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OLEFIN SYNTHESIS BY REACTION OF ALKYL PHENYL TELLURIDES WITH CHLORAMINE-T

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Alkyl phenyl tellurides reacted with chloramine-T in refluxing tetrahydrofuran to give olefins in high yields.

Recent years have seen the rapid development of organoselenium chemistry with a number of very useful synthetic procedures.[1] One of the major applications is based on the fact that alkyl phenyl selenides can be converted to olefins by syn elimination of selenoxide under very mild conditions. On the other hand, little have been known about organotelluriums with synthetic utility, though tellurium reagents are expected to behave like the other chalcogen counterparts. This is partially because they are often sensitive to oxidation. Seebach and Beck reported that oxidation of alkyl phenyl tellurides 1 with hydrogen peroxide led to no olefin via telluroxides.[2] Sharpless et al. found that by use of t-butyl hydroperoxide as an oxidant, telluroxide elimination occurred, but in poor yield.[3]

We now report that treatment of the tellurides 1 with excess chloramine-T 2 (N-chloro-N-sodio-4-methylbenzenesulfonamide) in refluxing tetrahydrofuran gave olefins 4 in high yields. The reaction presumably proceeds via adduct 3.

$$\underset{1}{RCH_2CH_2TePh} + \underset{2}{p\text{-}CH_3C_6H_4SO_2NClNa} \xrightarrow[THF]{} \underset{3}{RCH_2CH_2\overset{Ph}{\underset{NSO_2C_6H_4CH_3}{Te}}}$$

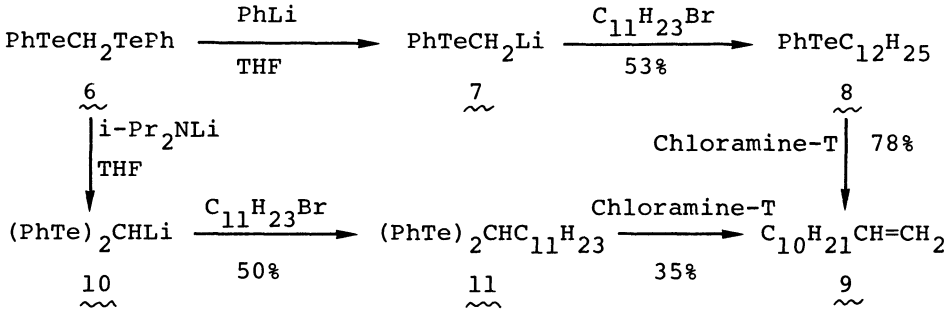
$$\xrightarrow{reflux} \underset{4}{RCH{=}CH_2} + \underset{5}{PhTeNHSO_2C_6H_4CH_3}$$

Table 1 summarizes some of the experimental results. The alkyl phenyl tellurides 1 were readily prepared in ca. 90% yields by treatment of a mixture of alkyl halides and diphenyl ditelluride with sodium borohydride in ethanol at room temperature under nitrogen.[4] Consequently, the present procedure provides an alternative method for the elimination of alkyl halides to alkenes. Homologated olefins can be prepared by a reaction of alkyl halides with phenyl telluromethyllithium 7 generated from bis(phenyltelluro)methane 6[5], followed by treatment with chloramine-T. The case of 1-dodecene 9 is illustrated in

Table 1. Yields of olefins by reaction of alkyl phenyl tellurides with chloramine-T.

Telluride	Olefin		Yield(%)
$n\text{-}C_{10}H_{21}TePh$	$n\text{-}C_8H_{17}CH{=}CH_2$		66 (86)[a]
$n\text{-}C_{12}H_{25}TePh$	$n\text{-}C_{10}H_{21}CH{=}CH_2$		78
$n\text{-}C_{14}H_{29}TePh$	$n\text{-}C_{12}H_{25}CH{=}CH_2$		89
$n\text{-}C_{15}H_{31}TePh$	$n\text{-}C_{13}H_{27}CH{=}CH_2$		75
$n\text{-}C_{12}H_{25}CH(CH_3)TePh$	$n\text{-}C_{12}H_{25}CH{=}CH_2$	(2.2)[b]	93
	$trans\text{-}C_{11}H_{23}CH{=}CHCH_3$	(1.0)[b]	

a) by gas chromatographic analysis.
b) molar ratio of the isomeric products.



Scheme. 1,1-Bis(phenyltelluro)dodecene 11, derived from bis(phenyltelluro)-methyllithium 10, also gave 1-dodecene 9 in lower yield by a similar treatment with chloramine-T. This reaction is considered to proceed via 1-dodecyl phenyl telluride 8, because 8 was formed as a product on treatment with a small amount of chloramine-T.

A reprensentative experimental procedure for the reactions of the tellurides with chloramine-T is as follows; A solution of 1-dodecyl phenyl telluride 1 ($R=C_{10}H_{21}$, 198 mg, 0.52 mmol) and commercial chloramine-T trihydrate 2 (300 mg, 1.0 mmol) in tetrahydrofuran (5 ml) was refluxed for 40 min in a nitrogen atmosphere. After evaporation of the solvent, the residue was treated with hexane (20 ml) and then filtered. The filtrate was passed through a short column of silica gel with hexane to give colorless oil of 1-dodecene, 68 mg (78%).

References and Notes

1) For reviews on synthetic organoselenium chemistry, see D. L. J. Clive, Tetrahedron, 34, 1049 (1978); H. J. Reich, Acc. Chem. Res., 12, 22 (1979).
2) D. Seebach and A. K. Beck, Chem. Ber., 108, 314 (1975).
3) K. B. Sharpless, K. M. Gorden, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, Chemica Scripta, 8A, 9 (1975).
4) All the tellurides are slightly yellow oils except 1-pentadecyl phenyl telluride, mp 26.5-27.5°C and were characterized by NMR and MS spectra and elemental analyses.
5) The synthesis and reactions of bis(phenyltelluro)methane 6 were carried out by modification of Seebach's method (reference 2).

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