Studies in Phosphinemethylene Chemistry. XII. Triphenylphosphine-*t*-butylmethylene and Triphenylphosphinetrimethylsilylmethylene[1]

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α-Proton transfer from $[(C_6H_5)_3PCH_2M(CH_3)_3]I$ *(M = Si and C) to triphenylphosphinemethylene was found to proceed essentially quantitatively in ether medium. Steric factors are believed responsible for this facile transylidation reaction. Reactions of triphenylphosphinetrimethylsilylmethylene and triphenylphosphine-t-butylmethylene thus formed with water, hydrogen bromide gas, and methyl iodide are described. Triphenylphosphine-t-butylmethylene reacted with benzaldehyde to give a mixture of cis- and trans-β-t-butylstyrene in 84% yield. Spin–spin coupling between* ^{31}P *and the γ-protons in the neopentylphosphonium salt and in neopentyldiphenylphosphine oxide was observed.*

In the initial paper of this series[3] we reported on the nucleophilic displacement of halide ion from various group IV-B organometallic halides and from mercuric bromide by triphenylphosphinemethylene. The reaction, for instance, in the case of trimethylbromosilane, was formulated as

$$(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}H_2 + (CH_3)_3SiBr \longrightarrow [(C_6H_5)_3\overset{+}{P}CH_2Si(CH_3)_3]\overset{-}{Br} \quad (1)$$

Characteristic of most of these reactions was the difficulty with which pure products were obtained, and the presence of methyltriphenylphosphonium halide as a contaminant in the crude products was noted.

In the intervening years Bestmann[4] discovered that "transylidation" (proton transfer from a phosphonium salt to a phosphinealkylidene reagent) occurs readily and that formation of the more highly stabilized phosphinealkylidene is favored.

$$(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}H_2 + [(C_6H_5)_3\overset{+}{P}CH_2R]\overset{-}{X} \longrightarrow (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HR + [(C_6H_5)_3\overset{+}{P}CH_3]\overset{-}{X} \quad (2)$$

R = stabilizing substituent, such as acyl or phenyl

In these laboratories it was demonstrated that such transylidations were equilibrium reactions, and that in the system involving triphenylphosphinemethylene and triphenylphosphinethylidene and their respective phosphonium salts, the $(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}H_2/(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HCH_3$ ratio was about 17.[5] A consideration of the facility with which such transylidations proceed prompted us to re-examine the triphenylphosphinemethylene–trimethylhalosilane reaction as a representative case of those reactions studied in part I.[3] It seemed possible that the complications encountered in the isolation of pure $[(C_6H_5)_3P^+CH_2Si(CH_3)_3]Br^-$ may have been due to intervening transylidation equilibria; that is, reaction 1 may have been followed by reaction 3.

$$[(C_6H_5)_3\overset{+}{P}CH_2Si(CH_3)_3]Br^- + (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}H_2 \longrightarrow [(C_6H_5)_3\overset{+}{P}CH_3]\overset{-}{Br} + (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HSi(CH_3)_3 \quad (3)$$

Thus on work-up with aqueous HBr a mixture of the methyl- and trimethylsilylmethylphosphonium salts would result.

A transylidation such as reaction 3 was considered a distinct possibility. Although one would expect the $+I$ inductive effect of the trimethylsilyl group to destabilize $(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}HSi(CH_3)_3$ relative to $(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}H_2$, a stabilization of the former by delocalization of negative charge into the silyl substituent by p_π–d_π overlap also seemed a possibility. Accordingly, the action of triphenylphosphinemethylene on (trimethylsilylmethyl)triphenylphosphonium iodide was studied.

It was found that *quantitative* transylidation occurred when triphenylphosphinemethylene and (trimethylsilylmethyl)triphenylphosphonium iodide (1:1 ratio) were stirred in ether at room temperature for 15 hr. Filtration of the reaction mixture gave methyltriphenylphosphonium iodide in nearly quantitative yields. The formation of triphenylphosphinetrimethylsilylmethylene and its presence in the yellow filtrate were demonstrated by the conversions 4, 5, and 6. Thus our original preparative procedure[3] was indeed complicated by competition of as yet unreacted trimethylbromosilane and already formed (trimethylsilylmethyl)triphenylphosphonium bromide for the phosphinemethylene reagent as it was being added. Our original procedure has been modified so as to be preparatively useful by using triphenylphosphinemethylene and the halosilane in 2:1 molar ratio. The silicon-substituted phosphinemethylene then can be treated with hydrohalic acid, preferably with HI for ease of phosphonium salt isolation, in order to obtain the desired silyl-substituted phosphonium cation.

It was of interest to inquire why the transylidation studied (reaction 3, but with halide ion = I^-) proceeded essentially quantitatively as written, *i.e.*, what factors contributed to the preferential formation of the silyl-substituted phosphinemethylene. An explanation involving $C_{p\pi}$–$Si_{d\pi}$ bonding seemed attractive as well as fashionable in terms of current ideas about bonding in

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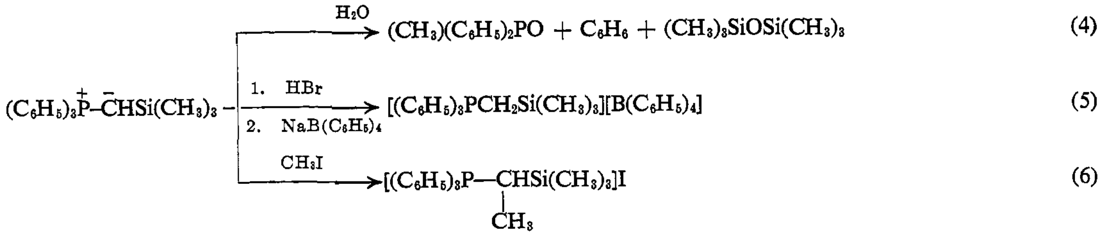
[1] Part XI: D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Am. Chem. Soc.*, 87, 3467 (1965).

[2] (a) Alfred P. Sloan Foundation Fellow 1962–1966; (b) Postdoctoral Research Associate, 1964–1965.

[3] D. Seyferth and S. O. Grim, *J. Am. Chem. Soc.*, **83**, 1610 (1961).

[4] H. J. Bestmann, *Chem. Ber.*, **95**, 58 (1962).

[5] D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Am. Chem. Soc.*, 87, 2847 (1965).



$$(C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}HSi(CH_3)_3 \begin{cases} \xrightarrow{H_2O} (CH_3)(C_6H_5)_2PO + C_6H_6 + (CH_3)_3SiOSi(CH_3)_3 & (4)\\ \xrightarrow[2.\ NaB(C_6H_5)_4]{1.\ HBr} [(C_6H_5)_3PCH_2Si(CH_3)_3][B(C_6H_5)_4] & (5)\\ \xrightarrow{CH_3I} [(C_6H_5)_3P\text{—}\underset{\substack{|\\ CH_3}}{C}HSi(CH_3)_3]I & (6)\end{cases}$$

$$2(C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}H_2 + (CH_3)_3SiCl \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}HSi(CH_3)_3 + [(C_6H_5)_3PCH_3]Cl \quad (7)$$

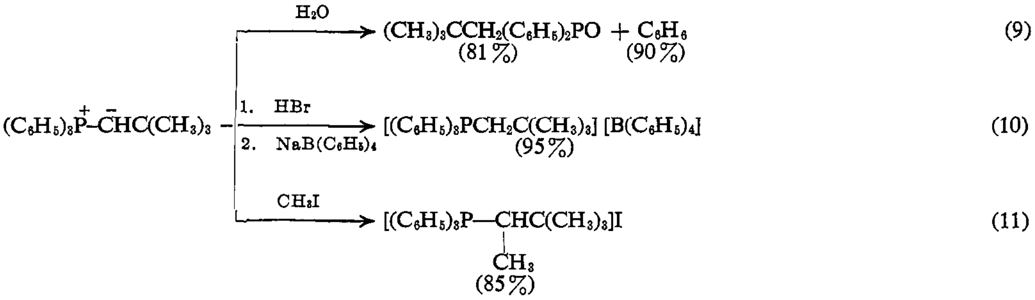
organosilicon compounds. Indeed, Miller[6] reported the isolation of trimethylphosphinetrimethylsilylmethylene as a colorless liquid and wrote resonance structures Ia, Ib, and Ic (R = CH_3) to describe this molecule.

$$\underset{\text{Ia}}{R_3\overset{+}{P}\text{-}\overset{-}{C}H\text{—}Si(CH_3)_3} \longleftrightarrow \underset{\text{Ib}}{R_3\overset{+}{P}\text{—}CH{=}\overset{-}{Si}(CH_3)_3} \longleftrightarrow \underset{\text{Ic}}{R_3P{=}CH\text{—}Si(CH_3)_3}$$

It is, however, dangerous to interpret the results of reactions of organosilicon species in terms of π-bonding effects if the possibility of steric effects being operative has not been eliminated. In the present case we are dealing with a "siliconeopentyl"-phosphonium salt in which the quaternary silicon and phosphorus atoms are separated by only a methylene group, and in such a structure one may find unusual reactivity caused not by electronic factors, but rather by steric factors. To obtain further information relating to this question, we prepared neopentyltriphenylphosphonium iodide, $[(C_6H_5)_3P^+CH_2C(CH_3)_3]I^-$ (in whose derived phosphinealkylidene analogous π-bonding effects (*i.e.*, Ib, Si replaced by C) would not be operative) and examined its reaction with triphenylphosphinemethylene.

As in the case of the silicon analog, transylidation between triphenylphosphinemethylene and neopentyltriphenylphosphonium iodide proceeded quantitatively as shown in eq. 8. After the methyltriphenylphosphonium iodide (yield about 90–95%) had been filtered, the deep orange filtrate was quenched in three separate experiments with water, anhydrous hydrogen bromide, and methyl iodide in order to establish the identity of the species present in solution. The results are given in eq. 9, 10, and 11.

$$[(C_6H_5)_3\overset{+}{P}CH_2C(CH_3)_3]I^- + (C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}H_2 \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}HC(CH_3)_3 + [(C_6H_5)_3\overset{+}{P}CH_3]I^- \quad (8)$$



$$(C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}HC(CH_3)_3 \begin{cases} \xrightarrow{H_2O} \underset{(81\%)}{(CH_3)_3CCH_2(C_6H_5)_2PO} + \underset{(90\%)}{C_6H_6} & (9)\\ \xrightarrow[2.\ NaB(C_6H_5)_4]{1.\ HBr} \underset{(95\%)}{[(C_6H_5)_3PCH_2C(CH_3)_3][B(C_6H_5)_4]} & (10)\\ \xrightarrow{CH_3I} [(C_6H_5)_3P\text{—}\underset{\substack{|\\ CH_3\\ (85\%)}}{C}HC(CH_3)_3]I & (11)\end{cases}$$

On the basis of inductive effects alone, one would not expect triphenylphosphine-*t*-butylmethylene to be favored in an equilibrium as described by eq. 8. As mentioned above, in transylidations triphenylphosphinemethylene is favored over triphenylphosphineethylidene, and further experiments showed that triphenylphosphinemethylene is favored over triphenylphosphineisopropylidene and triphenylphosphineisobutylidene, $(C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}(CH_3)_2$ and $(C_6H_5)_3\overset{+}{P}\text{-}\overset{-}{C}HCH(CH_3)_2$, respectively. However, the adjacent quaternary phosphorus and carbon centers in neopentyltriphenylphosphonium iodide should cause severe steric crowding of the methylene protons. It is possible that such crowding could elongate the methylene C–H bonds. The result would be a weaker methylene C–H bond and an increased acidity of the methylene protons over those in methyltriphenylphosphonium iodide.[7] Furthermore, loss of a methylene proton in conversion to triphenylphosphine-*t*-butylmethylene should help to relieve this crowding. The structure of a phosphinealkylidene in which the negative charge on the methylene carbon can only be displaced into phosphorus d-orbitals by a π-bonding mechanism has yet to be determined, and so no information is available concerning the geometry of substituents on the methylene carbon (a planar or nonplanar $\geqslant P{=}CHR$ system?). Any deviation of the methylene carbon hybridization from sp^3 (as it must be in the phosphonium salt) toward ($sp^2 + p$) as a result of $C_{p\pi}$–$P_{d\pi}$ overlap would also contribute to relief of steric crowding at the methylene carbon. We conclude that in reaction 8 we are dealing with a case of "steric assistance."[10]

With the larger silicon atom (covalent radius 1.17 Å. *vs.* 0.77 Å. for carbon) in the (trimethylsilylmethyl)-triphenylphosphonium salt such "steric assistance" in reaction 3 should not be as great as in the case of the neopentyl compound, but the steric factor still should result in a noticeable effect. It is not possible to assess the individual contributions of such a steric effect and C–Si π-bonding of the type mentioned to the observed transylidation reaction. We feel, however,

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(6) N. E. Miller, *J. Am. Chem. Soc.*, **87**, 390 (1965).

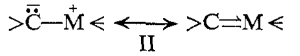
(7) An explanation in terms of an elongation of the N–H bond in phosphoramides of the type RR'P(=O)NHR'' as the bulk of R'', due to increasing branching, increased was given to account for the decrease of ν_{N-H} from 3441 cm.$^{-1}$ for R'' = CH_3 to 3418 cm.$^{-1}$ for R'' = isopropyl to 3400 cm.$^{-1}$ for R'' = *t*-butyl.[8] For a related example see ref. 9.

(8) R. A. Nyquist, *Spectrochim. Acta*, **19**, 713 (1963).

(9) G. Singh and H. Zimmer, *J. Org. Chem.*, **30**, 313 (1965).

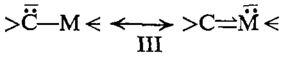
(10) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

that the π-bonding contribution is much less important than the steric factor. Of the two possibilities for delocalizing the negative charge on the methylene carbon atom, Ib and Ic (R = phenyl), the latter should be more important by far, since by C → P π-bonding one is neutralizing the positive charge on phosphorus, while by C → Si π-bonding one is placing excess negative charge on silicon. The greater importance of π-bonding in a system such as II as compared to π-bonding in a system such as III is well documented.



$$>\overset{-}{\ddot{C}}-\overset{+}{M}< \longleftrightarrow >C\overset{\rightharpoonup}{=}M<$$

II

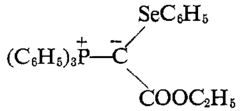


$$>\overset{-}{\ddot{C}}-M< \longleftrightarrow >C\overset{\rightharpoonup}{=}\overset{-}{\ddot{M}}<$$

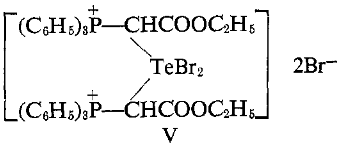
III

As one example may be cited the extremely facile Michael-type additions of nucleophilic reagents to vinylsulfonium[11] and vinylphosphonium[12,13] salts as compared with the much more sluggish addition of nucleophiles to vinylsilanes.[14] In a system where an alkyl-substituted, neutral silicon atom and a positively charged phosphorus atom are adjacent to a carbon atom bearing a lone electron pair, charge delocalization should occur almost exclusively from carbon to phosphorus (form Ic).

It is not possible to determine whether transylidations of the type described above complicated matters in the reactions of triphenylphosphinemethylene with triphenylgermanium bromide, trimethyltin bromide, dimethyltin dibromide, and mercuric bromide,[3] or with diphenylbromophosphine, phenyldibromophosphine, and dimethylbromostibine,[15] without further experimental work. If our ideas about the importance of steric factors are correct, those reactions of halides of the larger metals (Sn, Hg, and Sb) with triphenylphosphinemethylene may not have been complicated by such transylidations, but the reactions of the phenylbromophosphines with triphenylphosphinemethylene very likely were followed by transylidation. The work of Petragnani and de Moura Campos[16] is pertinent. These authors found that the reaction of triphenylphosphinecarboethoxymethylene with phenylselenenyl bromide, C_6H_5SeBr, gave the selenium-substituted phosphinemethylene IV *via* transylidation, but that the reaction of this Wittig reagent with tellurium tetrabromide gave only the phosphonium salt V.

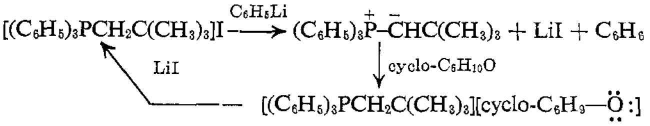


IV



V

We have investigated briefly the possibility of using triphenylphosphine-*t*-butylmethylene in the Wittig olefin synthesis. This reagent was generated by the action of phenyllithium on neopentyltriphenylphosphonium iodide and treated in the usual way with benzaldehyde. An 84% yield of β-*t*-butylstyrene (23.8% *cis* and 76.2% *trans* isomer) was obtained. The reaction of triphenylphosphine-*t*-butylmethylene with cyclohexanone, on the other hand, did not result in formation of olefin. Instead the starting phosphonium iodide was regenerated in high yield, presumably by the path outlined below.[16a]



The use of triphenylphosphinetrimethylsilylmethylene in the Wittig reaction has been investigated by Gilman and Tomasi,[17] but this is a subject which requires reinvestigation in view of their use of a 1:1 triphenylphosphinemethylene–trimethylchlorosilane stoichiometry, followed by addition of 1 equiv. of phenyllithium. Our studies on this aspect are continuing.

The n.m.r. spectra of our neopentylphosphorus derivatives also are of interest. Spin–spin coupling of phosphorus (^{31}P) with protons through four bonds has been a subject of recent interest. For example, Cotton and Schunn[18] have observed ^{31}P–^{1}H coupling of about 2 c.p.s. through four bonds (P–C–C–C–H) in the sodium and zinc salts of diethoxyphosphonylacetylmethane. Long-range P–H coupling has been found in P–N–C–C–H systems, but it was absent in compounds containing the P–N–N–C–H system.[19] Siddall and Prohaska[20] have reported P–H coupling through four bonds (P–O–C–C–H) in the case of diethyl phenylphosphate and diethyl phenylphosphite. This, however, is questionable because of the presence of a magnetically asymmetric center in these compounds which would result in a complex ABC_3 system with nonequivalent methylene protons.[21,22] Recently Hendrickson, *et al.*,[23] studied the proton resonance spectra of isobutyltriphenylphosphonium iodide

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[11] W. von E. Doering and K. C. Schreiber, *J. Am. Chem. Soc.*, **77**, 514 (1955).

[12] P. T. Keough and M. Grayson, *J. Org. Chem.*, **29**, 631 (1964).

[13] E. E. Schweizer and R. D. Bach, *ibid.*, **29**, 1746 (1964).

[14] M. Prober, Abstracts, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1956, p. 53-O; U. S. Patent 2,835,690 (1958); *Chem. Abstr.*, **52**, 18216 (1958).

[15] D. Seyferth and K. A. Brändle, *J. Am. Chem. Soc.*, **83**, 2055 (1961).

[16] N. Petragnani and M. de Moura Campos, *Chem. Ind.* (London), 1461 (1964).

[16a] Note Added in Proof. A referee has questioned why the triphenylphosphine-*t*-butylmethylene reagent should abstract a proton from cyclohexanone in view of the apparently sterically unfavorable neopentyltriphenylphosphonium salt structure. Our studies showed triphenylphosphinemethylene to be a stronger base than triphenylphosphine-*t*-butylmethylene. However, we have no data for a similar comparison between triphenylphosphine-*t*-butylmethylene and the cyclohexanone-derived anion. The ylid in its reaction with cyclohexanone is converted to the sterically less favorable neopentylphosphonium salt, but the Wittig reaction transition state (or the intermediate betaine) may be even less favorable in terms of steric crowding. With benzaldehyde, triphenylphosphine-*t*-butylmethylene has no alternative to attack at the carbonyl group; it can, however, abstract the acidic α-proton from cyclohexanone. In view of our lack of knowledge of the ultimate fate of the cyclohexanone-derived anion and the probability of its consumption in irreversible reactions with cyclohexanone, nothing can at present be said about the relative acidities of cyclohexanone and the neopentyltriphenylphosphonium cation. Further studies of the reactions of triphenylphosphine-*t*-butylmethylene with aldehydes and ketones clearly are required.

[17] H. Gilman and R. A. Tomasi, *J. Org. Chem.*, **27**, 3647 (1962).

[18] F. A. Cotton and R. A. Schunn, *J. Am. Chem. Soc.*, **85**, 2394 (1963).

[19] (a) F. Kaplan, G. Singh, and H. Zimmer, *J. Phys. Chem.*, **67**, 2509 (1963); (b) H. Zimmer and G. Singh, *J. Org. Chem.*, **29**, 1579 (1964).

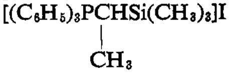
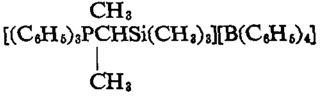
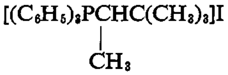
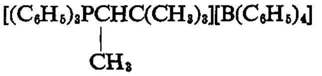
[20] T. Siddall and C. Prohaska, *J. Am. Chem. Soc.*, **84**, 3467 (1962).

[21] H. Finegold, *ibid.*, **82**, 2641 (1960).

[22] J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

[23] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

Table I. New Phosphorus Compounds Prepared in this Study

Compound	M.p., °C.	Analysis, %					
		C		H		I	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
$[(C_6H_5)_3PCH_2Si(CH_3)_3]I$	168–169	55.46	55.16	5.46	5.52	26.68	26.79
$[(C_6H_5)_3PCH_2Si(CH_3)_3][B(C_6H_5)_4]$	195–197	82.66	82.78	6.89	7.19		
$[(C_6H_5)_3PCH_2C(CH_3)_3]I$	209	60.00	60.04	5.65	5.75	27.61	27.29
$[(C_6H_5)_3PCH_2C(CH_3)_3][B(C_6H_5)_4]$	229–231	86.53	86.48	7.06	7.03		
 $[(C_6H_5)_3P\underset{\underset{\displaystyle CH_3}{\vert}}{C}HSi(CH_3)_3]I$	176–178	56.32	55.82	5.72	5.92	25.92	25.46
 $[(C_6H_5)_3P\underset{\underset{\displaystyle CH_3}{\vert}}{C}HSi(CH_3)_3][B(C_6H_5)_4]$	179–180	82.72	82.54	7.04	7.08		
 $[(C_6H_5)_3P\underset{\underset{\displaystyle CH_3}{\vert}}{C}HC(CH_3)_3]I$	215–216	60.76	60.49	5.91	6.10	26.80	26.76
 $[(C_6H_5)_3P\underset{\underset{\displaystyle CH_3}{\vert}}{C}HC(CH_3)_3][B(C_6H_5)_4]$	187–189	86.51	86.28	7.21	6.92		
$(C_6H_5)_2P(O)CH_2C(CH_3)_3$	164	75.00	74.68	7.72	7.71		

and acetomethyltriphenylphosphonium chloride, both of which have a P–C–C–C–H system. No P–H coupling through four bonds was observed, and these investigators concluded that phosphorus does not undergo spin–spin coupling with γ-protons. Our present study of the proton resonance spectra of the compounds prepared during the course of this investigation are of interest in this context. Pertinent data are presented in Table II.

In the case of neopentyltriphenylphosphonium iodide and neopentyldiphenylphosphine oxide we observed long range $^{31}P-^{1}H$ coupling through four bonds. It was comparatively easy to observe such small (0.50–0.76 c.p.s.) coupling because of the simplicity of these spectra. No coupling between phosphorus and γ-protons was observed in the case of α,β,β-trimethylpropyltriphenylphosphonium iodide or with (trimethylsilylmethyl)- or (α-trimethylsilylethyl)triphenylphosphonium iodide. This leads to a possible explanation that the expected small coupling of phosphorus to γ-protons readily vanishes if there are slight, unfavorable changes in hybridization around the phosphorus atom, which can be introduced through substitution along the P–C–C–C–H sequence. This serves to explain the lack of coupling between P and γ-H in acetomethyltriphenylphosphonium chloride, but leaves the lack of observed coupling in the isobutylphosphonium salt unexplained.

A listing of the compounds prepared is given in Table I.

Experimental

General Comments. Microanalyses were carried out by Dr. S. M. Nagy, M.I.T. Microchemical Laboratory. Infrared spectra were recorded using a Perkin-Elmer 337 grating spectrophotometer and n.m.r. spectra using a Varian Associates A-60 n.m.r. spectrometer. Solvents were distilled from calcium hydride before use. All experiments involving formation or reactions of phosphinemethylene or organolithium reagents were carried out under an atmosphere of prepurified nitrogen.

Preparation of Starting Materials. Trimethylsilylmethyl iodide was prepared by the method of Whitmore and Sommer,[24] neopentyl iodide by the procedure of Whitmore, *et al.*[25] It was found advantageous to use tetrahydrofuran as solvent in the preparation of neopentylmagnesium chloride.

Preparation of Triphenylphosphinemethylene.[26] Methyltriphenylphosphonium bromide (0.05 mole) and sodamide (2.0 g.) were stirred in about 200 ml. of anhydrous liquid ammonia. The ammonia was allowed to evaporate while the mixture was being stirred. The residual yellow solid was extracted with about 300 ml. of anhydrous ether and the solution was filtered through a glass wool plug into a storage buret under nitrogen. The triphenylphosphinemethylene solution was standardized by the method of Ross and Denney.[27]

(Trimethylsilylmethyl)triphenylphosphonium Iodide. A mixture of 0.03 mole of triphenylphosphine and 0.045 mole of iodomethyltrimethylsilane was stirred and heated gently at reflux for 2 hr. The dark brown solid obtained was dissolved in the minimum amount of chloroform and poured into 500 ml. of ethyl acetate. The product, 14 g. (98%), separated as white crystals. An analytical sample was recrystallized from ethanol–ethyl acetate. An infrared spectrum (KBr pellet) showed 3035 (w), 2948 (w), 2830 (w), 2785 (w), 1588 (w), 1487 (w), 1435 (s), 1254 (m), 1250 (m), 1155 (w), 1112 (m), 1100 (m), 993 (w), 856 (s), 828 (s), 795 (m), 769 (w), 754 (m), 713 (m), 694 (m), 687 (s), 650 (w), 642 (w), 580 (w), 519 (s), 496 (w), and 474 (w) cm.$^{-1}$.

(Trimethylsilylmethyl)triphenylphosphonium tetraphenylborate was prepared by reaction of the phosphonium iodide and sodium tetraphenylborate in methanol. It was recrystallized from methylene chloride–ethyl acetate–ether.

Neopentyltriphenylphosphonium Iodide. A mixture of 0.03 mole of triphenylphosphine and 0.045 mole of neopentyl iodide was heated at reflux, with stirring, for 24 hr. The mixture was cooled to room temperature and poured into 300 ml. of ethyl acetate. The product, 12 g. (87%), separated as white crystals. An analytical sample was recrystallized from chloroform–ethyl acetate. Its n.m.r. spectrum (Table II)

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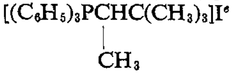
Table II. Proton Magnetic Resonance Data[a]

Compound	δ^b Hα	Hβ	Hγ	Phenyl protons	$J_{P,H}{}^c$ Hα	Hβ	Hγ
$[(C_6H_5)_3PCH_2Si(CH_3)_3]I$	3.19 (doublet, 2 H)	...	0.07 (singlet, 9 H)	7.58–8.25	18.4	...	...[d]
 $[(C_6H_5)_3P\underset{\displaystyle CH_3}{\underset{\vert}{C}}HSi(CH_3)_3]I^e$	4.33 (octet, 1 H)	1.43 (quartet, 3 H)	−0.07 (singlet, 9 H)	7.50–8.25	18.3	20.0	...[d]
$[(C_6H_5)_3PCH_2C(CH_3)_3]I$	3.81 (doublet, 2 H)	...	1.03 (doublet, 9 H)	7.58–8.25	12.8	...	~0.76
 $[(C_6H_5)_3P\underset{\displaystyle CH_3}{\underset{\vert}{C}}HC(CH_3)_3]I^e$	5.00 (octet, 1 H)	1.55 (quartet, 3 H)	0.98 (single, 9 H)	7.50–8.50	13.2	20.0	...[d]
$(C_6H_5)_2P(O)CH_2C(CH_3)_3$	2.32 (doublet, 2 H)	...	1.08 (doublet, 9 H)	7.25–8.00	10.6	...	~0.50

[a] Spectra were obtained in deuteriochloroform. [b] Chemical shifts are in p.p.m. downfield from an internal standard of TMS. [c] Coupling is in c.p.s. [d] No coupling between phosphorus and protons was observed. [e] Coupling between α and β protons was 7.0 c.p.s.

served to confirm its structure. An infrared spectrum (KBr) showed 3040 (w), 2950 (w), 2870 (w), 1592 (w), 1490 (w), 1447 (s), 1370 (w), 1330 (w), 1231 (w), 1184 (w), 1154 (w), 1140 (w), 1109 (s), 1098 (s), 1024 (w), 994 (m), 830 (w), 820 (w), 812 (m), 790 (w), 746 (s), 729 (m), 711 (w), 700 (m), 686 (s), 676 (m), 610 (w), 537 (s), 506 (s), 488 (m), and 468 (w) cm.$^{-1}$.

Reaction of Triphenylphosphinemethylene with (Trimethylsilylmethyl)triphenylphosphonium Iodide. To a mixture of 7.52 ml. of 0.266 *N* triphenylphosphinemethylene (2.5 mmoles) in ether was added 2.5 mmoles of the phosphonium iodide and another 45 ml. of ether. The mixture was stirred for 20 hr. under nitrogen and then was filtered into another flask. The residual solid was crystallized from chloroform–ethyl acetate to give methyltriphenylphosphonium iodide (yields from 90 to 100%), m.p. 185–186° (lit.[28] m.p. 184–186°), undepressed mixture melting point with an authentic sample and identical infrared and n.m.r. spectra.

The yellow filtrate was treated as follows in three separate reactions.

(*a*) *Reaction with Water.* To the filtrate was added 0.2 ml. of distilled water with stirring. The yellow color was discharged immediately. The reaction mixture was heated at reflux for 15 min. and then distilled *in vacuo* into a receiver at −78°. The residue was extracted with boiling cyclohexane to give 0.47 g. (87%) of methyldiphenylphosphine oxide, m.p. 111° (lit.[29] 109–111°), mixture melting point with an authentic sample undepressed, identical infrared spectrum as an authentic sample.

The filtrate was acidified with dilute hydrochloric acid and refluxed for several hours. G.l.c. analysis showed that benzene (88%) and hexamethyldisiloxane (92.5%) had been formed. These products were identified by means of their g.l.c. retention times and infrared spectra.

(*b*) *Reaction with Hydrogen Bromide.* Dry, gaseous HBr was passed through such a filtrate until the yellow color had been discharged. The light yellow solid (1.03 g., 97%) that precipitated was filtered. All attempts to recrystallize it from chloroform–ethyl acetate or ethanol–ethyl acetate gave only oils. The oil could, however, be converted to a tetraphenylborate in methanol solution. This product had m.p. 195–197° after recrystallization. Its mixture melting point with authentic $[(C_6H_5)_3PCH_2Si(CH_3)_3][B(C_6H_5)_4]$ was undepressed, and its infrared spectrum was identical with that of authentic material.

(*c*) *Reaction with Methyl Iodide.* To such a filtrate was added 0.02 mole of methyl iodide with stirring. A white solid precipitated immediately. The mixture was heated at reflux for 30 min. The solid product was filtered, yield 1.08 g. (88%). Three recrystallizations from chloroform–ethyl acetate gave analytically pure (α-trimethylsilylethyl)triphenylphosphonium iodide. Its proton magnetic resonance spectrum was in agreement with this structure. A tetraphenylborate derivative was prepared by the usual procedure.

Reaction of Triphenylphosphinemethylene with Trimethylchlorosilane, 2:1 Molar Ratio. In a three-necked flask fitted with condenser, magnetic stirrer, and pressure-equalizing addition funnel was placed 0.01 mole of triphenylphosphinemethylene in 100 ml. of ether. To this solution was added with stirring 0.005 mole of freshly distilled trimethylchlorosilane (Dow Corning Corp.). A white solid precipitated immediately. The mixture was heated at reflux for 2 hr. and then filtered under nitrogen into another flask. The residual solid, 1.5 g. (96%), was identified as methyltriphenylphosphonium chloride. An analytical sample was recrystallized from chloroform–ethyl acetate, m.p. 220–221°. During crystallization it took on a molecule of water, as shown by analysis and its n.m.r. spectrum. *Anal.* Calcd. for $C_{19}H_{18}ClP \cdot H_2O$: C, 69.00; H, 6.05; Cl, 10.43. Found: C, 69.48; H, 5.72; Cl, 10.20. Its n.m.r. spectrum consisted of a doublet at 3.26 p.p.m. (J = 13.4 c.p.s., 3 H), phenyl absorption from 7.50 to 8.00 p.p.m. (15 H); the protons of the water of crystallization appeared at 2.87 p.p.m. A sample also was converted by reaction with aqueous potassium iodide to the known methyltriphenylphosphonium iodide, m.p. 185–186°.

To the filtrate from the reaction mixture was added an excess of methyl iodide. The white precipitate which resulted (2.0 g., 82%) was identified as (α-trimethylsilylethyl)triphenylphosphonium iodide by mixture melting point with an authentic sample and by conversion to its tetraphenylborate (mixture melting point).

Reaction of Triphenylphosphinemethylene with Neopentyltriphenylphosphonium Iodide. To 2.5 mmoles of triphenylphosphinemethylene in 50 ml. of ether was added 2.5 mmoles of neopentyltriphenylphosphonium

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iodide, and the resulting mixture was stirred at room temperature. In about 1 hr. the original yellow color changed to deep orange. The mixture was stirred an additional 2 hr. and the orange solution then was filtered into another flask under nitrogen pressure. The residue was recrystallized from chloroform–ethyl acetate to give methyltriphenylphosphonium iodide, m.p. and m.m.p. 185–186°. Its yield in three different runs ranged from 90 to 95%.

The orange filtrate was treated as follows in three separate reactions.

(*a*) *Reaction with Water.* To the filtrate was added 0.2 ml. of water with stirring. The color was discharged immediately. The mixture was heated at reflux for 15 min. and the volatile components then were separated by a trap-to-trap distillation *in vacuo*. G.l.c. analysis of the distillate showed that benzene (identified by its retention time and infrared spectrum) had been produced in 90% yield. The residue was extracted with about 5 ml. of boiling cyclohexane and filtered. On cooling the filtrate, a white solid separated, 0.55 g. (81%) of neopentyldiphenylphosphine oxide. An analytical sample was recrystallized from cyclohexane. Its structure is supported by the n.m.r. spectrum. The infrared spectrum (KBr) showed 3090 (w), 3050 (w), 3020 (w), 2985 (w), 2960 (w), 2925 (w), 2870 (w), 1480 (w), 1475 (w), 1470 (w), 1440 (s), 1390 (w), 1370 (m), 1287 (w), 1239 (m), 1187 (s), 1177 (s), 1131 (m), 1110 (m), 1100 (m), 1070 (w), 1023 (w), 995 (w), 935 (w), 811 (m), 780 (m), 745 (m), 722 (s), 705 (s), 697 (s), 680 (w), 612 (w), 550 (s), 503 (s), 470 (w), and 430 (w) cm.$^{-1}$.

(*b*) *Reaction with Hydrogen Bromide.* Dry HBr gas was passed through such a filtrate until the orange color was completely discharged. A light yellow solid, 0.98 g. (95%), separated. Attempts to recrystallize it from chloroform–ethyl acetate–ether resulted in oils. It therefore was characterized as its tetraphenylborate derivative, m.p. and m.m.p. 229–231°.

(*c*) *Reaction with Methyl Iodide.* To the orange filtrate from a 2.5-mmole scale reaction was added 0.02 mole of methyl iodide with stirring. A white solid precipitated almost immediately. The mixture was heated at reflux for 30 min. and filtered to give 1.0 g. (85%) of product, α,β,β-trimethylpropyltriphenylphosphonium iodide. Recrystallization from chloroform–ethyl acetate–ether gave an oil which slowly crystallized on standing to give solid with m.p. 215–216°. Its n.m.r. spectrum was in agreement with the structure proposed. A tetraphenylborate derivative was prepared.

Preparation of Triphenylphosphinetrimethylsilylmethylene by the Action of Phenyllithium on (Trimethylsilylmethyl)triphenylphosphonium Iodide. To 0.01 mole of phosphonium salt in 200 ml. of diethyl ether was added with stirring 0.01 mole of phenyllithium in ether (0.65 *N* solution). A yellow color appeared immediately. The mixture was stirred for 30 min. at room temperature and then was quenched with 0.02 mole of methyl iodide. A white solid precipitated and the yellow color disappeared. The reaction mixture was heated at reflux for 30 min. and was filtered to give 4.5 g. (92%) of (α-trimethylsilylethyl)triphenylphosphonium iodide. The product was identified by mixture melting point with authentic material, by means of its n.m.r. spectrum, and by conversion to its tetraphenylborate derivative, m.p. 179–180°.

Preparation of Triphenylphosphine-t-butylmethylene by the Action of Phenyllithium on Neopentyltriphenylphosphonium Iodide. To the phosphonium salt (5 mmoles) in 100 ml. of ether was added 5.0 mmoles of ethereal phenyllithium. The solution immediately became deep orange in color. It was stirred at room temperature for 30 min.

(*a*) *Reaction with Methyl Iodide.* To such a solution containing about 5 mmoles of triphenylphosphine-*t*-butylmethylene was added 10 mmoles of methyl iodide. A white solid precipitated and the orange color was immediately discharged. The solid was collected (1.16 g., 97%) and identified as α,β,β-trimethylpropyltriphenylphosphonium iodide by mixture melting point and by means of its n.m.r. spectrum.

(*b*) *Wittig Reaction with Benzaldehyde.* To about 5 mmoles of the phosphinemethylene reagent prepared in this manner was added 5 mmoles of freshly distilled benzaldehyde. The orange color was discharged immediately and the reaction mixture was heated at reflux for 15 hr. Volatile materials were separated by a high-vacuum trap-to-trap distillation. The distillate was analyzed by g.l.c. (20% General Electric Co. SE-30 silicone gum on Chromosorb P) using *o*-xylene as internal standard. It was established that a mixture of the β-*t*-butylstyrene isomers had been formed in 84% yield, and that the product contained 23.8% of the *cis* isomer (which had the shorter g.l.c. retention time) and 76.2% of the *trans* isomer. Both were isolated by g.l.c. and fully characterized:

cis-β-t-Butylstyrene had $n^{25}\text{D}$ 1.5075. *Anal.* Calcd. for $C_{12}H_{16}$: C, 90.00; H, 10.00. Found: C, 90.23; H, 9.90. The infrared spectrum (pure liquid) showed 3080 (w), 3060 (w), 3020 (w), 2995 (m), 2960 (s), 2910 (m), 2872 (m), 1600 (w), 1500 (m), 1480 (m), 1470 (m), 1450 (w), 1415 (w), 1380 (w), 1365 (m), 1228 (w), 1200 (m), 1070 (w), 1025 (w), 915 (w), 893 (w), 825 (w), 750 (m), 730 (m), 694 (s), and 654 (w) cm.$^{-1}$; ultraviolet spectrum (in ethanol), $\lambda_{\max}$ at 226 mμ (ϵ 6463).

In the n.m.r. (CCl_4) spectrum, phenyl protons appeared as a singlet at 7.33 p.p.m., the olefinic proton α to the phenyl group as a doublet (J = 13.2 c.p.s.) at 6.54 p.p.m., the olefinic proton β to the phenyl group as a doublet (J = 13.2 c.p.s.) at 5.67 p.p.m., and the *t*-butyl group as a singlet at 1.00 p.p.m.

trans-β-t-Butylstyrene had $n^{25}\text{D}$ 1.5214. *Anal.* Found: C, 90.17; H, 9.93. The infrared spectrum (pure liquid) showed 3070 (w), 3060 (w), 3025 (m), 2960 (s), 2900 (m), 2865 (m), 1650 (w), 1600 (w), 1500 (m), 1480 (m), 1470 (m), 1450 (m), 1400 (w), 1370 (s), 1265 (m), 1200 (w), 1070 (w), 1025 (w), 980 (m), 966 (s), 940 (w), 920 (w), 905 (w), 840 (w), 740 (s), and 690 (s) cm.$^{-1}$; ultraviolet spectrum (in ethanol), $\lambda_{\max}$ at 250 mμ (ϵ 18,290), 283 (1310), 292 (845).

In the n.m.r. (CCl_4) spectrum phenyl protons appeared at 7.10–7.30 p.p.m., the olefinic protons as a sharp singlet at 6.20 p.p.m., and the *t*-butyl group as a singlet at 1.10 p.p.m. We have here an extreme example of an AB-type spectrum. Such an observation had been made by us previously in the case of *trans*-C_6H_5-

CH=CHSn$(CH_3)_3$,[30] and a similar example is provided by the n.m.r. spectrum of *trans*-propenylbenzene.[31]

The well-established rule[32] that simple *trans* olefins show ultraviolet absorption at longer wave lengths and with higher extinction coefficients than the corresponding *cis* isomers, as well as the often-applied generalization that a strong band in the infrared spectrum between 990 and 965 cm.$^{-1}$ is indicative of the *trans* structure,[33] were applied in the structural assignments above.

(*c*) *Attempted Wittig Reaction with Cyclohexanone.* To 5 mmoles of triphenylphosphine-*t*-butylmethylene in *ca.* 100 ml. of ether was added 5 mmoles of cyclohexanone. The color of the solution was discharged immediately with concurrent separation of a thick, white precipitate. The reaction mixture was heated at reflux for 15 hr. Volatiles then were removed by a trap-to-trap distillation *in vacuo.* G.l.c. analysis of the distillate did not show the expected *t*-butylmethylenecyclohexane. The solid residue was extracted with chloroform and filtered directly into 200 ml. of ethyl acetate. The white, crystalline solid which separated (1.90 g., 82.6%) was identified as neopentyltriphenylphosphonium iodide by mixture melting point and by means of its n.m.r. spectrum.

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Synthesis and Reactivity in the Benzocalicene Series[1]

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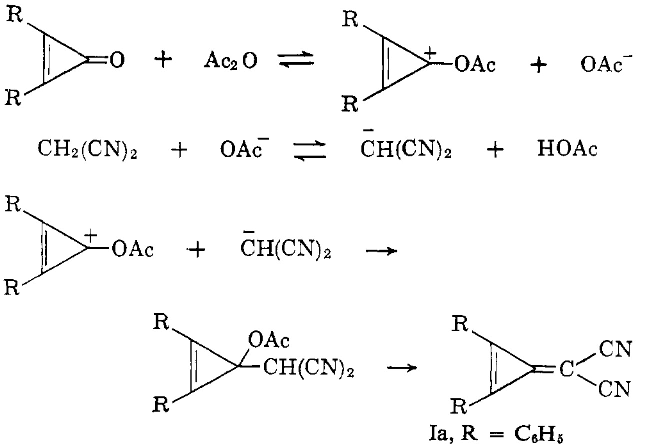
Indene-1-carboxylic acid esters and amide react with di-n-propylcyclopropenone in acetic anhydride at 120° to give 13–22% yields of the crystalline benzocalicene esters (IVb,c) and nitrile (IVe), respectively. The spectra, dipole moment, and other physical properties of these substances signify a stable and strongly polarized conjugated π-electron system. Reaction of the methyl ester IVb with N-bromosuccinimide or bromine has given the monosubstitution product V (R = CO_2CH_3). Under Vilsmeier–Haack conditions the methyl ester IVb is converted to a $C_{23}H_{27}O_2N$ enamine assigned the structure VII on the basis of spectroscopic evidence. With dimethyl acetylenedicarboxylate the ester IVb undergoes apparent cycloaddition and rearrangement to give a mixture of trimethyl 1,2-dipropylphenanthrene-3,4,9-tricarboxylate (XI) and its isomer XII.

Synthesis. The recent observation[2,3] that malononitrile condenses with disubstituted cyclopropenones in acetic anhydride to give dicyanomethylenecyclopropenes (Ia and Ib) suggested the possibility of employing a parallel method to achieve synthesis of that theoretically interesting[4] but elusive[5] class of compounds based on the calicene (II) nucleus. If our views of the mechanism of the malononitrile condensation were correct as depicted, the synthesis of calicenes would require the use of a cyclopentadiene derivative having an acidity comparable to that of malononitrile (pK_a = 11.2).[6] Simple acyl- or carbalkoxy-substituted cyclopentadienes would probably satisfy this requirement, but such compounds normally exist as dimers rather than as monomers in solution.[7] Our initial attempts toward calicene synthesis therefore utilized the more stable and



Ia, R = C_6H_5
Ib, R = $CH_2CH_2CH_3$

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