(2,4-DI-(TERT-BUTYL)-6-METHYLPHENYL)DITHIOPHOSPHORANE

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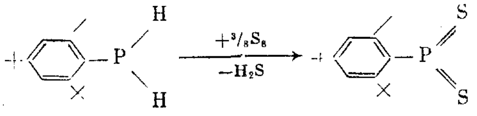
Use of the 2,4-di-(tert-butyl)-6-methylphenyl radical permits stabilization of the corresponding dithiophosphorane (I). The analogous diselenophosphorane could not be detected as the monomer. This compound undergoes intramolecular addition of the C—H bond of the ortho-tert-butyl group at the P=Se bond with formation of the corresponding diselenophosphonic acid (III). Intermediate selenophosphine oxide (IV) was trapped as its salt with triethylamine (V).

One of the most successful methods for stabilization of phosphorus compounds in an unusual coordination involves the introduction of two tert-butyl groups in the ortho positions in aryl phosphorus compounds (kinetic stabilization principle). Dithiophosphorane [1] and diselenophosphorane [2] were obtained for the first time by this method.

It was of interest to study the requirement of two o-tert-butyl groups for stabilization of the compounds indicated above and the effect of a decrease in the steric hindrance on the stabilization.

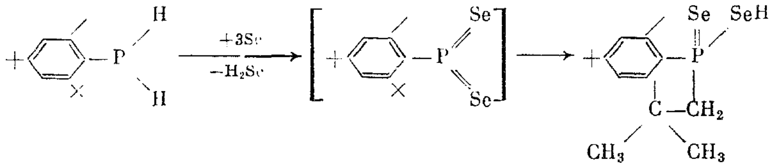
For this purpose, we used an arylphosphine, in which one O-tert-butyl group is replaced by a methyl group, for the synthesis of a monomeric dithiophosphorane. (2,4-Di-(tert-butyl)-6-methylphenyl)dithiophosphorane (I) was obtained by analogy to the work of Navech et al. [3]



(I)

Phosphorane (I) was obtained in quantitative yield as a bright orange, hygroscopic solid. The ^{31}P NMR spectrum shows a chemical shift (CS) at 285.2 ppm. This downfield value of the CS is characteristic for such compounds with a tricoordinated, pentavalent phosphorus atom [4]. The electron impact mass spectrum of (I) shows a molecular ion peak with m/z 298. Phosphorane (I) may be stored for months in an argon atmosphere.

Thus, the replacement of one o-tert-butyl group by a methyl group does not affect the stabilization of dithiophosphorane. However, this substitution is significant for stabilization of the corresponding diselenophosphorane (II). We did not detect (II) in reaction mixtures obtained in attempts to synthesize this compound.



(II) (III)

Intermediate diselenophosphorane (II) apparently undergoes intramolecular addition of the C—H bond of one of the methyl groups of the ortho-tert-butyl fragment at the P=Se bond with formation of the corresponding diselenophosphonic acid (III). Similar intramolecular

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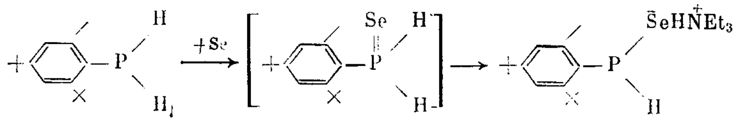
reactions have been studied extensively for dithiophosphoranes [5,6]. A singlet at 78.3 ppm is observed in the ^{31}P NMR spectrum of (III) in o-$Cl_2C_6H_4$. This value is close to that observed for analogous dithio derivatives: 76.1 (CH_2Cl_2) [5] and 75.0 ppm (CH_2Cl_2) [6]. The PMR spectrum of (III) in $CDCl_3$ displays two methyl groups as a singlet at 1.73 ppm and methylene group at 2.53 ppm as a multiplet instead of an O-tert-butyl group. The ortho-methyl group is seen as a singlet at 2.23 ppm.

If the reaction of selenium with (2,4-di-(tert-butyl)-6-methylphenyl)phosphine is carried out in triethylamine, intermediate selenophosphine oxide (IV) may be trapped as its salt with triethylamine (V).



(IV) (V)

The ^{31}P NMR spectrum of (V) shows a signal at −41.6 ppm with $^1J_{PH}$ = 472.5 Hz. The IR spectrum has a band at 2710 cm^{-1}, characteristic for the R_3HN^+ group.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a Bruker M-250 spectrometer, while the PMR spectra were taken on a Varian T-60 spectrometer. The IR spectra were taken on a UR-20 spectrometer. The mass spectra were taken on an MKh-1310 mass spectrometer, μ = 70 eV with precise measurement of the ion masses. All the operations were carried out in argon.

(2,4-Di-(tert-butyl)-6-methylphenyl)dithiophosphorane (I). A mixture of 2.63 g (0.011 mole) (2,4-di-(tert-butyl)-6-methylphenyl)phosphine [7] and 1.06 g (0.033 mole) sulfur in 10 ml toluene was heated at reflux for 40 min. The solvent was then evaporated in vacuum and 20 ml hexane was added. Unreacted sulfur was filtered off and hexane was removed in vacuum. The residue crystallized upon standing. The crystals were filtered off to give 3.12 g (94%) (I), mp 87-88°C. ^{31}P NMR spectrum in toluene: 285.2 ppm, m/z 298 (25%). Found: P, 10.24%. Calculated for $C_{15}H_{23}PS_2$: P, 10.40%.

1,2-(3-Methyl-5-tert-butylbenzo)-5,5-dimethyl-Δ^1-3-hydroseleno-3-phospholene-3-selenone (III). A mixture of 2.52 g (0.011 mole) (2,4-di(tert-butyl)-6-methylphenyl)-phosphine and 2.8 g (0.035) mole selenium in 10 ml toluene was heated at reflux for 12 h. The precipitate formed was separated from selenium. The yield of (III) was 1.47 g (34%). In an attempt to determine the melting point of this compound, it was found to decompose at 145°C. ^{31}P NMR spectrum in o-$Cl_2C_6H_4$: 78.3 ppm. PMR spectrum in $CDCl_3$ (δ, ppm): 1.33 s (9H, p-t-Bu), 1.73 s (6H, CH_3 at C^4), 2.52 s (3H, o-CH_3), 2.53 m (2H, CH_2 at C^5), 6.97-7.25 m (2H, aromatic protons). Found: P, 7.4%. Calculated for $C_{15}H_{23}PSe_2$: P, 7.87%.

Triethylammonio-(2,4-di-(tert-butyl)-6-methylphenyl)phosphine Selenoxide (V). A sample of 2.85 g (0.035 mole) selenium was added to 2.84 g (0.012 mole) (2,4-di-(tert-butyl)-6-methylphenyl)phosphine in 10 ml triethylamine. After 24 h, the white precipitate formed was separated from selenium to give 3.2 g (64%) (V), mp 173°C (dec.). ^{31}P NMR spectrum: −41.6 ppm, $^1J_{PH}$ = 472.5 Hz. Found: N, 3.3%. Calculated for $C_{21}H_{40}NPSe$: N, 3.36%.

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