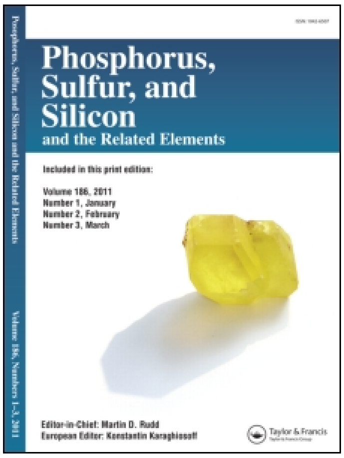

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Addition of Lithium Dialkylcuprates to Vinylphosphonic Acid Esters Nucleophilic Properties of Adducts

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SHORT COMMUNICATION

Addition of Lithium Dialkylcuprates to Vinylphosphonic Acid Esters Nucleophilic Properties of Adducts

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Addition of dialkylcuprates to α,β,unsaturated compounds has now been extensively applied as a simple and effective way for carbon–carbon bond formation.[1] It has been shown unequivocally that this reaction is highly regioselective and involves participation of an olefinic rather than conjugated system as an acceptor of the organometallic nucleophile.[2] In contrast to the reactions of lithium dialkylcuprates with α,β-unsaturated carbonyl and sulphonyl compounds, reactions with α,β-unsaturated phosphoryl compounds have not been a subject of broader interest. Only the addition of lithium dialkylcuprates to phosphine oxides containing allenyl groups has been described.[2a]

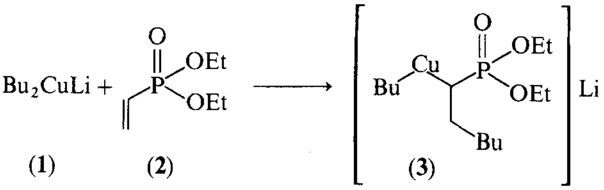
In recent years, a reaction sequence in which lithium dialkylcuprate adducts of α,β-unsaturated carbonyl compounds are utilized in nucleophilic substitutions has gained significant synthetic importance.[3] It is noteworthy that the nucleophile has been exclusively the ligand of an adduct derived from an α,β-unsaturated compound—an equivalent of the enolate anion. The addition and substitution are usually carried out in one synthetic operation which enables the easy introduction of two different vicinal groups to a carbon skeleton of the activated olefin.

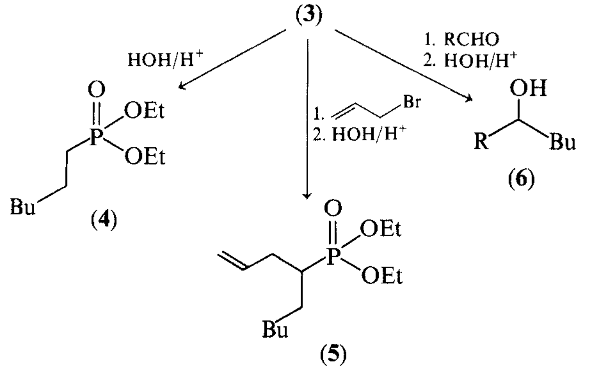
In a search for a convenient method for the synthesis of alkylphosphonic acid esters incorporating complex carbon chains we have tried to take an advantage of the addition-substitution sequence starting from vinylphosphonic acid esters. In the present communication we wish to report the result of preliminary studies on the reaction of lithium dibutylcuprate (**1**) with diethyl vinylphosphonate (**2**) and to characterize nucleophilic properties of the products formed.

Although vinylphosphonic acid esters include two reactive centres located at the terminal carbon and phosphorus which are able to participate in nucleophilic addition and nucleophilic substitution respectively, the adduct **3** turned out to be the only product resulting from treatment of **1** with equimolar amount of (**2**) in ether solution at $-70°$. It should be emphasised that in a similar situation organolithium compounds, e.g. methyllithium take part in nucleophilic substitution at phosphorus exclusively.[4]

There seems to be no doubt that (**3**) has the structure of an organocopper complex with two different ligands comprising carbon–carbon bonds as it was previously postulated for this type of compound.[2] The adduct (**3**) has been found to react with electrophilic reagents in two pathways. In each of them a different organic ligand is involved as a nucleophile. The preferable way depends on the type of electrophile.

Thus (**3**) treated with water in ether solution at $-70°$ is readily converted into diethyl hexylphosphonate (**4**), |86%; b.p. 78°/0.4; ^{31}P NMR ($CHCl_3$), δ 31.9;^{1} H NMR (90 MHz $CDCl_3$), δ 0.88 (*t*, 3H, $J_{H-H} = 6.2$ Hz), 1.32 (*t*, 6H, $J_{H-H} = 7.0$ Hz), 1.24–2.0 (*m*, 10H), 4.09 (*q*, 4H, $J_{H-H} = 7.0$ Hz); MS: 222 (M^+), 152, 137, 125|. Under the same conditions it reacts almost quantitatively with alkyl halides, e.g. with allyl bromide affording diethyl 4-nonen-1-ylphosphonate (**5**), |68%; b.p. 86/0.4; ^{31}P NMR ($CHCl_3$), δ 35.5; MS: 262 (M^+),

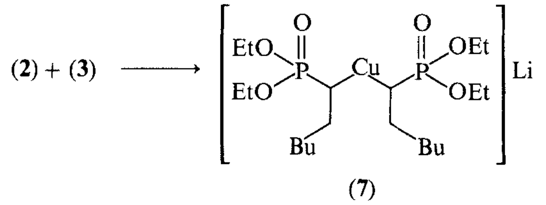




6a—R—phenyl
6b—R—ethyl

205, 177, 165, 137, 125|. On the other hand the reaction of (**3**) with aldehydes, e.g. with benzaldehyde or propionaldehyde gives solely 1-phenylpentanol-1 (**6a**)[5] (90%) and heptanol-3 (**6b**)[5] (82%) respectively.

From the point of view of synthetic utility the reaction of **3** with **2** is unquestionably the most attractive. In this transformation the butyl ligand of **3** acting as nucleophile results in the formation of the secondary adduct **7** that contains two identical organophosphorus groups with saturated extended chains. If one equivalent of **1** is treated with two equivalents of **2** the same product is obtained in the yield comparable to that of the stepwise procedure. Both alkyl groups of **1** can thus be entirely exploited as nucleophiles in the addition to α,β-unsaturated compound. Such a type of addition has not been hitherto observed.



Formation of (**7**) has been explicitly proved by the results of its reactions with electrophiles. The adduct (**7**) reacts with water in ether solution at −70° to produce (**4**) (80%) and with allyl bromide given (**5**) (65%). It is remarkable, however, that all attempts to add (**7**) to aldehydes have failed. Other transformations of (**7**) with electrophiles are currently being investigated.

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