Supplementary Material Available. EPR spectra will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6279.

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Bis(trimethylphosphoranylidene)methane, $(CH_3)_3PCP(CH_3)_3$

Sir:

Currently there is considerable interest in the chemistry of both the bis(triphenylphosphoranylidene)ammonium cation,[1] **1**, and the isoelectronic bis(triphenylphosphoranylidene)methane molecule,[2] **2**. This interest is based on some unexpected observations. (1) The cation **1** has been found by X-ray studies to vary strongly in its structure, depending on the nature of the anion and the type of the crystal lattice.[1] The PNP bond angle may range between 134.6 and 180°, and two different bond angles may be met in one and the same unit cell (!).[1b] (2) The crystals of compound **2** were also demonstrated[2b] to contain two different types of molecules, with PCP valence angles of 143.8 and 130.1°. (3) Moreover, compound **2** is unusual in showing the rare phenomenon of triboluminescence[2a] (i.e., to emit visible light upon touching of the crystals).

$$\underset{\mathbf{1}}{(C_6H_5)_3P{=}N{=}P(C_6H_5)_3{}^+} \qquad \underset{\mathbf{2}}{(C_6H_5)_3P{=}C{=}P(C_6H_5)_3}$$

It was concluded[1a,2a] from these observations, that there should be only a delicate energy balance associated with angle deformation in these species, similar and related to the energy characteristics of bond deformations in the isoelectronic siloxanes $R_3SiOSiR_3$.[3]

To contribute to this discussion, we report here some of the properties of $(CH_3)_3P{=}C{=}P(CH_3)_3$ and its synthesis, which was impossible to accomplish via the traditional methods employed previously[2] for the hexaphenyl analog **2**. We reported earlier[4] on $(CH_3)_3P{=}N{=}P(CH_3)_3{}^+$.

Difluorotrimethylphosphorane[5] undergoes a smooth reaction with trimethylsilylmethylene trimethylphosphorane[6] under mild conditions, in benzene solvent, resulting in about an 80% yield of fluorotrimethylsilane and fluoro(trimethylphosphoranylidene)methyltrimethylphosphorane (**3**) (eq 1a). Alternatively, this compound is obtained in high yield from the reaction of 1:2 molar amounts of $(CH_3)_3PF_2$ and $(CH_3)_3PCH_2$ (eq 1b). This precursor, **3**, mp. 74°C, is a covalent nonsalt-like species, soluble in benzene and other nonpolar solvents. In solution it appears to be a fluxional molecule in which the fluorine atom is subject to rapid site exchange at the phosphorus atoms. This renders the ^{31}P nuclei equivalent even at temperatures as low as −90°C, and no ^{19}F-couplings are observed:[7] ^1H NMR (in benzene at 30°C) $\delta(H_3C)$ 0.93 ppm, $A_9XX'A_9'$, $N = 11.3$ Hz;[8] $\delta(HC)$ −0.14, t, $J(PCH) = 21.5$ Hz. ^{31}P NMR, $\{^1H\}$ −32.8, s.

Anal. Calcd for $C_7H_{19}FP_2$: C, 45.65; H, 10.40. Found: C, 45.31; H, 10.57.

$$(CH_3)_3P{=}CH{-}Si(CH_3)_3 + (CH_3)_3PF_2 \xrightarrow[78^{\circ}C]{\text{benzene}} \underset{\mathbf{3}}{(CH_3)_3P{=}CH{-}P(CH_3)_3F} + (CH_3)_3SiF \qquad (1a)$$

$$2(CH_3)_3P{=}CH_2 + (CH_3)_3PF_2 \longrightarrow \underset{\mathbf{3}}{(CH_3)_3P{=}CH{-}P(CH_3)_3F} + [(CH_3)_4P]F \qquad (1b)$$

With methylene dichloride, an instantaneous reaction (eq 2) was observed, even at −80°C, which converted **3** into the corresponding chloride, **4**, mp 168°C dec.[9] This chloride is salt-like in character and therefore differs in all its physical and spectral properties from the fluoride (**3**): ^1H NMR (in CH_2Cl_2 at 30°C): $\delta(H_3C)$ 2.0, $A_9XX'A_9'$, $N = 12.8$;[8] $\delta(HC)$ 0.65, t, $J(PCH) = 5.0$ Hz; ^{31}P NMR, $\{^1H\}$ 10.5, s.

Anal. Calcd for $C_7H_{19}ClP_2$: C, 41.91; H, 9.55. Found: C, 42.37; H, 9.79.

$$(CH_3)_3P{=}CH{-}P(CH_3)_3F \xrightarrow[-CH_2F_2]{CH_2Cl_2} \underset{\mathbf{4}}{[(CH_3)_3P{=}CH{-}P(CH_3)_3]Cl} \qquad (2)$$

When an intimate mixture of **3** and sodium hydride is heated to the melting point of **3**, hydrogen is rapidly evolved and a colorless liquid can be distilled from the reaction mixture under vacuum. This product ($bp_{0.1}$ 41°C, mp ca. 0°C), **5**, which is extremely reactive, was identified as **5** by elemental analysis, ^1H, ^{13}C, and ^{31}P NMR, and mass spectra: ^1H NMR (in benzene) $\delta(H_3C)$ 1.21, $A_9XX'A_9'$, $N = 11.3$; ^{31}P NMR, $\{^1H\}$ −29.6, s; ^{13}C NMR, $\{^1H\}$ $\delta(CH_3)$ 23.9, AXX′, $N = 52$;[10] $\delta(C)$ 10.8, t, $J(PC) = 32$ Hz.

Anal. Calcd for $C_7H_{18}P_2$: C, 51.21; H, 11.05. Found: C, 50.84; H, 11.02. Parent ion mass: calcd 164.2, found 164 (MS, M^+).[11]

$$(CH_3)_3P{=}CH{-}P(CH_3)F + NaH \xrightarrow[\Delta]{\text{neat}} (CH_3)_3P{=}C{=}P(CH_3)_3 + H_2 + NaF \qquad (3)$$

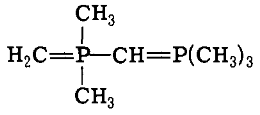
The compound **5** is one of the most air-sensitive compounds of the whole ylide series. Traces of air will immediately turn samples brown. Strict adherence to inert gas methods is necessary. The general chemical behavior of the ylide is characterized by a very strong basicity, which makes it a powerful deprotonating agent and a good nucleophile, and exceeds both the hexaphenyl analog and the simple monoylides.

Although there is no ambiguity about the structure of the hexaphenyl analog, in the case of **5** three isomers must be considered (**5**, **5a**, **5b**). The magnetic resonance spectra clearly indicate only the presence of **5**. Since prototropy has been demonstrated to be facile in ylide systems,[12] it follows that the "cumulated" (allene-type) ylide **5** is more stable than both the "conjugated" and the "isolated" double ylides **5a, b**.

Our results do not yet provide information on the valence angle at the central carbon atom in **5**, but a large angle

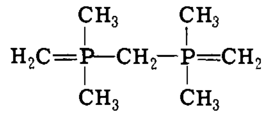
$(CH_3)_3P{=}C{=}P(CH_3)_3$

5



$$H_2C{=}\underset{CH_3}{\overset{CH_3}{P}}{-}CH{=}P(CH_3)_3$$

5a



$$H_2C{=}\underset{CH_3}{\overset{CH_3}{P}}{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{P}}{=}CH_2$$

5b

(>120°) is supposed to be essential for an effective delocalization of the high negative charge into the P-C-P π-system:

$$(CH_3)_3P{=}C{=}P(CH_3)_3 \longleftrightarrow \begin{matrix}(CH_3)_3\overset{+}{P}{-}\underline{C}^{-}{=}(CH_3)_3\\(CH_3)_3P{=}\underline{C}^{-}{-}\overset{+}{P}(CH_3)_3\end{matrix} \longleftrightarrow$$

$$(CH_3)_3\overset{+}{P}{-}\underline{C}^{2-}{-}\overset{+}{P}(CH_3)_3$$

Addition of excess ethereal hydrochloric acid to a solution of **5** in ether affords the bisphosphonium salt **6**, $[(CH_3)_3PCH_2P(CH_3)_3]Cl_2$, which is easily characterized. With 1 equiv of HCl only the monochloride **4** is obtained.

Other chemical reactions and the coordination chemistry of **5** are under investigation.

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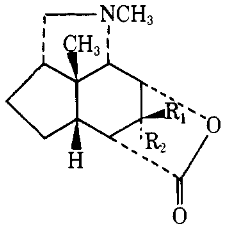
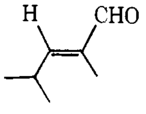
Diene Isomerization in a Diels-Alder Reaction. The Synthesis of 8-*epi*-Dendrobine

Sir:

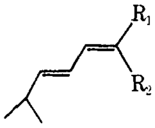
Dendrobine (**1a**) is representative of the unique lactone alkaloids produced by *Dendrobium nobile* Lindl, having both skeletal structure and pharmacological properties similar to those of picrotoxin.[1] Several total syntheses of dendrobine have been reported.[2] We now report the synthesis of an epimer of dendrobine (**1b**) resulting from diene isomerization in an intramolecular Diels-Alder reaction.



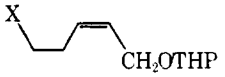
1a, $R_1 = CH(CH_3)_2$; $R_2 = H$
b, $R_1 = H$; $R_2 = CH(CH_3)_2$



2



3a, $R_1 = CH_3$; $R_2 = CH_2OH$
b, $R_1 = CH_3$; $R_2 = CHO$
c, $R_1 = CH_3$; $R_2 = CH_2CN$
d, $R_1 = CH_2OH$; $R_2 = CH_3$



4a, X = OH
b, X = Br
c, X = I

Directed aldol condensation[3] of isobutyraldehyde and ethylidene-*tert*-butylamine produced trans aldehyde **2** (50%). Sequential reaction of **3** at −70° with ethylidenetriphenylphosphine, butyllithium, and formaldehyde gas[4] gave a 16:1 mixture of dienols **3a** and **3d** (40%); assignment of configuration was based on a coupling constant of 14 Hz for the disubstituted double bond protons and a chemical shift for the aldehyde proton in **36** of 10.27 ppm as compared with 9.51 ppm for the aldehyde obtained from the minor isomer.[5] Reaction of **3a** with methyllithium-*p*-toluenesulfonyl chloride-lithium chloride[7] followed by heating the crude chloride with lithium iodide and cuprous cyanide ($HMPA-H_2O$, 60°, 16 hr) gave the corresponding nitrile **3c** (49%).

Alcohol **4a** was prepared in 54% yield by treating the sodium salt of propargyl THP ether with ethylene oxide, followed by Lindlar[8] reduction of the triple bond. Conversion of **4a** via **4b** (Ph_3PBr_2, pyridine, 83%) to the iodo compound **4c** (NaI, acetone, 88%) proceeded smoothly. Rapid addition of **4c** in HMPA-THF (−25°) to a solution of the anion of **3c** in THF at −25° (prepared from **3c** and lithium isopropylcyclohexylamide) afforded the triene **5a** in 80% yield following dry column chromatography. High pressure liquid chromatography (HPLC) showed that **5a** was homogeneous.

Hydrolysis of **5a** ($H_2SO_4-H_2O$, THF) gave the alcohol **5b** (56%) which was directly oxidized to aldehyde **5c** ($CrO_3\cdot$pyr, CH_2Cl_2, 84%).[9] HPLC analysis revealed that **5b** and **5c** were contaminated with ~15% of the trans allylic alcohol and trans aldehyde, respectively. Oxidation[10] of **5c** ($NaCN-AcOH-MnO_2$, MeOH) followed by preparative HPLC gave pure triene ester **5d** in 40% yield.

Reflux of **5d** in *o*-dichlorobenzene for 3 days afforded **6a** (25%) and **6b** (24%) after preparative HPLC. Configuration of the cyano group was assigned based on the chemical shift of the 7a-methyl group of the corresponding *N*-methyl amides[2b] (prepared by reaction of the nitrilium salt with water[10]). Thus the methyl group appears at 1.23 ppm in **6c** as compared with 0.97 ppm in **6d**, in accord with Inubushi's assignment of the upfield methyl group to the cis amide-methyl group configuration.[2b] Relative configuration of the remaining asymmetric centers was presumed to follow from the stereochemistry of the starting triene ester—a presump-