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Oxygen-Induced Transmetallation of Organoboranes with Diphenyl Ditelluride[1]

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Diphenyl ditelluride rapidly reacted with trialkylboranes in the presence of oxygen to give alkyl phenyl tellurides in high yields. The facile reaction proceeds via a free-radical mechanism induced by a stoichiometrical amount of oxygen. A combination of this transmetallation with hydroboration provides an alternative method for hydrotelluration of olefins.

The introduction of a tellurium functional group into organic substrates is one of the key steps in organic syntheses on tellurium-based methodology.[2] Nucleophilic substitutions of tellurolate species and electrophilic additions of tellurium (IV) species are widely and exclusively used.[3] Free-radical reactions have potential for this purpose, but have been little studied.[4-6] Organic ditelluride has a high ability for trapping alkyl radicals,[4] and therefore, may be used for the preparation of alkyl telluride via a free-radical process. In this regard, we have explored the radical reaction of organoboranes with diphenyl ditelluride (**1**). Here we wish to report oxygen-induced transmetallation of organoboranes with **1**, which in combination with hydroboration provides an alternative to hydrotelluration of olefins (Scheme 1).

$$\mathrm{RCH{=}CH_2} \xrightarrow{\mathrm{BH_3}} \mathrm{(RCH_2CH_2)_3B} \xrightarrow[\mathrm{O_2,\ THF}]{\mathrm{PhTePh}\ (\mathbf{1})} \mathrm{RCH_2CH_2TePh}$$

Scheme 1.

Organoboranes have been known to undergo facile free-radical chain reactions initiated by oxygen, light, or chemical initiators.[7] However, neither ultraviolet light nor AIBN could induce the reaction of trialkylborane with **1**. In contrast, oxygen rapidly did it. Thus, as soon as oxygen gas was introduced at a rate of 15–20 mL/min into a flask containing a solution of triethylborane (1.0 mmol) and **1** (1.0 mmol) in 10 mL of dry tetrahydrofuran (THF), an exothermic reaction occurred and was almost complete in 3 min. GLPC analysis indicated the formation of 1.0 mmol of ethyl phenyl telluride, that is, one alkyl group of the borane was converted into ethyl phenyl telluride. A similar reaction in a stream of air required 2 h to achieve the quantitative conversion. Moreover, a stop of the air stream in the course discontinued the formation of ethyl phenyl telluride, and the reintroduction of air resumed the smooth reaction. These results obviously indicate that this transmetallation is not a radical chain reaction but a stoichiometrical reaction with oxygen. Although disulfides can also react with organoboranes, the reaction is known to proceed via a radical chain mechanism.[8] In order to clarify the differences in reactivity among a series of diphenyl dichalcogenides, we investigated competitive reactions. Hexadecyl phenyl telluride was preferentially formed from the air-induced reactions of trihexadecylborane with an equimolar mixture of **1** and disulfide or diselenide (Scheme 2). In addition, a similar competitive reaction between diselenide and disulfide afforded mainly the corresponding selenide. The selectivity thus follows the active order of the dichalcogenides for trapping an alkyl radical[4] and the inverse order of the chalcogene–chalcogene bond dissociation energies.[9]

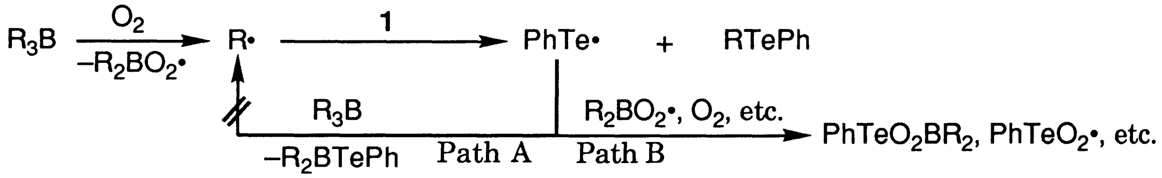
$$[CH_3(CH_2)_{15}]B + PhXXPh + PhYYPh \xrightarrow[rt,\ 2\ h]{Air} CH_3(CH_2)_{15}XPh + CH_3(CH_2)_{15}YPh$$

X	Y	$CH_3(CH_2)_{15}XPh$	$CH_3(CH_2)_{15}YPh$
X = Te	Y = Se	58%	5%
X = Te	Y = S	59%	< 2%
X = Se	Y = S	41%	< 2%

Scheme 2.

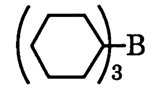
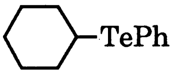
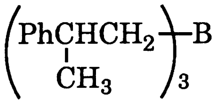
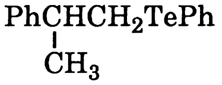
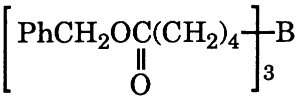
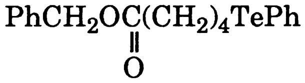
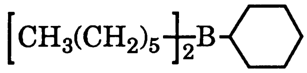
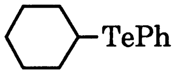
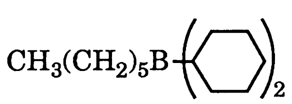
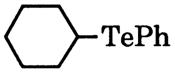
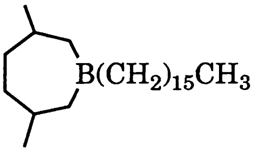
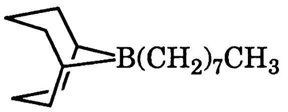
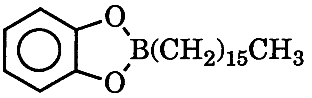
A reasonable mechanism for the transmetallation is proposed in Scheme 3. An alkyl radical generated from trialkylborane with oxygen must attack **1** by S_H2 mechanism to form the corresponding telluride. This step is very rapid presumably due to relatively high stability of resulting phenyltelluro radical to precede a competitive reaction with other dichalcogenide or well-known autoxidation of organoborane with oxygen.[10] If phenyltelluro radical is capable of attacking trialkylborane with liberation of alkyl radical, the latter species might then continue the chain reaction (Path A). However, the low reactivity of phenyltelluro radical[6] as well as the weak affinity of tellurium for boron seems to be unable to promote the propagation reaction. The phenyltelluro radical probably recombines with the same species to form **1** or reacts with excess oxygen or borylperoxyl radical to form tellurenyl peroxides (Path B).[11]

As summarized in Table 1, trialkylboranes prepared in situ by hydroboration of olefins smoothly transferred one alkyl group to tellurium in a stream of oxygen.[12] This method results in overall hydrotelluration of olefins and provides an expedient entry to otherwise not readily accessible organotellurium derivatives. Not only simple alkenes but also those containing the functional groups which were resistant to hydroboration were converted to the corresponding alkyl tellurides (Runs 1–7). A secondary alkyl group was transferred in



Scheme 3.

Table 1. Reaction of organoboranes with diphenyl ditelluride (**1**) in a stream of oxygen[a)]

Run	Organoborane	Temp/°C	Time/h	Product	Yield/%[b)]
1	$[CH_3(CH_2)_5]_3B$	0	0.5	$CH_3(CH_2)_5TePh$	83
2	$[CH_3(CH_2)_{15}]_3B$	rt	0.5	$CH_3(CH_2)_{15}TePh$	95
3		0	0.5		83
4	 $(PhCH(CH_3)CH_2)_3B$	0	0.5	 $PhCH(CH_3)CH_2TePh$	64
5	$[Br(CH_2)_5]_3B$	0	0.5	$Br(CH_2)_5TePh$	74
6	 $[PhCH_2OC(=O)(CH_2)_4]_3B$	0	0.5	 $PhCH_2OC(=O)(CH_2)_4TePh$	76
7	$[PhCH_2O(CH_2)_6]_3B$	0	0.5	$PhCH_2O(CH_2)_6TePh$	99
8		0	0.5	 $CH_3(CH_2)_5TePh$	39 39
9		0	0.5	 $CH_3(CH_2)_5TePh$	78 11
10	Ph_3B[c)]	rt	25	PhTePh	13
11		0	0.5	$CH_3(CH_2)_{15}TePh$	42
12		0	1	$CH_3(CH_2)_7TePh$	23
13		rt	48	$CH_3(CH_2)_{15}TePh$	14
14	$Ph_2B(CH_2)_{15}CH_3$	rt	1	$CH_3(CH_2)_{15}TePh$ PhTePh	64 33

a) The reaction was carried out with 1.0 mmol of an organoborane, prepared in situ by hydroboration of the corresponding olefin, and 1.0 mmol of **1** in THF. b) Isolated yield based on a maximum of 1 mol of alkyl phenyl telluride per 1 mol of an organoborane. c) Commercial triphenylborane was used.

preference to a primary alkyl group (Runs 8 and 9). In contrast to the behavior of trialkylboranes, triphenylborane exhibited only a very slow reaction (Run 10). Although this transmetallation is simple to use, only one of the three alkyl groups can be transferred from the organoborane. This is a limitation in synthetic applications, since the maximum yield based on starting olefin is 33%. To solve this problem we tested several mixed organoboranes. When *B*-alkyl boracyclanes were used, the yields of desired alkyl phenyl telluride were considerably low due to competitive reactions of the boracyclane moieties (Runs 11 and 12). The reaction of *B*-alkyl catecholborane was slow and complex (Run 13). A good result was obtained in the reaction of *B*-alkyl diphenylborane (Run 14).

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11) After the reaction of triethylborane (1.0 mmol) with **1** (1.0 mmol) in a stream of oxygen, the reaction solution still contained 0.18 mmol of **1**. Moreover, the hydrazine treatment of the aqueous alkaline solution after work-up of the reaction mixture gave a considerable amount of **1** (0.27 mmol), suggesting the conversion of some diphenyl ditelluride into tellurenyl peroxides or derivatives in higher oxidation state.
12) All new compounds were characterized by elemental and spectroscopic analyses.

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