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PREPARATION OF ALKYL HALIDES VIA ORGANOTELLURIUMS[1)]

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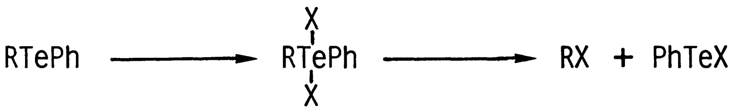
The conversion of phenyltelluroalkanes to haloalkanes was studied in connection with the homologation of alkyl halides. Similar reactions of 1,1-bis(phenyltelluro)alkanes provided a new synthetic method of aldehydes.

Very recently much attention has been given to organotelluriums.[2)] However, most of the researches have been undertaken to introduce tellurium into organic compounds, and little has been known about the transformation of organotelluriums which is applicable to organic synthesis.[3)] Seebach and Beck reported that tellurium stabilized the neighboring carbanion and allowed the formation of a new carbon-carbon bond like sulfur and selenium.[4)] Furthermore, we demonstrated its application to homologated olefin synthesis.[5)] We now report the conversion of phenyltelluro group to halogen in connection with the homologation of alkyl halides.[6)]

Treatment of phenyltelluroalkanes 1 with sulfuryl chloride, bromine, or iodine readily gave the corresponding tellurium dihalides 2, which were subsequently heated at 70-100°C in dimethylformamide to afford alkyl halides 3 smoothly. Although the pyrolysis was considered to occur via 1,2-halogen shift, the yields were much improved by the addition of alkali metal or ammonium halides (Table 1).[7)]

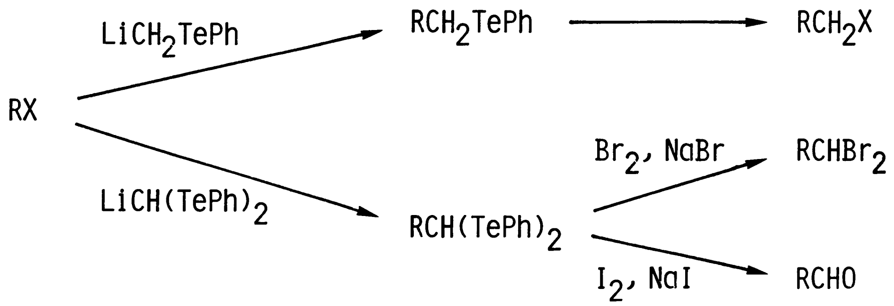


$$\mathrm{RTePh} \longrightarrow \mathrm{R}\underset{\mathrm{X}}{\overset{\mathrm{X}}{\mathrm{Te}}}\mathrm{Ph} \longrightarrow \mathrm{RX} + \mathrm{PhTeX}$$

1 2 3 4

Although phenyltellurium halide 4 seemed to be formed as another fragment of the pyrolysis, diphenylditelluride was isolated instead. On the other hand, a simple treatment of 1 with methyl iodide and sodium iodide in dimethylformamide at 55°C provided an alternative method of the iodination (see also Table 1).

Reaction of alkyl halides with phenyltelluromethyllithium gave 1-phenyltelluro alkanes in moderate yields.[4,5] Thus the present procedure can be successfully applied to the homologation of alkyl halides.



A similar sequence using bis(phenyltelluro)methyllithium as a reagent in the preceding reaction may provide a synthetic route to 1,1-dihaloalkanes. Actually the conversion of 1,1-bis(phenyltelluro)alkanes to 1,1-dibromoalkanes proceeded in the same way (Table 2). On the other hand, the same treatment with iodine and sodium iodide produced aldehydes in high yields (Table 3). The reaction turned out to occur under much milder conditions (60 min at room temperature or 15 min at 60°C). Formation of aldehydes was also found in attempted dichlorination (negligible yield) or diiodination using methyl iodide (moderate yield). These results provide not only a new synthetic method of aldehydes, but also a novel development of bis(phenyltelluro)methyllithium as a synthetic equivalent of formyl carbanion.

Typical experimental procedures are as below.

Halogenation via tellurium dihalide. Into a stirred solution of 1-phenyltelluro hexadecane 172 mg (0.40 mmol) in 2 ml of carbon tetrachloride was slowly added a solution of sulfuryl chloride 0.10 ml (1.24 mmol) in 2 ml of carbon tetrachloride at 0°C under nitrogen. The mixture was stirred for 10 min at room temperature, and then the solvent and the excess reagent were evaporated. The residual colorless solid of hexadecylphenyltellurium dichloride was mixed with sodium chloride 30 mg (0.51 mmol) and dimethylformamide 2 ml, and heated with stirring at 100°C for 1 h under nitrogen. It was quenched with water and extracted with hexane. The extract was dried ($MgSO_4$) and filtered through a short column of silica gel to give a colorless oil of 1-chlorohexadecane 96 mg (92%).

Table 1 Conversion of phenyltelluroalkanes (RTePh) to haloalkanes

R	Chlorination[a,c] Yield %	Bromination[a,d] Yield %	Iodination[a,e] Yield %	Iodination[b,f] Yield %
n-$C_{11}H_{23}$	89	93	71	88
n-$C_{12}H_{25}$	91	95	81	87
n-$C_{14}H_{29}$	90	95		90
n-$C_{16}H_{33}$	92	93	74	88
$Ph(CH_2)_2$	77	59		75
$Ph(CH_2)_3$	79	75		85
$C_{12}H_{25}CH(CH_3)$	83	91	85	83

a) Halogenation via tellurium dihalide.

b) Direct iodination by methyl iodide and sodium iodide.

Temperature: c) 100°C; d) 70°C; e) 85°C; f) 55°C.

Solvent: c) DMF; d) DMF or EtOH; e) CH_3CN or THF; f) DMF or THF.

Table 2. Conversion of 1,1-bis(phenyltelluro)alkanes, $RCH(TePh)_2$ to 1,1-dibromoalkanes

R	Yield %
n-$C_{11}H_{23}$	82
n-$C_{12}H_{25}$	85
n-$C_{14}H_{29}$	81
n-$C_{16}H_{33}$	76
$Ph(CH_2)_3$	81

Table 3. Conversion of 1,1-bis(phenyltelluro)alkanes, $RCH(TePh)_2$ to aldehydes

R	Yield %
n-$C_{11}H_{23}$	86
n-$C_{12}H_{25}$	88
n-$C_{14}H_{29}$	93
n-$C_{16}H_{33}$	92
$Ph(CH_2)_3$	77

Bromination and iodination via tellurium dihalide were carried out in the essentially same way as described in the above chlorination.

Iodination with methyl iodide and sodium iodide. Methyl iodide 0.20 ml (3.21 mmol) and sodium iodide 75 mg (0.50 mmol) were successively added into a solution of 1-phenyltellurododecane 149 mg (0.40 mmol) in 2 ml of dimethylformamide under nitrogen. The mixture was stirred for 10 min at room temperature and then for 2 h at 55°C. It was quenched with water and extracted with hexane. The extract was dried ($MgSO_4$) and filtered through a short column of silica gel to give a colorless oil of 1-iodododecane, 103 mg (87%).

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7) The improved yields are given in Table 1. The yields in the absence of additives were 50-60%.

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