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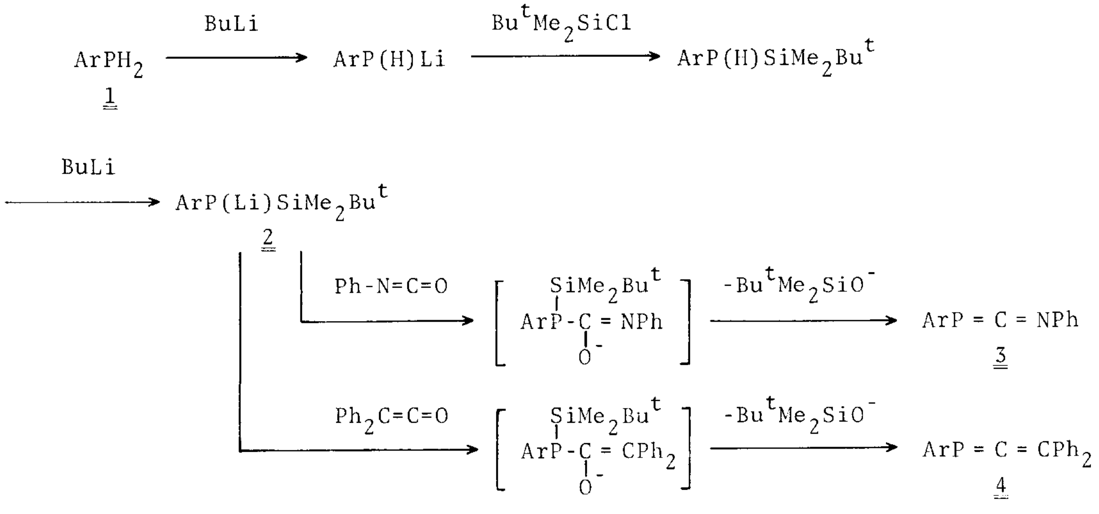
ISOLATION AND CHARACTERIZATION OF SOME VERY STABLE 1-PHOSPHA-ALLENES: STERICALLY PROTECTED IMINOMETHYLENE- AND ETHENYLIDENEPHOSPHINES

Masaaki Yoshifuji,* Kozo Toyota, Katsuhiro Shibayama, and Naoki Inamoto
Department of Chemistry, Faculty of Science, The University of
Tokyo, Hongo, Tokyo 113, Japan

Abstract: Very stable iminomethylenephosphine (**3**) and ethenylidenephosphine (**4**) were obtained by steric protection with the 2,4,6-tri-tert-butylphenyl group and some of the spectroscopic data are described.

The phosphorus compounds in low coordination state have been of current interest because of their unusual physicochemical properties. Very recently, Kolodiazhnyi, Wentrup et al., and Appel et al. reported the preparation and characterization of compounds with the -P=C=N-[1,2] and -P=C=O[3] groups. These reports prompt us to describe our preliminary results on the related 1-phospha-allene compounds which are well-sterically protected causing extraordinarily thermally stable and crystalline materials.

Our present report concerns the use of the 2,4,6-tri-tert-butylphenyl group attached on a phosphorus atom as a protective group for reactive sites. The reaction sequence for obtaining such compounds was as follows, as described for the preparation of similar methylenephosphines.[4]



(Ar = 2,4,6-$Bu^t_3C_6H_2$)

2,4,6-Tri-tert-butylphenylphosphine (1) was lithiated with butyllithium at -78 °C in THF, silylated with tert-butyldimethylsilyl chloride at room temperature, lithiated again with butyllithium at room temperature successively, and the reaction mixture was allowed to react with phenyl isocyanate at -78 °C to give an orange-red homogeneous solution. The solution was concentrated and chromatographed over silica-gel (hexane) to give yellow crystals of N-phenyl-P-(2,4,6-tri-tert-butylphenyl)iminomethylenephosphine (3) in 29% yield based on the phosphine 1, after recrystallization from pentane. 3: mp 90 - 92 °C; ^{1}H NMR ($CDCl_3$) δ 7.43 (d, $^4J_{PH}$ = 2.2 Hz, 2H, arom-Ar), 7.3 - 7.1 (m, 5H, Ph), 1.67 (s, 18H, o-Bu^t), and 1.30 (s, 9H, p-Bu^t); ^{31}P NMR ($CDCl_3$, from external 85% H_3PO_4) δ_P -106.2 ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 209.4 ppm (d, $^1J_{PC}$ = 27.4 Hz, P=C=N); IR (KBr) $\nu_{P=C=N}$ 1845 cm^{-1}; UV (hexane) λ_{max} (ε) 258 (32600), 288 (8700), and 415 nm (490); MS m/e 379 (M^+); Mol Wt (C_6H_6) 330.

The present heterocumulene (3) is very thermally stable, can be purified through column chromatography, and is monomeric even at room temperature, in contrast to those compounds reported by Wentrup et al., the dimerization of which starts to occur at -55 °C. Addition of water to 3 in $CDCl_3$ in an NMR sample tube did not cause any decomposition of the material, however, on standing for a few days some hydrolysis seemed to have occurred resulting 2,4,6-tri-tert-butylphenylphosphine oxide (δ_P -10.0 ppm, t, $^1J_{PH}$ = 490.7 Hz).[5]

The strong IR band at 1845 cm^{-1} seems to be characteristic for the asymmetric stretching vibration of the P=C=N group.[1,2]

The phosphorus NMR chemical shifts in low-coordination state normally show very low δ_P values, i.e., -P=P- (600 - 460 ppm),[6] -P=P(S)- (∿250 ppm),[7] -P=C< (270 - 120 ppm),[4,8] -P=N- (∿470 ppm),[9] -P=P(O)- (∿200 ppm),[10] -P=As- (670 - 530 ppm),[11] and so on. The unusual high-field chemical shift of 3 corresponds to those for the phosphides,[4] indicating a contribution of phosphide or unusual bonding character of the -P=C=N- moiety. Similar high-field chemical shift was recently reported for t-Bu-P=C=O (δ_P -180 ppm, -90 °C) as a reaction intermediate.[3]

Very similarly, the silylated phosphide 2 was allowed to react with diphenylketene to give 2,2-diphenylethenylidene-P-(2,4,6-tri-tert-butylphenyl)phosphine (4) in 58% yield based on the phosphine 1 as colorless crystals. The 1-phospha-allene of this type was obtained for the first time as a stable compound. 4: mp 160 - 161.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.39 (d, $^4J_{PH}$ = 1.8 Hz, 2H, arom-Ar), 7.24 (s, 10H, Ph), 1.50 (s, 18H, o-Bu^t), and 1.32 (s, 9H, p-Bu^t); ^{31}P NMR ($CDCl_3$) δ_P 72.1 ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 237.6 (d, $^1J_{PC}$ = 26.6 Hz, P=C=C) and 128.3 ppm (d, $^2J_{PC}$ = 6.4 Hz, P=C=C); UV (hexane) λ_{max} (ε) 242 (30000), 263 (27300), and 337 nm (4100); MS m/e 454 (M^+); Mol Wt (C_6H_6) 457.

The phospha-allene 4 thus obtained is extraordinarily stable toward heat, light and atmospheric moisture or oxygen.

Compared with those compounds with the -P=C< moiety,[4,8] the observed phosphorus chemical shift of 4 was not extremely low.

The ^{13}C chemical shift of the central carbon of the hetero-cumulene for 4 appeared at very low field as expectedly, however, the observed spin-spin coupling constants between the phosphorus atom and carbon atoms through one and two bonds were unexpectedly small.

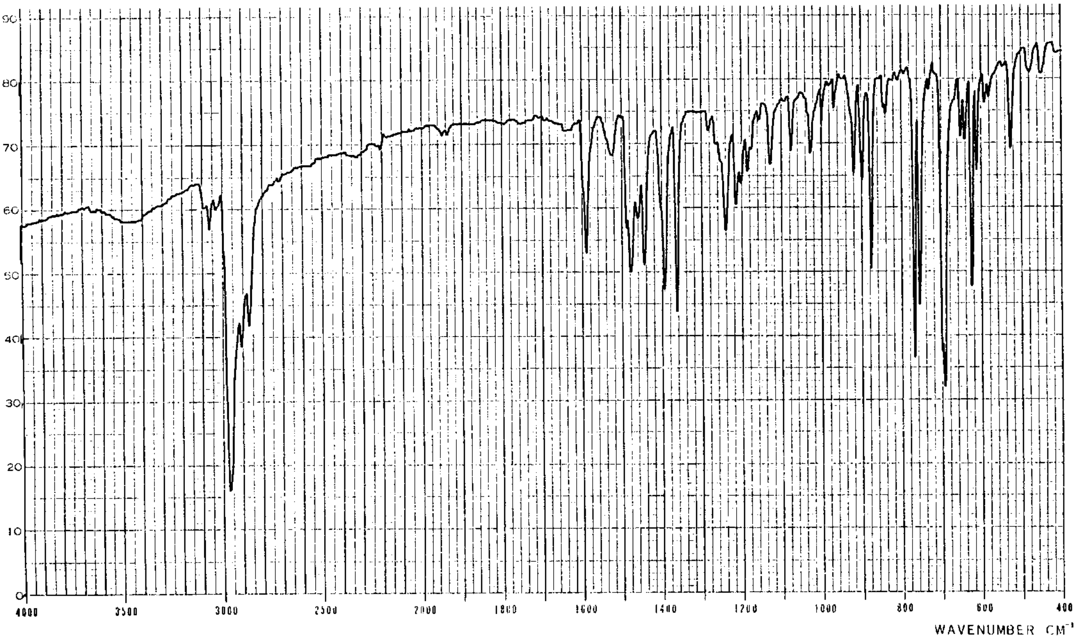


Figure 1. IR (KBr) of Ar-P = C = CPh_2 (4)

In contrast to the IR spectrum of 3, 4 showed no significant bands in the 1600 - 2300 cm^{-1} region (Fig.1), where many antisymmetric X=C=Y stretchings are observed.[12] It might be said that there is only little, if any, contribution of 4A form in 4, whereas in 3 there is fairly large contribution of dipolar form of 3A which may give rise to a high IR intensity of the X=C=Y stretching. These assumptions interpret both results of ^{31}P NMR chemical shifts and IR data. The assignments of the characteristic IR frequencies of the P=C=C group should be reserved for further investigation.

$$\underset{3}{-P=C=N-} \leftrightarrow \underset{3A}{-P^{-}-C\equiv N^{+}-} \qquad \underset{4}{-P=C=C<} \leftrightarrow \underset{4A}{-P^{+}\equiv C-C^{-}<}$$

The crystal structures of both 3 and 4 are quite of interest theoretically and the X-ray analyses are in progress now.

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