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NON-WITTIG TYPE REACTION OF TEBBE REAGENT WITH ACYL CHLORIDE[1]

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Abstract: Reactions between Tebbe reagent and acyl chlorides proceeded in non-Wittig type manner, giving the corresponding methyl ketones. A possible reaction mechanism is discussed.

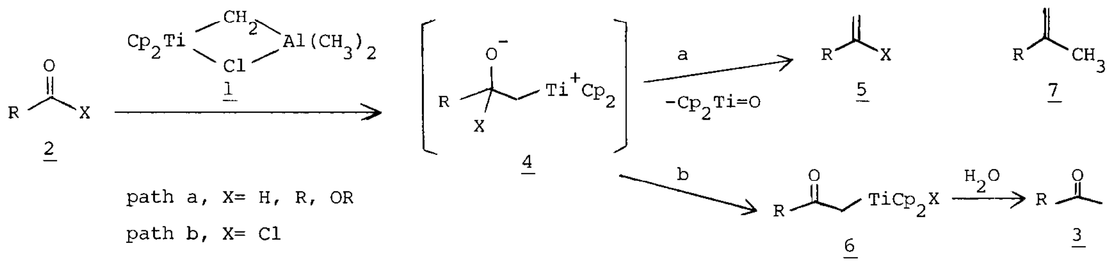
Recently, biscyclopentadienyl titanium-μ-chloro-μ-methylidene bismethyl aluminum 1 (Tebbe reagent) and its aluminum free analogues have received considerable attention[2-6]. Mostly were their reactions with carbonyl-containing compounds such as ketones, aldehydes and esters in Wittig-type manner to yield the corresponding methylenated products. Previously, we reported a successful, general route for the preparation of the Tebbe reagent and performed its subsequent methylenation reaction with carbonyls in one pot[7]. These results prompted us to investigate the reactions of Tebbe reagent with some carbonyls carrying better leaving groups. We found that the major product of the reaction of Tebbe reagent with an acyl chloride was the corresponding methyl ketone 3 (Table I). The expected Wittig-type reaction product, vinyl chloride, was not produced in any detectable amount. This result described the first example of the Tebbe reagent to react with a carbonyl functionality in a non-Wittig type manner.

Table I. Reaction of Tebbe reagent with acyl chloride[a]

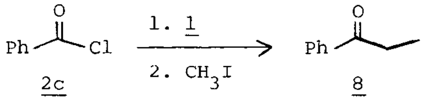
Entry	Acyl Chloride[b]		Product[c]		Yield[d,e]%
a	decanoyl chloride	2a	2-undecanone	3a	47
b	phenylacetyl chloride	2b	phenyl acetone	3b	35
c	benzoyl chloride	2c	acetophenone	3c	42
d	o-methylbenzoyl chloride	2d	o-methylacetophenone	3d	47
e	m-methylbenzoyl chloride	2e	m-methylacetophenone	3e	49
f	p-methylbenzoyl chloride	2f	p-methylacetophenone	3f	64
g	m-methoxybenzoyl chloride	2g	m-methoxyacetophenone	3g	59

a. reaction condition: acyl chloride 2 (1.25 mmol) in toluene/THF (2:1, 6 ml) was added dropwise at -40°C to the solution of Tebbe reagent 1 (2.5 mmol) in toluene (10 ml) generated as described previously[7]. After stirring at -40°C for 30 min and then at room temperature for 3 hr, a few drops of 15% NaOH were added to the reaction mixture and worked up in the usual manner
b. all acyl chlorides were freshly distilled before use
c. all products gave satisfactory MS and/or NMR spectra
d. flash-distilled yields, not optimized
e. we encountered some difficulties when adipoyl chloride was reacted with Tebbe reagent in which case no ketone product was detected

The different turn-out of the reaction of Tebbe reagent with acyl chloride from other types of carbonyls can be rationalized by the following proposed mechanism. Presumably, when Tebbe reagent is reacted with a carbonyl-containing compound, the reactive methylene-titanium ylid, $Cp_2Ti{=}CH_2$, tends to undertake nucleophilic attack at the carbonyl carbon, giving the intermediate 4. For most types of carbonyl carbon, the intermediate eliminates titanium oxide species to yield the methylenated product 5. However, in the case of acyl chloride, the situation becomes somewhat different because chloride ion, being a very good leaving group, allows the intermediate 4 to undergo a different type reaction, i.e. to lose chloride ion. In this case, it leads to the next intermediate 6 which is a titanium enolate. Upon aqueous work up, the corresponding methyl ketone 3 is formed. A good evidence for enolate 6 to be a reaction intermediate is that no isopropenyl compound 7 was detected in any case. Therefore, it seems to suggest that free methyl ketone 3 was not formed until aqueous work up.



To further support the assumption that intermediate 6 was involved in the reaction, benzoyl chloride was reacted with Tebbe reagent in usual manner. Before aqueous work-up, excess of methyl iodide was added and the reaction mixture was allowed to stir in a polar solvent system for another 4 hr. As expected, propiophenone 8 was obtained in significant amount as a result of the C-methylation of the titanium enolate. The synthetic utility of the possible generation of a methyl enolate directly from an acyl chloride is under active study.



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