and 4. The equilibrium favors the *cis*-monoadsorbed substrate (catalyst surface bonded equatorially), as expected, considering that the effective size of the catalyst probably is greater than that of phenyl. Desulfurizations of similar stereochemistry have been noted.[5] Equilibrium 3, −3 conceivably could take place at a step on the surface or by a rollover mechanism connecting the monoadsorbed species between adjacent surface sites.[2b] The low percentages of greater than D_1 product in the above-described deuteriogenolyses indicate that steps 5, −5 are not intervening seriously.

If the above interpretations are basically correct, we are required to conclude that the hydrogenolyses of acetate on Pt and Pd–C catalysts (expt 4 and 5), which occur stereospecifically with inversion of configuration, do not pass through the monoadsorbed state resulting from step 1. The monoadsorbed species from Ic and It equilibrate configurationally on these catalysts and proceed to stereoconvergent product. Consequently, these hydrogenolyses happen by some *direct substitution process* (step 6) A similar mechanism probably occurs on Ni(R) catalyst (expt 6).

The Ni(R)-catalyzed hydroxyl and methoxyl hydrogenolyses (expt 3 and 7) occur stereospecifically with retention of configuration. Hydrogenolysis of It-2,2,6,6-d_4 containing 83% D_4 gave IIt containing 65% D_4 under reaction conditions which led to 6% loss of D_4 in IIt initially containing 66% D_4 This indicates that these reactions may proceed *via* steps 1 + 2 with minor divergence through step 5 and negligible equilibration (3, −3). The Ni(R) desulfurizations (expt 8, 10, and 12) differ in that local poisoning of the catalyst upon step 1 leads to local hydrogen desorption, retarding steps 2 and 4 and allowing equilibrium (3, −3) to be reached. The observation that deuterium exchange of the benzylic hydrogen of (+)-2-phenylbutane occurs[6] with retention of configuration using deuterated Ni(R) and about 12.5 times as fast as the over-all isotopic exchange is compatible with the hydroxyl hydrogenolysis mechanism proposed above. During the isotopic exchange, excursions through steps 5, −5 and 3, −3 do not compete seriously with steps 1 + 2.

Acknowledgment. Support of this work from the Petroleum Research Fund (Grant No. 1536) of the American Chemical Society is gratefully acknowledged.

(5) E. L. Eliel and S. Krishnamurthy, *J. Org. Chem.*, **30**, 848 (1965).
(6) W. A. Bonner and T. W. Greenlee, *J. Am. Chem. Soc.*, **81**, 3336 (1959).
(7) A. P. Sloan Foundation Research Fellow.

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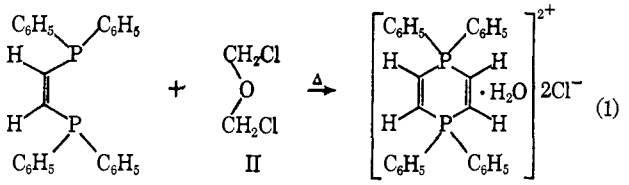
Received December 16, 1966

Two Syntheses of the Four-π-Electron 1,4-Diphosphoniacyclohexadiene-2,5 System

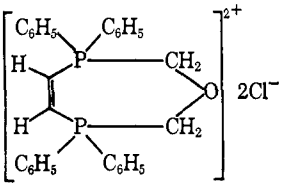
Sir:

We wish to report the formation of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexadiene-2,5 dichloride (IIIa) by reaction of *cis*-vinylenebis(diphenylphosphine)[1] (I) with bis(chloromethyl) ether (II) (eq 1).



(1)

Compound IIIa, mp 251–253° (from ethyl acetate–methanol) (*Anal.* Calcd for $C_{28}H_{24}Cl_2P_2 \cdot H_2O$: C, 65.75; H, 5.09; Cl, 13.89; P, 12.13. Found: C, 64.56; H, 5.11; Cl, 14.53; P, 11.96) gave an infrared spectrum exhibiting bands at 1430 and 1105 cm^{-1}, typical of a phenylphosphonium salt. The absence of a band between 1120 and 1250 cm^{-1} verified that no phosphoryl group was present. Both the water solubility and positive aqueous silver nitrate test supported the phosphonium salt structure. Treatment of IIIa with aqueous sodium picrate gave an immediate precipitate of the dipicrate IIIb, mp 235–237° (from acetonitrile) (*Anal.* Calcd for $C_{40}H_{28}N_6O_{14}P_2$: C, 54.67; H, 3.19; N, 9.57; Cl, 0.00. Found: C, 54.59; H, 3.39; N, 9.65; Cl, 0.00), showing that all of the halogen in IIIa as ionic. Although the calculated analysis for IIIa is identical with that of the expected product 3,3,6,6-tetraphenyl-1-oxa-3,6-diphosphoniacycloheptene-4 dichloride (IV), the absence of a carbon–oxygen single bond stretching band in the infrared spectrum makes assignment of this structure to III untenable.

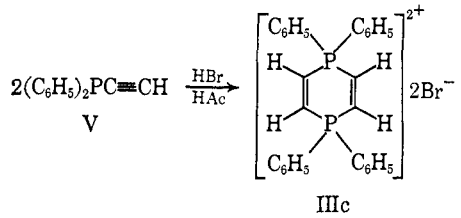


IV

Furthermore, solutions of IIIa in methanol-d_4 gave 60-MHz proton nmr spectra showing only a phenyl complex centered at τ 2.1 and three peaks at τ 0.53, 0.97, and 1.42. Cyclic and acyclic *cis*-vinylenebis(diphenylphosphonium) salts have been observed to exhibit a "pseudo-triplet" downfield from the phenyl protons.[2,3] In the previous examples, however, the center peak was much broader and shallower than in the case of IIIa in which the ratio is 1:2:1. The ratio of phenyl protons to this "triplet" was exactly 5:1 in IIIa. Increase of temperature did not change this ratio. Use of trifluoroacetic acid as the solvent led to essentially the same nmr spectrum, showing that neither exchange with methanol-d_4 nor protonation by trifluoroacetic acid occurs. If IIIa actually had structure IV, the nmr spectrum would show a signal at τ ~4.0 for the methylene protons.[4]

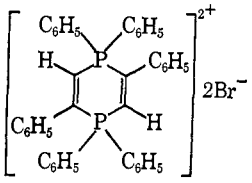
The novelty of this synthetic path made it desirable to produce IIIa by a more unequivocal route. Recent production of the 2,5-diphenyl derivative of III by treatment of diphenyl(phenylethynyl)phosphine with HBr in glacial acetic acid[3] suggested extension of this method to diphenylethynylphosphine[5] (V) (eq 2). A

(1) A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).
(2) A. M. Aguiar and H. Aguiar, *ibid.*, **88**, 4090 (1966).
(3) A. M. Aguiar, K. C. Hansen, and G. S. Reddy, *ibid.*, **89**, 3067 (1967).
(4) A. M. Aguiar, K. C. Hansen, and J. T. Mague, *J. Org. Chem.*, **32**, 2383 (1967).
(5) C. Charrier, M. P. Simonnin, W. Chodkiewwicz, and P. Cadiot, *Compt. Rend.*, **258**, 1537 (1964).



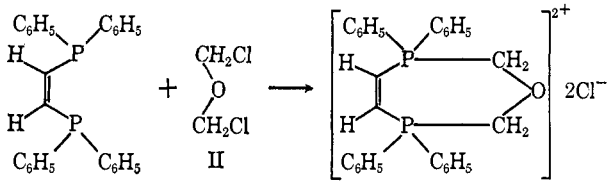
(2)

better yield of IIIc, mp 306–308° dec (from acetonitrile–methanol), was obtained by this method. Identical infrared and proton nmr spectra were obtained for IIIa and IIIc. Both gave the same picrate (IIIb), as shown by melting point and mixture melting point determinations. Simple phosphonium salts exhibit ^{31}P nmr shifts (relative to an external standard of 85% H_3PO_4) of between −20 and −40 ppm.[6] Vinylphosphonium salts, on the other hand, display increased shielding of the phosphorus nucleus.[2] The first example of a phosphonium salt displaying a positive ^{31}P nmr shift was reported recently[3] (VI).



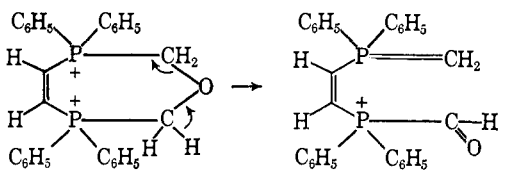
VI, +3.5 ppm

Methanol solutions of IIIa exhibited a ^{31}P nmr shift of +16.0 ppm, relative to an external standard of 85% H_3PO_4. This result is consistent, as in the case of VI, with delocalization of the four π electrons over the phosphorus 3d orbitals. Preliminary X-ray crystallographic studies of IIIa showed that it belongs to the tetragonal crystal system. Further crystallographic work is being carried out at Tulane University by Professor Charles J. Fritchie, Jr., to verify the expected planarity of the system. A silicon analog, 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene-2,5, has been shown to be planar.[7] Although the mechanism of formation of IIIa has not been established, it may involve initial formation of the expected oxadiphosphoniacycloheptene (IV) (eq 3).



(3)

Loss of one of the acidic methylene protons[2] would lead to an ylide which would decompose into an open ylide aldehyde (eq 4). Intramolecular reaction of these

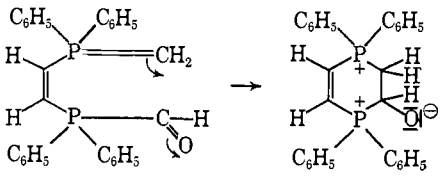


(4)

(6) S. O. Grim, W. McFarlane, E. F. Davidoff, and T. J. Marks, *J. Phys. Chem.*, 70, 581 (1966).

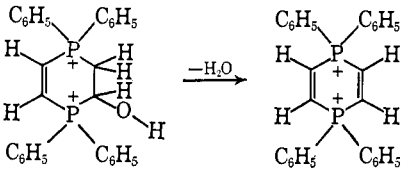
(7) N. G. Bokij and J. T. S. Truchkov, *Zh. Struckt. Khim. SSSR*, **6**, 571 (1965).

functional groups would give a betaine structure which, due to steric constraint, could not undergo decomposition to an olefin and phosphine oxide typical of the Wittig reaction (eq 5). After protonation, the resultant



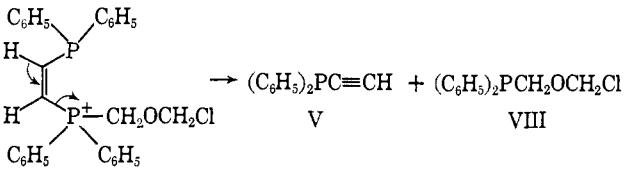
(5)

alcohol would be expected to lose water due to the acidity of the methylene protons[2] (eq 6).



(6)

There is also the possibility that the monophosphonium salt VII undergoes elimination to give diphenylethynylphosphine (eq 7). Reaction of diphenyl-



(7)

ethynylphosphine with hydrogen chloride (produced by decomposition of II or VIII) would lead to III. Formation of IIIc, as in the case of VI, probably involves a series of acid-catalyzed Michael-type additions of a tertiary phosphine to an alkynylphosphine.[8]

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(8) L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956); H. Hoffman and H. J. Diehr, *Chem. Ber.*, **98**, 364 (1965); D. Allen, J. C. Tebby, and D. H. Williams, *Tetrahedron Letters*, 2361 (1965).

(9) NASA Fellow, 1964–1967.

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The Photolysis of Bullvalene[1]

Sir:

Current interest in $C_{10}H_{10}$ hydrocarbons[2] and in the class of compounds $(CH)_{10}$ in particular[3] prompts us to

(1) Thanks are due the Lilly Research Laboratories for their generous support of this work.

(2) (a) M. Pomerantz, *J. Am. Chem. Soc.*, **88**, 5349 (1966); (b) M. Pomerantz, *ibid.*, **89**, 694 (1967); (c) J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967); (d) J. A. Elix, M. V. Sargent, and F. Sondheimer, *ibid.*, **89**, 180 (1967).

(3) (a) G. Schröder, *Angew. Chem.*, 77, 774 (1965); (b) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Letters*, 1017 (1966); (c) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966); (d) M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967); (e)