Peroxide-induced α-Elimination of Organic Halides from Organotellurium(IV) Halides

By Sakae Uemura* and Shin-ichi Fukuzawa
(*Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan*)

Summary Treatment of organotellurium(IV) halides with t-butyl hydroperoxide in 1,4-dioxan, acetic acid, or acetonitrile affords the corresponding organic halides in good to moderate yields presumably as the result of a 1,2-halogen shift.

The well established β-elimination giving olefins from organoselenium(II) compounds by oxidation[1] does not proceed well with organotellurium(II) compounds.[2] In the latter case some alcohols are formed, presumably as the result of a 1,2-oxygen shift in either the intermediate telluroxide or the tellurone.[2] We now report a novel peroxide-induced α-elimination of organic halides from easily accessible organotellurium(IV) halides,[3] namely, the removal of halogen and an alkyl or aryl group from Te. The reaction may, apparently, be considered as a 1,2-halogen shift.

In a typical experiment, a homogeneous 1,4-dioxan (5 ml) solution containing 2-chlorocyclohexyltellurium trichloride (**1**; X = Cl) (1 mmol) and t-butyl hydroperoxide (70%; 2 mmol) was stirred at reflux for 30 min, during which period a pale yellow solid was precipitated. After the usual work-up procedure, g.l.c. analysis revealed the formation of *trans*-1,2-dichlorocyclohexane (**2**; X = Cl) (0·86 mmol, 86% yield) and its *cis*-isomer (0·06 mmol, 6% yield). No olefinic product was obtained. The reaction proceeded in acetic acid or acetonitrile also, although the yield was lower. Similarly, from the corresponding tri-iodide (**1**; X = I), *trans*-1,2-chloroiodocyclohexane (**2**; X = I) was obtained. Application of the reaction to various aryltellurium(IV) trihalides (**3**) and (**5**) resulted in the formation of the corresponding aryl halides (**4**) and (**6**) with the halogen atom selectively replacing the tellurium group. Here, acetic acid was a better solvent than 1,4-dioxan. When *p*-methoxyphenyl-2-chlorocyclohexyltellurium dichloride (**7**) was similarly treated in acetic acid, both (**2**; X = Cl) and (**4**; R = MeO,

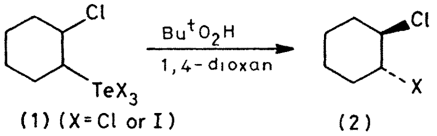


TABLE α-Elimination from Te of organic halides by oxidation of various organotellurium(IV) halides

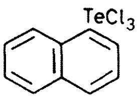
Te compound	Oxidant	Solvent	Time/h	Product	Yield/%
(**1**, X = Cl)	$\mathrm{Bu^tO_2H}$	1 4-Dioxan	0 5	(**2**, X = Cl)	92[a]
(**1**, X = Cl)	$\mathrm{Bu^tO_2H}$	AcOH	2	(**2**, X = Cl)	84[a]
(**1**, X = Cl)	$\mathrm{Bu^tO_2H}$	MeCN	0 5	(**2**, X = Cl)	51[a]
(**1**, X = I)	$\mathrm{Bu^tO_2H}$	1,4-Dioxan	1 5	(**2** X = I)	64[b]
(**3**, R = MeO, X = Cl)	$\mathrm{Bu^tO_2H}$	AcOH	1	(**4**, R = MeO, X = Cl)	53
(**3** R = MeO, X = Cl)	$\mathrm{Bu^tO_2H}$	1,4-Dioxan	2	(**4**, R = MeO, X = Cl)	30
(**3**, R = Me, X = Cl)	$\mathrm{Bu^tO_2H}$	AcOH	1 5	(**4**, R = Me, X = Cl)	25
(**3**, R = MeO, X = Br)	$\mathrm{Bu^tO_2H}$	AcOH	1 5	(**4**, R = MeO, X = Br)	5
(**5**)	$\mathrm{Bu^tO_2H}$	AcOH	1	(**6**)	42
(**7**)	$\mathrm{Bu^tO_2H}$	AcOH	1	(**2**, X = Cl) (**4**, R = MeO, X = Cl)	55[a] 22[c]
(**8**, R = H)	$\mathrm{Bu^tO_2H}$	MeCN	1	(**9**, R = H)	20[d]
(**8**, R = Ph)	$\mathrm{Bu^tO_2H}$	MeCN	1	(**9** R = Ph)	30[d]
(**1**, X = Cl)	$\mathrm{H_2O_2}$	1,4-Dioxan	1 5	(**2**, X = Cl)	67[a]
(**1**, X = Cl)	$\mathrm{PhC(Me)_2OOH}$	1,4-Dioxan	0 7	(**2**; X = Cl)	44[e]
(**1**, X = Cl)	*m*-$\mathrm{ClC_6H_4CO_3H}$	AcOH	2	(**2**, X = Cl)	40[a]

[a] *trans* . *cis* = 94—95 5—6 [b] *trans*-Isomer only [c] Another product is anisole, 6% [d] *Z* *E* = 9 1, smaller amounts (than of the *E*-isomer) of two or three unidentified compounds were also formed [e] *cis*-Isomer not determined

X = Cl) were obtained in 55 and 22% yield, respectively This result shows that the alkyl group is more labile to α-elimination than the aryl group


(3)


(4)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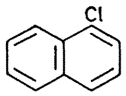
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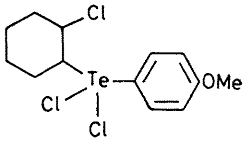
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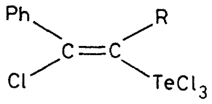
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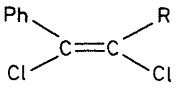
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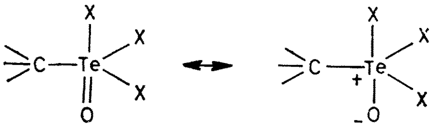
The *Z*-vinyltellurium compound (**8**) afforded mainly the dichloro compound of the *Z*-isomer (**9**), revealing that α-elimination occurs with retention of configuration in this case The reaction of (**1**) also proceeded when hydrogen peroxide, cumene hydroperoxide, or *m*-chloroperbenzoic acid were used instead of t-butyl hydroperoxide, but the yield of (**2**) was generally lower α-Elimination from (**3**), however, did not occur when these other oxidants were used Typical results are shown in the Table In all cases neither acetate nor alcohol was formed The precipitated white to pale yellow solid seems to be composed of tellurium(IV) oxide and/or oxo halides, since it showed hardly any absorption in the i r spectrum or C and H in combustion analyses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Although the reaction scheme is not yet clear, one possibility seems to be the oxidation of organotellurium(IV) halides to the corresponding unstable intermediate organotellurium(VI) compounds such as (**10**) in which a 1,2-halogen shift may occur rapidly to give the organic halide The formation of alcohols in the oxidation of some alkylphenyltellurides has been explained by assuming a 1,2-oxygen shift in either the intermediate telluroxide or tellurone as described above,[2] so for this α-elimination mechanism to hold a 1,2-halogen shift would have to be an easier process than a 1,2-oxygen shift A scheme involving a radical species such as $\mathrm{R\dot{T}e(OR')X_3}$ which eliminates RX may be ruled out since the product yield decreased on addition of iron(II) lactate or sulphate (which may give t-butoxyl or hydroxyl radicals through Fenton's reaction) [†] Attack of an active electrophilic halogen of t-butyl hypohalite (which might be formed *in situ*) on a carbon–tellurium bond may also be excluded, since the reaction of (**3**, R = MeO, X = Cl) with t-butyl hypochlorite, prepared separately, in acetic acid or 1,4-dioxan gave only a trace amount of (**4**, R = MeO, X = Cl)

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[†] We have recently found that the photolysis of (**3** R = MeO X = Cl) (high pressure Hg lamp) gave a good yield of (**4**, R = MeO X = Cl) Here, the addition of di-t-butyl peroxide did not have any effect on the yield of the product in spite of the ready formation of the t-butoxyl radical and thus the possible subsequent formation of $\mathrm{R\dot{T}e(OBu^t)X_3}$

[1] For example, D L J Clive, *Tetrahedron*, 1978, **34**, 1049, H J Reich, in 'Oxidation in Organic Chemistry,' Part C, ed W S Trahanovsky, Academic Press, New York, 1978, ch 1

[2] K B Sharpless, K M Gordon, R F Lauer, D W Patrick, S P Singer, and M W Young, *Chemica Scripta*, 1975, **8A**, 9, and references cited therein

[3] For the preparation of organotellurium(IV) halides employed here, see K J Irgolic 'The Organic Chemistry of Tellurium,' Gordon and Breach, New York, 1974, S Uemura, H Miyoshi, and M Okano, *Chem Lett* , 1979, 1357