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NEW FUNCTIONAL WITTIG REAGENT FOR THE FORMYLOLEFINATION OF ALDEHYDES AND KETONES

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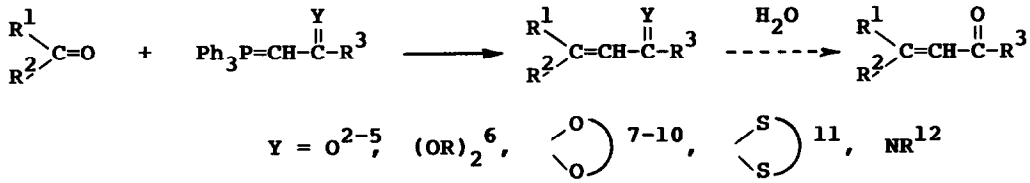
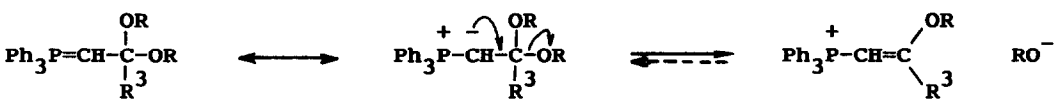
Abstract : *Wittig's reagent for n + 2 homologation of aldehydes and ketones into α,β-unsaturated aldehydes via the corresponding hydrazones is described.*

Wittig reaction with functionalized ylids is a powerful tool for the n + 2 homologation of aldehydes and ketones. It affords first intermediates with a protected carbonyl function which are easily hydrolyzed into the corresponding α,β-unsaturated carbonyl derivatives[1-12].

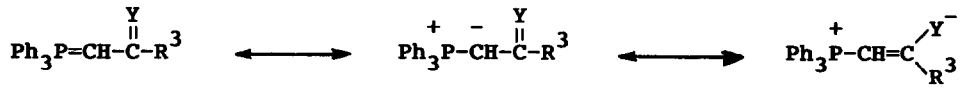


Y = O[2-5], $(OR)_2$[6], [7-10], [11], NR^{12}

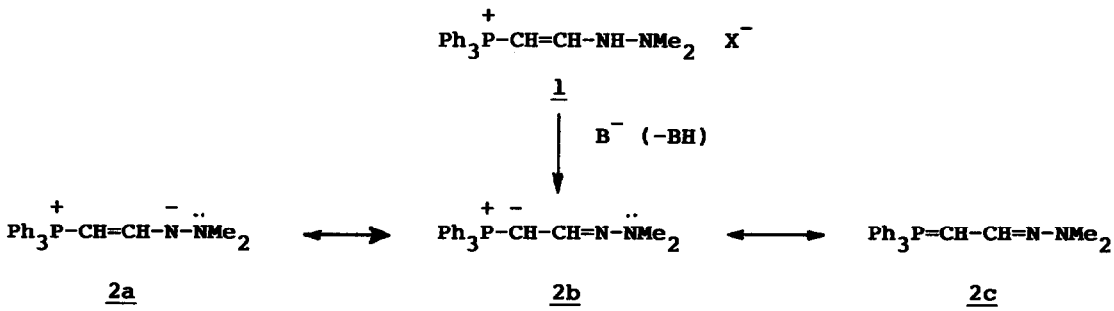
With aldehydes the yields are generally good but with ketones they are low and even very often no reaction is detected[1-12]. With the ketal or thioketal ylids |Y = $(OR)_2$, $(SR)_2$| the limitations arise probably from a reversible β-elimination reaction which decreases the concentration of the reactive ylid.



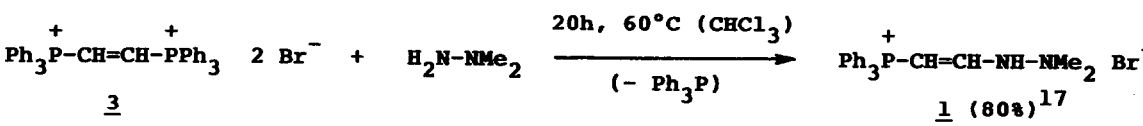
But in the case of keto or imino-ylids, the lack of reactivity results likely from the too efficient stabilization of the ylid by delocalisation of the anionic charge on the Y group.



We describe now the synthesis and reactivity of a new β-functionalized phosphonium salt 1 of the imino type (Y = NR) in which the 2a form of the ylid, unreactive in the Wittig process, is destabilized by the α-effect[13] in favor of the reactive form 2b.



Salt 1 was synthesized through a previously described method which involves the reaction of an active hydrogen compound on 1,2-vinylene bisphosphonium salt 3 in the presence of a base[14-16]. Salt 3 is prepared by adding acetyl bromide to triphenylphosphine in dry chloroform at reflux[14]. Thus under nitrogen we add an excess of 1,1-dimethylhydrazine to salt 3 in anhydrous chloroform at 60°C during 20 hrs. Beside the expected phosphonium salt 1, secondary products are formed by decomposition of the phosphonium salt 3[15,16].



We tested this mixture in the Wittig reaction without further purification[18]. The general procedure is as follows : under nitrogen, the ylid is formed at 35°C by reacting in dry THF an excess (5.13 g) of the crude salt 1 with 1.35 g (12 mmol) of KOtBu. After 1 hr, the aldehyde or the ketone (10 mmol) is introduced in the mixture and the reaction is run further for 20 hrs at 35°C for the aldehydes and 20 hrs at reflux for the ketones.

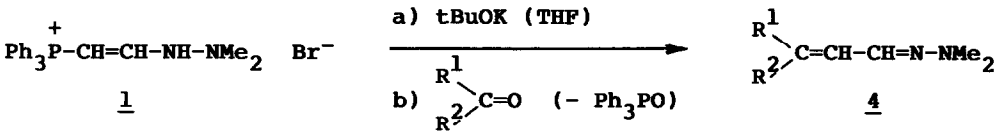
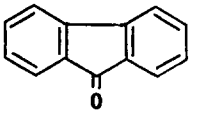


Table. **Synthesis of compounds 4**

	R^1	R^2	Yields (80%)
4a	H	Ph	82
4b	H	Ph-CH=CH-	80
4c	H	nC_7H_{15}-	80
4d	Me	Ph	27
4e	Ph	Ph	8
4f			74

The α,β-unsaturated hydrazones 4 are purified by column chromatography on silica gel (Table)[19].

They may be readily converted into the α,β-unsaturated carbonyl compounds by one of the numerous method described in the literature[20]. They can also be used in synthesis, for example as activated dienes in Diels-Alder reactions[21].

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16 - ibid 14, 73 (1982).
17 - The yield in salt 1 is determined by ^{31}P-NMR.
18 - Purification by crystallization is quite tedious and results in strong lowering of the yield.
19 - Elemental analysis and spectra (IR, ^{1}H RMN, Mass) are in agreement with the structure assigned.
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21 - See for example B. SERCKX-PONCIN, A.M. HESBAIN-FRISQUE, L. GHOSEZ, Tetrahedron Letters 23, 3261 (1982).

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