$ mechanism with metal–halogen exchange as a competing or, in some cases, dominant factor.[1a,b,d,5]

In the course of preparing cyclopropylmethyldimethylphosphine from bromomethylcyclopropane and potassium dimethylphosphide, we noted the anticipated product was formed together with a comparable amount of 3-butenyldimethylphosphine. Inasmuch as this result suggested a predominant radical path, we were prompted to undertake a mechanistic study to determine whether one-electron steps were involved in these couplings and, if so, whether conditions could be found to enhance the $S_N2$ component. We report herein CIDNP and product distribution evidence that alkyl, allylic, and benzylic halides do, in fact, react with diorganophosphides via a mechanism involving substantial radical participation, the degree of which is highly sensitive to the nature of the phosphide, substrate, and halide employed.

## Experimental Section

All manipulations and reactions were performed in an atmosphere of nitrogen. Solvents were distilled from sodium benzophenone ketyl before use. Benzene-$d_6$ and 1,2-dimethoxyethane-$d_{10}$ were dried over calcium hydride and distilled in vacuo prior to use in NMR experiments.

1-Bromo-5-hexene was obtained from Tridom-Fluka and 1-chloro-5-hexene from ICN. Bromomethylcyclopropane was prepared by the literature method.[6] All other halides were readily obtainable from a number of common sources. Potassium diphenylphosphide,[7] *lithium dimethylphosphide*,[8] and *sodium dimethylphosphide*[8] were prepared by the literature procedures. $^{31}P$ and $^{1}H$ NMR experiments were performed on a Varian XL-100 spectrometer. Analysis of organophosphide/organic halide reactions was performed utilizing a Data General Nova 2 computer hardwired to an AEI MS 1073 dual-beam mass spectrometer/gas chromatograph. Mass spectra of isolated phosphines were obtained on an AEI MS-9 spectrometer. Product distribution analyses for the bromomethylcyclopropane and 1-halo-5-hexene reactions were performed on an F & M 720 gas chromatograph with a ¼ in. × 8 ft, 3.8% SE-52 column. Response factors were determined for each of the products using *n*-decane or *n*-undecane as internal standards. Analyses were performed by adding a stoichiometric amount of organic halide to a 2-mL volumetric flask capped with a septum and containing a known amount of organophosphide in THF. GLC measurements were initiated immediately after adding the internal standard and diluting to the mark. Representative preparative scale reactions are given below.

**Potassium Dimethylphosphide.** Following a modification of the preparation of sodium dimethylphosphide,[8] 5.7 g of tetramethylbiphosphine[2i] (47 mmol) and 6.6 g of potassium (0.17 g-atom) in 150 mL of THF were stirred for 10 h under reflux to produce a deep red solution. After cooling and filtration through Celite, the volume was

reduced in vacuo to 50 mL and 70 mL of dioxane was added, precipitating the product. Two washings with ethyl ether afforded a light yellow, pyrophoric solid (4.4 g, 36%). Variable amounts of dioxane were retained, although after prolonged drying under high vacuum, the $^1H$ NMR spectrum showed no appreciable dioxane of solvation. An analytical sample was recrystallized from hot dioxane: $^1H$ NMR (THF-$d_8$) $\delta$ 1.22 (d, $J_{PH}$ = 3 Hz); $^{31}P$-{$^1H$} NMR (DME/benzene) 117.5 ppm (s).

Anal. Calcd for $C_2H_6KP$: C, 23.99; H, 6.04. Found: C, 23.42; H, 6.40.

**Potassium Diisopropylphosphide.** Diisopropylphosphine[9] (12.15 g, 0.103 mol) and potassium hydride (4.0 g, 0.10 mol) were heated in 125 mL of refluxing THF for 20 h. Filtration through Celite and evaporation of the THF gave an amorphous solid, which was washed with hexane and treated with 5 mL of dioxane. Drying in vacuo gave a yellow solid (4.0 g, 25%). An analytical sample was prepared by recrystallization from a small amount of dioxane: $^1H$ NMR (THF-$d_8$) $\delta$ 1.1 (m, 12 H), 2.33 (m, 2 H); $^{31}P$-{$^1H$} NMR (DME/benzene) −23.2 ppm (s).

Anal. Calcd for $C_6H_{14}KP$: C, 46.12; H, 9.03. Found: C, 44.65; H, 8.59.

**Cyclopropylmethyldimethylphosphine.** A solution of potassium dimethylphosphide was prepared by refluxing 15.9 g of tetramethylbiphosphine[2i] (0.130 mol) with 11.9 g of freshly cut potassium in 120 mL of THF for 16 h. The orange solution was decanted from excess potassium and cooled to −78 °C. Dropwise addition of 29.1 g of bromomethylcyclopropane in 100 mL of THF over a 3-h period gave a thick, white slurry. After warming to 25 °C, the reaction mixture was hydrolyzed by cautious addition of 40 mL of water and treated with 30 mL of ether. After separation of the organic phase, the aqueous solution was extracted with an additional 20 mL of ether. The pooled extracts were washed with 20 mL of saturated aqueous sodium chloride, dried ($MgSO_4$), and fractionally distilled. The fraction boiling at 105–132 °C was collected (17.0 g, 68%) and shown to be a mixture of cyclopropylmethyldimethylphosphine and 3-butenyldimethylphosphine (54/46) by GLC analysis. Separation was effected by spinning band distillation. Cyclopropylmethyldimethylphosphine: bp 119–120 °C; mass spectrum *m/e* 116.0748 (calcd for $C_6H_{13}P$, 116.0755); $^1H$ NMR (DME-$d_{10}$) $\delta$ 0.37 (m, 4 H), 0.89 (d, 6 H, $J_{PCH}$ = 2.8 Hz), 1.20 (m, 2 H), the unique ring proton is obscured by the P-methyl groups; $^{31}P$-{$^1H$} NMR (DME/benzene) 53.4 ppm (s). 3-Butenyldimethylphosphine: bp 114–116 °C; mass spectrum *m/e* 116.0741 (calcd for $C_6H_{13}P$, 116.0755); $^1H$ NMR (DME-$d_{10}$) $\delta$ 0.90 (d, 6 H, $J_{PCH}$ = 2.4 Hz), 1.30 (m, 2 H), 2.05 (m, 2 H), 4.89 (m, 2 H), and 5.73 (m, 1 H); $^{31}P$-{$^1H$} NMR (DME/benzene) 53.4 ppm (s).

**5-Hexenyldimethylphosphine.** To a solution of sodium dimethylphosphide (84.0 mmol) in 60 mL of $NH_{3(l)}$[2i] was added 9.84 g of 1-chloro-5-hexene (83.0 mmol) dropwise over a 20-min period. The ammonia was allowed to evaporate overnight and the product distilled directly from the residue (95%): bp 170–172 °C; mass spectrum *m/e* 144.1067 (calcd for $C_8H_{17}P$, 144.1068); $^1H$ NMR ($CDCl_3$) $\delta$ 0.92 (d, 2 H, $J_{PCH}$ = 2.0 Hz), 1.4 (m, 6 H), 1.9 (m, 2 H), 4.9 (m, 2 H), and 5.6 (m, 1 H); $^{31}P$-{$^1H$} NMR (DME/benzene) 54.2 ppm (s).

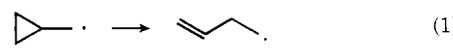
Other phosphines were prepared analogously to cyclopropylmethyl- or 5-hexenlydimethylphosphine: butyldimethylphosphine[1d] [$^{31}P$-{H} NMR (DME/benzene) 52.3 ppm (s)]; cyclohexyldimethylphosphine;[10] ethyldimethylphosphine;[1d] allyldimethylphosphine[11] (from allyl *chloride*) [$^{31}P$-{$^1H$} (DME/benzene) 54.2 ppm (s)]; cyclopentylmethyldimethylphosphine [mass spectrum *m/e* 144.1068 (calcd for $C_8H_{17}P$ 144.1068); $^1H$ NMR ($CDCl_3$) $\delta$ 0.92 (d, 6 H $J_{PCH}$ = 2.5 Hz), 1.13 (m, 2 H), 1.47 (br m, 9 H); $^{31}P$-{$^1H$} NMR (DME/benzene) 54.2 ppm (s)]; *tert*-butyldimethylphosphine;[12] diphenylbutylphosphine;[1d] diisopropylbutylphosphine [mass spectrum *m/e* 174.1542 (calcd for $C_{10}H_{23}P$, 174.1537); $^{31}P$-{$^1H$} NMR (DME/benzene) −2.5 ppm (s)]; benzyldimethylphosphine[13] (from benzyl *chloride*) [$^{31}P$-{$^1H$} NMR (DME/benzene) 46.9 ppm (s)]; cyclopropylmethyldiphenylphosphine [mass spectrum *m/e* 240.1059 (calcd for $C_{16}H_{17}P$, 240.1069); $^{31}P$-{$^1H$} NMR (DME/benzene) 16.9 ppm (s)].

**CIDNP Spectra.** $^1H$ CIDNP spectra were obtained for the reaction of bromomethylcyclopropane with potassium dimethyl phosphide[14] in dimethoxyethane-$d_{10}$ by mixing the halide with the phosphide solution in a 5-mm tube directly in the probe of the spectrometer. As soon as the halide was deposited and spinning resumed, a kinetics program was initiated which collected individual transients at the rate of ten per minute.

Mixing problems encountered in $^{31}P$ NMR experiments due to density differences were overcome by fitting each tube with a capillary pipet cut to a length such that the capillary end extended one-third of the way below the surface of the solution. This was held in place by a tight-fitting septum which also served to seal the $^{31}P$ NMR tube from the atmosphere. It was possible to deposit an appropriate amount of organic halide in the pipet portion of this apparatus and avoid mixing with the phosphide solution while the field was locked and an initial spectrum acquired. A small volume of nitrogen injected into the pipet with the assembly still in the probe effected mixing and the spectra were collected in the normal manner.

## Results and Discussion

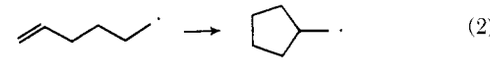
Inasmuch as the cyclopropylcarbinyl radical is known to undergo rapid ring opening[15,16] (eq 1), the formation of substantial amounts of 3-butenyldimethylphosphine from the reaction of bromomethylcyclopropane and potassium dimethylphosphide (Table I, reaction 1) suggested radical



(1)

participation in these coupling reactions. Subsequently, we observed CIDNP[17] when the reaction was monitored by $^1H$ NMR, confirming radical involvement. The spectra were, however, too complex and unresolved to be of any mechanistic use.

Because of the complexity of the spectra and the short duration of polarization,[18] detection and interpretation of CIDNP in the $^1H$ NMR spectra of the coupling reactions of diorganophosphides with organic halides was, in general, difficult. Since $^{31}P$ longitudinal relaxation times are typically longer than those of protons,[19,20] we utilized $^{31}P$ NMR as a more leisurely probe for CIDNP. Additionally, a technique was employed which allowed accumulation of data during mixing of the reagents. Moreover, the simplicity of the spectra facilitate interpretation of the CIDNP phenomenon (vide infra). For these reasons, we employed $^{31}P$ NMR as a rapid technique for assessing radical participation with a wide variety of substrates.[22] While it is clear that CIDNP implies radical combination as a product-forming step,[17] we will assume that, for these systems, a lack of CIDNP implies a nonradical path. This assumption is supported by product studies. For instance, in those cases amenable to use of 1-halo-5-hexene as a substrate $^{31}P$ CIDNP, when observed, was accompanied by cyclization; lack of CIDNP correlated with negligible cyclization. Since the 1-hexenyl radical is known to cyclize[23] (eq 2), this behavior is consistent with the assumption.

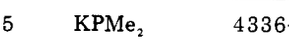
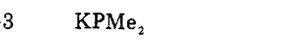
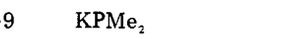
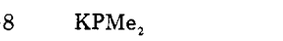
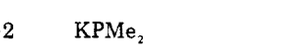
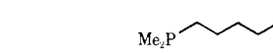
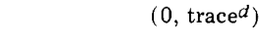
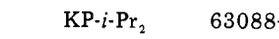
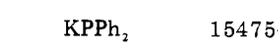
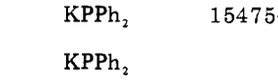
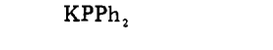
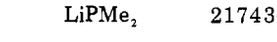
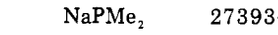
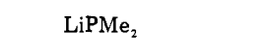
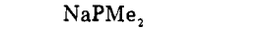
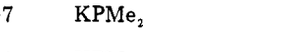
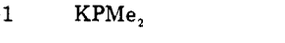


(2)

Further, the observation of CIDNP was generally accompanied by formation of side products (predominant, in some cases) attributable to radical couplings. These products were generally absent in reactions which exhibited no CIDNP.

In order to assess the effect of the halide on the course of the reaction of a constant alkali metal dialkylphosphide with alkyl halides, we investigated a series of reactions of potassium dimethylphosphide with *n*-butyl chloride, bromide, and iodide. Inspection of Table I (reactions 2, 3, and 4) shows that in all cases, the predominant product was *n*-butyldimethylphosphine. However, CIDNP was observed only for reactions 3 and 4; see Figure 1. Further, small amounts of tetramethylbiphosphine (with enhanced emission) and octane were formed with the bromide and iodide, but not for *n*-butyl chloride. The reaction of potassium dimethylphosphide with 1-chloro-5-hexene and the bromo analogue gave the cyclization product (i.e., cyclopentylmethyldimethylphosphine) only with the organic bromide (Table I, reactions 5 and 6). This result establishes that the course of these coupling reactions is highly dependent on the nature of the halide in the organic substrate; *i.e., significant radical participation occurs only for organic bromides and iodides.* Alkyl chlorides presumably react by an $S_N2$ mechanism. We note that this observation is of synthetic significance. For this method, alkyl chlorides are

Table I. Reactions of Diorganophosphides with Organic Halides

| Reaction | Organic halide | Registry no. | Alkali metal phosphide | Registry no. | Products (0, [a] +, [b] −, [c] %[d,e]) |
|---|---|---|---|---|---|
| 1 |  | 7051-34-5 | $KPMe_2$ | 4336-59-8 |  (−, 34[d]),  (?,[f] 30[d]) |
| 2 |  | 109-69-3 | $KPMe_2$ | |  (0, 100[e]) |
| 3 |  | 109-65-9 | $KPMe_2$ | |  (−, 93[e]), $(Me_2P)_2$ (+, 2[e]), octane (trace[d]) |
| 4 |  | 542-69-8 | $KPMe_2$ | |  (−, 29[e]), $(Me_2P)_2$ (+, 71[e]) |
| 5 |  | 928-89-2 | $KPMe_2$ | |  (0, 96[d]),  (0, trace[d]) |
| 6 |  | 2695-47-8 | $KPMe_2$ | |  (−, 65[d]),  (?,[f] 14[d]), $(Me_2P)_2$ (+, trace[e]) |
| 7 |  | | $KP\text{-}i\text{-}Pr_2$ | 63088-98-2 |  (−, 100[e]) |
| 8 |  | | $KPPh_2$ | 15475-27-1 |  (0, 100[e]) |
| 9 |  | | $KPPh_2$ | |  (0, 100[d,e]) |
| 10 |  | | $LiPMe_2$ | 21743-25-9 |  (−, 100[e]), $(Me_2P)_2$ (+, trace[e]) |
| 11 |  | | $NaPMe_2$ | 27393-70-0 |  (−, 100[e]) $(Me_2P)_2$ (+, trace[e]) |
| 12 |  | | $LiPMe_2$ | |  (0, 100[e]) |
| 13 |  | | $NaPMe_2$ | |  (0, 100[e]) |
| 14 |  | 106-95-6 | $KPMe_2$ | |  (−, 5[e]), $(Me_2P)_2$ (+, 95[e]), hexadiene (20[d]) |
| 15 |  | 100-39-0 | $KPMe_2$ | |  (−, trace[e]), $(Me_2P)_2$ (+, 98[e]), bibenzyl (31[d]) |
| 16 |  | 507-19-7 | $KPMe_2$ | |  (−, 44[e]), $(Me_2P)_2$ (+, 56[e]) |
| 17 | PhBr | 108-86-1 | $KPMe_2$ | | $Me_2PPh$ (0, 70[e]), $(Me_2P)_2$ (0, 30[e]) |
| 18 |  | 74-96-4 | $KPMe_2$ | |  (−, 89[e]), $(Me_2P)_2$ (+, 11[e]) |
| 19 |  | | $KPPh_2$ | |  (0, 100[e]) |

[a] 0 = no CIDNP observed. [b] + = enhanced absorption. [c] − = enhanced emission. [d] Yields determined by GLC and based on $MPR_2$. [e] Yields determined by $^{31}P$ NMR and based on $MPR_2$. [f] Obscured by other products, see text.

the preferred substrate for the preparation of tertiary phosphines incorporating groups prone to radical rearrangements.

While rates for $S_N2$ and radical mechanisms generally have the same halide dependence,[24] it appears that, in these instances, the rate for $S_N2$ processes is less affected than that for the radical process by progressing to the lighter congeners.

The effects of varying the organic substituent of the diorganophosphide are illustrated by the reactions of *n*-butyl bromide with potassium dimethyl-, diisopropyl-, and diphenylphosphides (Table I, reactions 3, 7, and 8). CIDNP is observed with the potassium dialkylphosphides, but not with potassium diphenylphosphide. Moreover, ring opening does not occur when bromomethylcyclopropane is used as the substrate (reaction 9), in contrast to reaction 1. Hence, the degree of radical participation is affected by the electronegativity of the organic substituent bound to the phosphide. Inasmuch as the oxidation potential of the diorganophosphide is anticipated to be strongly dependent on group electronegativities, this is consistent with an electron-transfer mechanism operating for dialkylphosphides and absent with diarylphosphides, in keeping with the CIDNP observations.

CIDNP was observed in the reactions of *n*-butyl bromide with lithium, sodium, and potassium dimethylphosphides (Table I, reactions 10, 11, and 3). Additionally, CIDNP is not observed in the reactions of *n*-butyl chloride with the same series (reactions 12, 13, and 2). Thus, no measurable effect is attributed to the metal; i.e., any changes in degree of aggregation or ion pairing due to variation of alkali metal do not strongly affect choice of mechanism.[25]

The results above clearly establish a one-electron component in the reactions of alkyl bromides and iodides with dialkylphosphides, apparently in competition with an $S_N2$ path (predominant for alkyl chlorides). The one-electron path is characterized by observation of CIDNP in the $^{31}P$ NMR resonance of the coupling product and by the presence of side products indicative of radical recombinations (e.g., tetramethylbiphosphine, which itself exhibits CIDNP). For allyl and benzyl bromides, these side products are dominant (Table I, reactions 14 and 15). In both cases, only traces of the tertiary phosphines are received; the major products are tetrameth-

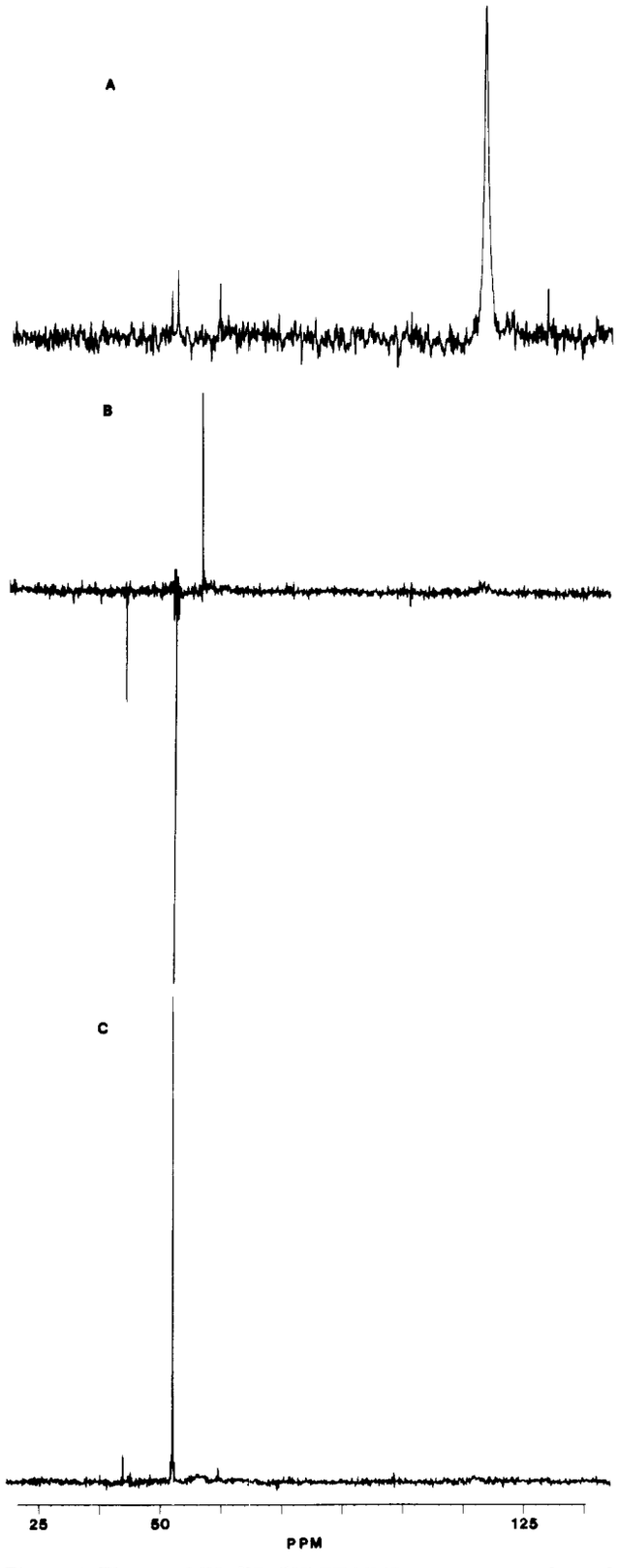
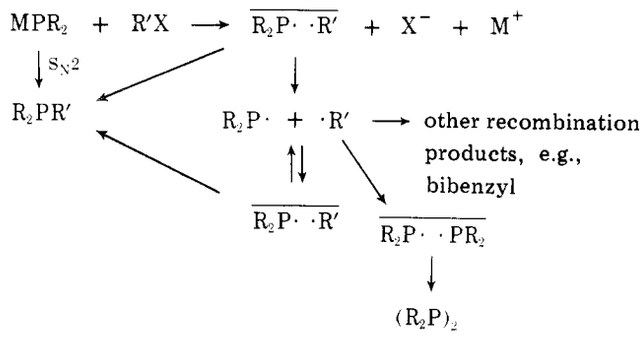



**Figure 1.** The 40.5-MHz $^{31}P-\{^1H\}$ FT NMR spectrum of: K[$PMe_2$] in benzene-$d_6$/1,2-dimethoxyethane: (a) before reaction; (b) after addition of *n*-butyl bromide (one transient 15 s after addition); (c) after relaxation. The resonance at 52.3 ppm is *n*-butyldimethylphosphine; the signal at 59.6 ppm is tetramethylbiphosphine.

ylbiphosphine and hexadiene or bibenzyl. *tert*-Butyl bromide gives a poor yield of *tert*-butyldimethylphosphine (reaction 16). The favored product is, again, tetramethylbiphosphine. Thus, the yield of the tertiary phosphine depends directly on the established order of radical stability.[24]

Phenyldimethylphosphine is formed from aryl halides in good yields without CIDNP. Tetramethylbiphosphine is a detectable side product, but also fails to exhibit CIDNP when formed (Table I, reaction 17).

These results constitute strong evidence that a product-forming step involving radical pair combination, presumably preceded by electron transfer, is in competition with an $S_N2$ process. Further, the choice of mechanism depends in a systematic way on the nature of the halide and the properties of the organic groups. The scheme below, in which the coupling




product arises from either a radical pair with initial singlet spin correlation or via a nonradical path, is consistent with the data. The *g* values for dialkylphosphinyl radicals do not appear to have been reported. However, that for $(C_6H_5)_2P\cdot$ is 2.009.[26] Since hydrocarbon radicals have *g* values close to that of the free electron in the absence of strongly electron-withdrawing groups,[27] $\Delta g > 0$. Further, the hyperfine interaction, $A_{^{31}P}$, is anticipated to be greater than zero.[22] Therefore, the $^{31}P$ resonance of products derived by recombination of the initial singlet correlated geminate pair should exhibit enhanced emission,[17] as observed. The net emission should be reduced, to some degree, by the recombination of secondary pairs with uncorrelated spins and opposite polarization. Tetramethylbiphosphine must result from collapse of a symmetric radical pair with $\Delta g = 0$; any polarization observed must arise in the primary pair with recombination of the escaped, free dimethylphosphinyl radicals occurring before nuclear relaxation is complete.[28] Hence, any polarization observed in the biphosphine must occur with sign opposite that of the primary product, i.e., enhanced absorption, as is found. The apparent exception to this scheme is cyclopentylmethyldimethylphosphine. Since the rate of ring closure of the hexenyl radical (ca. $10^5$ $s^{-1}$)[23] is substantially slower than that of geminate recombination (ca. $10^{10}$ $s^{-1}$),[17,29] the ring-closed species must be an excape product derived from a radical pair with initially uncorrelated spins and should appear with polarization opposite that of 5-hexenyldimethylphosphine, i.e., enhanced absorption. However, cyclopentylmethyldimethylphosphine and 5-hexenyldimethylphosphine are not resolved in their 40.5-MHz $^{31}P$ NMR spectra. Even under high-resolution conditions, mixtures appear as a single resonance.[31] Presumably, the *A* polarization of the ring-closed product is outweighed by the *E* polarization of ring-opened product. $^{13}C$ NMR spectra, in which the products are distinct, would be capable of resolving this point. However, CIDNP proved too weak to observe within the required solubility limits. $^1H$ NMR were complex and overlapping and of little value.[32]

The dialkylphosphinyl radical, $R_2P\cdot$, invoked in this scheme, has been implicated in the photoinitiated addition of secondary phosphines and biphosphines to alkenes[34] and in the photolytic oxidation of tetraphenylbiphosphine with ethanol.[35]

Metal–halogen exchange of the type established for alkyl lithium–benzyl halide reactions[36] has been proposed as being

responsible for the formation of coupling products in the reaction of dialkylphosphides with chlorophenylacetylene,[37] 1-bromo-2-diethylaminoethane,[38] 1,2-dibromoethane,[16] and aryl halides.[16] The principal evidence is the formation of tetraalkylbiphosphines and organic coupling products.[16] Our results clearly establish that observation of these products is insufficient evidence to propose metal–halogen exchange. In most cases (vide supra) these products are radical derived. However, that the steady formation of tetramethylbiphosphine and phenyldimethylphosphine occurs without CIDNP in the reaction of potassium dimethylphosphide with phenyl bromide (reaction 16) suggests that exchange *may* occur in

$$KPMe_2 + PhBr \rightleftharpoons PhK + BrPMe_2$$

$$PhK + KPMe_2 \rightarrow PhPMe_2$$

$$BrPMe_2 + KPMe_2 \rightarrow Me_2PPMe_2$$

this and other instances. In this regard, we examined the reaction of PhLi with $ClPMe_2$ via $^{31}P$ NMR. Phenyldimethylphosphine is formed without CIDNP as would be required. The intimate mechanism of addition of alkyl- and arylphosphides to aryl[4,16] and vinylic substrates[2e,39] is not clarified by our results, although they do allow the possibility of metal–halogen exchange.

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**Registry No.**—Tetramethylbiphosphine, 3676-91-3; potassium, 7440-09-7; diisopropylphosphine, 20491-53-6; potassium hydride, 7693-26-7; cyclopropylmethyldimethylphosphine, 63059-20-1; 3-butenyldimethylphosphine, 55831-90-8; 5-hexenyldimethylphosphine, 63059-21-2; butyldimethylphosphine, 55842-34-3; allyldimethylphosphine, 26681-86-7; allyl chloride, 107-05-1; cyclopentylmethyldimethylphosphine, 63058-99-1; diisopropylbutylphosphine, 63059-00-7; benzyldimethylphosphine, 13954-37-5; benzyl chloride, 100-44-7; cyclopropylmethyldiphenylphosphine, 63059-01-8.

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$$R'\cdot + PR_2^- \rightarrow R'PR_2^-\cdot$$

$$R'PR_2^-\cdot + R'X \rightarrow R'PR_2 + R'X^-\cdot$$

$$R'X^-\cdot \rightarrow R'\cdot + X^-$$

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