

One striking inconsistency with the proposed scheme is the very negative entropy of activation. A 1,5 hydrogen shift in a planar cyclic diene should occur with little reorganization in the transition state and consequently should have $\Delta S^\ddagger \approx 0$. Actually, large negative entropies of activation for 1,5 hydrogen shifts have been noted for a number of other cyclic dienes such as 7-deuterio-,³⁰ 7-phenyl-,³⁰ and 7-methoxytropilidenes,³¹ 1,4,6-cyclooctatriene,³² and 1-deuterio-2,4-cyclooctadiene.³³ These can be rationalized as involving a lack of experimental precision in the kinetic measurements,³⁴ however, we believe this is unsatisfactory. Clearly, the simple scheme proposed above for **4** requires elaboration, and further studies are in progress.

One other interesting aspect of the 1,5 hydrogen shift in cyclopentadienes is its fast rate even though there is about a 50-kcal difference between the activation energy for rearrangement and the corresponding carbon-hydrogen bond dissociation energy. The enhanced rates of hydrogen migration for the cyclopentadienes can be ascribed to the unique closed cyclopentadienyl molecular orbital pattern which is developed in the transition state.

Conclusion

In the above we have shown how a combination of techniques involving a common pyrolytic process can be

(30) A. P. ter Borg, H. Kloosterziel, and N. van Meurs, *Rec. Trav. Chim.*, **82**, 717 (1963).

(31) T. Nozoe and K. Takahashi, *Bull. Chem. Soc. Japan*, **38**, 665 (1965).

used to characterize directly a simple but relatively inaccessible reactive free radical. The information obtained encompasses thermodynamic, spectroscopic, and chemical properties. Although our primary purpose here is the illustration of the techniques of FVP by summarizing our work on one species (**1**), some of the other reactive intermediates or thermal processes currently being studied in our laboratory can be listed. These include cyclobutadiene³⁵ and its isomers, the thermal decarbonylation of phenoxy radicals³⁴ and a variety of related thermal rearrangements,³⁶ simple π radicals such as the benzyl radical,³⁷ and finally the synthesis and characterization of some "unusual" hydrocarbons.

The work described here has involved a number of collaborators. The mass spectroscopic experiments were designed and carried out by Paul Schissel with the help of D. J. McAdoo and P. F. D'Angelo. The esr and optical spectroscopic experiments were carried out by P. H. Kasai, E. B. Whipple, C. L. Angell, and D. McLeod. In the early stages of our work, W. Weltner, Jr., offered helpful encouragement and advice. The chemical experiments were carried out by D. W. McNeil and M. E. Kent. Finally, F. P. Lossing has been especially helpful throughout our work particularly with respect to the interpretation of our mass spectral results.

(32) W. R. Roth, *Ann.*, **671**, 25 (1964).

(33) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters*, 999 (1968).

(34) K. Eggers, *J. Am. Chem. Soc.*, **89**, 3691 (1967).

(35) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *ibid.*, **91**, 1875 (1969).

(36) E. Hedaya, M. E. Kent, D. W. McNeil, F. P. Lossing, and T. McAllister, *Tetrahedron Letters*, **30**, 3415 (1968).

(37) C. L. Angell, E. Hedaya, and D. McLeod, Jr., *J. Am. Chem. Soc.*, **89**, 4214 (1967).

Carbophosphoranes

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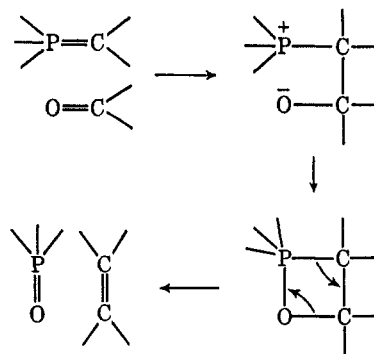
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Extensive research¹⁻⁴ on phosphonium ylides, $(C_6H_5)_3P=CXY \leftrightarrow (C_6H_5)_3P^+-C^-XY$, during the past 15 years has demonstrated broad synthetic utility resulting from their reactivity in the manner of carbanions and the ability of phosphorus to assume pentavalency and to form strong phosphorus-oxygen bonds. These characteristics are particularly evident in Wittig reactions¹⁻⁴ in which nucleophilic attack of such ylides on aldehydes or ketones yields olefins and triphenylphosphine oxide by way of acyclic betaines and four-membered-ring intermediates.



(1) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

(2) A. Maercker, *Org. Reactions*, **14**, 270 (1965).

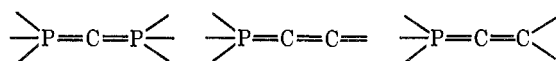
(3) H. J. Bestmann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 583, 645, 830 (1965).

(4) S. Trippett, *Quart. Rev. (London)*, **17**, 406 (1963).

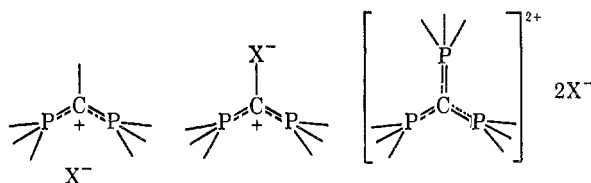
For the special case of phosphoranes having the general structure $(C_6H_5)_3P=C=Z$, heterocumulene reactivity is also significant. Research on such carbophos-

phoranes was initiated independently by Ramirez⁵ and by Matthews⁶ with the synthesis of a bis ylide, hexaphenylcarbodiphosphorane, $(C_6H_5)_3P=C=P(C_6H_5)_3$ (**1**). Other cumulated phosphoranes have since been obtained from **1** including triphenylphosphoranylidene-ketene, $(C_6H_5)_3P=C=C=O$ (**2**),⁷ and triphenyl-2,2-bis(trifluoromethyl)vinylidenephosphorane, $(C_6H_5)_3P=C=C(CF_3)_2$ (**3**).⁸

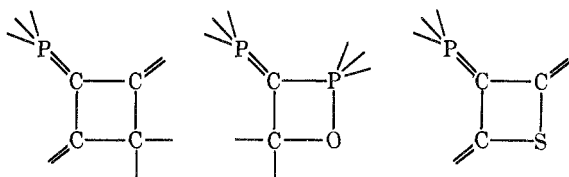
The existence of these carbophosphoranes with molecular skeletons of types



has made available new classes of compounds possessing P-C bonds with bond orders ranging from 1 to 2, including mesomeric salts having two or three phosphorus atoms bonded to a single carbon atom



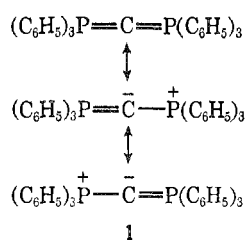
and cyclic phosphoranes with four-membered-ring structures such as



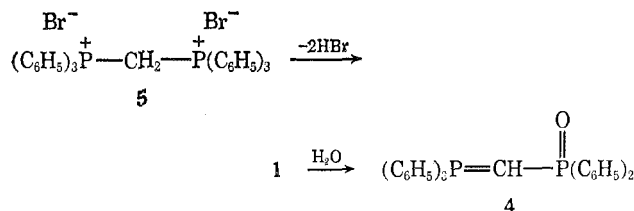
In this Account we discuss the results—often unexpected—obtained from synthetic, mechanistic, and structural studies of these intriguing organophosphorus compounds.

Hexaphenylcarbodiphosphorane

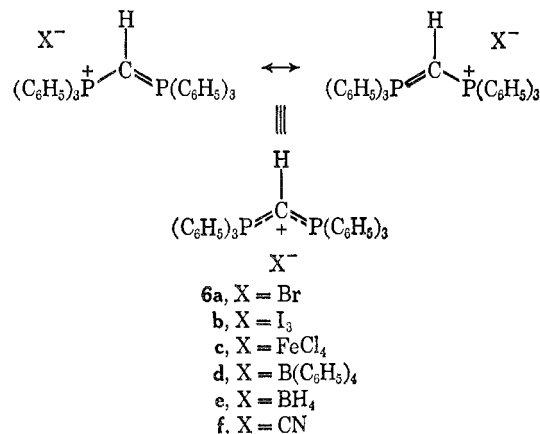
Hexaphenylcarbodiphosphorane (**1**)^{5,6,9-12} is a stable,



reactive solid that has the uncommon property of being triboluminescent—a bright green flash is emitted when yellow crystals of **1** are prodded under nitrogen.¹⁰ In water, **1** dissolves completely to form a diacid base. Colorless crystals of the phosphoranylphosphorane **4** are eventually deposited.^{5,12}



Hexaphenylcarbodiphosphorane is readily prepared^{5,6,9-12} by successive dehydrobromination of methylenebis(triphenylphosphonium bromide) (**5**). As weak a base as sodium carbonate converts **5** to the stable salt **6a** which then yields **1** after more drastic treatment with lithium butyl^{9,10} or potassium metal.^{5,12}



Physical and chemical evidence shows that **6** is better represented as a mesomeric phosphoranion¹³ salt than as an ylide with a phosphorane-phosphonium salt structure. A single phosphorus nmr absorption^{5,6} ($\delta^{31}P$ -21.2 ppm) for **6a** (compare -18.4 ppm for **5** and +4.3 ppm for **1**)¹¹ indicates equivalency of the two phosphorus atoms while the stability expected of the symmetrical structure **6** was demonstrated by inertness of the salts toward reaction with acetone or hot aqueous carbonate.¹⁷

Other phosphoranion salts were prepared by metathesis reactions of **6a** and by direct addition of proton acids or alkyl halides to **1**.¹⁰ Phosphoranion halides can further be converted to deeply colored salts possessing complex anions by the addition of halogens or metal halides.¹⁰ For example, dark brown crystals of the triiodide **6b** are formed from the iodide and iodine, and a red-gold tetrachloroferrate (**6c**) from the chloride and ferric chloride. Some of the phosphoranion com-

(5) F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Am. Chem. Soc.*, **83**, 3539 (1961).

(6) C. N. Matthews, U. S. Patent 3,262,971 (July 26, 1966).

(7) C. N. Matthews and G. H. Birum, *Tetrahedron Lett.*, 5707 (1966).

(8) G. H. Birum and C. N. Matthews, *J. Org. Chem.*, **32**, 3554 (1967).

(9) C. N. Matthews, J. S. Driscoll, J. E. Harris, and R. J. Wineman, *J. Am. Chem. Soc.*, **84**, 4349 (1962).

(10) J. S. Driscoll, D. W. Grisley, Jr., J. V. Pustinger, J. E. Harris, and C. N. Matthews, *J. Org. Chem.*, **29**, 2427 (1964).

(11) G. H. Birum and C. N. Matthews, *J. Am. Chem. Soc.*, **88**, 4198 (1966).

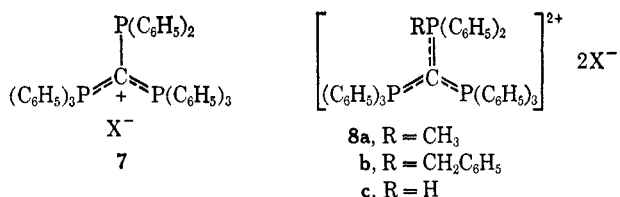
(12) F. Ramirez, J. F. Pilot, N. B. Desai, C. P. Smith, B. Hansen, and N. McKelvie, *ibid.*, **89**, 6273 (1967).

(13) In this Account we are using the term "phosphoranion" more broadly than in the past^{5,12} to designate mesomeric phosphorane-phosphonium salts having two or three phosphorus atoms bonded to a single carbon atom. The systematic name of the phosphoranion bromide **6a** is [(triphenylphosphoranylidene)methyl]triphenylphosphonium bromide.

pounds are photochromic, particularly the colorless tetraphenylboronate **6d** which rapidly becomes orange-red when exposed to ultraviolet light, the appearance of color being accompanied by the formation of a radical species with an epr g value of 2.0065.^{9,10}

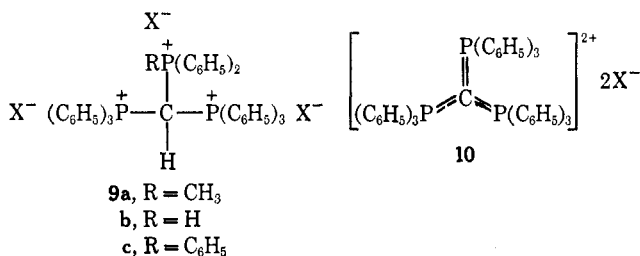
A possible use of phosphoranium cations for solubilization is suggested¹⁴ by the ease with which the borohydride **6e** effected reduction of organic compounds in mixed solvents such as benzene-ethanol (10:1) and hexane-ethanol (1:1). Ready metathesis reactions with the cyanide **6f** as well as smooth halogenation reactions with complex halogen salts should similarly be facilitated in a variety of solvents.

The first characterized examples of compounds having three phosphorus atoms bonded to a single carbon atom were synthesized¹¹ from **1** by nucleophilic displacement¹⁸ of chloride from chlorodiphenylphosphine. Reaction of the resulting tertiary phosphine **7**



(X = Cl) with alkyl or benzyl halides yielded the doubly charged salts **8**. Phosphorus nmr spectra of **7** contain characteristic multiplets for spin coupling of two equivalent phosphorus atoms with an unlike phosphorus atom, *i.e.*, a doublet ($\delta^{31}\text{P}$ -26.0 ppm) for the two equivalent atoms and a 1:2:1 triplet ($\delta^{31}\text{P}$ +1.5 ppm) for the single trivalent atom. For the dication salt **8a** two moderately broad peaks ($\delta^{31}\text{P}$ -25.1, -22.0 ppm) with a 2:1 area ratio indicated that the dications have mesomeric structures in which two positive charges are delocalized over three pentavalent phosphorus centers.

Further evidence for mesomeric structures possessing maximum delocalization of charge lies in the stability of the dications in strong acid solutions. In trifluoroacetic acid, nmr spectra of **8a** gave no indication that triphosphonium salts **9a** were present. The dication



could be dissolved in solutions containing hydriodic acid or fluoroboric acid and then recovered unchanged. When **7** was dissolved in trifluoroacetic acid, nmr spectra showed that a proton had been taken up readily

to form the dication **8c** but there was no evidence that further protonation had occurred to give the triphosphonium salt **9b**.

The inertness of mesomeric dications in strong acids contrasts with the behavior of mesomeric monocations **6**. Protonation of **6** to give diphosphonium salts **5** occurs readily as shown by equilibrium studies ($\text{p}K_a = 4.5$),^{5,12} by isolation of diphosphonium salts in high yield from hydrochloric acid,¹⁶ and by nmr spectral evidence in trifluoroacetic acid. The dication **8** apparently possesses considerably more resonance stabilization than the monocation **6**, and, in addition, would be expected to exhibit greater coulombic repulsion. As a result of these factors it seems likely that triphosphonium salts—if they can exist at all—would be among the strongest of organic acids.

Further reactions with the tertiary phosphine **7** (X = Cl) were attempted in order to synthesize the symmetrical mesomeric dication **10** related to the hypothetical triphosphonium salt **9c**. While alkyl halides and benzyl halides react readily with **7** to give mesomeric dications, as already described, it was found that aryl halide reactions did not yield **10**. For example, iodobenzene and **7** under various conditions gave complex mixtures in which the cleavage product **6** could be detected. Reaction of **7** with diphenyliodonium chloride also yielded uncharacterized mixtures containing **6**. Addition of benzenediazonium fluoroborate to **7** led to formation of a red salt **11**, which decomposed at 220° to yield **7** (X = BF₄) instead of **10**, presumably through elimination of nitrogen, boron trifluoride, and fluorobenzene. Other tertiary phosphine reactions carried out on **7** (see Figure 1) included complex formation, as with mercuric chloride to give **12**, oxidation by *t*-butyl hydroperoxide to give the phosphine oxide **13**, reaction with elemental sulfur to give the phosphine sulfide **14**, and addition of chlorine to give the dichlorophosphine **15** which can be readily hydrolyzed to **13**. Attempts to convert some of these compounds to **10** by applying known methods¹⁷ of phosphonium salt synthesis have so far been unsuccessful, probably because the crowded phosphorus functional groups of the mesomeric precursors are sterically shielded from attack by the various bulky phenylating agents used.

In a more direct approach, displacement of halogen from trihalomethanes by excess triphenylphosphine might be expected to yield **10** by spontaneous dehydrohalogenation of initially formed triphosphonium salts **9c**. In past research on the reactions of triphenylphosphine with polyhalomethanes, however, no evidence for the formation of **9** or **10** has been reported. In some cases major products obtained were diphosphonium salts **5** and mesomeric salts **6** which presumably resulted from nucleophilic attack of triphenylphosphine

(14) C. N. Matthews and J. S. Driscoll, *Chem. Ind. (London)*, 1282 (1963).

(15) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing Co., New York, N. Y., 1967.

(16) D. W. Grisley, Jr., J. C. Alm, and C. N. Matthews, *Tetrahedron*, **21**, 5 (1965).

(17) Houben-Weyl, "Methoden der Organische Chemie," Band 12/1, "Organische Phosphorverbindungen," Part 1, Georg Thieme Verlag, Stuttgart, 1963, p 79.

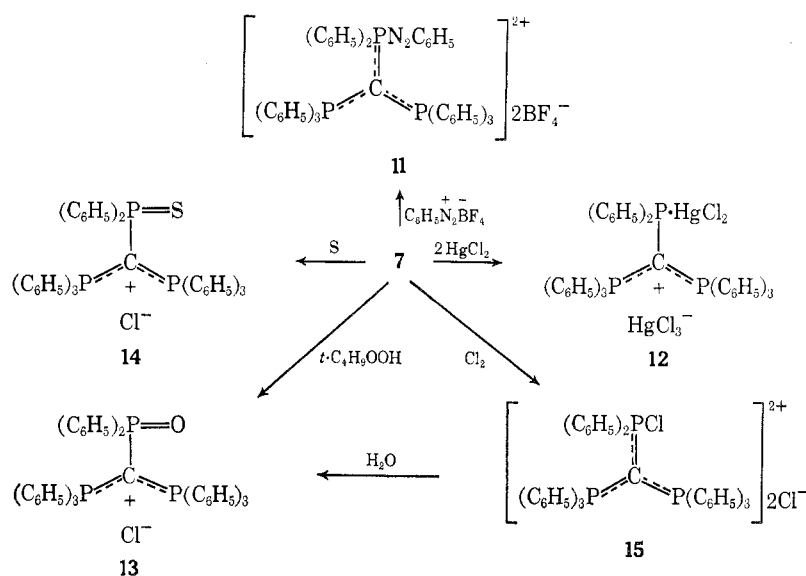
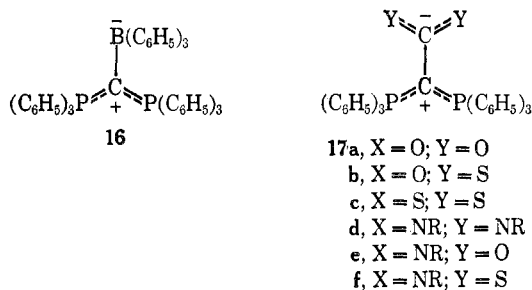


Figure 1. Phosphoranium salts synthesized from [(diphenylphosphino)(triphenylphosphorylidene)methyl]triphenylphosphonium chloride (7).

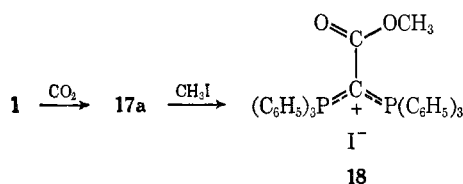
on the positive halogen centers of dihalomethyltriphenylphosphonium intermediates.^{16,18,19}

Triphenylphosphoranylideneketene

Phosphoranium inner salts **16** and **17** are readily formed by nucleophilic attack of **1** on Lewis acids such as boron triphenyl,⁹ or on cumulated compounds such as carbon dioxide,²⁰ carbon disulfide,²⁰ carbonyl sulfide,²⁰ carbodiimides,¹² isocyanates,¹² and isothiocyanates.²¹ For example, when gaseous carbon dioxide is dispersed in a stirred solution of **1** in dry diglyme under nitrogen at room temperature, a white solid (**17a**)



is precipitated and can be converted to the ester **18** by reaction with methyl iodide.²⁰ In hot diglyme **17a**



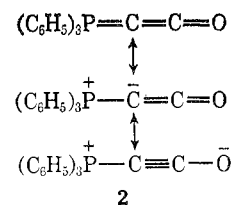
(18) H. Hoffman and H. J. Diehr, *Angew. Chem. Intern. Ed. Engl.*, **3**, 737 (1964).

(19) B. Miller in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Wiley-Interscience, New York, N. Y., 1965, p 133.

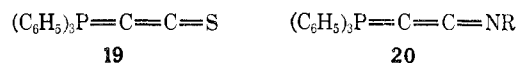
(20) C. N. Matthews, J. S. Driscoll, and G. H. Birum, *Chem. Commun.*, 736 (1966).

(21) G. H. Birum and C. N. Matthews, *Chem. Ind. (London)*, 653 (1968).

yielded equimolar amounts of triphenylphosphine oxide and triphenylphosphoranylideneketene (**2**).^{10,20} The inner salts **17c** and **17f** can similarly be decomposed to



triphenylphosphoranylideneethioketene (**19**)^{10,20} and triphenylphosphoranylideneketenimine (**20**),²¹ respectively.



Crystal structure studies²² show that **2** is monomeric. The bond lengths in the cumulated chain are remarkably short and, instead of being linear, the chain is bent to an angle of 145.5° at the carbon atom nearest the phosphorus. For **19** the corresponding angle is 168.0° (see Figure 2), a further structural difference being that the approximately linear C=C=S group is staggered whereas the C=C=O group in **2** eclipses a P—C bond.^{22,23} The difference in the P=C=C angle and in the P—C length in **19** compared with **2** can be attributed^{22,23} to the decrease in $d_\pi-\pi$ bonding²⁴ brought about by the greater electron-withdrawing power of sulfur. Phosphorus nmr absorption might therefore be expected to occur further downfield with the sulfur analog, as in triphenylphosphine sulfide ($\delta^{31}\text{P} -43.9$ ppm) compared with triphenylphosphine oxide ($\delta^{31}\text{P} -23.4$ ppm). The reverse is actually the case for **2**

(22) J. J. Daly and P. J. Wheatley, *J. Chem. Soc., A*, 1703 (1966).

(23) J. J. Daly, *ibid.*, 1913 (1967).

(24) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965.

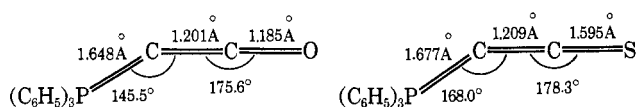
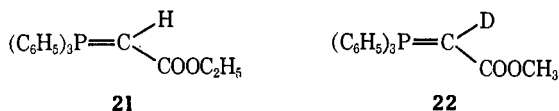


Figure 2. Bond lengths and bond angles of triphenylphosphoranylidene ketene (**2**) and triphenylphosphoranylidene thioketene (**19**).

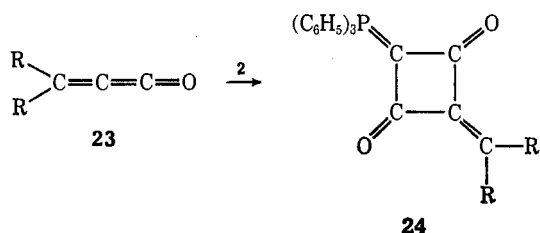
($\delta^{31}\text{P}$ -2.6 ppm) and **19** ($\delta^{31}\text{P}$ +7.7 ppm). Correlation of chemical shifts with structure in quadruply connected organophosphorus compounds²⁵ continues to be problematic, the most obvious anomaly¹ being the near identity of shifts ($\delta^{31}\text{P}$ -20 ppm region) due to phosphonium salts, phosphoranium compounds, and related ylides derived from triphenylphosphine.

Addition reactions take place readily with these versatile heterocumulenes.⁷ For example, in cold ethanol **2** was converted to the ylide **21**, while in methanol-*d* the corresponding deuterated ylide **22** was obtained. These facile additions of active hydrogen (or deuterium) compounds illustrate a general method for forming



β -ketoalkylidene triphenylphosphoranes, ylides that have been shown to be useful synthetic intermediates.¹⁻⁴ Imidazole and methyl mercaptan, for example, add to **2** and **19** to yield ylides that are not easily obtainable by standard methods.

Other reactions of **2** lead to a variety of cyclic organophosphorus compounds.²⁶ Because **2** can be regarded as both a ketene and an ylide it was of particular interest to investigate reactions with aldehydes and ketones, carbonyl compounds that normally give β -lactones with ketenes²⁷ and olefinic products with phosphorus ylides.¹ Phosphorane-substituted 1,3-cyclobutanediones were obtained as final products, indicating that **2** had reacted successively first as an ylide and then as a ketene. The initial step, presumably, was a Wittig reaction leading to previously unknown methyleneketenes (**23**) which then added rapidly to **2** to give the 1,3-cyclobutanediones **24**.²⁸ The over-all reaction proceeded readily at room temperature with aldehydes (*e.g.*, *p*-nitrobenzaldehyde) and with active



(25) J. R. Van Wazer and J. H. Letcher in "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Wiley-Interscience, New York, N. Y., 1967, p 169.

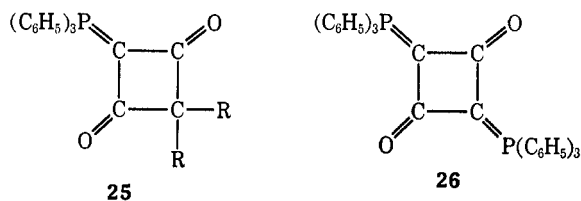
(26) G. H. Birum and C. N. Matthews, *J. Am. Chem. Soc.*, **90**, 3842 (1968).

(27) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967.

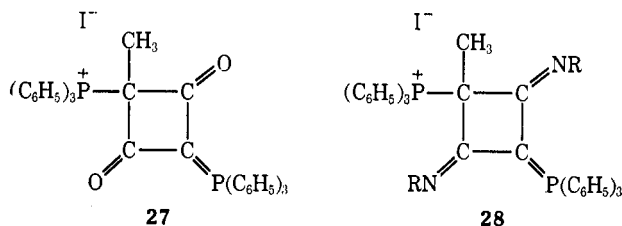
(28) The question remains open as to whether these heterocumulene cycloadditions proceed stepwise or in a concerted manner following the Woodward-Hoffmann rules.

ketones (*e.g.*, hexafluoroacetone) but not with less active ketones such as acetone and fluorenone.

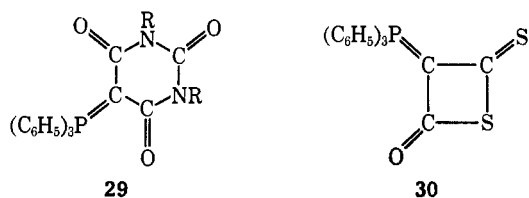
Evidence that the products have carbocyclic rather than lactone structures was provided by ir, uv, nmr, and mass spectra; by the resistance of the compounds to attack by reagents such as concentrated trifluoroacetic acid, aniline in boiling benzene, and hot acidified methanol; and by the marked similarity of **24** to the products **25** obtained by cycloaddition of **2** to ketenes (*e.g.*, **25**, R = C₆H₅),²⁶ by addition of carbon suboxide to diphenylmethylenetriphenylphosphorane followed by rearrangement (**25**, R = C₆H₅),²⁹ and by displacement reactions of triphenylphosphine with 1,2-dichloroperfluorocyclobutene (**25**, R = F).³⁰



The symmetrical cyclic dimer of **2** would also be expected to be stabilized by resonance between conjugated cyclobutanone and cyclobutenone structures.³¹ Attempts to synthesize **26** directly from **2** by uv irradiation, heating, or treatment with acids and bases, however, were unsuccessful, although a methyl iodide adduct of the hypothetical dimer was unexpectedly formed when **2** was treated with methyl iodide.²⁶ This phosphonium salt is apparently the end product (**27**) of a reaction sequence involving ylide formation from **2** and methyl iodide followed by further attack on **2** and subsequent ring closure. Analogous salts (**28**) were prepared from methyl iodide and triphenylphosphoranylidene ketenimines (**20**).²¹ Other types of cyclic phospho-



ranes formed from **2**²⁶ include stable six-membered-ring 2:1 adducts (**29**) synthesized from aromatic isocyanates and an unstable thiolactone (**30**) resulting from treatment of **2** with carbon disulfide.



(29) H. F. van Woerden, H. Cerfontain, and C. F. van Valkenburg, *Rec. Trav. Chim. Pays-Bas*, **88**, 158 (1969).

(30) (a) S. E. Elzey, Jr., U. S. Patent 3,359,321 (Dec 19, 1967); (b) R. F. Stockel, F. Megson, and M. T. Beachem, *J. Org. Chem.*, **33**, 4395 (1968).

(31) For convenience we have represented the carbocyclic products as cyclobutanediones rather than ionic cyclobutenones although betaine structures may more accurately describe the electron distribution for these β -carbonyl-stabilized ylides.

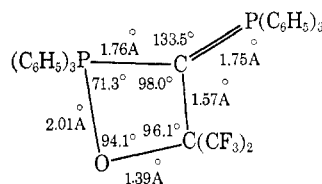
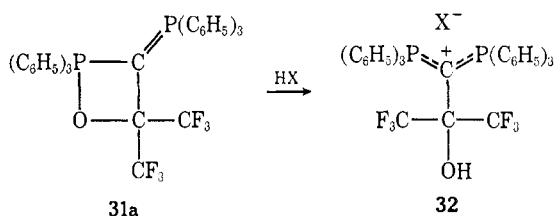


Figure 3. Bond lengths and bond angles of 4,4-bis(trifluoromethyl)-2,2,2-triphenyl-3-(triphenylphosphoranylidene)-1,2-oxaphosphetane (**31a**).

Triphenyl-2,2-bis(trifluoromethyl)-vinylidenephosphorane

The few intermediates that have been isolated from Wittig reactions of alkylidetriphenylphosphoranes and carbonyl compounds have been shown to have acyclic phosphobetaine structures.^{1,32} Examples include an adduct of methylenetriphenylphosphorane and benzaldehyde—isolated as a hydrobromide salt^{32a}—and a stable inner salt from isopropylidetriphenylphosphorane and diphenylketene which could be alkylated on carbon by methyl iodide.^{32b} These ionic intermediates subsequently yielded Wittig products as expected, presumably by electron redistribution following intramolecular ring closure.

The only stable cyclic Wittig intermediate so far reported was obtained by the reaction of hexaphenylcarbodiphosphorane (**1**) with hexafluoroacetone.³³ The oxaphosphetane structure **31a** was assigned to this 1:1

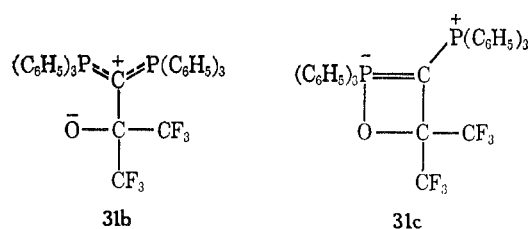


adduct on the basis of its phosphorus nmr spectrum. Two doublets ($\delta^{31}\text{P}$ -7.3 ppm, $+54.0$ ppm) of equal areas and coupling constants are consistent with spin-spin coupling of two nonequivalent phosphorus atoms, the doublet at -7.3 ppm having a chemical shift close to the value found for exocyclic phosphorus ylides²⁶ and the other at $+54.0$ ppm being in the region characteristic of cyclic structures having phosphorus covalently bonded to five substituents.³³ Although X-ray crystallographic studies³⁴ (see Figure 3) show that the planar four-membered-ring system has a long P-O bond and essentially equal bonds from the phosphorus atoms to the carbon atom, substantial contributions from ionic structures such as **31b** and **31c** appear to be ruled out by the nmr evidence (^{31}P , ^1H , ^{19}F) as well as by the failure of the adduct to be alkylated by methyl iodide. Ring opening of **31a** could be effected by acid treatment to give phosphonium salts (**32**) having equivalent phosphorus atoms ($\delta^{31}\text{P}$ -22 ppm).

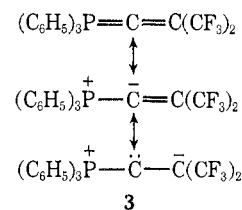
(32) (a) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954); (b) G. Wittig and A. Haag, *ibid.*, **96**, 1535 (1963).

(33) G. H. Birum and C. N. Matthews, *Chem. Commun.*, 137 (1967).

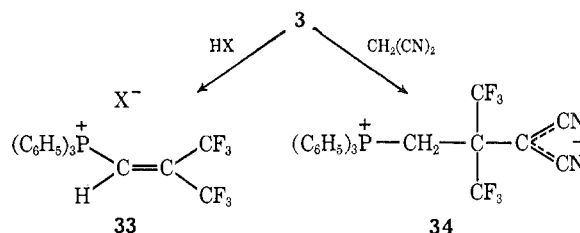
(34) G. Chiofolla and J. J. Daly, *J. Chem. Soc., A*, 568 (1968).



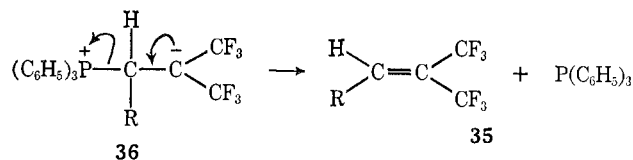
Warming **31a** in inert solvents to complete the Wittig sequence yielded equimolar amounts of triphenylphosphine oxide and triphenyl-2,2-bis(trifluoromethyl)vinylidenephosphorane (**3**),^{8,33} a reactive phosphorane that possibly has carbenoid as well as ylide character.



Addition of strong acids such as anhydrous hydrogen chloride to **3** gave bis(trifluoromethyl)vinylphosphonium salts (**33**). With malononitrile, the inner salt **34** was obtained instead, presumably through rearrangement of an ylide formed by way of a salt (**33**, $\text{X} = \text{CH}(\text{CN})_2$) possessing a highly nucleophilic anion.



Reactions of **3** with alcohols, phenols, mercaptans, and amines followed a different course. High yields of vinyl compounds (**35**)—bis(trifluoromethyl)vinyl ethers and vinyl sulfides and enamines—were obtained, possibly by spontaneous elimination of triphenylphosphine from adducts (**36**) formed by carbenoid insertion of **3**. Three types of products can thus be synthesized



RH = alcohols, phenols, mercaptans, amines

from active hydrogen compounds and **3**: vinylphosphonium salts, phosphonium inner salts, and olefins.⁸

Reactions with ketones and aldehydes also take place readily to give complex mixtures of products not yet characterized. Differences from the behavior of **2** would be expected, as has been shown with diphenylketene which, with **3**, yielded a stable butatriene (**37**)

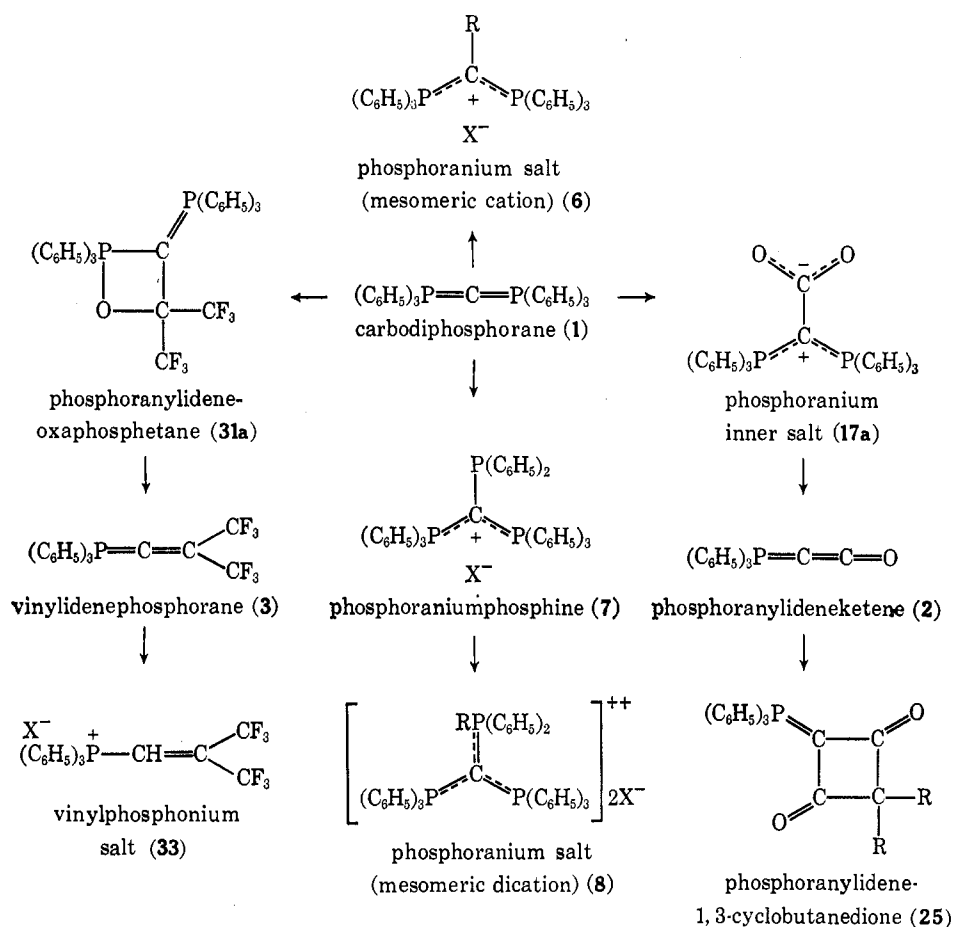
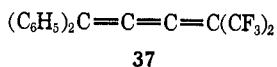


Figure 4. Representative phosphoranes, phosphonium salts, and phosphonium salts synthesized from hexaphenylcarbodiphosphorane.



via a Wittig reaction instead of a cyclic adduct.⁸

Summary

Interrelationships of the major types of compounds discussed in this Account are outlined in Figure 4.

Starting with the triboluminescent bis ylide hexaphenylcarbodiphosphorane (1), other carbophosphoranes have been synthesized, including triphenylphosphoranylideneketene (2) from an inner salt adduct (17a) of 1 and carbon dioxide, and triphenyl-2,2-bis(trifluoromethyl)vinylidenephosphorane (3) by a Wittig reaction between 1 and hexafluoroacetone that proceeded *via* a stable four-membered-ring intermediate (31a). Phosphonium salts 6, 7, and 8—mesomeric phosphorane-phosphonium salts with two or three phosphorus atoms bonded to a single carbon

atom—were also prepared by nucleophilic reactions of 1. Some phosphonium salts are photochromic. Surprisingly, 2 and its thioketene analog, 19, are not linear but have very short multiple bonds with $\text{P}=\text{C}=\text{C}$ angles of 145.5 and 168.0°, respectively. Cyclic phosphoranes with substituted 1,3-cyclobutanedione structures such as 25 result from reactions of 2 with active carbonyl compounds and, unexpectedly, when 2 is treated with methyl iodide. Alcohols, mercaptans, and amines readily add to 2 to form β -ketoalkylidenetriphenylphosphoranes whereas with 3 the products obtained are bis(trifluoromethyl)vinyl ethers and vinyl mercaptans and enamines, together with triphenylphosphine.

The availability of these structurally diverse organophosphorus compounds should be a stimulus to further experimental and theoretical investigations of the nature of double bonding between carbon and phosphorus.