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1,4-Addition of Diisobutylaluminium Benzenetellurolate to α,β-Unsaturated Carbonyl Compounds and Aldol Reaction of Resulting Aluminium Enolates[1]

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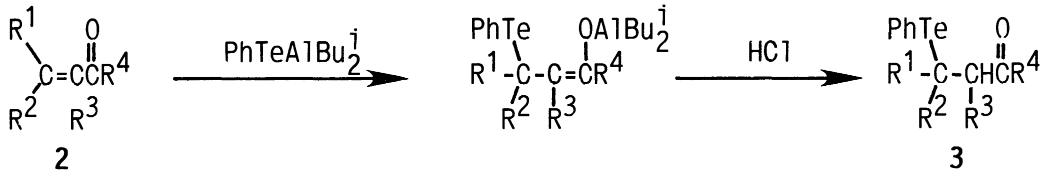
Diisobutylaluminium benzenetellurolate, prepared from diphenyl ditelluride and diisobutylaluminium hydride, easily added to α,β-unsaturated carbonyl compounds in 1,4-fashion to give β-phenyltelluro carbonyl compounds. The intermediate aluminium enolates reacted with aldehydes to give aldol adducts. Subsequent telluroxide elimination resulted in the formation of α-substituted α,β-unsaturated carbonyl compounds.

Recently, much attention is focused on utilization of organotellurium compounds for organic synthesis.[2] Organotellurolate anions are the most commonly used reagents for the introduction of an organotellurium functionality into organic structures. Aluminium tellurolate reagents have never been, however, described in literature in contrast to the unique and useful reactivities of aluminium thiolates and selenolates.[3-7] We now wish to report the first preparation of aluminium tellurolate, its 1,4-conjugate addition to α,β-unsaturated carbonyl compounds, and an application of this reaction to the preparation of α-substituted α,β-unsaturated carbonyl compounds.

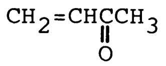
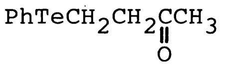
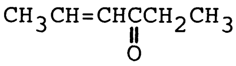
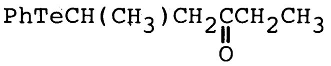
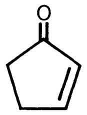
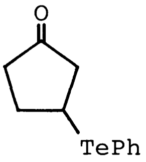
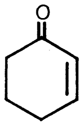
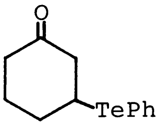
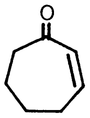
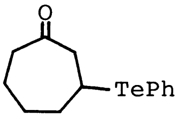
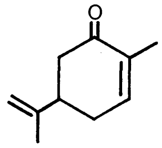
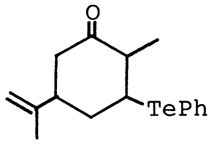
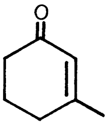
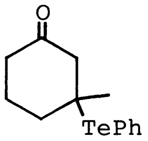
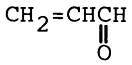
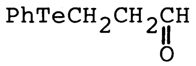
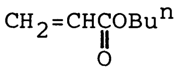
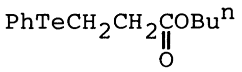
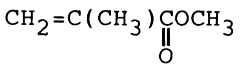
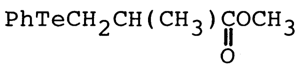
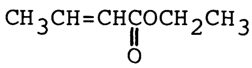
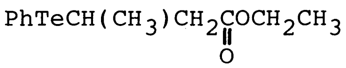
After unsuccessful attempts to generate aluminium tellurolates by means of several methods such as trialkylalane with elemental tellurium and dialkylaluminium chloride with benzenetellurolate or phenyltellurotrimethylsilane, we found that diisobutylaluminium benzenetellurolate (**1**) was conveniently prepared by treatment of a tetrahydrofuran (THF) solution or a solid of diphenyl ditelluride with double the molar quantity of diisobutylaluminium hydride (1 mol dm^{-3} hexane solution) at room temperature for 0.5 h under an argon atmosphere.[6] The completion of the conversion was ascertained by the observation of a theoretical amounts of gas evolution. Aluminium tellurolate 1 was so highly sensitive to air

$$\mathrm{PhTePh} + 2(\underline{i}\text{-}\mathrm{Bu})_2\mathrm{AlH} \longrightarrow \underset{\mathbf{1}}{2\mathrm{PhTeAlBu}^{\underline{i}}_2} + \mathrm{H_2}$$



2 **3**

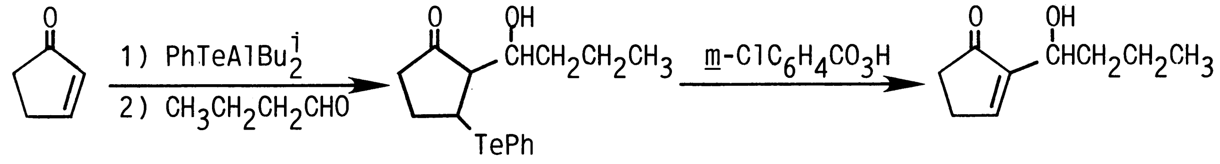
Table 1. Reaction of α,β-unsaturated carbonyl compounds with diisobutylaluminium benzenetellurolate (**1**)[a]

Run	Substrate	Solvent	Product	Yield/%
1	 $CH_2{=}CH\underset{O}{\underset{\Vert}{C}}CH_3$	THF	 $PhTeCH_2CH_2\underset{O}{\underset{\Vert}{C}}CH_3$	84
2	 $CH_3CH{=}CH\underset{O}{\underset{\Vert}{C}}CH_2CH_3$	THF	 $PhTeCH(CH_3)CH_2\underset{O}{\underset{\Vert}{C}}CH_2CH_3$	53
3		THF		87
4		THF CH_2Cl_2 hexane toluene		65 52 36 50
5		THF		71
6		THF		26
7		THF		0
8	 $CH_2{=}CH\underset{O}{\underset{\Vert}{C}}H$	THF	 $PhTeCH_2CH_2\underset{O}{\underset{\Vert}{C}}H$	47
9	 $CH_2{=}CH\underset{O}{\underset{\Vert}{C}}OBu^n$	THF	 $PhTeCH_2CH_2\underset{O}{\underset{\Vert}{C}}OBu^n$	63
10	 $CH_2{=}C(CH_3)\underset{O}{\underset{\Vert}{C}}OCH_3$	CH_2Cl_2	 $PhTeCH_2CH(CH_3)\underset{O}{\underset{\Vert}{C}}OCH_3$	44
11	 $CH_3CH{=}CH\underset{O}{\underset{\Vert}{C}}OCH_2CH_3$	CH_2Cl_2	 $PhTeCH(CH_3)CH_2\underset{O}{\underset{\Vert}{C}}OCH_2CH_3$	26

a) The reaction was carried out with 1.0 mmol of a substrate and 1.2 mmol of **1** at -78 °C for 0.5 h.

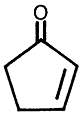
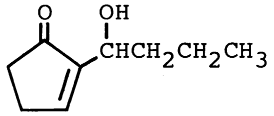
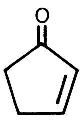
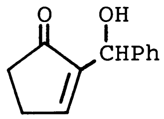
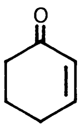
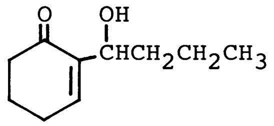
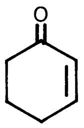
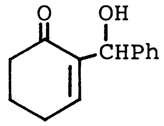
and moisture that it was used in situ like the other aluminium chalcogenolates for further reactions. When to the resulting colorless solution was added a solution of α,β-unsaturated carbonyl compound 2 at -78 °C, 1,4-conjugate addition smoothly proceeded for 0.5 h, and β-phenyltelluro carbonyl compound 3 was obtained after quenching with a degassed 2 mol dm^{-3} aqueous solution of HCl at the same temperature. Although the first Michael-type addition induced by an organotellurium reagent was recently found by Ohe et al. on treatment of α,β-unsaturated ester and nitrile with sodium benzenetellurolate, the reaction was applicable only to $CH_2{=}CHCO_2C_2H_5$, $CH_2{=}C(CH_3)CO_2C_2H_5$, $CH_2{=}CHCN$, and $CH_2{=}C(CH_3)CN$.[8)] On the other hand, the present conjugate addition provides a variety of examples for α,β-unsaturated ketones, aldehydes, and esters, as summarized in Table 1.[9)] Terminal and cyclic enones were converted to the corresponding β-phenyltelluro ketones in fair to good yields. Alkyl substituents on the double bond led to a lowering of the reactivity owing to steric and electronic effects. Conjugated enal also gave β-phenyltelluro aldehyde, but the yield was moderate probably because of competitive 1,2-addition to the aldehyde moiety. Furthermore, this reaction was successfully applicable to α,β-unsaturated esters in contrast to use of aluminium thiolate which formed the corresponding thiocarboxylic S-esters.[4,5)]

Organoaluminium enolates are recognized as a highly potential agent of aldol reaction.[5,7,10)] The aluminium enolate derived from the present conjugate



4 5 6

Table 2. α-Hydroxyalkylation of α,β-unsaturated carbonyl compound involving a sequence of 1,4-addition, aldol reaction, and subsequent telluroxide elimination

Run	Substrate	Aldehyde	Product	Yield/%
1		$CH_3CH_2CH_2CHO$		76
2		PhCHO		89
3		$CH_3CH_2CH_2CHO$		51
4		PhCHO		47

addition to 2-cyclopentenone (**4**) also underwent aldol reaction with butanal in THF at -78 to -30 °C for 3 h to give α-hydroxyalkyl carbonyl compound **5** in 74% yield. The synthetic potentiality of aldol adduct **5** possessing a functional phenyltelluro group at β-position was successfully demonstrated by its conversion into **6**, telluroxide-elimination product, in 87% yield on treatment with m-chloroperbenzoic acid[11] at room temperature for 1 h. The overall transformation therefore provides hydroxyalkylation of α,β-unsaturated carbonyl compound at α-position. The overall yield (64%) of **6** was improved up to 76% based on **4** by omitting the purification of aldol adduct **5**, because **5** was found to be somewhat unstable and to decompose partially during purification. Some results of this three-step conversion are shown in Table 2. Further investigation on the chemical properties of aluminium tellurolate **1** as well as the aldol adducts is now under way.

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