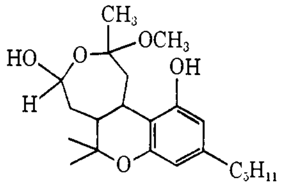
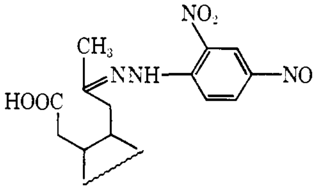
378.2402), and in addition included peaks at 360 ($M^+ - H_2O$), 346 ($M^+ - CH_3OH$), 331, and 288 (base) which are completely explicable on the basis of structure **3**.

The methyl singlet at 1.41 ppm and the hemiacetal proton at 4.84 ppm are in agreement with literature values in similar compounds.[13] Similarly, the slight shift in the position of *gem*-dimethyl groups in **3** is in accordance with that reported by Gaoni and Mechoulam in the case of 1-methoxyhexahydrocannabinol.[9b]

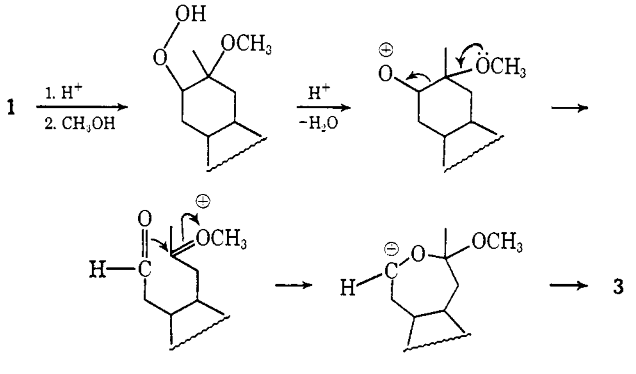
3 gives a positive test with Tollens reagent. This is taken as confirmation of the presence of a hemiacetal function in **3**. Moreover, it furnished a resinous 2,4-dinitrophenylhydrazone of the acid[14] **4** ($C_{27}H_{34}N_2O_8$; *m/e* 542) which was purified by chromatography on thick silica gel plates. We submit that the most reasonable interpretation of the mechanism of formation of **3** is



3



4



Similar rearrangements of hydroperoxides are known in the literature.[15] In confirmation of this proposed mechanistic scheme, **3** was also formed when **1** was treated with a catalytic amount of *p*-toluenesulfonic acid in methanol for 16 hr.

Isolation of similar compounds in the Δ^1- and Δ^6-*trans*-tetrahydrocannabinol series is in progress.

Acknowledgment. The authors wish to thank Drs. R. Lyle and P. Dowd for helpful discussions, Dr. P. Levins for nmr and mass spectral data, and JEOLCO, Inc., for decoupling experiments. We also wish to acknowledge the financial support of Arthur D. Little, Inc.

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[13] L. J. Dolby, C. A. Elliger, S. Esfandiori, and K. S. Marshall, *J. Org. Chem.*, **33**, 4508 (1968); N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Vol. I, Varian Associates, Palo Alto, Calif., 1962, p 143.

[14] We believe this is formed by oxidation of 3 to the corresponding lactone followed by ring opening. Oxidative properties of 2,4-dinitrophenylhydrazine are known; see, *e.g.*, D. Welti and D. Whittaker, *Chem. Ind.* (London), 968 (1962).

[15] E. G. E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Inc., Princeton, N. J., 1961, p 54.

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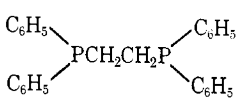
A New Synthesis of Polytertiary Phosphines and Arsines

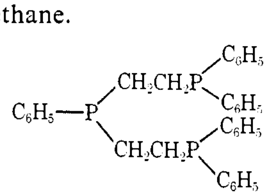
Sir:

The base-catalyzed addition of phosphorus–hydrogen bonds to carbon–carbon multiple bonds is an important reaction in organophosphorus chemistry.[1] This communication reports an extension of this reaction to the preparation of novel polytertiary phosphines by the base-catalyzed addition of phosphorus–hydrogen bonds to vinylphosphines and ethynylphosphines. Many of the new polytertiary phosphines prepared by this synthetic method are useful multidentate ligands in coordination chemistry.

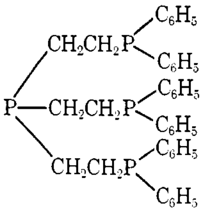
A commonly used chelating ditertiary phosphine is 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (I), previously[2] prepared by reaction of an alkali metal diphenylphosphide with 1,2-dichloroethane. The reaction between stoichiometric quantities of diphenylphosphine and diphenylvinylphosphine in boiling benzene for 20 hr in the presence of 5–10% phenyllithium catalyst gives an 80% yield of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (I), mp 139–140° (lit.[2] mp 140–142°). The infrared spectrum of I prepared from diphenylphosphine and diphenylvinylphosphine was identical with that of material prepared from lithium diphenylphosphide and 1,2-dichloroethane.



I



II



III

This new preparative method is particularly useful for the preparation of novel tridentate and tetradentate chelate polytertiary phosphines with $-CH_2-CH_2-$ bridges between the phosphorus atoms. The chelating tritertiary phosphine[3] $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ (II), mp 129–130° (lit.[2] mp 131–132°), can be obtained in 50–90% yields either from $C_6H_5PH_2$ and $(C_6H_5)_2PCH{=}CH_2$ or from $(C_6H_5)_2PH$ and $C_6H_5P(CH{=}CH_2)_2$ in boiling benzene using a phenyllithium or, preferably, a potassium *t*-butoxide catalyst; these new methods for preparing II are much more efficient than its previously[2] reported preparation from sodium diphenylphosphide and phenylbis(2-bromoethyl)phosphine. Similarly the new chelating tetratertiary phosphine[3] $P[CH_2CH_2P(C_6H_5)_2]_3$ (III),[3] mp 129–130°, can be prepared in 60–75% yields from $(C_6H_5)_2PH$ and $(CH_2{=}CH)_3P$ or in lower yields from PH_3 and $(C_6H_5)_2PCH{=}CH_2$; in the latter case the reaction is carried out using phenyllithium catalyst in a sealed stainless steel cylinder at 100° for 36 hr. A chelating tetratertiary phosphine

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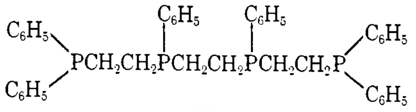
[1] K. Sasse in "Methoden der Organischen Chemie," Houben-Weyl, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1963, pp 25–28.

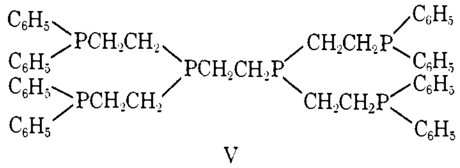
[2] W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).

[3] The new compounds gave satisfactory analyses for all elements. The ^{31}P nmr spectra were consistent with the proposed structures.

isomeric to III is $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (IV),[3] mp 155–158°, which may be prepared in 56% yield from $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$[4] and $(C_6H_5)_2PCH{=}CH_2$ in boiling benzene for 24 hr in the presence of a potassium *t*-butoxide catalyst. Further extension of this new synthesis results in the preparation of the potentially hexadentate ligand $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ (V), mp 138–140°, in ~20% yield from $H_2PCH_2CH_2PH_2$[5] and excess $(C_6H_5)_2PCH{=}CH_2$; the hexatertiary phosphine V is the first known potentially hexadentate tertiary phosphine ligand.[6]

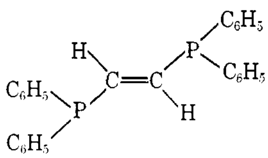


IV

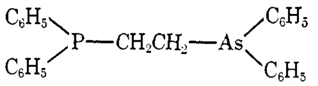


V

In an attempt to explore the possible utility of the new synthetic method for preparing phosphines with $-CH{=}CH-$ bridges, the reaction between $(C_6H_5)_2PH$ and $(C_6H_5)_2PC{\equiv}CH$[7] was investigated (boiling benzene, 14 hr, phenyllithium catalyst). A 66% yield of *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (VI)[8] was obtained; identification of this material as the *trans* isomer was based on its infrared and nmr spectra[8] and upon its reaction with $CH_3Mo(CO)_3C_5H_5$ to give a (diphos)$[Mo(CO)_2(COCH_3)C_5H_5]_2$ rather than a (diphos)$_2Mo(CO)_2$ derivative.[9] This result suggests that base-catalyzed addition of the phosphorus–hydrogen bond across the carbon–carbon triple bond of an ethynylphosphine is stereospecific resulting in the *trans* isomer. Unfortunately unsaturated tertiary phosphines such as VI cannot act as chelating agents because of the unfavorable relative locations of the phosphorus atoms.[10]

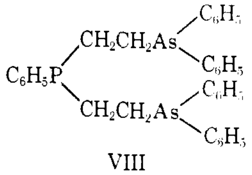


VI

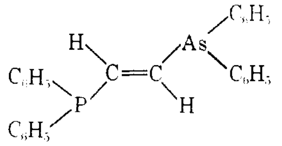


VII

Another extension of this new synthetic technique enables the preparation of unusual "mixed" tertiary phosphine–arsines by addition of diphenylarsine to a vinylphosphine or ethynylphosphine using a potassium *t*-butoxide catalyst[11] in boiling benzene. Thus the reaction of $(C_6H_5)_2AsH$ with $(C_6H_5)_2PCH{=}CH_2$ gives a 65% yield of 1-diphenylphosphino-2-diphenylarsinoethane, $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ (VII),[3] mp 116–118°. Similarly the reaction of $(C_6H_5)_2AsH$ with $C_6H_5P(CH{=}CH_2)_2$ gave a 62% yield of $C_6H_5P[CH_2CH_2As(C_6H_5)_2]_2$ (VIII),[3] mp 160–162°. Reaction of $(C_6H_5)_2AsH$ with $(C_6H_5)_2PC{\equiv}CH$ gives a 66% yield of *trans*-$(C_6H_5)_2PCH{=}CHAs(C_6H_5)_2$ (IX),[3] mp 95–96°. The proton nmr spectrum of IX besides exhibiting a strong phenyl resonance at τ 2.7–2.8 exhibits two overlapping doublets at τ 3.07 (J = 14.5 cps) and τ 3.10 (J = 16 cps) indicating a slight chemical shift difference between the two vinyl protons arising from the fact that one is bonded to a carbon bonded to phosphorus and the other is bonded to a carbon bonded to arsenic.



VIII



IX

An investigation of the complexes formed by these polytertiary phosphines and arsines upon reaction with metal carbonyl and metal halide derivatives is currently in progress.

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-68-1435 and to the University of Georgia Office of General Research for the support of P. N. K. during the course of this work. We also thank Dr. R. C. Taylor for providing samples of $C_6H_5PH_2$ and $H_2PCH_2CH_2PH_2$.

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(4) (a) K. Issleib and H. Weichmann, *Ber.*, **101**, 2197 (1968). (b) The starting material $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ can also be prepared in ~21% yield by cleavage of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ with sodium metal in liquid ammonia.

(5) L. Maier, *Helv. Chim. Acta*, 49, 842 (1966).

(6) For a report of a hexadentate polytertiary arsine ligand, see C. M. Harris and J. V. Kingston, *Chem. Commun.*, 965 (1968).

(7) C. Charrier, M. P. Simonnin, W. Chodkiewicz, and P. Cadiot, *Compt. Rend.*, **258**, 1537 (1964).

(8) A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, 86, 2299 (1964).

(9) R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, **8**, 1792 (1969).

(10) R. B. King and A. Efraty, *ibid.*, in press.

(11) Phenyllithium could not be used as a catalyst for reactions of $(C_6H_5)_2AsH$.

(12) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(13) Postdoctoral Research Associate.

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The Stability of Isoindoles

Sir:

Interest both in the synthesis[1] and the stability[1a,2] of isoindoles has grown considerably in recent years. Yet in spite of the resurgence of synthetic activity and the long history of this class of compounds[3] it was only a short time ago that the first isolable N-unsubstituted isoindoles were reported;[1a,c] all of these compounds bore one or more aryl groups in the pyrrole ring. Indeed, it is a striking fact that there is no example to date in the literature of an isolable isoindole in which the pyrrole moiety is free of substituents. To be sure, the parent compound, isoindole,[1b] and its relative, benz[*f*]-isoindole,[1d] have been prepared recently, but they are known only in solution. This situation has raised the

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(1) For examples: (a) D. F. Veber and W. Lwowski, *J. Amer. Chem. Soc.*, **86**, 4152 (1964); (b) R. Kreher and J. Seubert, *Z. Naturforsch.*, **20b**, 75 (1965); (c) J. C. Emmett and W. Lwowski, *Tetrahedron*, **22**, 1011 (1966); (d) J. Shields and J. Bornstein, *Chem. Ind.* (London), 1404 (1967); (e) C. O. Bender and R. Bonnett, *J. Chem. Soc.*, 3036 (1968); (f) M. E. Mann and J. D. White, *Chem. Commun.*, 420 (1969).

(2) (a) J. Kopecky, J. E. Shields, and J. Bornstein, *Tetrahedron Lett.*, 3669 (1967), and references cited therein; (b) R. C. Anderson and R. H. Fleming, *ibid.*, 1581 (1969).

(3) R. C. Elderfield and T. N. Dodd, Jr., in "Heterocyclic Compounds," Vol. III, R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, N. Y., 1952, p 275 ff.