

PREPARATION OF ALKYL HALIDES VIA ORGANOTELLURIUMS¹⁾

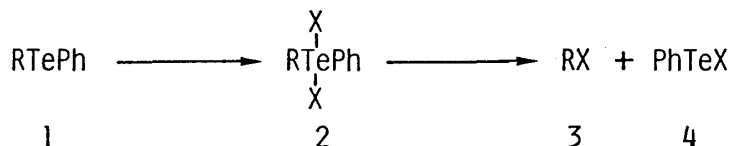
Kiyofumi CHIKAMATSU, Tetsuo OTSUBO, Fumio OGURA,* and Hachiro YAMAGUCHI

Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Saijo, Higashi-Hiroshima 724

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 sulfonyl 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⁾



Although phenyltellurium halide 4 seemed to be formed as another fragment of the pyrolysis, diphenylditelluride was isolated instead. On the other hand, a simple

Table 1 Conversion of phenyltelluroalkanes (R₂TePh) to haloalkanes

R	Chlorination ^{a,c}	Bromination ^{a,d}	Iodination ^{a,e}	Iodination ^{b,f}
	Yield %	Yield %	Yield %	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) CH₃CN 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 (MgSO₄) and filtered through a short column of silica gel to give a colorless oil of 1-iodododecane, 103 mg (87%).

Acknowledgement. The authors thank Prof. Soichi Misumi for helpful discussions and Yamada Science Foundation for financial support.

References

- 1) Organotelluriums Part III. Part I, ref. 5; Part II, F. Ogura, H. Yamaguchi, T. Otsubo, and K. Chikamatsu, *Synth. Commun.*, 12, 131 (1982).
- 2) K. J. Irgolic, "The Organic Chemistry of Tellurium," Gordon and Breach, New York (1974); *J. Organometal. Chem.*, 203, 367 (1980) and references cited therein.
- 3) For a recent review, see S. Uemura, *Kagaku*, 36, 381 (1981).
- 4) D. Seebach and A. K. Beck, *Chem. Ber.*, 108, 314 (1975).
- 5) T. Otsubo, F. Ogura, H. Yamaguchi, H. Higuchi, Y. Sakata, and S. Misumi, *Chem. Lett.*, 1981, 447.
- 6) The pyrolytic^a, photolytic^b, oxidative^c, and substitutional^d conversion of trichlorotelluro group to halogen has already been reported, but the pyrolytic conditions are severe compared to those of the present phenyltelluro case;
a) M. Ogawa and R. Ishioka, *Bull. Chem. Soc. Jpn.*, 43, 496 (1970); b) S. Uemura and S. Fukuzawa, *Chem. Lett.*, 1980, 943; c) *ibid.*, *J. Chem. Soc., Chem. Commun.*, 1033 (1980); d) S. Uemura, H. Miyoshi, and M. Okano, *Chem. Lett.*, 1979, 1357; S. Uemura, S. Fukuzawa, M. Wakasugi, and M. Okano, *J. Organometal. Chem.*, 214, 319 (1981).
- 7) The improved yields are given in Table 1. The yields in the absence of additives were 50-60%.