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DIALKYLTELLURONIUM ALLYLIDE AS A NOVEL REAGENT FOR SYNTHESIS OF α,β-UNSATURATED EPOXIDES

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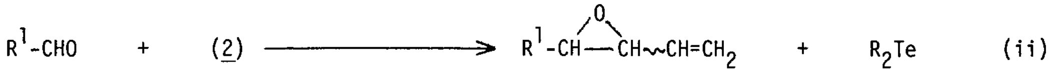
Summary: Reaction of dialkyltelluronium allylide with aldehydes gave rise to α,β-unsaturated epoxides with moderate Z-selectivity and in good yields.

In recent years there has been remarkable interest in the development of new synthetic methods using organotellurium compounds.[1] However, only little attention has been paid to telluronium ylides[2] as a reagent for carbon-carbon bond formation, in contrast to the intense investigation and general utility of sulfonium, sulfoxonium, and selenonium ylides.[3] Recently, we described a new synthesis of α,β-unsaturated carboxylic esters based on the olefination of carbonyl compounds with dialkyltelluronium carbethoxymethylide——a stabilized telluronium ylide.[4] In this letter, we wish to report that the reaction of aldehydes with dialkyltelluronium allylide —— a moderately stabilized telluronium ylide —— gives rise to α,β-unsaturated epoxides in good yields.

First, attempts to generate diphenyltelluronium allylide by proton abstraction of allyldiphenyltelluronium bromide[5] were unsuccessful due to its ready decomposition to diphenyl telluride and allyl bromide on treatment with base.

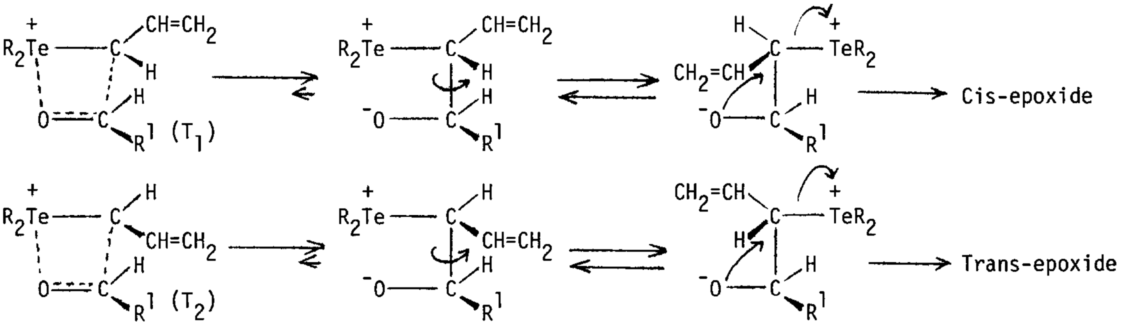
On the other hand, we found that dialkyltelluronium allylide (2a; R=Me), (2b; R=Bu^n), (2c; R=Bu^i), and (2d; R=cyclohexyl) were generated on treatment of the corresponding salts (1a), (1b), (1c), and (1d) with strong base, and reacted with aldehydes to give α,β-unsaturated epoxides. Allyldiisobutyltelluronium bromide (1c), which is most convenient for manipulation and gives the best results, is readily available as stable colorless crystals by the reaction of diisobutyl telluride and allyl bromide in dry ether for 3 days at room temperature; mp 94.5-95.5°C; 78% yield. Diisobutyltelluronium allylide (2c) generated by the action of potassium tert-butoxide on (1c) in THF at -78°C, reacted with aldehydes to give α,β-unsaturated epoxides and diisobutyl telluride (Table 1). Similarly, the reaction of diisobutyltelluronium 3,3-

$$\underset{(\underline{1})}{R_2\overset{+}{Te}\text{-}CH_2CH{=}CH_2}\ Br^- \xrightarrow{KOC(CH_3)_3} \underset{(\underline{2})}{R_2\overset{+}{Te}\text{-}\overset{-}{C}HCH{=}CH_2} \qquad (i)$$



$$R^1\text{-}CHO + (\underline{2}) \longrightarrow R^1\text{-}CH\overset{O}{\text{—}}CH\sim CH{=}CH_2 + R_2Te \qquad (ii)$$

dimethylallylide ($\underline{2e}$) with benzaldehyde gave 2-[(2-methyl)-1-propenyl]-3-phenyloxirane in 63% yield (entry 5). As shown in Table 1, the cis/trans ratios in the reaction with aromatic aldehydes were effected by both electronic and steric factors. While cis-selectivity was moderate in entries 1 and 6-11, it was less when the phenyl ring was substituted by strong electron-attacting group (entry 12) or in the ortho-position (entry 13-17). This reaction can be also applied to aliphatic aldehydes in moderate yields (entry 19-24). However, a readily enolizable aldehyde, 2-phenylpropionaldehyde, was transformed into 2-methyl-2-phenyl-4-pentenal in 82% yield under the same conditions, probably by way of prior proton transfer from the aldehyde to ($\underline{2c}$) and subsequent allylation of the resultant enolate with ($\underline{1c}$).[6]



Scheme I

The mechanism illustrated in the Scheme I would account for the cis-selective stereochemical course of the carbonyl epoxidation with ($\underline{2}$). Given the postulate that the reaction proceeds via four-membered transition states (T_1) and (T_2), it might be anticipated that (T_2) is destabilized relative to (T_1) by steric interaction between the vinyl and R^1 groups. Importance of electrostatic interaction between the telluronium positive charge and carbonyl oxygen may be deduced from the decrease in cis-selectivity with ($\underline{2d}$) (entry 4). Probably, the bulky cyclohexyl group on tellurium in ($\underline{2d}$) prevents the interaction of the telluronium positive charge and carbonyl oxygen.

In addition to the synthetic utility for preparation of α,β-unsaturated epoxides,[7] this

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

Entry	Aldehyde	Reagent	% Yield[b]	cis/trans[c]
1	Benzaldehyde	(2a)	65	83:17
2	Benzaldehyde	(2b)[d]	42	82:18
3	Benzaldehyde	(2c)	82	85:15
4	Benzaldehyde	(2d)	64	64:36
5	Benzaldehyde	(2e)	63	60:40
6	4-Methylbenzaldehyde	(2c)	75	80:20
7	4-Methoxybenzaldehyde	(2c)	64	83:17
8	Piperonal	(2c)	78	87:13
9	Vertraldehyde	(2c)	65	88:12
10	3-Pyridine-carboxaldehyde	(2c)	85	78:22
11	4-Chlorobenzaldehyde	(2c)	80	75:25
12	4-Nitrobenzaldehyde	(2c)	94	58:42
13	2-Methylbenzaldehyde	(2c)	65	60:40
14	2-Methoxybenzaldehyde	(2c)	83	63:37
15	2-Chlorobenzaldehyde	(2c)	86	50:50
16	2,4,6-Trimethylbenzaldehyde	(2c)	58[e]	57:43
17	6-Bromopiperonal	(2c)	84	45:55
18	1-Naphthaldehyde	(2c)	80	82:18
19	Cyclohexanecarboxaldehyde	(2c)	55	78:22
20	Cyclohexene-4-carboxaldehyde	(2c)	57	80:20
21	Heptanal	(2c)	38	68:32
22	Decanal	(2c)	35	65:35
23	3-Phenylpropionaldehyde	(2c)	30	64:36
24	2-Methyl-2-phenylpropionaldehyde	(2c)	56[f]	85:15

[a] All reactions were performed as described in detail in the text. [b] Values reported are for isolated α,β-unsaturated epoxides. Dialkyl telluride was obtained in each entry, but the yield was not determined. [c] Determined by ^{1}H-NMR. [d] Allyldi-n-butyltelluronium bromide (1d) used was not pure, since it was oil and thus could not be purified by recrystallization. [e] Starting aldehyde (28%) was recovered. [f] Starting aldehyde (30%) was recovered.

reaction is of mechanistic interest in view of the first demonstration that telluronium ylides can give rise to either alkenes or epoxides depending upon their stabilities.

A typical experimental procedure is as follows. Allyldiisobutyltelluronium bromide (1c) (0.87 g, 2.4 mmol) and potassium tert-butoxide (0.269 g, 2.4 mmol) were placed in a reaction vessel under nitrogen atmosphere, and dry THF (4 ml) was added with stirring at -78°C. After a few minutes, a solution of benzaldehyde (0.216 g, 2 mmol) in THF (2 ml) was added dropwise, and the reaction mixture was slowly allowed to warm to room temperature. Normal work-up followed by column chromatography on silica gel gave diisobutyl telluride (0.55 g, 95% based on the used salt; eluted by hexane) and 2-phenyl-3-vinyloxirane (0.356 g, 82%; cis/trans=85:15; eluted by 5% ether/hexane).[7a]

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