

NOTE

THE CLEAVAGE OF TETRAHYDROFURAN BY LITHIUM DIMETHYLPHOSPHIDE

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Issleib and Tzschach¹ have reported that lithium diethylphosphide, $\text{Li}^+[(\text{C}_2\text{H}_5)_2\text{P}]^-$ decomposes when allowed to remain in contact for long periods of time with tetrahydrofuran to give a yellow, uncharacterized product. In contrast to these results, Hewertson and Watson² suggested that lithium diethylphosphide does not undergo a chemical reaction with tetrahydrofuran, but that the solvent causes ionization of the Li-P bond. We have found that lithium dimethylphosphide, in apparent contrast to the results reported for lithium diethylphosphide², undergoes a fairly rapid, nearly quantitative reaction with tetrahydrofuran to give $(\text{CH}_3)_2\text{PCH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{O}^-\text{Li}^+$. This compound was not characterized, but was further allowed to interact with trimethylchlorosilane, to give $(\text{CH}_3)_2\text{P}(\text{CH}_2)_4\text{OSi}(\text{CH}_3)_3$ in 91% yield.

EXPERIMENTAL

Infrared spectra were obtained on pure liquid films using a Perkin-Elmer 237 B spectrophotometer. The ¹H NMR spectra were taken in benzene as solvent with tetramethylsilane as an internal reference using a Varian A-60 spectrophotometer. The ³¹P NMR spectra were obtained on a Varian HA-100 NMR spectrometer with 85% H_3PO_4 as an external reference.

All reactions were carried out under an atmosphere of dry, oxygen free nitrogen.

Tetramethyldiphosphine was prepared according to the method of Maier³, by heating tetramethyldiphosphine disulfide⁴ with tributylphosphine.

In a manner almost identical to the procedure described for the preparation of lithium diethylphosphide², a mixture of 10.9 g (0.089 moles) of tetramethyldiphosphine and 1.84 g (0.267 moles) of lithium metal were refluxed in 100 ml of tetrahydrofuran. The color of the mixture became bright yellow. After heating for 6 h, excess lithium was removed by filtration. A 28.9 g (0.267 moles) sample of trimethylchlorosilane dissolved in 50 ml of tetrahydrofuran was then added drop by drop to the filtered mixture. This resulting mixture was then heated until refluxing for an additional 30 minutes to insure completion of the reaction. It was filtered and the solvent was removed by distillation at atmospheric pressure. The remaining liquid was fractionally distilled at 20 mm pressure. A 33 g fraction was isolated which boiled at 108°. Analysis by GLPC indicated the purity of this fraction to be greater than 99%.

Characterization of this product showed it to be $(\text{CH}_3)_2\text{P}(\text{CH}_2)_4\text{OSi}(\text{CH}_3)_3$, (yield, 91%). The infrared spectrum displays the expected absorptions for the molecule $(\text{CH}_3)_3\text{SiO}(\text{CH}_2)_4\text{P}(\text{CH}_3)_2$. A strong peak at 1250 cm^{-1} may be assigned to a symmetric C-H deformation characteristic of Si-CH₃. Another very strong peak at 1100 cm^{-1} is assigned to C-O stretch⁵ characteristic of SiOC, other absorptions were recorded at (cm^{-1} , intensity): 2950, 2890, 2850 vs; 2800, 2725, 1475, 1450 w; 1425 m; 1375 w; 1285 m; 1050 s; 1000 w; 965 m; 935, 900 s; 875, 850 vs; 750 s; 710 m.

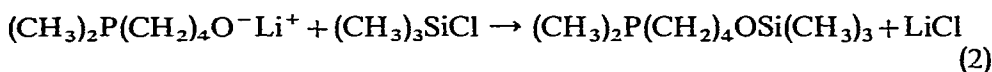
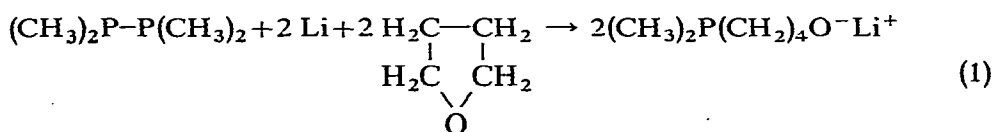
The ¹H NMR spectrum showed a peak at $\delta -0.08$ ppm which was assigned to the methyl protons on silicon, a doublet ($J(\text{PH})=2.5$ cps) which was assigned to methyl protons on phosphorus at $\delta -0.87$ ppm, broad peaks at $\delta -1.42$ ppm were assigned to the methylene protons attached to phosphorus and broad peaks at $\delta -3.58$ ppm which were assigned to the methylene protons attached to oxygen. Integration gave a ratio of the methyl protons on silicon to the methyl protons of phosphorus of 3.0:2.0. The ³¹P NMR spectrum showed a single absorption at $\delta +53.6$ ppm relative to H_3PO_4 .

Analysis: Found: C, 52.30; H, 11.08; P, 14.79; mol.wt. 226 (by vapor pressure osmometry in benzene. $\text{C}_9\text{H}_{23}\text{PSiO}$ calcd.: C, 52.40; H, 11.16; P, 15.04; mol.wt. 206.

DISCUSSION

Although both SiOC and POC have absorptions at 1100 cm^{-1} the ³¹P NMR and ¹H NMR showed definitely that the compound was of the type R_2PC instead of R_2POC . Compounds of the latter type have ³¹P chemical shifts in the region of -100 ppm relative to H_3PO_4 ⁶ and ¹H chemical shifts at about -1 ppm with coupling constants of about 7 cps⁷, whereas compounds of the former type have ³¹P chemical shifts in the region of $+50$ ppm and ¹H chemical shifts around -0.9 ppm with coupling constants around 2.8 cps. Therefore the band at 1100 cm^{-1} can be assigned to SiOC and indicates the formula of the compound to be $(\text{CH}_3)_3\text{SiO}(\text{CH}_2)_4\text{P}(\text{CH}_3)_2$.

The reactions which were observed may be described according to the equations



The cleavage of dioxane by lithium diphenylphosphide has been suggested previously⁸. In a similar manner, it has been shown that alkyl- and arylphosphides can cleave ethylene oxide⁹, and other cyclic ethers¹⁰. Also, it has been shown that while $\text{Li}^+[\text{AsR}_2]^-$ will convert tetrahydrofuran to $\text{R}_2\text{As}(\text{CH}_2)_4\text{OH}$ after hydrolysis¹¹, no such reaction will occur with $\text{Li}^+[(\text{cyclo-C}_6\text{H}_{11})_2\text{P}]^-$, even after refluxing the mixture for days¹⁰. This report of the cleavage of tetrahydrofuran by lithium dimethylphosphide is the first substantiated reported of such a reaction.

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