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Abstract

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ON THE ADDITION OF LITHIUM DIALKYLPHOSPHIDES TO VINYLACETYLENE HYDROCARBONS

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It had previously been established that lithium dialkylamides add to vinylacetylene hydrocarbons with the formation, after treatment of the adducts with water, of allenic or acetylenic amines (^{1}).

To elucidate the behavior, under the same conditions, of other compounds of the type R_2E—Li, where E is an element of group V of the periodic system, we studied the reactions of vinylacetylene and of two of its homologs–vinylmethyl- and vinylethylacetylenes–with lithium diethyl- and lithium dibutylphosphides.

Lithium dialkylphosphides were first obtained in 1959 by the action of lithium phenyl on dialkylphosphines (^{2}). Of the reactions of these compounds, only their interaction with aromatic ketones has been described (^{3}).

As a result of the addition of lithium dialkylphosphides to vinylacetylene hydrocarbons, one might have expected the formation of acetylenic, allenic, or 1,3-diene tertiary phosphines. Since in all cases studied up to the present, in the reactions of vinylacetylenes with lithium alkyls (^{4}) and lithium amides (^{1}), the radical always adds to the terminal atom of the conjugated system, the most probable products were phosphines of normal structure (I), (II), and (III, with R = H).

$$R—C \equiv C—CH_2—CH_2—PR_2, \tag{I}$$

$$R—CH = C = CH—CH_2—PR_2, \tag{II}$$

$$R—CH = CH—CH = CH—PR_2. \tag{III}$$

In reality, the addition of lithium phosphides to vinylacetylene proceeded in all three possible directions, whereas in the case of vinylmethyl- and vinylethylacetylenes exclusively, or almost exclusively, allenic tertiary phosphines (II) were obtained.

Fig. 1. IR transmission spectra: 1 —phosphine from vinylacetylene; 2 —1-diethylphosphinopentadiene-2,3; 3 —1-diethylphosphinohexadiene-2,3; 4 —1-dibutylphosphinohexadiene-2,3; 5 —tributylphosphine

Figure 1: Fig. 1. IR transmission spectra: 1 —phosphine from vinylacetylene; 2 —1-diethylphosphinopentadiene-2,3; 3 —1-diethylphosphinohexadiene-2,3; 4 —1-dibutylphosphinohexadiene-2,3; 5 —tributylphosphine

The tertiary phosphine obtained by treating with water the adduct of lithium dibutylphosphide to vinylacetylene undoubtedly contained 1-dibutylphosphinobutyne-3 (I, R = H). Its infrared spectrum showed the characteristic frequencies of a terminal acetylenic group (2120 and 3318 cm^{-1}), together with the frequencies of allenic (1960 and 905 cm^{-1}) and 1,3-diene (1560–1600, 3083 cm^{-1}) groupings. By the usual determination (^{5}), about 40% of acetylene (I) was found in it. However, the substance was not a pure phosphine.

The acetylenic phosphine (I, R = H) could have been formed as a result of 3,4-addition of the lithium dialkylphosphide (at the double bond), or as a result of isomerization of the allenic adduct (II, R = H). It is also possible that addition of the lithium dialkylphosphide occurs not to free vinylacetylene, but to lithium acetylide. In that case, addition of a second lithium atom to the same carbon atom is unlikely.

In the infrared spectra of the tertiary phosphines obtained from vinylmethyl- and vinylethylacetylenes in about 35% yield, there were intense frequencies characteristic of an allenic grouping (about 1960 and 870 cm^{-1}, curves 2–4). The frequencies of the acetylenic bond were completely absent from the spectra; the frequencies of the conjugated system of double bonds were either absent or were very weak and doubtful. Most likely they···

belonged to phosphines of type (III), formed as a result of isomerization of adducts of type (II).

It is noteworthy that vinylmethyl- and vinylethylacetylenes behave identically in the reaction with lithium phosphides. Meanwhile, under the action of lithium dialkylamides, vinylethylacetylene also gave allene adducts, whereas vinylmethylacetylene gave chiefly dimer and polymers.

Fig. 1. IR transmission spectra: 1 —phosphine from vinylacetylene; 2 —1-diethylphosphinopentadiene-2,3; 3 —1-diethylphosphinohexadiene-2,3; 4 —1-dibutylphosphinohexadiene-2,3; 5 —tributylphosphine.

Along with tertiary phosphines, in all cases higher-boiling products containing phosphorus are formed in significant amounts. Details—

but we did not study them; however, we believe that they are higher telomers of the phosphines isolated by us. We observed similar telomerization in the reaction of amines with vinylacetylene (^{1}).

In the course of the investigation it was established that lithium dialkylphosphides readily react with halogen derivatives to form unsaturated tertiary phosphines. This reaction had not previously been carried out with lithium dialkylphosphides, although it is known that lithium phosphide readily forms primary phosphines with halogen derivatives (^{6}). By the action of lithium diethylphosphide on butyl chloride we obtained diethylbutylphosphine; similarly, tributylphosphine was obtained from lithium dibutylphosphide and butyl chloride.

The indicated property of lithium dialkylphosphides compelled us to pay special attention to ensuring that, in the preparation of the lithium alkyls used by us for the synthesis of lithium dialkylphosphides, unreacted alkyl chloride did not remain.

Phosphines with an allenic grouping are described for the first time. In general, there are few data in the literature on the chemistry of unsaturated phosphines. For example, trivinyl- and triallylphosphines are known, as are phosphines with unsaturated or aryl and allyl radicals ($^{7-9}$). All of them were obtained from phosphorus chlorides and organometallic compounds. Literature data on reactions of addition of phosphines and phosphites to unsaturated hydrocarbons are likewise not numerous.

The allenic tertiary phosphines obtained by us were fairly mobile colorless liquids with an odor characteristic of phosphines. They showed exaltation of molecular refraction. In air they rapidly oxidized and resinified, acquiring a brown color; in an argon atmosphere they remain unchanged for a long time. We were unable to hydrogenate them over palladium.

Experimental Part

Lithium dialkylphosphides were prepared by the interaction of equivalent amounts of butyllithium (^{13}) and dialkylphosphines in ether. The dialkylphosphines were obtained by reduction with lithium aluminum hydride of the products of interaction of phosphorus thiochloride with magnesium bromoalkyls (^{14}). In contrast to the procedure indicated above (^{12}), we did not isolate the product of interaction of phosphorus thiochloride with magnesium bromobutyl, but subjected the entire reaction mixture to reduction, after decomposition of the organomagnesium complex with water and drying it over $CaCl_2$.

To 75 ml of an ethereal solution of butyllithium (0.08–0.1 g-mole), with mechanical stirring, was added a solution of the dialkylphosphine (0.08 g-mole in 25 ml of ether), and after 30 min the corresponding hydrocarbon (0.08 g-mole) was introduced dropwise into the resulting solution of lithium dialkylphosphide. Warming and yellowing of the mixture were observed. After stirring for 30 min the mixture was poured into ice water. The ethereal solution of phosphines, separated from the aqueous layer and dried, was subjected to distillation. The phosphines were usually distilled within narrow limits (1°). All work was carried out in an argon atmosphere.

Addition of lithium dibutylphosphide to vinylacetylene. From the above-mentioned amounts of reagents, 1.6 g (10%) of phosphine and 2.5 g of polymers were obtained. Phosphine (1-dibutylphosphinobutyne-3 with impurities). B.p. 95-96°/5 mm, d_4^{20} 0.8448; n_D^{20} 1.4830.

Found, %: C 73.85; 73.92; H 12.17; 12.08; P 13.20
$C_{12}H_{23}P$. Calculated, %: C 72.68; H 11.69; P 15.62

IR spectrum: 725 medium, 783 medium, 905 strong, 966 weak, 1005 medium, 1035 weak, 1052 weak, 1094 weak, 1200 weak, 1281 weak, 1339 weak, 1376 medium, 1415 medium, 1460 strong, 1563-1600 weak, 1816 weak, 1960 very weak, 2120 weak, 2860 very strong, 2873 very strong, 2927 very strong, 2957 very strong, 3083 weak, 3318 strong cm^{-1}.

Addition of lithium diethylphosphide to vinylmethylacetylene. 4.5 g of phosphine and 4.5 g of residue were obtained. 1-Diethylphosphinopentadiene-2,3. B.p. 60–61°/5 mm, d_4^{20} 0.8697; n_D^{20} 1.5050. *MR* found 54.01; calculated 53.07.

Found %:	C 69.50; 69.05; H 11.16; 10.98; P 19.49; 19.22
$C_9H_{17}P$. Calculated %:	C 69.20; H 10.97; P 19.83

IR spectrum: 720 s., 745 s., 786 med., 862 v.s., 975 s., 997 s., 1025 s., 1060 w., 1134 w., 1180 w., 1234 med., 1281 s., 1368 s., 1415 s., 1455 v.s., 1965 s. cm^{-1}.

Addition of lithium diethylphosphide to vinylethylacetylene. 4.6 g of phosphine and 7.3 g of residue were obtained. 1-Diethylphosphinohexadiene-2,3. B.p. 78–79°/5 mm, d_4^{20} 0.8569, n_D^{20} 1.5025. *MR* found 58.78; calculated 57.69.

Found %:	C 70.74; 70.30; H 11.23; 11.34; P 18.10; 17.95
$C_{10}H_{19}P$. Calculated %:	C 70.55; H 11.25; P 18.20

IR spectrum: 730 med., 763 s., 818 med., 855 w., 876 v.s., 950 w., 993 w., 1036 med., 1067 med., 1140 w., 1185 med., 1240 med., 1282 med., 1325 med., 1378 med., 1414 med., 1458 v.s., 1648 w., 1955 s. cm^{-1}.

Addition of lithium dibutylphosphide to vinylethylacetylene. 5 g of phosphine and 7.5 g of residue were obtained. 1-Dibutylphosphinohexadiene-2,3. B.p. 125–126°/5 mm, d_4^{20} 0.8534; n_D^{20} 1.4952. *MR* found 77.38; calculated 76.16.

Found %:	C 73.88; 74.69; H 11.96; 12.39 P 13.24; 13.06
$C_{14}H_{27}P$. Calculated %:	C 74.29; H 12.02; P 13.69

IR spectrum: 724 v.s., 782 s., 818 s., 876 v.s., 895 s., 965 s., 987 s., 1019 w., 1037 med., 1065 med., 1091 med., 1139 w., 1180 med., 1198 med., 1225 w., 1278 s., 1324 med., 1340 w., 1378 s., 1410 s., 1445 s., 1465 s., 1648 w., 1955 s. cm^{-1}.

Preparation of trialkylphosphines. By the action of an ethereal solution of butyl chloride on an ethereal solution of lithium diethylphosphide, diethylbutylphosphine was obtained in 60% yield. B.p. 41–42°/5 mm, 106–107°/100 mm, d_4^{20} 0.8094; n_D^{20} 1.4600, which agrees with the literature data (15). Tributylphosphine was obtained in an analogous manner. B.p. 96–97°/5 mm, 135.5–136°/32 mm, 146–147°/50 mm, d_4^{20} 0.8191; n_D^{20} 1.4632, which also agrees with the literature data (16).

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