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SYNTHESIS AND REACTIVITY OF NEW ORGANOPHOSPHORUS COMPOUNDS

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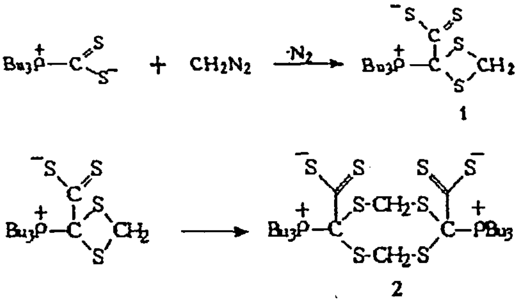
Abstract Synthesis of functionally substituted organophosphorus compounds on the basis of reactions of the tri-n-butylphosphine/carbon disulfide, tri-n-butylphosphine/phenylisothiocyanate, tris(dimethylamino)phosphine/phenylisothiocyanate adducts with a wide range of different dipolarophiles are reported. The development of application of S-Li tri-n-butylphosphonio-dithioformiate derivatives to the synthesis of new types of organophosphorus compounds are reported.

In 1861 A.W.Hofmann reported on the violently exothermic reaction between the newly discovered trialkylphosphines and carbon disulfide to give red crystalline adducts. Over the succeeding century the chemistry of this class of compounds was little studied. In 1971 Hartzler[1] reported on the formation of 2-alkylidene-1,3-dithioles as a result of interaction of the tributylphosphoniodithiofor-miate adduct with acetylene carbo-xylate in the presence of aromatic aldehyde. Cava[2] reported that the intermediate ilide can be stabilized by formation of stable phosphonium salt, if the reaction is carried out in the presence of absolute HBF. In 1992 the papers of R.A.Aitken[3] appeared on the reactions of the phosphoniodithioformiate cycloaddition to 1,3-dipolarophiles.

We have undertaken a detailed study of the cycloaddition reactions of adducts with a wide range of different dipolarophile. Reaction of diazomethane with tributylphosphoniodithioformiate proceeds at temperatures from 0 C to room temperatures for several minutes. The data NMR ^{31}P (48 ppm), ^{13}C (235 ppm CSS, 94 ppm P=C, 75 ppm CH_2). IR (1045 cm^{-1}, CSS$^-$) may correspond both to monomeric (1) or dimeric (2) products, but its molecular weight corresponds to dimeric form (2):



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Reaction of tributylphosphoniodithioformiate with diazomethane at temperatures from -40 C to -20 C give somewhat different results. Yellow noncrystallizing oil is formed. In the NMR ^{31}P spectrum two signals are observed at +48 ppm similar to phosphonium salt (2) and at +44 ppm with the ratio 2:1. Obviously the latter signal may be assigned to phosphonium ylide (3) which most probably has also a dimeric form (4):

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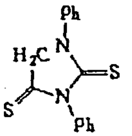
The reaction of tributylphosphoniophenylisothiocyanate with diazomethane proceeds differently from dithioformiate derivative. Nonphosphorus product (5) was isolated from the reaction mixture.



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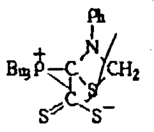

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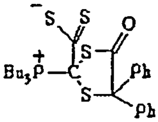
The remaining reaction mixture is a yellow viscous oil containing two compounds with the chemical shifts of +52 (tributylphosphineazine) and +49 ppm (phosphonium salt (6)) in the ratio 10:1.

Interaction of diphenylketene with tributylphosphoniodithioformiate preceeds analogously as interaction of diazomethane. Reaction proceeds at room temperature in several minutes. According to NMR ^{31}P and ^{13}C and IR spectroscopy the mixture of four phosphorus containing compounds is formed. These are phophonium salt (7) (+44 ppm), ylide (8), (+34 ppm), phosphonium salt (9) (+48 ppm) and tributylphosphine oxide.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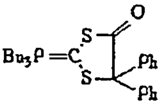
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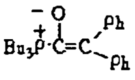
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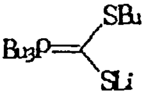
In both cases with diazomethane and diphenylketene, the formed ylides may serve as good Wittig reagents for formation of heterocyclic structures.

Analysis of literature shows that the interest to metallated phosphorus ylides is explained by their synthetic potential, by the possibility to regulate stereochemical aspects of Wittig reaction with aldehydes and ketenes.

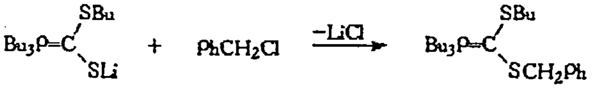
Interaction of tributylphosphoniodithioformiate with butyllithium easily proceeds at temperatures from -70 to -40 C in several minutes. The reaction mixture shows one ^{31}P phosphorus signal at +40 ppm corresponding to phosphonium ylides. The obtained lithium derivative of tributylphosphoniodithioformiate is highly reactive, thus afterwards it was studied in situ without its isolation from the solution.



$$Bu_3P{=}C(SBu)(SLi)$$

Our further study deals with synthetic application of the above lithium ylide.

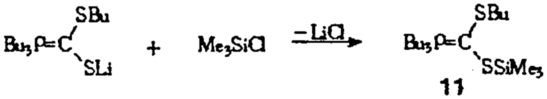
Interaction of benzyle chloride with Li-ylide proceeds at -20 C with formation of the single product, transparent colorless oil, dithioalkyidenphosphorane (10) with the chemical shift +32.5 ppm.



$$Bu_3P{=}C(SBu)(SLi) + PhCH_2Cl \xrightarrow{-LiCl} Bu_3P{=}C(SBu)(SCH_2Ph)$$

10

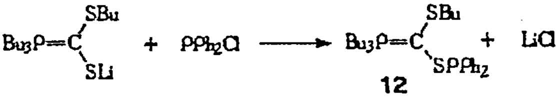
Interaction of lithium Li-ylide with trimethylchlorosilane gives ylide (11) with a quantitative yield, which is yellow liquid oil.



$$Bu_3P{=}C(SBu)(SLi) + Me_3SiCl \xrightarrow{-LiCl} Bu_3P{=}C(SBu)(SSiMe_3)$$

11

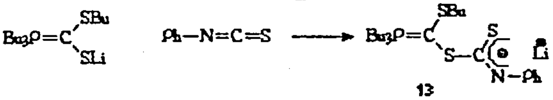
Reaction of Li-ylide with diphenylchlorophosphine results in formation of phosphonium ylide (12) with the yield 90% containing trivalent phosphorus atom, (δ_P 49 ppm, 28 ppm)



$$Bu_3P{=}C(SBu)(SLi) + PPh_2Cl \longrightarrow Bu_3P{=}C(SBu)(SPPh_2) + LiCl$$

12

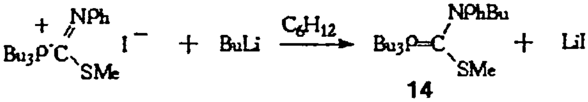
Ylide reacts with phenylisothiocyanate via pseudoacylation giving metallated ylide (13) with a high yield. (δ_P 41 ppm)



$$Bu_3P{=}C(SBu)(SLi) \quad Ph{-}N{=}C{=}S \longrightarrow Bu_3P{=}C(SBu){-}S{-}C(S^{\ominus})(N{-}Ph)\ Li^{\oplus}$$

13

Phosphonium salt, obtained from tributylphosphoniophenylisocyanate and methyl iodide with small admixture of tributylmethylphosphonium iodide, gives phosphonium ylide (14) with the enamine nitrogen atom when treated by butyllithium.



$$Bu_3\overset{+}{P}C({=}NPh)(SMe)\ I^- + BuLi \xrightarrow{C_6H_{12}} Bu_3P{=}C(NPhBu)(SMe) + LiI$$

14

Thus, the studies of metallation reactions of the tributylphosphine/carbon disulfide adduct, phosphonium salts with butyllithium allowed us to find a new convenient one-pot method of synthesis of functional alkylidenphosphoranes.

REFERENCES

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2. M.P.Cava, J.Org.Chem.,44, 930 (1979).
3. R.A.Aitken, S.V.Raut, G.Ferguson. Tetrahedron,48, 450 (1992)