Investigation of the Purity of Alkali Metal Diphenylphosphides and Their Reactions with Organic Halides. Evidence for Single Electron Transfer

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For the first time the purity of lithium, sodium, and potassium diphenylphosphide, prepared by various methods, has been evaluated using ^{31}P NMR spectroscopy. A method was developed to prepare each of the phosphides in a high state of purity. Highly pure potassium diphenylphosphide was then allowed to react with *p*-iodotoluene in order to determine the effect of purity on the $S_{RN}1$ nature of this reaction. The results were then compared with literature reports which used less pure $KPPh_2$. The mechanism of reaction of alkyl halides with pure alkali metal diphenylphosphides, using the radical probes 6-halo-5,5-dimethyl-1-hexenes and 1-halo-2,2-dimethylhexanes, was investigated. The results provide the first evidence to support single electron transfer (SET) in the reaction of an alkali metal diphenylphosphide with an alkyl halide. SET was found to be the major reaction pathway in the reaction of hindered alkyl iodides (neopentyl type). On the other hand, SET was found to be a minor pathway in the reaction of the corresponding alkyl bromides and chlorides with PPh_2^-. There was no evidence found for SET in the reactions of unhindered alkyl halides with PPh_2^- although SET participation cannot be rigorously excluded.

Introduction

Dialkyl- and diarylphosphide anions have been used extensively as powerful nucleophiles in reactions with alkyl halides to form substitution products in high yields.[1-4] For a long time, these reactions have been thought to proceed by a polar S_N2 mechanism. The reactions of aryl halides with lithium diphenylphosphide have been studied by Aguiar and co-workers,[5] and they found that substitution products were formed in high yields. In mechanistic studies these workers eliminated the possibility of a benzyne mechanism and a metal–halogen exchange mechanism, based on experimental results.

In 1977, Wreford and co-workers examined the reactions of dialkyl- and diarylphosphides with several alkyl halides, benzyl bromide, and bromobenzene using ^{31}P CIDNP and product analysis as a means of studying the mechanism of reaction.[6] They concluded that there was no evidence for radical involvement in the reaction of dialkylphosphides with aryl halides or of diarylphosphides with alkyl halides.

In 1979, Bunnett and Swartz investigated the reaction of potassium diphenylphosphide with a halobenzenes and halotoluenes.[7] In these studies, they obtained high yields of substitution products and concluded that these reactions are thermally induced radical-chain reactions that proceed by an $S_{RN}1$ mechanism. Except for these reports, there are no other reports of mechanistic studies of thermal reactions of organic halides with diorganophosphide ions.

Interestingly, there has been no attempt to determine the purity of the phosphides used in these studies when it is possible that impurities could play a significant role in the observed mechanism of reaction. Since different methods and solvents were reported in the literature[1,5-7] for the preparation of diphenylphosphides and since the purity of these phosphides had not been determined by previous workers, we decided to evaluate some of the preparative methods in order to determine the purity of the phosphides obtained and to determine what effect, if any, purity of the phosphides would have on the product yield and mechanistic pathway of the reaction.

There are various methods reported for the preparation of alkali metal diphenylphosphides.[1] In Aguiar's work,[5] the lithium salt was prepared by the phenyl cleavage of triphenylphosphine with lithium metal in THF. Wreford[6] prepared various alkali metal phosphides by cleavage of the corresponding tetrasubstituted bisphosphines with the appropriate alkali metal in THF or by the reaction of dialkylphosphines with KH in THF. Bunnett[7] prepared potassium diphenylphosphide by the reaction of diphenylphosphine with t-BuOK in dimethyl sulfoxide.

In this study we report methods for the preparation of alkali metal diphenylphosphides in high purity, the effect of purity on reactions with *p*-iodotoluene, and for the first time evidence for SET in the reaction of a PPh_2^- with sterically hindered primary alkyl iodides.

Results and Discussion

Preparation and Purifity of Alkali Metal Diphenylphosphides. $LiPPh_2$ was prepared by the reaction of Ph_2PH with molar equivalents of various metalating agents such as n-BuLi, PhLi, and s-BuLi in THF as solvent (eq

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(6) Bangerter, B. W.; Beatty, R. P.; Kouba, J. K.; Wreford, S. S. *J. Org. Chem.* **1977**, *42*, 3247.

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1). In the use of lithium metal as the metalating agent,

$$Ph_2PH + RLi \xrightarrow[-78\ ^\circ C]{THF} \underset{(96\%\ \text{pure when R = s-Bu})}{Ph_2PLi} + RH \qquad (1)$$

a slight molar excess of the metal was used (eq 2). The

$$Ph_2PH + Li \xrightarrow{THF} \underset{(50\%\ \text{pure})}{Ph_2PLi} + 1/2H_2 \qquad (2)$$

product obtained by using lithium metal as a metallating agent showed a broad ^{31}P resonance between −20 and −30 ppm due to the combination of the salt and the unreacted phosphine. In addition, there were resonances at −3, −113, and +89 ppm. The purity of the salt was calculated from the relative integration of its ^{31}P NMR resonance with respect to the sum of integrations of all resonances of the sample and was expressed as a percentage. The salt obtained by this method was no more than 50% pure. When n-BuLi was used, the resulting salt showed a sharp resonance at −21.8 ppm and was shown to be 84% pure. This solution also contained 5% tetraphenylbisphosphine and 9% of a compound which appeared at +89 ppm. High purity lithium diphenylphosphide was prepared using PhLi and s-BuLi as metalating agents. The use of PhLi resulted in 91% pure $LiPPh_2$, while the use of s-BuLi produced a 96% pure product. Once again the resonance at +89 ppm accounted for the remainder of the material.

Sodium diphenylphosphide was prepared by treatng diphenylphosphine with a slight molar excess of metallic sodium in THF at room temperature (eq 3). The product

$$Ph_2PH + Na \xrightarrow{THF} \underset{(99\%\ \text{pure})}{Ph_2PNa} + 1/2H_2 \qquad (3)$$

obtained showed a resonance at −20.2 ppm and was >99% pure. Potassium diphenylphosphide was prepared (a) by treating diphenylphosphine with a slight molar excess of potassium metal in THF at −78 °C (eq 4) and (b) by reacting

$$Ph_2PH + K \xrightarrow{THF} \underset{(100\%\ \text{pure})}{Ph_2PK} + 1/2H_2 \qquad (4)$$

equimolar amounts of diphenylphosphine and t-BuOK in DMSO (eq 5). The salt obtained by method (a) was 100%

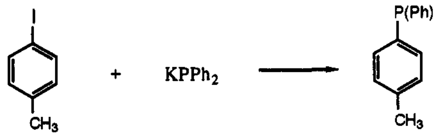
$$Ph_2PH + t\text{-}BuOK \xrightarrow{DMSO} \underset{(98\%\ \text{pure})}{Ph_2PK} + t\text{-}BuOH \qquad (5)$$

pure and showed only a single ^{31}P resonance at −9.6 ppm, and that obtained by method (b) showed two resonances, one at +75.8 and the other at −2.2 ppm, in the ratio of 1:3 and a third minor resonance at +10 ppm. The resonances at +75.8 and −2.2 ppm together accounted for 98% (*vide infra*) of the product.

In order to analyze some of the extraneous minor ^{31}P resonances mentioned above, various samples were hydrolyzed with water and the ^{31}P NMR spectra of hydrolyzed samples analyzed. From this study, it was evident that the resonances at +89 ppm, from samples of $LiPPh_2$ in THF, and −75.8 ppm, from $KPPh_2$ in DMSO, are due to the respective compounds and not due to any impurities. Both these resonances and the major resonances (−21.8 and −2.2 ppm) disappeared upon hydrolysis and were replaced by a single resonance at −39.9 ppm, corresponding to diphenylphosphine. The ^{31}P resonances are probably due to the original compound in some form of a solvate or a different state of aggregation or to some compound that forms Ph_2PH on hydrolysis. All ^{31}P NMR results were reproducible when samples of the same concentration were compared at the same temperature. Also, GC analysis of the hydrolyzed samples showed only Ph_2PH and its oxide.

The conclusion of these preparative studies is that we have developed better methods for the preparation of $LiPPh_2$ (96% pure), $NaPPh_2$ (>99% pure), and $KPPh_2$ (100% pure) than previously reported. Such high purity diphenylphosphides were necessary in order to carry out mechanistic studies in which small traces of impurities might alter the course of reactions.

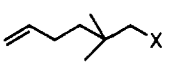
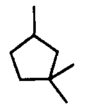
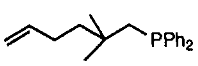
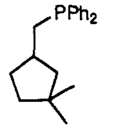
Effect of Purity of $KPPh_2$ on Reaction with *p*-Iodotoluene. Since Bunnett[7] has already shown that *p*-iodotoluene reacts with $KPPh_2$ by an electron-transfer mechanism, we chose this reaction to determine the affect of purity of $KPPh_2$ on product formation and the mechanism of this reaction. Repetition of the reaction of *p*-iodotoluene with a sample of $KPPh_2$, prepared by method (b) under the reaction conditions described by Bunnett,[7] gave a 79% yield of the product (eq 6), which is in agreement with Bunnett's results. When a sample prepared by method (a) was used for the same reaction, only a 42% yield of the substitution product was formed, together with a 50% yield of toluene. Although these results were surprising at first, they are consistent with remarks made by Bunnett and our own experience in working with THF. Although the phosphide sample made by method (a) was purer than that made by method (b), the former sample was prepared in THF, and therefore the reaction was conducted in THF. The aryl radicals produced in the reaction abstracted hydrogen atoms from the α-carbons of THF to produce toluene which reduced the yield of the substitution product. An attempt to carry out the reaction in DMSO necessitated the removal of THF under vacuum and the addition of DMSO. This resulted in 75% pure $KPPh_2$, which when allowed to react with *p*-iodotoluene, produced substitution product in 50% yield and toluene in 20% yield. The presence of 20% of toluene is indicative of incomplete removal of THF, perhaps that which was coordinated with $KPPh_2$. This study, in addition to supporting Bunnett's mechanism, points out that the yield of substitution product depends mainly on the solvent and less on the purity of the phosphide.



(6)

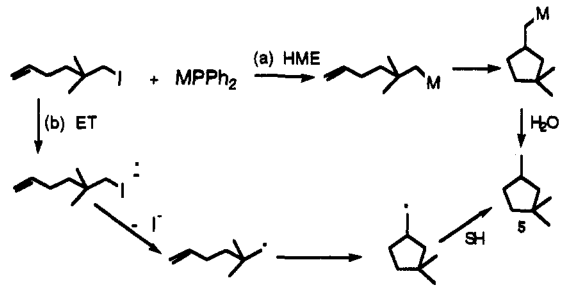
The Mechanism of Reaction of Alkyl Halides with PPh_2^-. Reactions of 6-Halo-5,5-dimethyl-1-hexenes with Alkali Metal Diphenylphosphides. Wreford and co-workers[6] have concluded that the reactions of alkyl halides with alkali metal diphenylphosphides do not involve radical intermediates. This conclusion was based on a study involving a limited number of halides. It was felt necessary to study this reaction further by the use of alkyl halides possessing a cyclizable radical probe. The first study involved sterically hindered alkyl halides in an

Table I. Reactions of 6-Halo-5,5-dimethyl-1-hexenes with MPPh$_2$ in THF[a]

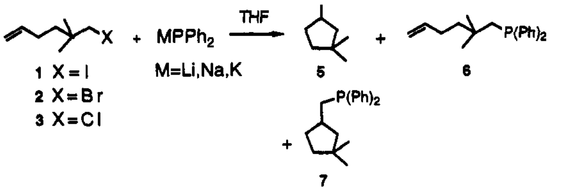
entry		MPPh$_2$ M			
1	I	Li	9 (0)[b]	43	48
2	I	Na	11 (0)[b]	22	67
3	I	Na	4 (11)[c]	22	70
4	I	Na	4 (12)[d]	22	70
5	I	K	7 (0)[b]	17	75
6	I	K[e]	0	24	75
7	Br	Li	0	96	trace
8	Br	Na	0	99	trace
9	Br	K	0	89	10
10	Cl	Na[f]	0	trace	0
11	Cl	K[g]	0	58	5

[a] All reactions were conducted at 25 °C; initial [halide] = 0.066 M, initial [MPPh$_2$] = 0.133 M for 30 min (iodide), 130 min (bromide) in a > 4 h (chloride). [b] Figures in parentheses indicate % d_1 for the reactions quenched with MeOD or D_2O. [c] % d_1 when the reaction was conducted in THF-d_8 quenched with MeOH. [d] % d_1 when the reaction was conducted in THF-d_8 and quenched with MeOD. [e] KPPh$_2$ was prepared by method b, and the reaction was conducted in DMSO. [f] The reaction was stopped after 4 h; 98% of starting halide was recovered. [g] The reaction was stopped after 52 h; 7% of the starting halide was recovered. [h] None of the straight-chain hydrocarbon 4 was formed in any of these reactions.

Scheme I



attempt to detect single electron transfer (SET) under optimum conditions. Reactions of halides **1**–**3** with 2 molar equiv of MPPh$_2$ (M = Li, Na, K) were carried out in THF at 25 °C and the products characterized (eq 7). The results



(7)

of these studies are summarized in Table I. The phosphine products **6** and **7** were characterized after H_2O_2 oxidation to the corresponding phosphine oxides, and quantitative analyses were carried out using ^{31}P NMR and GC. The typical reaction times for complete disappearance of the iodide, bromide, and chloride, as monitored by GC, were 1 min, 90–100 min, and >48 h, respectively.

When the reactions were carried out under the conditions described in Table I, the only non-phosphorous-containing product was the cyclized hydrocarbon **5**. Only the reactions involving the alkyl iodide produced the corresponding cyclic substitution product in high yield; however, even the corresponding bromide and chloride produced this product in 10% and 5% yield, respectively. Examination of the origin of the cyclic hydrocarbon indicates that there are two possible pathways for the formation of **5** (Scheme Ia and b). Pathway (a), the halogen–metal exchange mechanism (HME), was tested by quenching the reaction mixtures within 5 min of mixing (reaction is over in 1 min) with deoxygenated MeOD or D_2O. As indicated in Table I, (entries 1, 2, and 5) there was no deuterium incorporation in **5**. Also, in the presence of *tert*-butylamine (TBA), used as a carbanion trap, the products and their yields remained the same as that in the absence of the trap. These results clearly eliminate the HME mechanistic pathway for the formation of **5**. Pathway (b), the single-electron-transfer mechanism (SET), involves an initial electron transfer from the nucleophile to the alkyl halide, followed by elimination of halide ion to produce the 2,2-dimethyl-5-hexen-1-yl radical. The cyclization of this radical is much faster ($k = 3.6 \times 10^{6}\ \mathrm{s}^{-1}$)[8] than the cyclization of 5-hexen-1-yllithium ($k = 2.0 \times 10^{-3}\ \mathrm{s}^{-1}$)[9] (which involves a carbanion cyclization). The cyclized radical could abstract α-H atoms from THF to form **5**. In order to test the radical nature of the intermediate, the reaction of the iodide with NaPPh$_2$ was carried out in THF-d_8 and quenched with deoxygenated MeOH. Under these conditions, the cyclic hydrocarbon **5** showed 11% d_1 incorporation (entry 3). The % d_1 incorporation in hydrocarbon **5** was within experimental error (12%) when the same reaction was carried out in THF-d_8 and quenched with MeOD (entry 4). These results confirm not only the involvement of a radical intermediate, but also provide supporting evidence for the absence of metal–halogen exchange. When the reaction was carried out using KPPh$_2$ in THF and the reaction mixture quenched with MeOD, 7% cyclized hydrocarbon was formed (entry 5); however, when the solvent was changed to DMSO (entry 6), a non-hydrogen atom donor, no hydrocarbon product was formed.

There are three possible pathways (Scheme II) for the formation of the substitution products: (a) a direct S_N2 pathway to form the straight-chain substitution product; (b) a metal–halogen exchange followed by the reaction of Ph$_2$PX, and (c) an electron-transfer mechanism. Neopentyl substrates react very slowly in S_N2 reactions, and yet the reaction of **1** and PPh$_2^-$ is over in 1 min. Furthermore, an S_N2 pathway does not explain the formation of any hydrocarbon or cyclized substitution product. On the basis of these considerations, it is not likely that the iodide reacted predominantly by an S_N2

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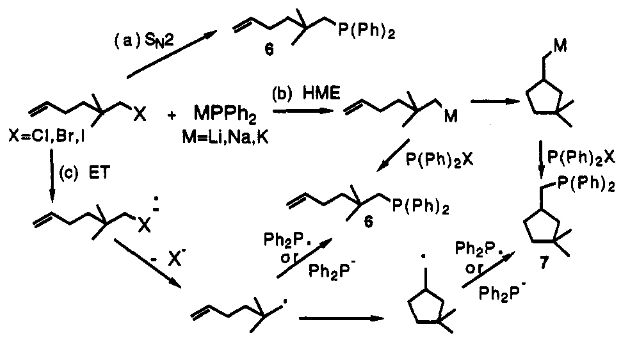
[8] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

[9] Bailey, W. F.; Nurmi, T. T.; Patricia, J. F.; Wang, W. *J. Am. Chem. Soc.* **1987**, *109*, 2442.

Scheme II



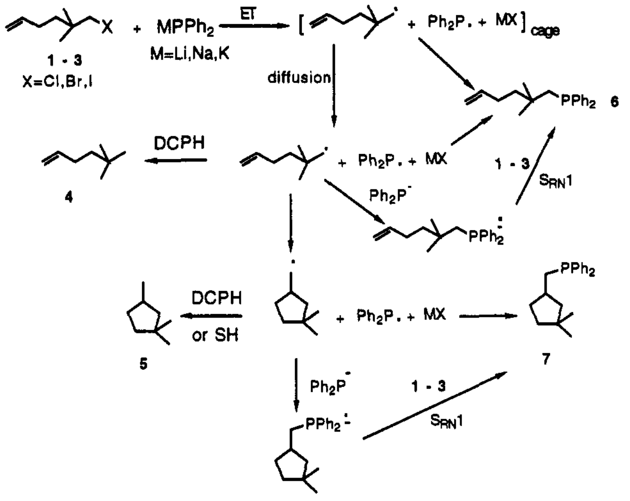
pathway. The S_N2 pathway might play a major role in the reactions of the chloride and bromide since these reactions are much slower. In these cases hydrocarbon is not formed, and cyclized substitution product is produced in low yield. The fact that the use of 10 molar equiv of TBA did not decrease the yield of the substitution products makes the metal–halogen exchange mechanism (pathway b) unlikely, as discussed earlier. When the alkyl bromide 2 was allowed to react with $LiPPh_2$ or $NaPPh_2$, only the straight-chain substitution product (entries 7,8) was formed; however, the reaction of 2 with $KPPh_2$ yielded the cyclic substitution product in 10% yield (entry 9). Once again the SET nature of the reaction of $MPPh_2$ with the alkyl iodide and alkyl bromide follows the order K > Na > Li.

The reaction of the alkyl chloride 3 with $NaPPh_2$ was sluggish and yielded only a trace of the straight-chain substitution product (entry 10) after 4 h; however, the reaction of 3 with $KPPh_2$, despite being slow, yielded 58% straight-chain substitution product and 5% cyclic substitution product (entry 11) after 52 h. On the basis of these results, it is concluded that the SET pathway for the reaction of $KPPh_2$ with the alkyl bromide and chloride is in effect, although it is probably minor compared to the corresponding iodide.

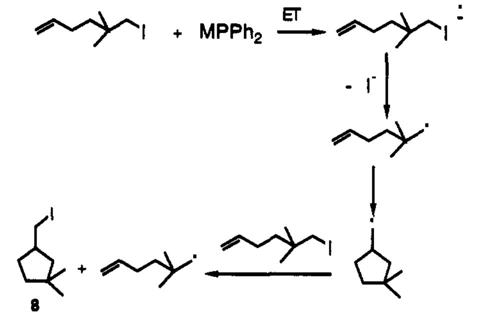
On the basis of all of the evidence so far, the most viable pathway in the reaction of 6-iodo-5,5-dimethyl-1-hexene with $MPPh_2$ (where M = Li, Na, K) is the SET mechanism. Significant evidence for this mechanism comes from results of the reaction of the iodide with $KPPh_2$ in the presence of the radical trap DCPH. This reaction resulted in a considerable increase in the yield of the cyclic hydrocarbon 5 (from 7 to 61%), with a concomitant decrease in the straight-chain and cyclic substitution products. In addition, the straight-chain hydrocarbon 4 was formed in 10% yield indicating that the straight-chain radical was trapped before it had a chance to cyclize or form the substitution product. These results strongly favor the involvement of radical intermediates and, hence, the SET mechanism.

The overall SET mechanism suggested for the reactions of hindered halides with diphenylphosphides is shown in Scheme III. The substitution products are formed by the coupling of the hydrocarbon radicals with either diphenylphosphide radical in the solvent cage or diphenylphosphide anion after diffusion of the straight-chain radical from the solvent cage (which can form 5–7). In the latter case, an $S_{RN}1$ mechanism would be operative. Evidence for geminate coupling inside the solvent cage leading to substitution product comes from results of the reaction of iodide 1 with $KPPh_2$ in DMSO, a solvent of higher viscosity than THF. The amount of 6 increased from 17% in THF to 24% in DMSO at the expense of a decrease in 5 from 7% in THF to 0% in DMSO. These results are in keeping with the principle that more radicals will diffuse out of the solvent cage in a solvent of lower viscosity, resulting in a greater chance to form products derived from cyclized radicals.

Scheme III



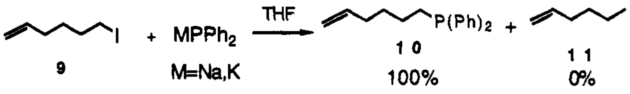
Scheme IV



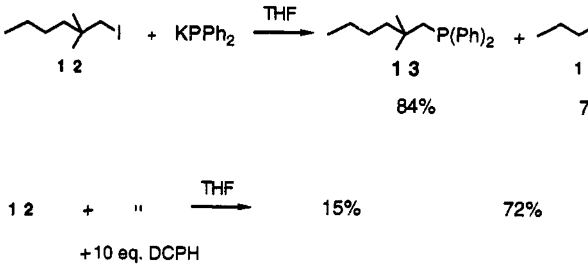
The possibility of a radical-chain process (Scheme IV) leading to the cyclization of the alkyl iodide 1 was investigated. The reaction of 1 molar equiv of iodide with 0.1 molar equiv of $NaPPh_2$ in THF resulted in 90% recovery of the unreacted halide (with no trace of the cyclized isomer 8), 7% of the substitution products, and 1% of the cyclic hydrocarbon. The fact that the reaction of 1 with $NaPPh_2$ is over in a matter of seconds indicated that the much slower halogen atom radical-chain process could not compete favorably with the pathway shown in Scheme III. These results suggest that a halogen atom radical chain process as a pathway to cyclized substitution product is not likely. Further results that strongly indicate that a halogen atom radical-chain process is not a factor in the formation of cyclized substitution product (7) are based on the reaction of the saturated counterpart of 1 which is compound 12. Compound 12 is not capable of cyclization, therefore, a halogen atom radical chain process (Scheme IV) is not possible, yet the evidence is clear that radicals are formed. These results will be presented in the next section.

Studies Involving Hindered and Nonhindered Saturated Alkyl Halides. In order to further investigate the electron-transfer nature of reactions of alkyl iodides with alkali metal phosphides, it was decided to study the reactions of hindered and nonhindered saturated primary iodides. Although the possibility of observing cyclized products is eliminated, the reaction was studied in order to observe products indicative of a radical precursor and also to observe the reaction under conditions where a halogen atom radical chain process is not possible.

The reaction of n-hexyl iodide with $MPPh_2$ (M = Na, K) both in the presence and in the absence of a radical trap, DCPH, resulted only in the formation of substitution product in 100% yield. The reaction of the corresponding unsaturated primary iodide **9** also resulted only in the formation of the straight-chain substitution product in 100% yield (eq 8). Both the saturated and unsaturated nonhindered primary alkyl iodides did not produce any hydrocarbon products *indicative of a radical precursor* (product **11** not observed). On the other hand, the reaction of 1-iodo-2,2-dimethylhexane (**12**) with $KPPh_2$ produced hydrocarbon **14** in 7% yield indicative of a radical precursor that has abstracted a hydrogen atom from THF (eq 9).



(8)



(9)

(10)

Also, isolation of compound **14** indicates that cyclized product **7** (eq 7) cannot be explained by a halogen atom radical chain process (Scheme IV) since the formation of **14** is not possible by such a process. In the presence of the radical trap, DCPH, the yield of hydrocarbon **14** increased from 7% to 72%, with an accompanied decrease of the substitution product **13** from 84 to 15%. These results are strongly supportive of a radical intermediate being trapped by DCPH (eq 10).

In the case of iodide **12**, the steric requirement of coupling might be responsible for the major escape of the radical from the cage. In any case, it appears, based on this work, that hindered primary alkyl iodides react with PPh_2^- predominantly by a SET pathway. The corresponding bromides and chlorides because of a less favorable reduction potential compared to the iodide may react predominantly by a S_N2 pathway. On the other hand, when the hindered nature of the primary alkyl halide is removed there is no evidence for a SET pathway; however, this possibility cannot be rigorously eliminated at this stage since geminate coupling in the solvent cage is possible.[10]

Since radical probe **1** has been used in our laboratory over the years to test for the SET nature of reactions involving various nucleophiles, an attempt was made to determine if any correlations exists between the ease of oxidation of these nucleophiles and the yield of cyclic products (both substitution and hydrocarbon products). The E^0 values of some nucleophiles used in this laboratory are given below.[11] The yield of cyclic products formed in the reactions of **1** with various nucleophiles was in the order:

E^0 values	(unknown)		1.0 (THF)		1.1–1.3 (THF)		0.3 (acetonitrile)
nucleophile	Ph_2P^-	>	Me_3Sn^-	>	$i\text{-}Pr_2N^-$	>	$C_2H_5S^-$
yield of cyclic products	80%		77%		48%		0%

In the case of LDA, it should be noted that a competing α-dehydrohalogenation reaction (carbene formation) was responsible for the lower amount of SET product, although the E^0 values for Me_3Sn^- and $(i\text{-}Pr)_2N^-$ are almost equal. On the basis of the above correlation, it might be inferred that diphenylphosphides have a comparable E^0 value compared to Me_3Sn^- which is known to be a very good one-electron donor.

Several attempts were made using cyclic voltammetry to measure the oxidation potential of Ph_2P^- for comparison with that of other nucleophiles. At a Pt button electrode, no well-defined redox reactions were observed for solutions of 3 mM $KPPh_2$ in THF containing 0.1 M $n\text{-}Bu_4N^+BF_4^-$ over the potential range 0.50 to −2.2 V vs the SCE. The current–voltage curves obtained on this solution were compared with those obtained for the supporting electrolyte alone. The data suggest that the double layer structure is significantly changed by the presence of $KPPh_2$, inferring adsorption of $KPPh_2$ (or Ph_2P^-) on the Pt surface. This observation may be the reason that the oxidation potential for Ph_2P^- has not been previously reported.

Cyclic voltammograms were also obtained on a 3 mM solution of **1** in dry THF. At fast potential sweep rates, an electrochemically reversible couple was observed at −0.80 V versus the saturated calomel electrode. From the correlation above and from the fact that the oxidation potential of Ph_2P^- must be negative of the reaction potential for **1**, we conclude that E^0 of Ph_2P^- is in the range −0.8 to −1.3 V. Indeed, our calculations of gas-phase oxidation potentials for $(CH_3)_2N^-$ are 0.98 eV and Ph_2P^- are 2.81 eV, indicating that Ph_2P^- should be a better one electron donor than $(CH_3)_2N^-$. Work to be published soon from this laboratory shows that $(i\text{-}Pr)_2N^-$ is a good one-electron donor.[12]

Experimental Section

Materials. Reagent-grade tetrahydrofuran (THF) was distilled immediately before use under nitrogen from deep puple solutions of sodium benzophenone ketyl. Dimethyl sulfoxide was distilled over calcium hydride at reduced pressure. Dicyclohexylphosphine (DCPH) from Alfa was purified by distillation at reduced pressure, and *tert*-butylamine (Aldrich) was distilled from calcium hydride under nitrogen. The alkyllithium solutions were purchased from Aldrich and used after standardization by Watson–Eastham titration.[13] Potassium *tert*-butoxide, prepared by reacting the alcohol with potassium metal, was sublimed prior to use. THF-d_8 in 1-mL ampules from Aldrich was used as received. MeOD (Aldrich) was deoxygenated prior to use.

General Procedures. All glassware and syringes were oven dried at 150 °C for at least 6 h and cooled under a flow of nitrogen prior to use. Transfer of reagents was performed by using syringes equipped with stainless steel needles. Air- and moisture-sensitive

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[10] Work recently completely by E. C. Ashby, X. Sun, and L. Tolbert indicate that radical coupling in the solvent cage is taking place when unhindered primary alkyl radicals are involved. This work will be reported shortly.

[11] Eberson, L. *Electron Transfer Reaction in Organic Chemistry*; Springer-Verlag: New York, 1987; pp 45–46.

[12] Ashby, E. C.; Park, B.; Patil, G. S.; Gadru, K.; Gurumurthy, R. *J. Org. Chem.*, in press.

[13] Watson, S. C.; Eastham, J. F. *J. Organometal. Chem.* **1967**, *9*, 165.

compounds were manipulated under argon or nitrogen, using glovebox, vacuum line, and Schlenk tube techniques.

Proton NMR spectra were recorded on a Gemini-300 MHz instrument using Me_4Si as an internal reference and the chemical shifts (δ) expressed in ppm. Phosphorous-31 NMR spectra were recorded on a Varian XL-400 MHz instrument operating at 161.895 MHz, using H_3PO_4 as an external standard, with resonances deshielded from the reference being reported as positive values. A pulse delay of 5 s was used. Triphenylphosphine and triphenylphosphine oxide were used as internal standards. Gas-liquid chromatography was accomplished with a FID detector and a 30-m × 0.25-mm DB-5 capillary column. GC response factors were determined relative to decane as a standard.

All phosphide solutions were standardized in triplicate by quenching a 1.00-mL solution in 10.0 mL of distilled water under nitrogen and titrating to a phenolphthalein endpoint with a standardized HCl solution. The solutions (0.2 M) were clear yellow-green or orange solutions without floating particles. The slight excess of the metals used settled and did not pose problems when the reagents were dispensed with syringes. The solutions were stored in a tightly sealed flask, with the exclusion of moisture and oxygen, in the refrigerator without any deterioration.

Lithium Diphenylphosphide from Diphenylphosphine and Alkyllithiums. To 20 mL of THF was added 0.74 g (4.0 mmol) of diphenylphosphine by means of a syringe under nitrogen and the resulting solution allowed to stir and equilibrate to the desired temperature. The optimum temperatures were −35 °C for reactions with n-BuLi and −78 °C for reaction with PhLi and s-BuLi. To the stirred solutions of the above was added a stoichiometric amount of the standardized alkyllithium solution dropwise by means of a syringe. The resulting solution was allowed to react for 4 h in the case of the n-BuLi reaction and 8 h in the case of the s-BuLi and PhLi reactions. A clear orange colored solution was obtained: ^{31}P NMR (THF, −78 °C) δ −21.5 (lit.[3] δ −23).

General Procedure for the Preparation of Alkali Metal Diphenylphsphides from Diphenylphosphine and Alkali Metal. To a round-bottom flask, fitted with a T-bore stopcock and stirring bar, was added 11–12 mmol of alkali metal and the flask flushed with the appropriate inert gas (argon or nitrogen). Fifty mL of freshly distilled THF was then added to the flask under an inert gas atmosphere. The solution was stirred and equilibrated to the desired temperature (optimum temperatures were 25 °C for Na and Li and −78 °C for the K reactions). To the resulting solution was added dropwise 1.86 g (10.0 mmol) of diphenylphosphine. After the addition, the solution was stirred for 8 h for the K and Na and 36 h for the Li reactions, at the temperatures mentioned, to yield the respective phosphides: ^{31}P NMR ($NaPPh_2$/THF, 25 °C) δ −24.5 (lit.[3] δ −24.4); ^{31}P NMR ($KPPh_2$/THF, −80 °C) δ −9.6 (lit.[3] δ −12.4).

Potassium Diphenylphosphide from Diphenylphosphine and t-BuOK. A solution of $KPPh_2$, prepared by the reaction of diphenylphosphine with an equimolar amount of t-BuOK in DMSO according to the procedure described bu Bunnett,[7] showed the following: ^{31}P NMR (DMSO, 25 °C) δ −2.2 and δ +75.8 in the ratio 3:1.

6-Iodo-5,5-dimethyl-1-hexene. This iodide, prepared in 90% yield according to the literature procedure,[14] exhibited the following: ^1H NMR ($CDCl_3$) δ 1.05 (s, 6H), 1.27–2.27 (m, 4H), 3.13 (s, 2H), 4.8–5.1 (m, 2H), 5.7–6.0 (m, 1H).

6-Bromo-5,5-dimethyl-1-hexene. This bromide, prepared in 70% yield according to the literature procedure,[14] exhibited the following: ^1H NMR ($CDCl_3$) δ 1.02 (s, 6H), 1.4–1.5 (m, 2H), 1.9–2.1 (m, 2H), 3.2 (s, 2H), 4.8–5.1 (m, 2H), 5.7–6.0 (m, 1H).

6-Chloro-5,5-dimethyl-1-hexene. This chloride, prepared in 75% yield according to the literature procedure,[14] exhibited the following: ^1H NMR ($CDCl_3$) δ 0.98 (s, 6H), 1.35–1.45 (m, 2H), 1.9–2.1 (m, 2H), 3.35 (s, 2H), 4.8–5.2 (m, 2H), 5.6–6.0 (m, 1H).

General Procedure for the Reaction of the 6-Halo-5,5-dimethyl-1-hexenes with Alkali Metal Diphenylphosphides. To 2.0 mL of a 0.2 M solution of phosphide ($LiPPh_2$ was prepared by the reaction of s-BuLi and Ph_2PH; $NaPPh_2$ and $KPPh_2$ were prepared by the reaction of respective metals with Ph_2PH) in THF was added dropwise 1.0 mL of a 0.2 M alkyl halide solution in THF at room temperature. Solutions of alkyl halides and phosphides were protected from light, and transfers were made via syringes. The reactions were conducted for 30 min with the iodide, 130 min with the bromide, and >4 h with the chloride. Reactions were quenched with deoxygenated anhydrous MeOH or H_2O, internal standards added, and GLC and ^{31}P NMR analyses performed. In reactions where MeOD or D_2O were used as quenching agents, an aliquot of the reaction mixture was quenched after 2–3 min and subjected to mass spectral analysis for % d_1 incorporation. A reaction with 4 mmol of the iodide and 8 mmol of $NaPPh_2$ was carried out in THF, and the mixture of crude products was oxidized with 5% H_2O_2 in CH_2Cl_2. The crude mixture of phosphine oxides of **6** and **7** was chromatographed over silica gel. Elution with a 90% EtOAc-10% MeOH mixture gave the individual oxides. **(2,2-Dimethyl-5-hexenyl)diphenylphosphine oxide**: ^1H NMR ($CDCl_3$) δ 1.05 (s, 6H), 1.45 (m, 2H), 2.0 (m, 2H), 2.3 (d, 2H, J = 11.1 Hz), 4.85–4.95 (m, 2H), 5.6–5.8 (m, 1H), 7.4–7.9 (m, 10H); ^{31}P NMR ($CDCl_3$) δ 27.9; mass spectrum *m/e* (relative intensity) 312 (M^+, 8.7), 297 (10.4), 257 (8.1), 215 (100), 202 (61.4), 201 (55.9), 125 (12.6), 77 (18.8), 47 (12.6).

[(3,3-Dimethylcyclopentyl)methyl]diphenylphosphine oxide: ^1H NM ($CDCl_3$) δ 0.88 (s, 3H), 0.97 (s, 3H), 1.2–1.4 (m, 3H), 1.6–1.8 (m, 3H), 2.3–2.4 (m, 3H), 5.6–5.8 (m, 1H), 7.4–7.8 (m, 10H); ^{31}P NMR ($CDCl_3$) δ 27.9; mass spectrum *m/e* 312 (M^+), 297, (9.9) 215 (100) 202, (60.1) 201, (31.7) 125, (11.5) 77, (16.6) 47 (10.2).

Electrochemistry. Cyclic voltammetric data were acquired with an EG&G Princeton Applied Research Corp. Model 273 potentiostat/galvanostat under the control of the Model 270 software package. A Pt-button working electrode, a Pt-wire counter electrode, and either a saturated calomel reference electrode or a silver/silver chloride electrode were used. The reference electrode was placed in a separate compartment to minimize aqueous contamination of electrochemical solutions from the reference electrode fill solution. The compartment was filled with supporting electrolyte (0.1 M n-$Bu_4N^+BF_4^-$ in dry THF) and was isolated from the electrochemical solution by a fritted glass disk. Voltammograms were obtained at potential sweep rates ranging from 0.020 to 10 V/s. Positive feedback was used to compensate for solution resistance at scan rates in excess of 0.2 V/s. Solutions used in electrochemical experiments were deoxygenated with solvent-saturated nitrogen and blanketed with nitrogen during all experiments.

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[14] Ashby, E. C.; Depriest, A. B.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* **1984**, *49*, 3545.