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A CONVENIENT NEW ROUTE FROM DIPHOSPHENE TO 1,3-DIPHOSPHA-ALLENE AND DYNAMIC NMR STUDIES OF THE 2,4,6-TRI-t-BUTYLPHENYL DERIVATIVE

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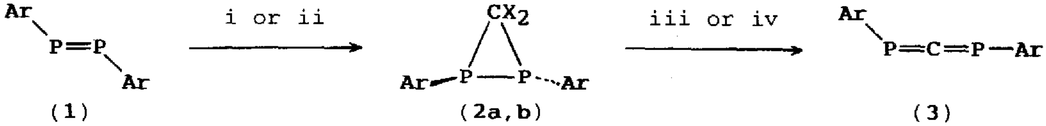
Abstract: Addition of dihalocarbenes to a diphosphene gave diphosphiranes which undergo rearrangement on treatment with alkyllithium reagents to afford 1,3-diphospha-allene; dynamic NMR studies on the allene are described.

1,3-Diphospha-allene is a new type of unusual organophosphorus compound of a cumulene frame having two phosphorus atoms in low coordination state protected by steric bulkiness. We have reported the first preparation and characterization of 1,3-bis(2,4,6-tri-t-butylphenyl)-1,3-diphospha-allene (**3**)1) via silyloxyphosphinophospha-ethylene.2) Karsch3) and Appel4) also reported the other preparative methods for **3**.

We now report a new convenient method for **3** from the E-diphosphene **1**.5) Our present method involves addition of dihalocarbenes6) to the P=P double bond of the diphosphene **1**, followed by ring opening of the resulting diphosphiranes **2** with alkyllithium reagents. The latter ring opening reactions have often been used for the preparation of allenes.7,8) The diphosphirane **2a** (0.0761 mmol) in 4.5 ml of ether (δ_P -69.5) was allowed to react with methyllithium (0.107 mmol) in ether (0.1 ml) at -78 °C and was immediately warmed up to room temperature with stirring for 45 min to give 62% yield of pure **3** (δ_P 141.7) after column chromatography (silica gel, pentane). The whole process could be carried out in a "one-pot" manner without isolation of **2**. For example, in the case of dibromodiphosphirane, **2b** (δ_P -70.3) was not purified for the further reaction using THF as a solvent and butyllithium in hexane was used for the final step to give 20% yield of **3** with 76% recovery of the diphosphene **1** after chromatographic separation. All spectral data including ^1H, ^{13}C, ^{31}P NMR and MS of **3** thus obtained were identical with those of an authentic sample.1)

We have observed racemization of **3** around the P=C=P axis9) with a mercury



Ar = 2,4,6-$Bu^t{}_3C_6H_2$; **a**: X=Cl, **b**: X=Br. Reagents: i, $CHCl_3$ + $KOBu^t$ or Bu^nLi; ii, $CHBr_3$ + $KOBu^t$ or CBr_4 + Bu^nLi; iii, MeLi; iv, Bu^nLi.

lamp and intramolecular cyclization reaction2) on heating in boiling toluene. We were successful in the first observation on the internal rotation about the P-C_{Ar} bond of this particular compound **3**. ^{1}H NMR spectra of 3 in $CDCl_3$ were obtained on a JEOL GX-270 at 270.166 MHz between at -60.0 and 56.7 °C. At -60.0 °C, o-t-butyl groups appeared as two singlets at δ 1.60 and 1.10 together with that of p-t-butyl at δ 1.29 in almost equal intensities. At 24 °C the o-t-butyl signals started to coalesce and finally at 56.7 °C they became a broad singlet at δ 1.36 whereas the signal due to p-t-butyl remained constant in shape as a sharp singlet at δ 1.29 during the temperature range mentioned above. By the method of line shape analysis,10) the rate constants (k) were obtained for the internal rotation about the P-C_{Ar} bond.11) From the plot of ln(k/T) vs. 1/T, at 8 different temperatures between 0.0 and 56.7 °C, the activation parameters are as follows (correlation factor for the Eyring plot r = 0.9998): $\Delta H^{\dagger}_{273}$ = 12.3 ± 0.2 kcal/mol and $\Delta S^{\dagger}_{273}$ = -6.4 ± 0.8 e.u. The first order rate constant k is 30.4 s^{-1} at 0 °C. Taking the Dreiding stereomodel of **3** into account, the two adjacent bulky aryl groups with o-t-butyl cogs might correlate each other to rotate in a gear mode.12)

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