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Synthesis of Enones and Cyclopropanes by the Reaction of Telluronium Ylides Generated from Bis(2-oxoalkyl)tellurium Dichlorides

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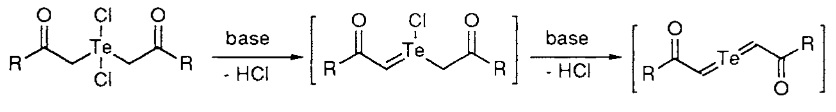
The reaction of bis(2-oxoalkyl)tellurium dichlorides (**1**) with a base gave either 1,4-dioxo-2-alkenes or 1,2,3-triacylcyclopropanes depending on the conditions employed. The reaction of **1** with LDA followed by the addition of an aldehyde led to the Wittig-type olefination to give *E*-α,β-unsaturated ketones in good yields. The cyclopropanes and 1,4-dioxo-2-alkenes could also be synthesized conveniently by a one-pot procedure from the corresponding ketones by the aid of $TeCl_4$ and LDA.

The reaction of ylides with carbonyl compounds is a very useful synthetic tool for the formation of carbon-carbon double bonds and for the construction of epoxide functionalities.1) As for the telluronium ylides, several strongly stabilized ylides have been isolated, but they do not react with carbonyl compounds.2) Suzuki and co-workers reported the first example of the Wittig-type reaction by use of moderately stabilized telluronium ylides.3) They revealed that telluronium ylides react more readily with carbonyl compounds than the analogous sulfonium and selenonium ylides affording olefins or epoxides selectively depending on the nature of the telluronium ylides.3a,b)

Since bis(2-oxoalkyl)tellurium dichlorides (**1**)4) are easily prepared by the reaction of $TeCl_4$ with ketones5b,c) or enol silyl ethers5a) and since they have two α-carbons bearing acidic hydrogens and two chlorine atoms on the tellurium, we envisaged that **1** would play as a synthetically useful precursor of a diylide **3** (or its synthon) by the treatment with a suitable base.6)

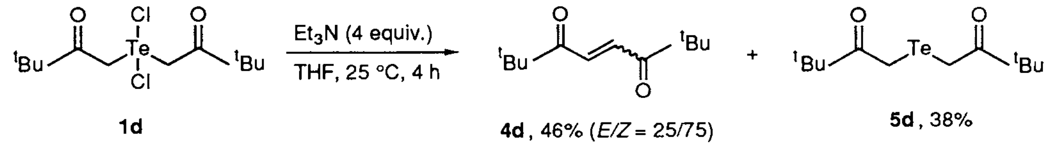


1 **2** **3**

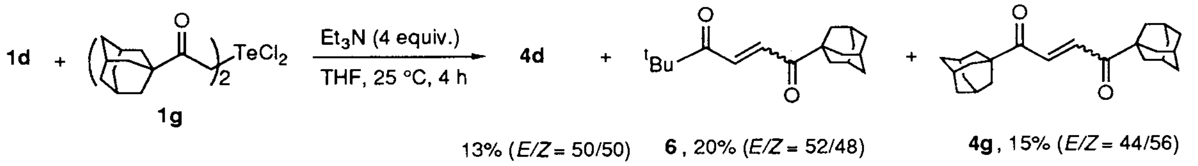
(1)

When bis(3,3-dimethyl-2-oxobutyl) tellurium dichloride **1d** was allowed to react with benzaldehyde in the presence of 4 equiv. of Et_3N in THF, the expected Wittig-type product, *E*-4,4-dimethyl-1-phenyl-1-penten-3-one, was not formed, but a coupling product (**4d**) and a telluride (**5d**) were obtained in 46% (*E*/*Z* = 25/75) and 38% yields, respectively (Eq. 2).7) When an equimolar mixture of **1d** and **1g** was treated with Et_3N under similar conditions, both the homo- and cross-coupling products were obtained with a ratio of **4d**/**6**/**4g** = 1/1.5/1.2, indicating that this coupling reaction might proceed intermolecularly.8)

In contrast to the results mentioned above, the Wittig-type reaction did take place when lithium diisopropylamide (LDA) was used as a base. For example, 2 equiv. of benzaldehyde was added at -78 °C to a pale yellow homogeneous solution prepared by the addition of **1c** to 2 equiv. of LDA at -78 °C in THF. No

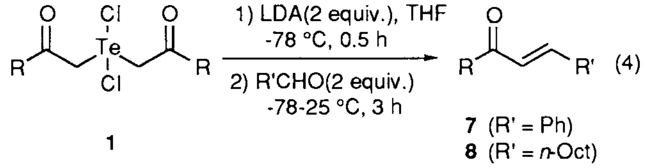


(2)



(3)

apparent change was observed at that temperature, but white precipitates began to deposit on warming to 25 °C. The mixture was stirred at 25 °C for 3 h and then subjected to column chromatography on silica gel to give 84% of *E*-4-methyl-1-phenyl-1-hexen-3-one (**7c**) based on benzaldehyde used. The use of nonanal afforded the corresponding enone (**8c**, 2-methyl-4-tridecen-3-one) in 71% yield. These results indicate that both of the two substituents on Te participated in the reaction with aldehydes. Under similar conditions, several *E*-α,β-unsaturated ketones were synthesized from **1** having primary (runs 1 and 2), secondary (run 3), tertiary alkyl (run 4) and aryl substituents (runs 5 and 6) and the results were summarized in Table 1. α,β-Unsaturated ketones were obtained in good yields except for the case of **1a**. The relatively low yields of products from **1a** may arise from the H-abstraction by LDA not only at the α-carbon but also at the γ-carbon. The mild conditions adopted for this reaction were also noticeable since the similar Wittig-type reactions of sulfonium and phosphonium ylides require much higher temperatures.[9]



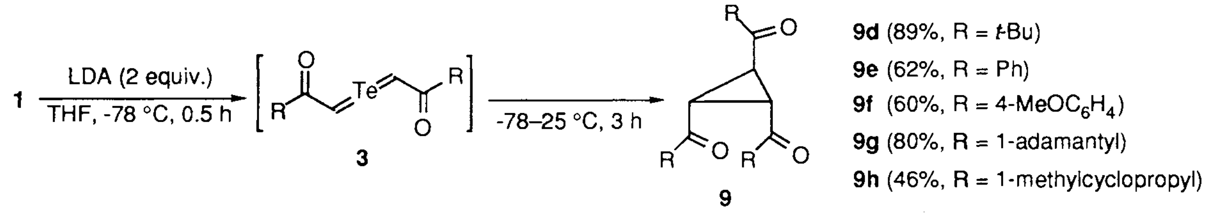
(4)

Table 1. Synthesis of α,β-Unsaturated Ketones

Run	1 (R)	Yield / %[a]	
		7	8
1	**1a** (Me)	42	48
2	**1b** (*i*-Bu)	75	70
3	**1c** (*i*-Pr)	84	71
4	**1d** (*t*-Bu)	62	61
5	**1e** (Ph)	75	74
6	**1f** (4-MeOC$_6$H$_4$)	89	88[b]

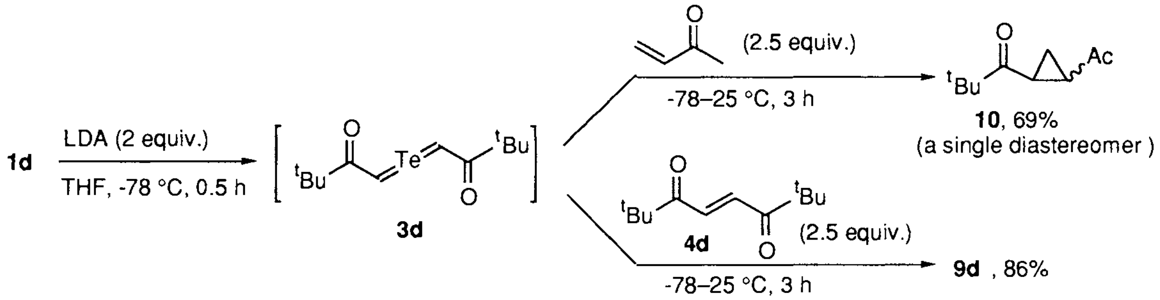
a) Isolated yield based on the aldehyde used. Only *E* - isomer was obtained. b) R' = *n*-Pr.

Since LDA is a strong base and white precipitates (likely to be LiCl) were formed in the reaction of **1d** with 2 equiv. of LDA in Et$_2$O at -78 °C, we would like to propose the formation of a diylide intermediate **3** as active species, although attempted isolation or characterization of **3** failed.[6] On warming the THF solution of **3** to 25 °C we found that **3** decomposed resulting in the formation of the *E*-isomer of 1,2,3-trisubstituted cyclopropane (**9**) with the deposition of metallic tellurium (Eq. 5). Bis(2-oxoalkyl)tellurium dichlorides carrying an aryl or tertiary alkyl group afforded the corresponding cyclopropanes **9** in good yields as shown below. However, **1a-c**, in which R is a methyl, primary or secondary alkyl group, gave complex results and the corresponding cyclopropanes **9a-c** could not be formed under similar conditions.



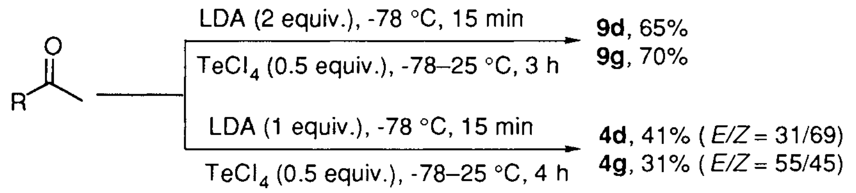
(5)

It is known that phenacyl sulfonium[9b-e] and selenonium ylides[9f,g] afford cyclopropanes upon heating via a Michael-type addition of the ylides to 1,2-diphenacylethylene generated in situ. The intermediacy of enones in the present cyclopropane formation was supported by the control experiments shown in Eq. 6, which showed that the reactions of methyl vinyl ketone and **4d** with **3d** gave corresponding cyclopropanes **10** and **9d** in good yields, where yields were calculated based on 2-oxoalkyl group on **1d**. Furthermore, when a THF solution of **3d** generated at -78 °C was quickly warmed to 0 °C and monitored by GC, **4d** was detected in substantial amounts at the early stage of the reaction and then it decreased as **9d** increased.[10]



(6)

Since **1** was expected to be generated by the reaction of $TeCl_4$ with an enolate, a one-pot synthesis of enones **4** and cyclopropanes **9** from ketones by the aid of $TeCl_4$ and LDA was examined. When $TeCl_4$ was added to a mixture of a ketone and LDA in THF with the molar ratio of 1/2/4 and the solution was warmed to 25 °C, **9d** and **9g** were obtained in 65% and 70% yields, respectively, indicating that **1** generated in situ reacted with the remaining LDA to afford **3**. On the other hand, when a stoichiometric amount of LDA to ketones was used, **4d** and **4g** were formed in 41% and 31% yields, respectively, under similar conditions. In this case, *i*-Pr_2NH generated in situ by the deprotonation of **1** with LDA played as the base to form the enones **4**. These procedures are convenient and would be useful for the facile preparation of 1,4-dioxo-2-alkenes **4** and cyclopropanes **9** from ketones by a one-pot method.



Scheme 1.

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4) Recent papers on the reaction of **1**: R. Tamura, H. Shimizu, N. Ono, N. Azuma, and H. Suzuki, *Organometallics*, **11**, 954 (1992); L. Engman, *Organometallics*, **5**, 427 (1986).

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6) Although the formation of **3** has not yet been confirmed and a possibility that the actual active species has some alternative structures (for example, a tetrasubstituted tellurium structure having intramolecular O-Te coordination) can not be ruled out, **3** is proposed as an active species in our working hypothesis and presented here in its diylene form.

7) It is interesting to note that the selenium analogues of **1** do not give any coupling products but undergo a Pummerer-like rearrangement to produce the corresponding α-chloroselenides under similar conditions. See for example: J. Nakayama and Y. Sugihara, *Chem. Lett.*, **1988**, 1317; L. Engman, J. Persson, and U. Tilstam, *Tetrahedron Lett.*, **30**, 2665 (1989).

8) This result does not contradict with an intramolecular coupling process if disproportionation of **1** was involved in this reaction.

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10) For example, (**4d** / **9d** / reaction time) = (12% / 10% / 10 min), (4% / 15% / 20 min), (4% / 19% / 40 min), (3% / 22% / 60 min), (2% / 30% / 120 min). Finally **9d** was obtained in 80% after stirring at 25 °C for 2 h.

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