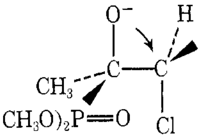
and β-ketophosphonate.[4,11,13] Similarly, the reactions of trialkyl phosphites with α-halo ketones give a variety of products depending on reaction conditions. Investigations of the mechanism of these reactions have led to little conclusive evidence about their mechanism.[19] Formation of the vinyl phosphate, epoxyphosphonate, and phosphate halohydrin is believed to result from attack by the phosphorus at the carbonyl carbon. Formation of the β-ketophosphonate results from attack at the α-halo carbon.

For the aliphatic α-halo ketones, formation of the epoxide is the favored course of the reaction. The phosphorus can attack the carbonyl carbon to form the intermediate halohydrin. The α carbon is free to rotate around its bond to the carbonyl carbon, positioning the halide trans to the oxygen which is involved in nucleophilic attack.



In the case of chlorocyclohexanone, the α carbon is not free to rotate. The preferred conformation of the molecule has the chlorine in an equatorial position. Attack by the phosphorus can result in chlorohydrin with hydroxyl and chlorine having either cis or trans stereochemistry; the trans can lead to epoxide through the axial–axial conformer (which has the phosphonate group equatorial), but the cis isomer cannot achieve the proper stereochemistry to generate epoxide so it would give vinyl phosphate by attack at phosphorus; we found a 50:50 mixture of epoxyphosphonate and vinyl phosphate.

For α-chloroacetophenone, the α carbon is free to rotate in epoxide formation. However, attack of the oxygen at phosphorus is also favorable owing to the formation of a conjugated system. Meisters and Swan, who found that sodium diethylphosphonate and α-chloroacetophenone in liquid ammonia gave a mixture of the epoxide and vinyl compounds, suggested that the polarity of the solvent was the determining factor.[11] They proposed that a more polar solvent would favor epoxide formation; however, our reaction in methanol gives no epoxide.

Acknowledgment. We thank Professor Max Tishler for encouragement and Dr. B. G. Christensen of Merck Sharp and Dohme Research Laboratories for allowing us access to unpublished research. This research was supported in part by a grant from Merck and Co., Inc.

Registry No.—**2,** 36432-35-6; **3,** 1445-84-7; **4,** 58074-07-0; **5,** 58074-08-1; **6,** 58074-09-2; **7,** 58074-10-5; **8,** 13176-31-3; chloroacetone, 78-95-5; 2-chloro-4,4-dimethyl-3-pentanone, 40955-58-6; chlorocyclohexane, 822-87-7; 1-chloro-3,3-dimethyl-2-butanone, 13547-70-1; α-chloroacetophenone, 532-27-4; 3-bromo-2-butanone, 814-75-5; dimethyl phosphonate, 868-85-9; diethyl phosphonate, 762-04-9; sodium methoxide, 124-41-4; sodium benzyloxide, 20194-18-7; dibenzyl phosphonate, 17176-77-1.

References and Notes

(1) D. Hendlin, E. O. Stapley, M. Jackson, H. Wallick, A. K. Miller, F. J. Wolf, T. W. Miller, L. Chaiet, F. M. Kahan, E. L. Foltz, H. B. Woodruff, J. M. Mata, S. Hernandez, and S. Mochales, *Science*, **166**, 122 (1969).

(2) B. G. Christensen, W. J. Leanza, T. R. Beattie, A. A. Patchett, B. H. Arison, R. E. Ormond, F. A. Kuehl, G. Albers-Schonberg, and O. Jardetzky, *Science*, **166**, 123 (1969).

(3) C. E. Griffin and S. K. Kundu, *J. Org. Chem.*, **34**, 1532 (1969).

(4) G. Sturtz, *Bull. Soc. Chim. Fr.*, 2333 (1964).

(5) F. M. Kahan, J. S. Kahan, P. J. Cassidy, and H. Kropp, *Ann. N.Y. Acad. Sci.*, **235**, 364 (1974).

(6) D. P. Wyman and P. R. Kaufman, *J. Org. Chem.*, **29**, 1956 (1964).

(7) E. R. Buchman and H. Sargent, *J. Am. Chem. Soc.*, **67**, 401 (1945).

(8) M. S. Newman, M. D. Farbman, and H. Hipsher, *Org. Synth.*, **3**, 188 (1960).

(9) F. Imura, *Nippon Kagaku Zasshi*, **78**, 48 (1957); *Chem. Abstr.*, **53**, 5185 (1959).

(10) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

(11) A. Meisters and J. M. Swan, *Aust. J. Chem.*, **18**, 168 (1965).

(12) D. Redmore, *Chem. Rev.*, **71**, 315 (1971).

(13) B. A. Arbuzov, V. S. Vinogradova, and N. A. Polezhaeva, *Dokl. Akad. Nauk SSSR*, **111**, 107 (1956); *Chem. Abstr.*, **51**, 8001 (1957); *Dokl. Akad. Nauk SSSR*, **121**, 641 (1958); *Chem. Abstr.*, **53**, 1180 (1959); *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 41 (1959); *Chem. Abstr.*, **53**, 15035 (1959); *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 832 (1960); *Chem. Abstr.*, **54**, 24454 (1960).

(14) K. Hunger, *Chem. Ber.*, **101**, 3530 (1968).

(15) B. G. Christensen, personal communication.

(16) E. J. Glamkowski, G. Gal, R. Purick, A. J. Davidson, and M. Sletzinger, *J. Org. Chem.*, **35**, 3510 (1970).

(17) V. S. Abramov and A. S. Kapustina, *J. Gen. Chem. USSR (Engl. Transl.)*, **27**, 1093 (1957); V. S. Abramov and R. N. Savintseva, *Khim. Org. Soedin. Fosfora, Akad. Nauk*, 129 (1967); *Chem. Abstr.*, **69**, 67465 (1968).

(18) T. Agawa, T. Kubo, and Y. Ohsiro, *Synthesis*, 27 (1971).

(19) P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965).

Conformation and Electronic Structure of the Lithium Adduct of Methylenephosphoranes

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NMR evidence is presented to show that lithium adducts are formed upon addition of *n*-butyllithium to methyltriphenylphosphonium iodide. The geometry of the lithium adduct to methylenephosphorane was examined by means of CNDO/2 molecular orbital calculations. The electronic structure of this molecule is compared to several other related molecules. The calculations suggest that the lithium does not perturb the electron distribution or conformation about the methylene group significantly compared to methylenephosphorane, with the exception that the phosphorus atom loses electron density in the adduct. Calculations of P–C couplings by the finite perturbation method support the proposed conformation.

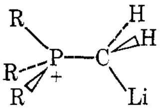
It has been previously established that lithium salts can bond to phosphorus–carbon ylides.[1] These compounds are the simplest type of a rich variety of organometallic compounds formed where the methylene carbanion of a phosphorus ylide bonds to a metal.[1a] However, there is very little reported on the nature of these adducts. From a proton NMR investigation it was proposed[1b] that the conformation of these lithium adducts was 1 since the C–H coupling of the methylene group was approximately the same as that found for phosphonium salts (see Table I). The C–H coupling for the salt-free ylide was, however, 15 Hz larger than that obtained for the lithium adduct.[1b] Evidence of both

Table I. NMR Properties of the Methylenephosphoranes and Their Related Salts[a]

Compd	Solvent	^{13}C chemical shift, ppm	^{31}P chemical shift, ppm	$^{1}J_{P-C}$, Hz[b]	$^{1}J_{C-H}$, Hz
$Me_3P{=}CH_2$[c]	C_6D_6	−1.5	2.1	90.5	149
$Ph_3P{=}CH_2$[d]		−4.1		100.0	153[e]
$Me_2EtP{=}CH_2$[f]	Neat				149
Me_3P^+–Me I^-[g]	$CDCl_3$	11.3	25.1	56.0	134[h]
Ph_3P^+–Me I^-	$CDCl_3$	11.4	21.1	57.1	
Ph_3P–CH_2Li I^-	C_6D_6–Et_2O 6:1	−4.1	22.1	51.9	133
	C_6D_6–Et_2O 1:1	−4.3	18.7	61.3	
	C_6D_6–Et_2O 1:6	−5.0		64.7	
Me_2EtP^+–CH_2Li Cl^-	C_6H_6				134

[a] The ^{13}C chemical shifts are relative to internal Me_4Si and refer to the methylene carbon (or methyl) carbon directly bonded to phosphorus. The ^{13}C and P–C couplings for the phenyl ring carbons in the different solvents for the lithium compounds are identical. [b] The digital resolution was ±0.1 Hz. [c] Values taken from H. Schmidbaur, W. Buchner, and D. Scheutzow, *Chem. Ber.*, **106,** 1251 (1973). [d] Y. Yamamoto and H. Schmidbaur, *J. Organomet. Chem.*, **97,** 479 (1975). [e] K. A. O. Starzewski and M. Feigl, *ibid.*, **93,** C20 (1975). [f] H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101,** 3556 (1968). [g] W. McFarlane, *Proc. R. Soc., London, Ser. A*, **306,** 185 (1968). [h] I. J. Petracek et al., *Tetrahedron Lett.*, 707 (1970).

experimental and theoretical nature is presented that indicates that structure 2 is a possible conformation of these lithium adducts. Furthermore, lithiated phosphoranes are always likely to be obtained when alkyllithium compounds are employed to generate methylenephosphoranes (and possible other nonstabilized phosphoranes), even under "salt-free" [2] conditions. This casts doubt on the validity of kinetic and stereochemical investigations with nonstabilized (ylides that do not contain electron-withdrawing groups on the carbon bearing the formal negative charge) phosphoranes.[3]



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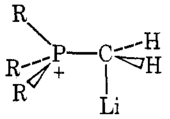


2

2a, R = H

Results and Discussion

The ^{13}C NMR of methylenetriphenylphosphorane along with those of several other ylides has previously been published.[4a] We now wish to correct that NMR data in light of our current findings, i.e., the previously reported ^{13}C chemical shifts and ^{31}P–^{13}C couplings for "methylenetriphenylphosphorane" are, in fact, those for the lithium adduct of the ylide. Listed in Table I are several NMR parameters that provide strong evidence for the formation of lithium salts from their corresponding ylides (for the preparation of the triphenyl substituted compounds, see the Experimental Section). That the compounds generated by the reaction of *n*-butyllithium with methyl phosphonium salts are not ylides is evidenced by the following facts.

1. The C–H coupling for the methylene group is essentially identical for the triphenyl- and dimethylethylmethylenephosphorane lithium adducts. However, the C–H coupling for methylenetrimethyl- and dimethylethylphosphorane, prepared by a desilyation process,[4b] is 15 Hz larger.

2. The directly bonded P–C coupling for the triphenyl substituted lithium compound is similar to that found for methyltriphenyl- and tetramethylphosphonium iodide. Methylenetrimethyl- (or triphenyl-) phosphorane, however, has a P–C coupling of 48.1–25.8 Hz larger than that found for the lithiated compound.[5]

3. The P–C coupling is strongly dependent on the concentration of ether as a solvent, implying coordination of lithium to the ether (vide infra).

4. The ^{31}P chemical shift of methylenetrimethylphosphorane is 2.1 ppm, shielded by 23.0 ppm from its phosphonium salt protomer. This is normal for nonstabilized ylides.[6] On the other hand, there is essentially no difference between the ^{31}P chemical shifts of the lithiated triphenylphosphorane and its phosphonium salt. The ^{31}P chemical shift of methylenetriphenylphosphorane in Me_2SO[6] and benzene[7] has been reported as 22.2 and 22.3 ppm, respectively, and thus (note the similarity with the phosphonium salt chemical shift) also provides evidence that the compound in these solvents is not the ylide, but rather the lithium adduct.

If the ^{31}P chemical shifts can be related in a qualitative sense to the electronic environment of the phosphorus nucleus,[8,9] then these data suggest that the phosphorus in the phosphonium salts and the lithium adducts is somewhat similar. The ^{13}C chemical shifts indicate substantial electron density on the carbon adjacent to the lithium which is comparable to that found for methyllithium (−11 to −15 ppm)[10] and methylenetrimethylphosphorane.

The conformation and electronic structure of the lithium adduct of methylenephosphorane was studied by CNDO/2 molecular orbital calculations.[11] Figure 1 shows the four

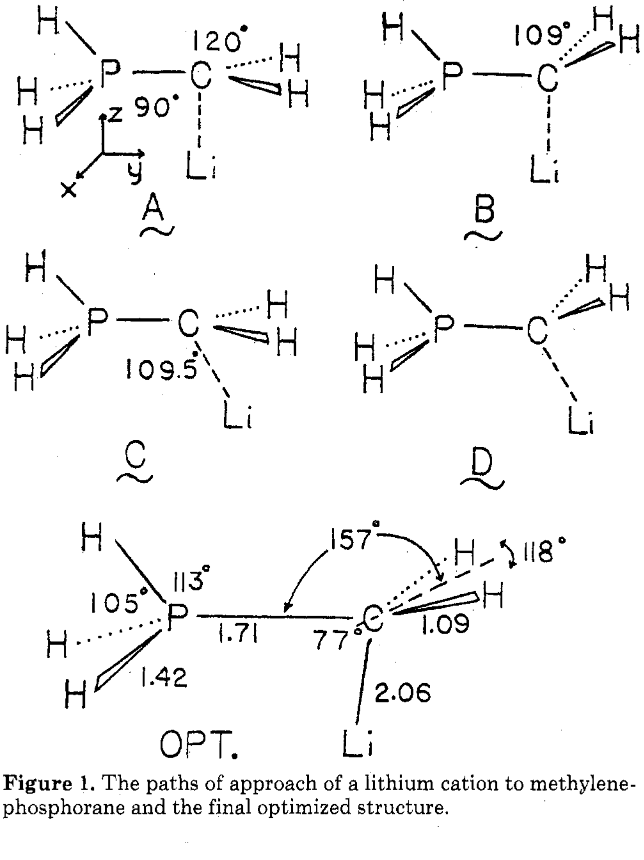


Figure 1. The paths of approach of a lithium cation to methylenephosphorane and the final optimized structure.

paths of approach for a lithium cation considered, as well as the final geometry optimized structure. Figure 2 shows the relative energies (using the spd basis set) for these paths. It is seen that there is a marked tendency for lithium to form a P–C–Li bond angle of 90°. This is analogous to the lithium complex of formaldehyde[12] as determined by ab initio molecular orbital calculations and underscores the ability of the phosphonium group to form σ_π type bonds both with and without d orbitals.[14] The CNDO/2 spd parameterization has given reliable geometries for phosphorus-containing molecules;[14–16] however, the CNDO/2 and INDO methods give bond angles with lithium that seem to be rather smaller than expected.[17] The difference in energy between the optimized structure in Figure 1 and one with a P–C–Li bond angle of 90° and the methylene group flattened onto the X–Y plane (**2a**) is only 3.5 kcal/mol. This probably represents a better fit (in accord with the NMR evidence and theoretical calculations thereof, described below) to the conformation of the lithiated phosphoranes in solution. The calculations do not take into account solvent–solute interactions; however, solvent coordination effects with lithium are mimicked below. The CNDO/2 method without d orbitals gives erroneously long P–C bond lengths,[14,15] so a geometry optimization with this basis set was not attempted.

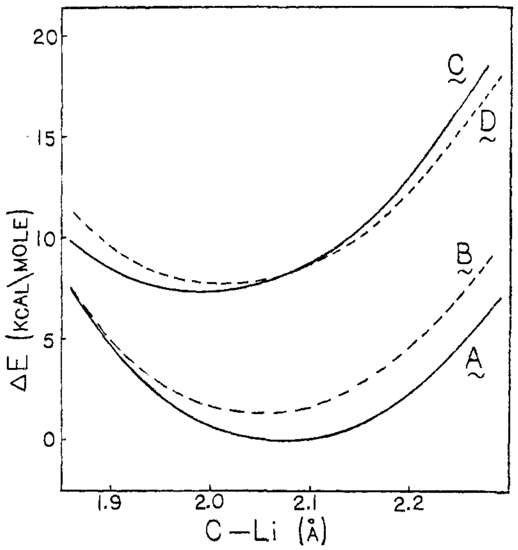


Figure 2. The relative energies of the lithium adduct with respect to the C–Li bond distance and the possible paths considered in Figure 1. The C–P bond distance is held constant at 1.68 Å. The letters refer to the paths considered in Figure 1.

The electron distribution for the lithium adduct of methylenephosphorane, the parent ylide, and its phosphonium cation is given in Figure 3. It is well known that the CNDO/2 level of approximation with a spd basis set overemphasizes d orbital importance,[18] so that deleting the d orbitals from the basis set will effectively bracket the "real" situation (the charges from the sp basis set are given in parentheses). The charges for methylphosphonium cation, **3**, and methylenephosphorane, **4**, represent those from totally optimized structures.[13] Molecular orbital calculations of a semiempirical, as well as ab initio, nature on **4** using assumed geometries have been previously published.[19] The charge distribution with and without d orbitals in Figure 3 is similar to these previous calculations.

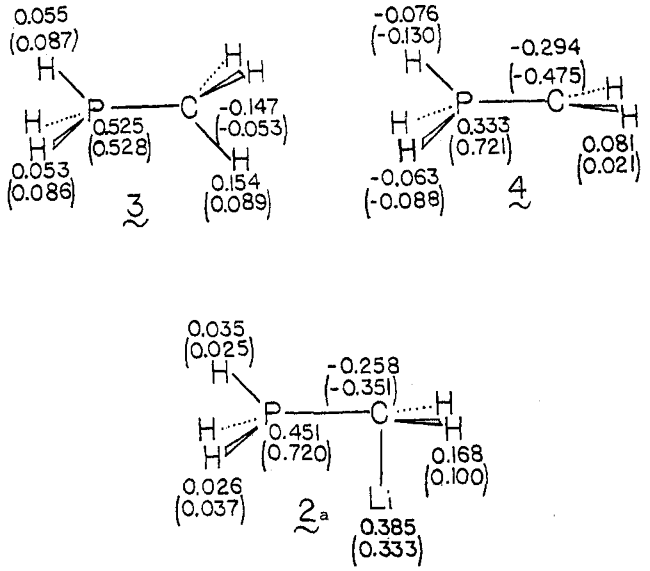
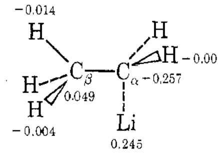


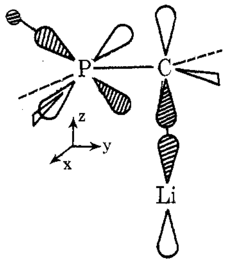
Figure 3. Electron distribution in the lithium adduct of methylenephosphorane and related molecules. The charges refer to those obtained with the spd basis set; those in parenthesis are from the sp basis set.

There are several details that merit attention in comparing the charges for the molecules in Figure 3. The carbon in **2a** loses only a small amount of charge compared to the ylide **4**. This is in accord with the similarity of the ^{13}C chemical shifts of the methylene carbons of methylenetrimethylphosphorane and the lithium adduct of methylenetriphenylphosphorane in Table I. The lithium atom also retains a good share of its positive charge. The major difference between the two basis sets is reflected on the charge on phosphorus for **2a**. The charge on phosphorus in the spd basis set approaches that of the phosphonium cation, **3**, which is consistent with the ^{31}P chemical shifts in Table I. The charge on phosphorus for **2a** (and **4**) is much too large in the sp basis set. The fact that phosphorus loses electron density in **2a** relative to **4** is a consequence of the lithium cation polarizing the molecule in a manner that alternates positive and negative charges relative to the site of substitution of the lithium.[20] This charge polarization effect is also apparent for the electron distribution in ethyllithium (using CNDO/2). The charge on the β carbon in the INDO approximation increases to 0.131 electrons while that for the lithium decreases to 0.207 (it might, therefore, be expected that the β carbon should be deshielded with respect to that of ethane in the ^{13}C NMR). For this calculation standard bond lengths and angles[21] were used with a C–Li bond distance of 2.05 Å.[22] The conformation of ethyllithium with a C–C–Li bond angle of 90° and C_α–C_β–H (H–C_α–H) bond angles of 109.47° (**5**) was 18.7 kcal/mol (17.8 kcal/mol with INDO) more stable than that with a C–C–Li bond angle of 109.47°. The conformation with a H–C–H and C–C–Li bond angles of 120 and 90°, respectively (analogous to **2a**) was less stable than that in **5** by 25.7 and 30.6 kcal/mol by CNDO/2 and INDO calculations, respectively.



5

The highest occupied molecular orbital in **2a** (5a′) is comprised of a p_Z orbital on carbon overlapping with a sp orbital on lithium and the d_{YZ} orbital on phosphorus. This is the only molecular orbital that contains significant involvement of the orbitals of lithium. There are also several low-lying unoccupied molecular orbitals consisting chiefly of d orbitals on phosphorus and p orbitals on lithium. The difference in the bond order between carbon and lithium, in **2a**, is 0.850 and 0.570 electrons (for the spd and sp basis sets, respectively) *less* than that in ethyllithium (using the CNDO/2 wave function). Therefore, the bonding between carbon and lithium in **2a** seems to lie between that of an ionic complex and a σ bond.



As a further check on the conformation of the lithium adduct of methylenephosphorane, the nuclear spin coupling of phosphorus to carbon was calculated by the finite perturbation method[23] using CNDO/2 wave functions.[24] This method has been shown to give reliable one-bonded P–C couplings for a variety of tetravalent phosphorus compounds.[14,26] The calculated P–C couplings in Table II are quite close to those given in Table I with the exception of the completely optimized structure of the lithium adduct of methylenephosphorane. A much better fit to the experimental values is found for **2a** where the P–C–Li bond angle is 90° and the methylene group lies in the *xy* plane (again, note that this conformation is only 3.5 kcal/mol less stable than the completely optimized one).[38] Any tipping of the methylene group out of this plane reduces the P–C coupling for both the lithium complex and methylenephosphorane[14] (the calculated P–C coupling for the structure analogous to **1** was −7.7 Hz). Note also that while all of the C–H couplings for **2a**, **3**, and **4** are smaller than those in Table I (this is normal with CNDO/2[29]), their relative magnitudes are correctly predicted. These calculations include only the Fermi contact contribution to the nuclear spin couplings. The spin dipolar and orbital contributions are felt by the present authors to contribute to a neglible extent for $^1J_{P-C}$ in tetravalent phosphorus compounds. This rests, in part, on the fact that the calculated P–C couplings are accurate in comparison to the experimental values for many tetravalent phosphorus compounds.[14,26] Also, $^1J_{P-C}$ follows trends similar to those found for $^1J_{C-C}$;[14] spin orbital and dipolar contributions have been shown by theoretical calculations to be insensitive to variations of $^1J_{C-C}$.[29b]

Table II. Calculated P–C, C–H, C–C Couplings, and Valence Shell s Orbital Bond Orders[a]

Compd	$^1J_{P-C}$, Hz	$P^2{}_{S_PS_C}$	$^1J_{C-H}$, Hz
$H_3P{=}CH_2$	114.7	0.2942	121.4
$H_3P^+{-}CH_3$	45.6	0.2266	88.5
$H_3P^+{-}CH_2Li$ totally optimized	6.4	0.2178	85.6
2	38.5	0.2351	84.9
	$^1J_{C-C}$	$P^2{}_{S_CS_C}$	$^1J_{C-H}$
CH_3CH_2Li, C–C–Li = 90°			
5 (HCH = 109°, C–C–H = 109°)	6.5	0.1953	74.0[b]
HCH = 120°, C–C–H = 120°	40.3	0.2396	140.6[b]
CH_3CH_3[c]	41.5	0.2490	122.1

[a] The calculations for the phosphorus compounds are of the CNDO type and those of ethyllithium and ethane are from the INDO approximation. All couplings were calculated to be positive. [b] The C–H couplings are for the methylene group of ethyllithium. [c] Values taken from G. E. Maciel, J. W. McIver, Jr., N. S. Ostund, and J. A. Pople, *J. Am. Chem. Soc.*, **92,** 1, 11 (1970).

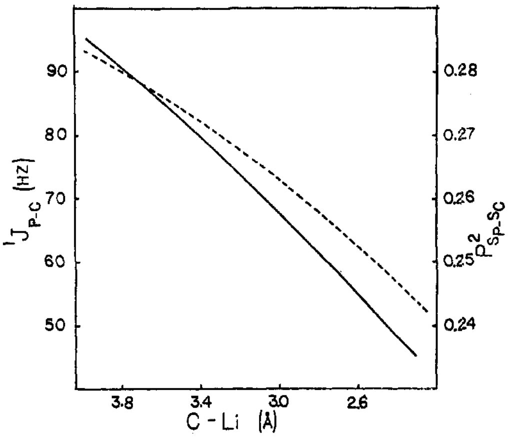
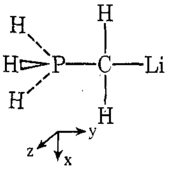


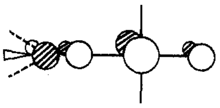
Figure 4. Calculated P–C couplings (solid line) and phosphorus 3s–carbon 2s bond orders (dashed line) as a function of the C–Li bond distance.

A decrease in C–C coupling when the methylene group is tipped out of the *xy* plane is also evident for ethyllithium. Thus, the C–C coupling drops from 40.3 to 6.5 Hz when the methylene group is tipped 60° from the *xy* plane by the INDO method. The CNDO values (not listed in Table II) also reproduce this trend; however, the calculated C–C and C–H couplings are smaller by factors of approximately 1.5 and 0.6, respectively. Note that the calculated C–H coupling for ethyllithium (in **5**) is somewhat smaller than that reported for methyllithium (98 Hz).[27] The directly bonded C–Li coupling of ethyllithium (in **5**) calculated by INDO was +20.7 Hz (+11.7 Hz with CNDO/2) and is in moderately good agreement to that found for methyllithium (15 Hz)[27] and *n*-butyllithium (14 Hz).[28] The calculated C–Li coupling is too large for ethyllithium with all tetrahedral angles (25.4 Hz) and too small for the conformation with the methylene group in the *xy* plane (7.4 Hz). Since the INDO method has been found to be remarkably accurate in calculations of C–C (and C–H) couplings for a large variety of systems[29] and the CNDO/2 results for ethyllithium parallel these, the assignment of conformation **2a** for the lithium adduct of methylenephosphorane is strengthened (i.e., the decrease in $^1J_{C-C}$ with tipping of the methylene group does not appear to be sensitive to the basis set used).

It is well known that alkyllithium compounds, methyllithium in particular, exist as dimers or tetramers in solution.[22] This is probably not the case for the lithium adduct of methylenetriphenylphosphorane for two reasons. First, the bulky triphenyl groups would be expected to oppose this tendency for steric reasons. Secondly, the P–C–H bond angle would have to approach 109° if dimerization occurred which according to our finite perturbation results would produce a very small P–C coupling, similar to that calculated for the totally optimized structure in Table II which is not observed experimentally. However, the lone pairs of a solvent such as ether ought to be coordinated with the lithium. Increasing the amount of ether might be expected to increase the coordination of the lithium to ether at the expense of weakening the carbon–lithium bond. Therefore, the 12.8-Hz increase in the P–C coupling of the lithium adduct of methylenetriphenylphosphorane with increasing concentration of ether reported in Table I may be explained in this manner.[30] Other ylides that can be prepared and recrystallized in the absence of lithium salts such as acetonylidenetriphenylphosphorane show no change in P–C couplings when the solvent and concentration was widely varied.[31] A similar solvent dependence of C–H coupling in benzyllithium has also been observed and discussed in terms of solvent coordination to the lithium.[32] To test the hypothesis that weakening the C–Li bond would increase the P–C coupling, a series of finite perturbation calculations were carried out on **2a**. The C–Li bond distance was decreased from 4.00 Å in steps of 0.25 Å with the P–C bond distance fixed at 1.68 Å (variations of the P–C bond distance in methylenephosphorane, for example, do not change the P–C coupling significantly[14]). The results of these calculations, as shown in Figure 4, agree nicely with this hypothesis. Furthermore, the s character in the C–H, C–C, and P–C bonds has been related to the C–H, C–C,[29] and P–C[26] couplings. It is evident from Figure 4 that the phosphorus 3s–carbon 2s bond order varies in an almost parallel manner to the calculated couplings. Therefore, this increase in the P–C coupling with respect to increasing C–Li bond distance is *not* a peculiarity of the finite perturbation method itself.

Finally, prompted by a report that ab initio calculations indicate that replacement of hydrogen for lithium atoms about methane remarkably stabilizes the square-planar conformation at carbon, relative to the tetrahedral one,[33] CNDO/2 calculations were carried out on the lithium adduct of methylenephosphorane to see if the molecule with a square-planar carbon might be stable. It was thought that the d_{YZ} orbital might appreciably interact with the highest occupied molecular orbital on a square planar carbon system thus stabilizing it (especially with the overemphasis of d orbitals in the CNDO/2 approximation), in a manner originally suggested by Hoffmann.[34] However, this conformation was found to be less stable by 65.7 and 69.3 kcal/mol relative to 2 with the spd and sp basis sets, respectively. Furthermore, this conformation was a saddle point on the energy surface, collapsing with no energy of activation to the optimized structure. Therefore, d orbitals on phosphorus provides only a 3.6 kcal/mol stabilization for the square planar carbon using the CNDO/2 approximation.





Conclusions

It is clear from the NMR evidence and theoretical calculations that the reaction of alkyllithium compounds with methyl-substituted phosphonium salts does not produce methylenephosphoranes, but rather, lithium salt adducts which possibly have the conformation 2. Other nonstabilized ylides such as ethylidene- or ispropylidenetriphenylphosphorane apparently do not form stable lithium adducts judging from the ^{13}C NMR and $^{31}P-^{13}C$ coupling evidence[8,14] if the solutions are stirred *for at least 2 h* after the alkyllithium reagent is added and before the final filtration. Certainly the rate data collected for the reactions of methylenephosphoranes are likely to be erroneous.[35] The fact that betaine intermediates are isolated from nonstabilized ylides but not from stabilized ylides has led to some conclusions regarding the relationships of the rates of the various steps in the Wittig reaction.[3,36] These conclusions are likely to be suspect since a lithium cation can stabilize the betaine by coordination with the oxyanion, if other alkylidenephosphoranes do indeed *initially* form lithium salt adducts. Likewise, the differences in the stereochemistry of the Wittig reaction using stabilized and nonstabilized ylides[3,37] may have to be reexamined.

Experimental Section

The solutions of the lithium iodide adduct of methylenetriphenylphosphorane were prepared in a drybox by dropwise addition of an equimolar amount (2.7 ml) of *n*-butyllithium in hexane (Alfa Chemicals) to a suspension of 2.0 g of recrystallized methyltriphenylphosphonium iodide (Aldrich) in 20 ml of diethyl ether (dried and distilled over NaH). The resulting red solution was stirred for approximately 2 h and concentrated in vacuo. The red solid was dissolved with the solvent listed in Table I to a concentration of 0.5 M and filtered several times through a pipette packed with glass wool. A plug was inserted into the NMR tube and the top filled with wax. No decomposition of the lithium adduct of the ylide was observed by ^{13}C NMR after several days; likewise no precipitate formed in the tube after this period of time. The ^{13}C and ^{31}P NMR were obtained on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. The ^{13}C and ^{31}P NMR data were taken at operating frequencies of 22.63 and 36.43 MHz, respectively. All calculations were carried out with a Burroughs B6700 computer.

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Registry No.—$Ph_3{}^+PMe\ I^-$, 2065-66-9; $Ph_3P^+CH_2Li\ I^-$, 57454-94-1; butyllithium, 109-72-8.

References and Notes

(1) (a) H. Schmidbaur, *Acc. Chem. Res.*, **8**, 62 (1975); (b) H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 3556 (1968).

(2) H. J. Bestmann, *Angew. Chem., Int. Ed. Engl.*, **4**, 583 (1965).

(3) For reviews see A. W. Johnson, "Ylid Chemistry", Academic Press, New York, N.Y., 1966, pp 152–187, and H. J. Bestmann and R. Zimmermann in "Organic Phosphorus Compounds", Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, pp 32–35.

(4) (a) T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, **97**, 940 (1975); (b) H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 595 (1967).

(5) There will obviously be differences due to substitution of the methyl for phenyl groups on phosphorus; however, these are considered to be generally quite small, e.g., compare $^1J_{P-C}$ for methyltriphenylphosphonium and tetramethylphosphonium iodide in Table I. Furthermore, calculations of $^1J_{P-C}$ for many hydrogen-substituted compounds agree very closely to experimental values for their methyl- and phenyl-substituted ones.[14]

(6) S. O. Grim, W. M. Farlane, and T. J. Marks, *Chem. Commun.*, 1191 (1967).

(7) H. Schmidbaur and M. Heiman, *Z. Naturforsch. B*, **29**, 485 (1974).

(8) T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, **97**, 2942, 2946 (1975).

(9) For example, the charges on phosphorus for phosphines as determined by semiempirical SCF molecular orbital calculations correlate well with ^{31}P chemical shifts; see R. Friedemann, W. Grundler, and K. Issleib, *Tetrahedron*, **26**, 2861 (1970); see, however, J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 819 (1966), **45**, 2916, 2926 (1966), for a differing interpretation.

(10) L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *J. Am. Chem. Soc.*, **91**, 1057 (1969).

(11) Quantum Chemistry Program Exchange, Program 141, Indiana University.

(12) F. Bernardi and G. F. Pedulli, *J. Chem. Soc., Perkin Trans. 2*, 194 (1975); note, however, that this minimum on the energy surface is 19 kcal/mol less stable than the other minimum found with a C–O–Li bond angle of 180°.

(13) The P–C, P–H, and C–H bond distances were 1.78, 1.42, and 1.09 Å, respectively, for **3**. The HPH and HCH bond angles were 105 and 109°, respectively. The P–H and C–H bond distances were identical for **4**. The P–C bond distance was 1.68 Å and HCH bond angle was 118° for **4**. The full details of the electronic structure and conformation of **3**, **4**, and several other ylides will be reported elsewhere.[14]

(14) (a) T. A. Albright, manuscripts submitted for publication. (b) The calculated values of $^1J_{P-C}$ for 37 tetravalent phosphorus compounds, including phosphonium cations, alkylidenephosphoranes, phosphine oxides, and sulfides, agree, generally to ±10% of their experimental values. The correlation coefficient between the calculated couplings and $P_{S_PS_C}{}^2$ was 0.974. *A recent experimental study of* $^1J_{P-C}$ *in a wide variety* of tetravalent phosphorus compounds has also shown the Fermi contact contribution to $^1J_{P-C}$ to be dominant which is consistent with the conclusions of ref 14a; see R. M. Lequian, M. J. Pouet, and M. P. Simonnin, *Org. Magn. Reson.*, **7**, 392 (1975).

(15) M. S. Gordon and L. Neubauer, *J. Am. Chem. Soc.*, **96**, 5690 (1974).

(16) J. F. Labarre and C. Leibovici, *J. Mol. Struct.*, **25**, 445 (1975).
(17) F. J. Marsch, B. G. Thomas, and M. S. Gordon, *J. Mol. Struct.*, **25**, 101 (1975).
(18) See, for example, W. Ensslin, H. Bock, and G. Becker, *J. Am. Chem. Soc.*, **96**, 2757 (1974), and S. Rothenberg, R. H. Young, and H. F. Schaefer, III, *ibid.*, **92**, 3243 (1970).
(19) R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Am. Chem. Soc.*, **92**, 3929 (1970); I. Absar and J. R. Van Wazer, *ibid.*, **94**, 2382 (1973); K. A. O. Starzewski, H. T. Dieck, and H. Bock, *J. Organomet. Chem.*, **65**, 311 (1974).
(20) Similar effects have been noted for other highly positive or negatively charged groups; see, for example, M. D. Gordon and J. F. Neumer, *J. Phys. Chem.*, **78**, 1868 (1974), and J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970, pp 119–126.
(21) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(22) N. C. Baird, R. F. Barr, and R. L. Datta, *J. Organomet. Chem.*, **59**, 65 (1973).
(23) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960, 2965 (1968).
(24) Quantum Chemistry Program Exchange, Program 224, Indiana University. This program was modified for second row atoms with and without d orbitals. The value chosen for the density of the 3s orbital at the phosphorus nucleus was 5.6251.[25]
(25) J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).
(26) G. A. Gray, *J. Am. Chem. Soc.*, **93**, 2132 (1971), and C. Giessner-Prettre and B. Pullman, *J. Theor. Biol.*, **48**, 425 (1974).
(27) L. D. McKeever, R. Waack, M. A. Doren, and E. B. Baker, *J. Am. Chem. Soc.*, **91**, 1057 (1969).
(28) L. D. McKeever and R. Waack, *Chem. Commun.*, 750 (1969).
(29) (a) See, for example, K. D. Summerhays and G. E. Maciel, *J. Am. Chem. Soc.*, **94**, 8348 (1972); G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *ibid.*, **92**, 1, 11 (1970); V. J. Bartuska and G. E. Maciel, *J. Magn. Reson.*, **5**, 211 (1971); **7**, 36 (1972). (b) A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971).
(30) An attempt was made to prepare methylenetriphenylphosphorane (or its lithium iodide adduct) in 100% benzene. Approximately 2 h after the introduction of *n*-butyllithium a large quantity of a yellow solid precipitated out which might possibly be the lithium iodide adduct (see ref 1).
(31) T. A. Albright, unpublished.
(32) R. Waack, L. D. McKeever, and M. A. Doren, *Chem. Commun.*, 117 (1969).
(33) P. v. R. Schleyer, symposium at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 7, 1975.
(34) R. Hoffmann, *Pure Appl. Chem.*, **28**, 181 (1971).
(35) For example, G. Wittig, H. D. Weigmann, and M. Schlosser, *Chem. Ber.*, **94**, 676 (1961); G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, **562**, 177 (1949); S. Tripett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961); A. Piskala, M. Zimmermann, G. Fouquet, and M. Schlosser, *Collect. Czech. Chem. Commun.*, **36**, 1489 (1971); D. Seyferth and G. Singh, *J. Am. Chem. Soc.*, **87**, 4156 (1965); and see M. Schlosser and K. F. Christmann, *Angew. Chem.*, **76**, 683 (1964), for related observations.
(36) There has been one report in the literature that nonstabilized ylides to not form betaines; see E. Vedejs and K. Snoble, *J. Am. Chem. Soc.*, **95**, 5778 (1973).
(37) W. P. Schneider, *Chem. Commun.*, 785 (1969), and references cited therein.
(38) A recent ^{1}H NMR study of the conformation of α-lithio sulfoxides also suggests the "carbanion" to be planar with coordination of lithium and not tetrahedral; see R. Lett and A. Marquett, *Tetrahedron Lett.*, 1579 (1975).

Metalation of Phosphine Imides with Organolithium Compounds

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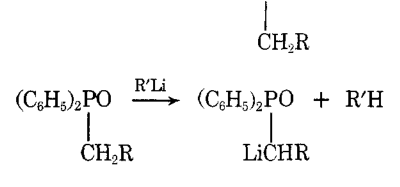
Phenyllithium metalates triphenylphosphine *N*-phenylimide (**1a**) in the ortho position of a *P*-phenyl group and diphenylalkylphosphine *N*-phenylimides on the α carbon of the alkyl group. Alkyllithium reagents react with triphenylphosphine *N*-phenylimide to give the ortho-metalated imide in addition to a competitive reaction which involves an initial displacement of phenyl by alkyl followed by α-metalations on the alkyl carbon (**9a** and **9b**). Displacement of a phenyl group is more pronounced with methyllithium than with *n*-butyllithium. Halogen-metal exchange is not observed in the reaction of *n*-butyllithium with triphenylphosphine *N*-(4-bromophenyl)imide.

Metalation of triphenylphosphine by *n*-butyllithium gives, subsequent to carbonation, an 8% yield of 3-carboxyphenyldiphenylphosphine.[1] Phenylsodium and triphenylphosphine yield 10% 5-phenyldibenzophosphole, presumably through the intermediacy of an ortho-metalated compound.[2] Alkylithium compounds metalate benzyldiphenylphosphine[3] and alkyldiphenylphosphines[4] on the α-alkyl carbon, methyl hydrogen being more easily displaced than methylene hydrogen. Alkylphosphine oxides metalate easily on an α carbon.[5a,b] Gilman and Brown reported that triphenylphosphine oxide is not metalated by phenyllithium or phenylmagnesium bromide.[1] Seyferth et al.[6a,b] have shown that alkyl Grignard or alkyllithium reagents displace a phenyl group from triphenylphosphine oxide, ultimately yielding an α-metalated diphenylalkylphosphine oxide. They present evidence that the overall reaction takes place in two steps:



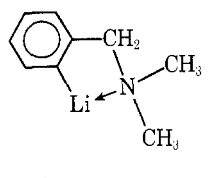
$$(C_6H_5)_3PO \xrightarrow{RCH_2Li} \underset{CH_2R}{(C_6H_5)_2PO} + C_6H_5Li$$

$$\underset{CH_2R}{(C_6H_5)_2PO} \xrightarrow{R'Li} \underset{LiCHR}{(C_6H_5)_2PO} + R'H$$

$R' = C_6H_5$ or RCH_2

Similar results were observed with triphenylphosphine sulfide.[7]

Intramolecularly directed metalation through coordination with nitrogen has been demonstrated in *N,N*-dimethylbenzylamine,[8] dimethylaminomethyl- and dimethylaminoethylferrocene,[9a,b] dimethylaminomethylpyridines,[10] and arylcarboxamides.[11,12] Further, many examples of the ortho-metalation reaction with transition metal complexes having nitrogen and phosphorous donor ligands exist.[13]



Since arylphosphine *N*-arylimides (**1**) are amenable to intramolecularly directed metalation through coordination on nitrogen and, more importantly, exhibit strong electronic effects in the rings attached to both nitrogen and phosphorous, they are interesting substrates for the study of electrophilic and nucleophilic metalations. The present paper describes our initial work pertaining to the reaction of organolithium compounds with phosphine N-arylimides.

Triphenylphosphine *N*-phenylimide (**1a**) is metalated by phenyllithium to give, after carbonation, a 62% yield of 2-diphenylphosphinylbenzoic acid (**2**).