

Preliminary communication

Reactivity of phosphonium diylids with esters and amides

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Abstract

The phosphonium diylid $(C_6H_5)_2P(CH_2)(CH_2Li)$ reacts readily with various esters and amides to give acylated phosphonium salts and Wittig products. In the case of *N,N*-dimethylbenzamide the reaction can be directed mainly to the Wittig products by protonation. Depending on the nature of the carbonyl group, unexpected reactions, such as conjugate additions to α,β -unsaturated compounds or enolization of α -hydrogenated amides, can also take place.

In the preceding paper [1], we reported the reactions of some diylids with ketones and aldehydes. The high nucleophilicity of diylids that we observed prompted us to investigate the corresponding reactions with esters and amides.

Non-stabilized phosphonium monoylids usually do not react with the esters or amides. Examples of Wittig type reactions of monoylids with such carbonyl compounds are known only for intramolecular reactions [2], and those of stabilized monoylids with activated esters [3,4], *N*-acylpyrroles [5], and *N*-sulfonyllactams [5,6], and take place only under drastic conditions.

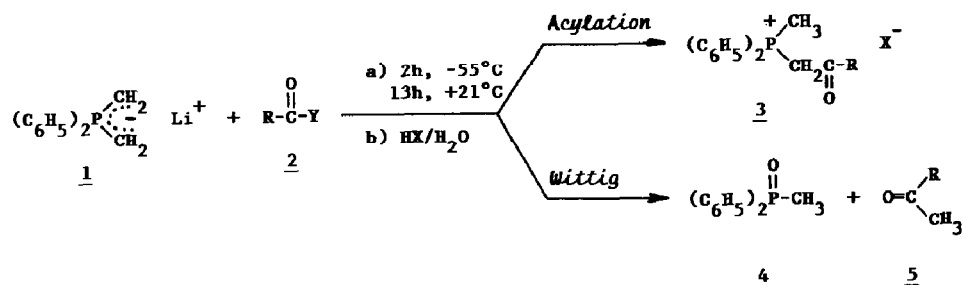
When compound **2** reacts in THF with one equivalent of diylid **1** [1] at $-50^\circ C$ the acylation products **3** and Wittig products **4** and **5** are obtained (after hydrolysis of the intermediate enamines), with the yields, which depend on Y, reported in Table 1.

Table 1

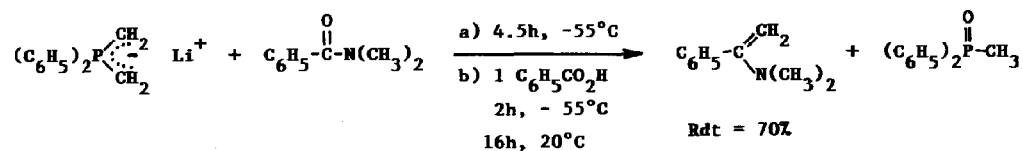
Reactions of phosphonium diylid **1** with esters and amides

2 : $R-C-Y$ \parallel O	3 Yield (%)	Other products
2a $C_6H_5COOC_2H_5$	96	—
2b $C_6H_5CON(CH_3)_2$	80	4 (20%); 5 (20%)
2c $C_6H_5CH=CHCOOC_2H_5$	46.5	6 (17.5%)
2d $C_6H_5CH=CHCON(C_2H_5)_2$	5	6 (80%)

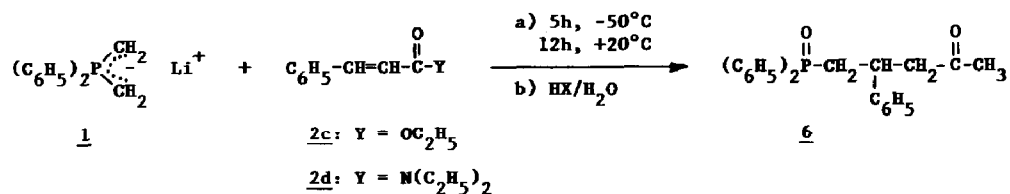
In contrast to the previously studied non-stabilized mono ylids, the diylid **1** reacts with the carbonyl function of the *N,N*-dimethylbenzamide **2b** at low temperature, and substantial amounts of Wittig products are obtained.



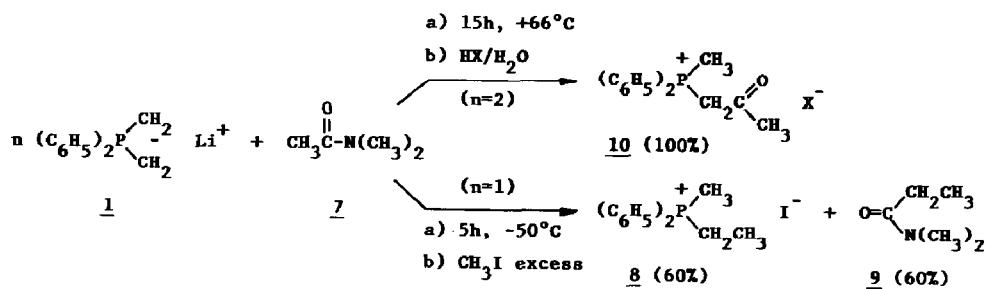
The Wittig reaction can even become predominant if one equivalent of benzoic acid is added at low temperature during the reaction.



The reaction of α,β -unsaturated ester **2c** and amides **2d** with diylid **1** gives, after hydrolysis, high yields of the unexpected product **6** (see Table 1). We assume that compound **6** results from successive reactions in which an initial 1,4-addition is followed by an intramolecular Wittig reaction which leads, after hydrolysis, to the δ -ketonic phosphine oxide **6**:



Another secondary process, rarely encountered in the reactions of phosphonium mono ylids, is enolization. This reaction can become predominant in the case of the diylids. Thus treatment of the *N,N*-dimethylacetamide **7** with one equivalent ($n = 1$) of **1** followed by methylation with methyl iodide and then hydrolysis, gives products **8** and **9** in 60% combined yield. Furthermore, reaction of two equivalents ($n = 2$) of diylid **1** with the amide **7** in boiling THF gives a ca. 100% yield of the acylation product **10** after hydrolysis. This last reaction ($n = 2$) shows the very high nucleophilicity of the diylid **1**, which can attack the enolate function:



We are now studying the reactions of phosphonium diylid with other substrates (such as urea, lactame, isocyanate, etc.), and also the effects of changing the metal present in the diylid.

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