2-Alkoxy-*trans*-cycloalkyltellurium(IV) Trihalides

M. E. SABIR ALI, M. AZAD MALIK
and BARRY C. SMITH*

Department of Chemistry, Birkbeck College (University of London), Gordon House, 29 Gordon Square, London WC1H 0PP (U.K.)

(Received February 28, 1989)

Tellurium tetrachloride reacts with cyclohexene in boiling carbon tetrachloride to give 2-chlorocyclohexyltellurium trichloride [1–3]. A preliminary X-ray crystal investigation by Cameron [4] established that the cyclohexyl group contains 1,2-*trans*-substituents, consistent with addition of $TeCl_3^+$ and Cl^- to the double bond. Some reactions of tellurium(IV) halides with cycloalkenes in the presence of alcohols are reported here.

Experimental

Alkoxycycloalkyltellurium Trihalides

In a typical reaction, cyclohexene (1.60 g, 19.5 mmol) was added to tellurium tetrachloride (5.00 g, 18.6 mmol) in carbon tetrachloride (50 cm^3) and alcohol (60 mmol). The mixture was boiled under reflux (2 h), cooled, filtered to remove traces of elemental tellurium, shaken with charcoal, and filtered. Evaporation under reduced pressure and recrystallisation of the product from light petroleum (boiling point 40–60 °C) gave colourless 2-alkoxy-*trans*-cycloalkyltellurium trichlorides or yellow 2-alkoxy-*trans*-cyclohexyltellurium tribromides. Preparative and analytical data are summarized in Table 1.

*Author to whom correspondence should be addressed.

Results and Discussion

Cyclohexene or cycloheptene reacts with tellurium tetrachloride or tellurium tetrabromide and an alcohol in carbon tetrachloride to give 2-alkoxycycloalkyltellurium trihalides. The X-ray crystal structure of 2-ethoxy-*trans*-cycloheptyltellurium tribromide shows two distinct forms [5]. Both have *trans*-equatorial substituents, consistent with the 1,2-*trans*-addition of $TeBr_3^+$ and OEt^- groups. Tellurium has a pseudo-octahedral configuration. Two bromides occupy *trans*-octahedral positions, the third bromine is *trans* to the co-ordinated oxygen, and a pair of non-bonding electrons is presumed to occupy the site *trans* to carbon.

Mass Spectra

The mass spectra of cyclohexene and cycloheptene contain base peaks corresponding to ions of relative molecular mass 81 and 95 respectively. The mass spectra of alkoxycycloalkyltellurium trihalides can be distinguished at a glance. Base peaks occur at M_r 81 and 95 for derivatives of cyclohexene and cycloheptene respectively. Molecular ion peaks correspond to the relative molecular mass minus the relative atomic mass of one halogen: M_r 313, 327 and 341 for methoxy-, ethoxy- and propanoxy-cyclohexyltellurium trichlorides; M_r 401, 415 and 429 for the corresponding tribromides; and M_r 327, 341 and 355

TABLE 1. Analysis of alkoxycycloalkyltellurium trihalides

Compound	Yield (%)	Melting point (°C)	Found (%)			Formula	Calculated (%)		
			C	H	Halogen		C	H	Halogen
$CH_3OC_6H_{10}TeCl_3$	77	120–121	23.98	3.69	30.85	$C_7H_{13}Cl_3OTe$	24.22	3.77	30.64
$C_2H_5OC_6H_{10}TeCl_3$	63	97–98	26.80	4.18	29.21	$C_8H_{15}Cl_3OTe$	26.60	4.18	29.45
n-$C_3H_7OC_6H_{10}TeCl_3$	37	67–68	28.98	4.49	28.44	$C_9H_{17}Cl_3OTe$	28.81	4.56	28.35
i-$C_3H_7OC_6H_{10}TeCl_3$	35	106–108	29.48	4.59	28.09	$C_9H_{17}Cl_3OTe$	28.81	4.56	28.35
$CH_3OC_6H_{10}TeBr_3$	64	142–143	17.32	2.67	49.99	$C_7H_{13}Br_3OTe$	17.50	2.73	49.89
$C_2H_5OC_6H_{10}TeBr_3$	65	119–120	19.59	3.07	47.99	$C_8H_{15}Br_3OTe$	19.43	3.06	48.47
n-$C_3H_7OC_6H_{10}TeBr_3$	33	109–110	21.37	3.32	46.99	$C_9H_{17}Br_3OTe$	21.25	3.37	47.14
i-$C_3H_7OC_6H_{10}TeBr_3$	32	124–125	21.27	3.39	46.89	$C_9H_{17}Br_3OTe$	21.25	3.37	47.14
$CH_3OC_7H_{12}TeCl_3$	51	103–104	26.61	4.17	29.74	$C_8H_{15}Cl_3OTe$	26.60	4.18	29.45
$C_2H_5OC_7H_{12}TeCl_3$	41	75–76	29.07	4.57	28.26	$C_9H_{17}Cl_3OTe$	28.81	4.56	28.35
n-$C_3H_7OC_7H_{12}TeCl_3$	84	oil	31.07	4.90	27.49	$C_{10}H_{19}Cl_3OTe$	30.86	4.92	27.33
i-$C_3H_7OC_7H_{12}TeCl_3$	49	93	30.97	4.98	27.37	$C_{10}H_{19}Cl_3OTe$	30.86	4.92	27.33
$C_2H_5OC_7H_{12}TeBr_3$	53	76–78	21.31	3.37	46.88	$C_9H_{17}Br_3OTe$	21.25	3.37	47.13

0020-1693/89/$3.50

for methoxy-, ethoxy- and propanoxy-cycloheptyltellurium trichlorides.

Fragments corresponding to cycloalkene plus alkoxy occur at M_r 113 or 127 (OMe), 127 or 141 (OEt), and 141 or 155 (OPr^n and OPr^i). Common fragments occur at M_r 130 (Te); 165 or 209 (TeX); 200 or 288 (TeX_2); 247 or 256 ($C_6H_{10}TeCl$ or $C_7H_{12}TeCl$); 278, 292 or 306 ($ROC_6H_{10}TeCl$); and 292, 306 or 320 ($ROC_7H_{12}TeCl$).

Proton NMR Spectra

The ^1H NMR spectra of cyclohexene and cycloheptene contain methylene proton multiplets in the region δ 1.5 to 2.0 ppm and alkenic proton bands near δ 5.7 ppm. The relevant data for alkoxycycloalkyltellurium trihalides are summarised in Table 2.

The protons which were alkenic originally (A and B) appear as well-resolved multiplets. The H–CTe protons (A) of alkoxycyclohexyltellurium trihalides and alkoxycycloheptyltellurium trichlorides show eight- and six-line signals respectively. The differences depend on whether *trans*-A–B coupling is less than *trans*-A–C coupling and greater than *cis*-A–D coupling, or whether *trans*-A–C and *cis*-A–D coupling are equal but less than *trans*-A–B coupling. Thus the signals consist of doublets of doublets of doublets or triplets of doublets. The H–COR protons (B) of these cyclohexyl and cycloheptyl derivatives appear at higher field as six-line signals in which *trans*-A–B and *trans*-B–E coupling are equal and greater than *cis*-B–F coupling. Thus these six-line signals appear as doublets of triplets. The splitting patterns of A and B protons of 2-ethoxycyclohexyltellurium tribromide and 2-ethoxycycloheptyltellurium trichloride appear as Figs. 1 and 2 respectively.

The α-methylene protons of ethanoxy and n-propanoxy derivatives are non-equivalent and appear as two sets of eight lines (quartets of AB signals) and two sets of six lines (triplets of AB signals) respectively. Similarly, the isopropanoxy derivatives contain non-equivalent methyl groups which appear as two doublets while the α-proton appears as a heptet.

Carbon-13 NMR Spectra

The ^{13}C NMR spectra of the alkoxycycloalkyltellurium trihalides contain lines corresponding to each of the ring carbons and each of the alkoxy carbons except in the case of isopropanoxycycloheptyltellurium trichloride, where the two methyl carbons produce a single line of double intensity. Chemical shift data are summarised in Table 3.

The C–Te and C–OR signals in alkoxycycloalkyltellurium trihalides appear at low field between δ 77 and 81 ppm. Changes from trichloride to tribromide in the cyclohexyl series cause the C–Te signals to shift to higher field. Other ring carbon atoms appear in the range δ 21–38 ppm. Chemical shifts of alkoxy carbons depend on their proximity to oxygen: α 56–75; β 15–25; γ *c.* 10 ppm.

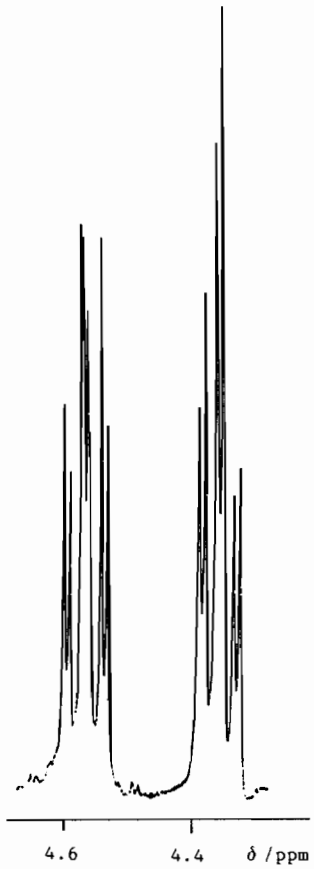

Fig. 1. ^1H NMR signals for A and B protons in 2-ethoxy-*trans*-cyclohexyltellurium tribromide.

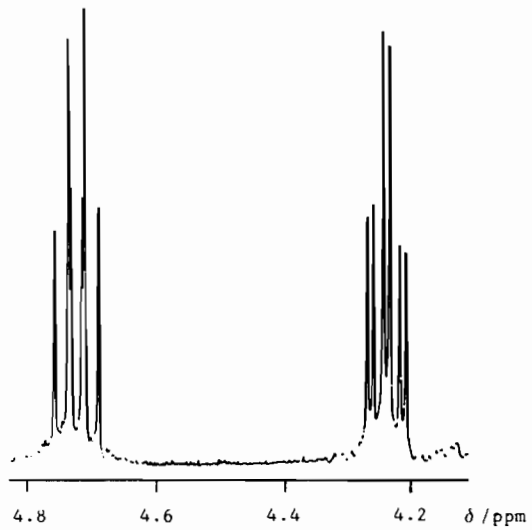

Fig. 2. ^1H NMR signals for A and B protons in 2-ethoxy-*trans*-cycloheptyltellurium trichloride.

TABLE 2. ^{1}H NMR data for alkoxycycloalkyltellurium trihalides in $CDCl_3$

Compound	HCTe(A) δ (ppm)	HCOR(B) δ (ppm)	^3J(A–D) (Hz)	^3J(A–C) (Hz)	^3J(A–B) ^3J(B–E) (Hz)	^3J(B–F) (Hz)	α δ (ppm)	β δ (ppm)	γ δ (ppm)	$^2J(\alpha_1-\alpha_2)$ (Hz)	$^3J(\alpha-\beta)$ (Hz)	$^3J(\beta-\gamma)$ (Hz)
$CH_3OC_6H_{10}TeCl_3$	4.43	4.15	3.7	12.3	10.9	4.0	3.51					
$C_2H_5OC_6H_{10}TeCl_3$	4.43	4.25	3.7	12.1	10.7	4.2	3.87 3.58	1.24		9.2	7.0	
n-$C_3H_7OC_6H_{10}TeCl_3$	4.45	4.23	3.7	12.2	10.8	4.1	3.75 3.49	1.61	0.95	9.0	6.6	7.1
i-$C_3H_7OC_6H_{10}TeCl_3$	4.41	4.34	3.6	12.0	10.7	3.8	3.98	1.24 1.23			6.1	
$CH_3OC_6H_{10}TeBr_3$	4.60	4.29	3.9	12.3	10.8	4.1	3.53					
$C_2H_5OC_6H_{10}TeBr_3$	4.57	4.36	3.7	12.4	10.9	4.0	3.86 3.57	1.22		9.1	7.0	
n-$C_3H_7OC_6H_{10}TeBr_3$	4.61	4.35	3.8	12.4	10.9	3.8	3.74 3.48	1.63	0.95	8.9	6.5	7.0
i-$C_3H_7OC_6H_{10}TeBr_3$	4.56	4.44	3.8	12.2	10.8	3.9	3.94	1.24 1.22			6.1	
$CH_3OC_7H_{12}TeCl_3$	4.74	4.14	8.5		10.3	4.0	3.61					
$C_2H_5OC_7H_{12}TeCl_3$	4.72	4.24	8.5		10.3	4.0	3.92 3.50	1.29		8.8	7.0	
n-$C_3H_7OC_7H_{12}TeCl_3$	4.76	4.24	8.5		10.2	3.8	3.73 3.56	1.61	0.99	8.7	6.7	7.4
i-$C_3H_7OC_7H_{12}TeCl_3$	4.70	4.40	8.5		10.1	4.1	4.12	1.33 1.30			6.2	

TABLE 3. ^{13}C NMR data for alkoxycycloalkyltellurium trihalides in $CDCl_3$

Compound	δ (ppm) for ring carbons							δ (ppm) for alkoxy carbons		
	CTe	COR						α	β	γ
$CH_3OC_6H_{10}TeCl_3$	80.50	80.13	32.32	27.70	25.89	23.23		56.87		
$C_2H_5OC_6H_{10}TeCl_3$	79.89	79.26	33.00	27.48	25.69	23.16		65.25	15.19	
n-$C_3H_7OC_6H_{10}TeCl_3$	80.33	79.44	32.98	27.51	25.74	23.18		71.13	22.99	10.50
i-$C_3H_7OC_6H_{10}TeCl_3$	79.79	77.76	33.97	27.36	25.49	23.18		71.73	23.67	
									22.29	
$CH_3OC_6H_{10}TeBr_3$	76.71	81.02	32.26	28.16	27.61	23.51		57.11		
$C_2H_5OC_6H_{10}TeBr_3$	76.46	79.93	32.93	27.87	27.29	23.45		65.62	15.25	
n-$C_3H_7OC_6H_{10}TeBr_3$	76.89	80.03	32.89	27.89	27.33	23.44		71.40	23.05	10.55
i-$C_3H_7OC_6H_{10}TeBr_3$	76.28	78.01	34.04	27.79	27.08	23.52		72.03	23.75	
									22.57	
$CH_3OC_7H_{12}TeCl_3$	82.29	83.57	33.00	27.86	25.08	24.64	24.41	58.58		
$C_2H_5OC_7H_{12}TeCl_3$	81.66	82.25	33.44	27.94	25.01	24.56	24.48	67.65	14.33	
n-$C_3H_7OC_7H_{12}TeCl_3$	81.90	82.17	33.39	27.90	25.40	24.98	24.47	73.28	23.91	10.44
i-$C_3H_7OC_7H_{12}TeCl_3$	81.01	79.38	33.98	27.93	25.00	23.00	21.08	74.01	24.43[a]	

[a]Double intensity.

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