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REGIO- AND STEREOSPECIFIC Z-IODO - AND Z-BROMOCHLORINATION OF ALKYLPHENYLACETYLENES VIA Z-CHLOROTELLURATION

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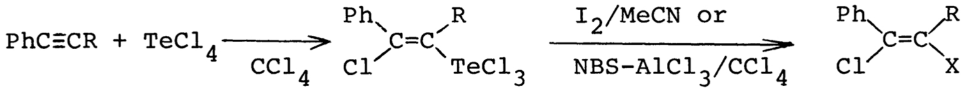
Reaction of alkylphenylacetylenes with tellurium(IV) tetrachloride in carbon tetrachloride gives Z-(2-chlorovinyl)tellurium (IV) trichloride derivatives in over 75% yield, which afford the corresponding Z-chloroiodoalkenes or Z-bromochloroalkenes in good yields by halogenodetelluration with iodine in acetonitrile or N-bromosuccinimide in carbon tetrachloride.

Although the reaction of phenylacetylene and diphenylacetylene with tellurium(IV) tetrachloride has been reported to give the vinyltellurium(IV) compounds, their structures have not yet been fully characterized.1) During a study of the regio- and stereochemistry of chlorotelluration of several acetylenes we have now found that the chlorotelluration of alkylphenylacetylenes and a subsequent halogenodetelluration gave a good yield of the corresponding Z-chloroiodoalkenes or Z-bromochloroalkenes in a high selectivity. The finding may add another interesting feature on the chemistry of organotellurium(IV) compounds, since a little is known concerning their use for organic syntheses.2,3)

The reaction of tellurium(IV) tetrachloride with an equimolar amount of alkylphenylacetylene (1; R=H, Me, Et, or Ph) in carbon tetrachloride at 76°C for 1 hr, followed by the removal of the solvent in vacuo, gave the corresponding Z-(2-chlorovinyl)tellurium(IV) trichloride derivatives (2) in over 75% yield as a solid or brown oil without any formation of dichloroalkenes. The crude (2) obtained here is analytically almost pure without any purification such as recrystallization or distillation: (2; R=H); ^{1}H-NMR(MeOD) δ 7.73(s, =C$\underline{\text{H}}$), ^{13}C-NMR(CDCl$_3$) δ 124.2(d, =$\underline{\text{C}}$H), mp 200°C(d). Found: C, 25.09; H, 1.71%. Calcd for $C_8H_6Cl_4Te$: C, 25.86, H, 1.63%. (2; R=Me); ^{1}H-NMR(CCl$_4$) δ 2.70(s, C$\underline{\text{H}}_3$), oil. Found: C, 27.74; H, 2.04%. Calcd for $C_9H_8Cl_4Te$: C, 28.04; H, 2.09%. (2; R=Et); oil. Found: C, 29.72; H, 2.31%. Calcd for $C_{10}H_{10}Cl_4Te$: C, 30.06; H, 2.52%. (2; R=Ph); ^{13}C-NMR(CDCl$_3$) δ 150.0(s, =$\underline{\text{C}}$-Te), mp 97-103°C. Found: C, 37.18; H, 2.34%. Calcd for $C_{14}H_{10}Cl_4Te$: C, 37.57; H, 2.25%. No regioisomer of (2) was detected in the crude product by ^{1}H- and ^{13}C-NMR.

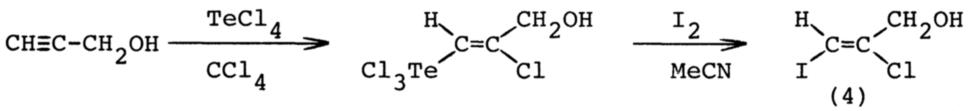
By treating the crude (2) with 1-2 mole equivalents of iodine in acetonitrile or methyl alcohol at reflux for 2 hr, iododetelluration occurred to produce the corresponding Z-chloroiodoalkenes (3; X=I) selectively. Treatment of (2; R=H) with N-bromosuccinimide-aluminium(III) chloride in carbon tetrachloride or copper(II) bromide in acetonitrile afforded (3; R=H, X=Br) in over 60% yield, while the reaction of (2; R=H) with bromine was unsuccessful for obtaining the same compound (yield <10%) under several conditions examined. Typical results are shown in Table. Appli-



(1) (2) (3; X=I or Br)

cation to propargyl alcohol also afforded only Z-chloroiodoalkene (4) (δ 6.53 for =C$\underline{H}$, 4.32 for C$\underline{H}_2$OH) in 40% yield; an authentic E-isomer of (4) (δ 6.47 and 4.42, respectively) was prepared selectively via chloromercuration with mercury(II) chloride in aqueous NaCl[4] followed by iododemercuration in acetonitrile.

Although halogenodemetallation of various vinylmetal compounds has been well known, the finding described here seems to be a first example of a successful


(4)

application to vinyltellurium(IV) compounds so far as we know.[2] Since halogenodemetallation of vinylmetal compounds usually proceeds with retention of configuration,[5] these results show that chlorotelluration of (1) and propargyl alcohol proceeded cis-stereospecifically and also regiospecifically. This method should be useful for selective cis-iodo- and cis-bromo-chlorination of alkylphenylacetylenes, because such reaction with several other reagents usually gives E-isomer (as a result of trans-addition) as a main product.[6]

Table. Z-Chloroiodination[a] and Z-bromochlorination[b] of (1) via chlorotelluration

(1)	Yield(%)[c] of (2)	Yield(%)[d] of (3; X=I)	(3; X=Br)
H	86	94	70
Me	>90	85	
Et	>90	60	
Ph	76	92[e]	60[f]

a) I_2/MeCN, reflux for 2 hr.
b) NBS-$AlCl_3$/CCl_4, reflux for 2 hr.
c) Isolated yield based on (1) charged.
d) Based on (2) in the case of R=H and Ph and on (1) in the case of R=Me and Et as determined by GLC analysis. Some of (3) were determined by ^{1}H- and ^{13}C-NMR spectra together with elemental analysis. Others were identical on the retention time of GLC and in spectral data with those of the authentic samples obtained by the reported methods.[6]
e) Mp 58°C. f) Contains E-isomer; Z/E=2.6/1.

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