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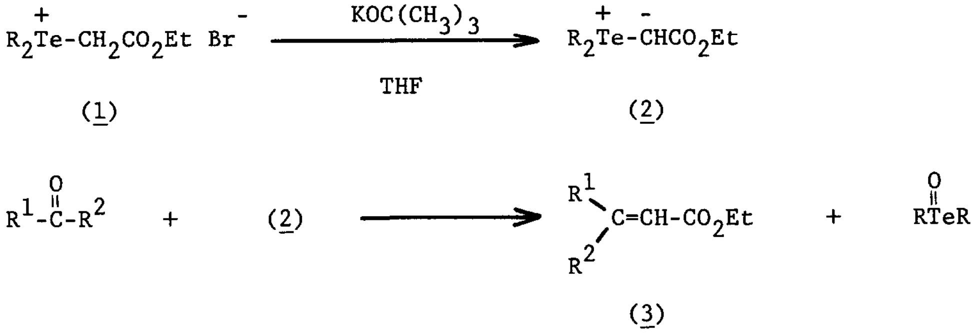
A New Synthesis of α,β-Unsaturated Carboxylic Esters Using Dialkyltelluronium Carbethoxymethylide

Atsuhiro Osuka*, Yasuo Mori, Hirohito Shimizu, and Hitomi Suzuki*
Department of Chemistry, Faculty of Science,
Ehime University, Bunkyo-cho, Matsuyama 790, Japan

Summary: Dialkyltelluronium carbethoxymethylide was found to condense with a variety of carbonyl compounds to yield α,β-unsaturated carboxylic esters in good yields.

The general utility of the reaction of the non-stabilized sulfonium and selenonium ylides with aldehydes and ketones to produce high yields of epoxides has been well documented in the last two decades.[1] However, the stabilized sulfonium ylides normally condense only with exceptionally reactive carbonyl partners.[2] Dimethylsulfonium carbethoxymethylide has been reported not to add to carbonyl groups of simple aldehydes and ketones, although its Michael type condensation with α,β-unsaturated systems to produce cyclopropane is well known.[3] Several highly stabilized and unreactive telluronium ylides have been described in the literature[4]; however, little is known about the reactivity of dialkyltelluronium carbethoxymethylide (2) towards carbonyl compounds.[5] In this letter, we wish to report a new and efficient method which allows the direct conversion of carbonyl compounds to α,β-unsaturated carboxylic esters using the telluronium ylide (2).

The carbethoxydialkyltelluronium bromides (1a; R=Me)[6a] and (1b; R=*n*-Bu)[6b] were reacted with strong bases to yield the corresponding telluronium ylides (2a) and (2b), which were found to condense with a variety of aldehydes and ketones to form the α,β-unsaturated esters in good yields (Table 1). In all cases, none of the α,β-epoxy esters, which are expected condensation products



from the reaction of sulfonium and selenonium ylides, were detected. It is significant to mention here that combination of carbethoxymethyldibutyltelluronium bromide and potassium *tert*-butoxide is reagent of choice due to its ready solubility in THF, absence of side-products, and high yields of the reaction. In the reactions with aldehydes, it was noted that the resulting α,β-unsaturated esters were predominantly of the E-configuration (entry 1-7, and 19). It is noteworthy that highly enolizable ketones such as cyclopentanone can also serve in the same capacity to give the desired product (entry 8). Results with isophorone oxide, benzalacetone, and *trans*-cinnamaldehyde (entry 14, 19, and 20) indicate that this method can be applied to a wide variety of substrates including α,β-epoxy ketones and enones. The condensation with 2-methylcyclohexanone, acetophenone, and 2-hexanone produced the E-isomer with moderate to good stereoselectivity (entry 10, 15, and 17). Although these results are interesting, a clear understanding is expected to evolve only after the systematic investigation, that is being currently undertaken with a view to optimize the stereoselectivity of the reaction, is completed.

Apart from its synthetic utility, this condensation reaction seems quite interesting in view of the fact that change of sulfur or selenium to tellurium causes a dramatic alternation in both the reactivity and the reaction course of ester-stabilized ylide with carbonyl compounds.

Experimental simplicity, absence of isomerized ester, easily available reagent and wide applicability make the present method a highly useful addition for the direct synthesis of α,β-unsaturated esters from carbonyl compounds.[7] Further studies on the reactions, properties, and synthetic applications of telluronium

Table 1. Synthesis of α,β-Unsaturated Carboxylic Esters[a]

Entry	Carbonyl Compounds	% Yield[b]	E/Z[c]
1	Benzaldehyde	75	$>$ 50:1
2	Benzaldehyde[d]	66	$>$ 50:1
3	Piperonal	73	$>$ 50:1
4	3,4-Dimethoxybenzaldehyde	76	$>$ 50:1
5	4-Chlorobenzaldehyde	80	$>$ 50:1
6	2-Bromo-4,5-methylenedioxybenzaldehyde	53	$>$ 50:1
7	Hexanal	52	19:1
8	Cyclopentanone	52	
9	Cyclohexanone	74	
10	2-Methylcyclohexanone	87	12:1
11	3-Methylcyclohexanone	83	1:1
12	4-Methylcyclohexanone	81	
13	4-*tert*-Butylcyclohexanone	90	
14	Isophorone oxide	80	1:2
15	Acetophenone	68	11:1
16	Benzophenone	52	
17	2-Hexanone	65	2.5:1
18	Pinacolone	55	$>$ 50:1
19	*trans*-Cinnamaldehyde	72	$>$ 50:1
20	Benzalacetone	56	2:1

[a] All reactions were performed as described in detail in the text. [b] Values reported are for isolated product. [c] E/Z ratio was determined by GC or ^{1}H-NMR. [d] Carbethoxymethyldimethyltelluronium bromide (1a) and *n*-butyllithium were used.

ylides will be reported in due course.

The reaction of (2b) with *trans*-cinnamaldehyde is typical. A solution of carbethoxymethyldibutyltelluronium bromide (1.23 g, 3 mmol) in dry THF (3 ml) was added dropwise to a solution of potassium *tert*-butoxide (0.337 g, 3 mmol) in THF (4 ml) at -20°C. After a few minutes, *trans*-cinnamaldehyde (0.264g, 2 mmol) was added over a period of one minute. The reaction mixture was stirred for 1 h at -20°C. After usual work-up, the product was purified by column chromatography on silica gel to give ethyl 5-phenylpenta-(2E, 4E)-

dienoate (0.291 g, 72%). GC and ^{1}H-NMR analysis of the product revealed > 98% purity.

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