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DIRECT SYNTHESES OF TERMINAL OLEFINS FROM THE REACTION OF 1-CHLOROMETHYLTRIMETHYLSILANE AND KETONES

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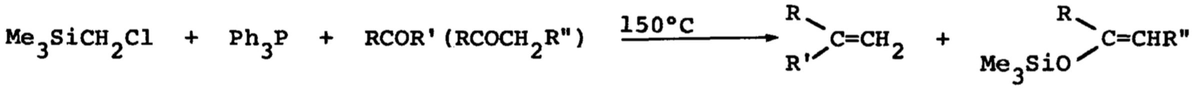
The reactions of ketones with 1-chloromethyltrimethylsilane in the presence of triphenylphosphine gave terminal olefins in good yields. The terminal olefins are formed through the Wittig type reactions of methylenetriphenylphosphorane with ketones.

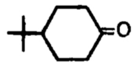
Methylenetriphenylphosphorane is often used for the syntheses of terminal olefins. However, the Wittig reaction involves several steps, i.e. initially preparation of phosphonium salts, then conversion of phosphonium salts into phosphonium ylids, and finally condensation with carbonyl compounds mostly under nitrogen atmosphere. We wish to report a direct conversion of ketones into terminal olefins using 1-chloromethyltrimethylsilane in the presence of triphenylphosphine. A mixture of benzophenone (1.01 mmol), triphenylphosphine (1.52 mmol), and 1-chloromethyltrimethylsilane (3.06 mmol) was heated in a sealed tube at 150°C for 10 min. without solvent. The reaction mixture separated into two layers. Triphenylphosphine oxide (280 mg, 100%) was separated as a white precipitate on addition of hexane to the reaction mixture. The hexane was evaporated and the residue was chromatographed on a silica gel column with petroleum ether. Evaporation of the solvent gave 142 mg(78%) of 1,1-diphenylethylene. Other ketones were also converted into terminal olefins. On the other hand, in the case of the ketones having α-hydrogens (acetophenone, or 4-t-butyl-cyclohexanone), the silyl enol ethers were produced with the terminal olefins.



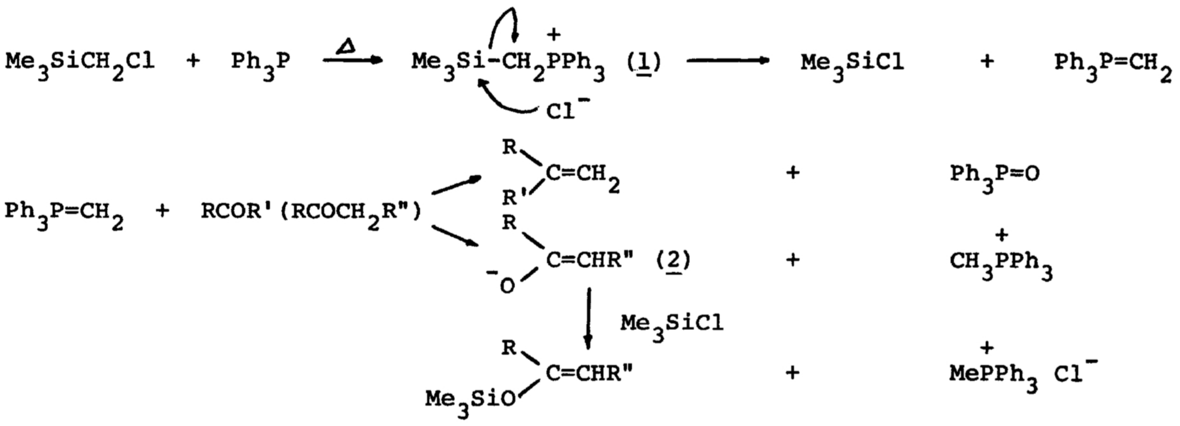
$$\mathrm{Me_3SiCH_2Cl} + \mathrm{Ph_3P} + \mathrm{RCOR'(RCOCH_2R'')} \xrightarrow{150^\circ\mathrm{C}} \mathrm{(R)(R')C{=}CH_2} + \mathrm{(R)(Me_3SiO)C{=}CHR''}$$

The results are summarized in Table 1. The methylenation using 1-chloromethyltrimethylsilane appears to be operationally simpler and cleaner than that of the original Wittig reaction. Triphenylphosphine is necessary for the formation of terminal olefins.

Table 1.[1)]

Ketone	Reaction time(min)	Conversion of ketone(%)	Olefin(%)	Silyl enol ether(%)
Ph_2CO	10	100	90(78)	-
$Me_3SiCOPh$	10	100	100(70)	-
$Et_3SiCOPh$	9	100	80(65)	-
Me_3CCOPh	10	51	41(24)	-
	60	91	62(57)	-
PhCOMe	10	62	47	15
	60	88	57	24
	15	71	52	24
	60	100	66	38

The initial reaction may involve the formation of trimethylsilylmethyltriphenylphosphonium chloride (1) in the reaction of 1-chloromethyltrimethylsilane and triphenylphosphine.[2)] The second step may be the cleavage of silicon-carbon bond of (1) by chloride ion to produce trimethylchlorosilane and methylenetriphenylphosphorane. The latter reacts either with carbonyl to give terminal olefin or α-hydrogen to produce enolate ion (2)[3)] which affords the silyl enol ether by the reaction with trimethylchlorosilane.



References

1) Yields were obtained by GLC analyses relative to the area of the known amounts of internal standards. Isolated yields (separation by column chromatography on silica gel) are given in parentheses.

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