Journal of Organometallic Chemistry, 268 (1984) 113–118
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE REACTION OF TRIMETHYLCHLOROSILANE WITH PHENYLTELLUROMAGNESIUM BROMIDE IN TETRAHYDROFURAN: CHARACTERISATION OF THE PRODUCTS BY ^{29}Si AND ^{125}Te NMR SPECTROSCOPY

C.H.W. JONES and R.D. SHARMA

Chemistry Department, Simon Fraser University, Burnaby, B.C., V5A 1S6 (Canada)

(Received November 17th, 1983)

Summary

The products of the reaction of Me_3SiCl with PhTeMgBr in THF have been identified with the aid of high resolution ^{29}Si and ^{125}Te NMR spectroscopy. In addition to the expected product $Me_3SiTePh$ (40%), the symmetrical telluride $(Me_3Si)_2Te$ (10%) and the ether $Me_3SiO(CH_2)_4TePh$ (45%) are also formed. The latter results from ring-opening of the solvent THF by Me_3SiCl followed by reaction of the product with PhTeMgBr.

Introduction

Phenyl trimethylsilyl telluride can be prepared by the reaction of Me_3SiCl with LiTePh [1] or PhTeMgBr [3,4]. In the latter case Hooton and Allred [3] found that, on reaction in ether, the symmetrical disproportionation product $(Me_3Si)_2Te$ was formed in low yield rather than the desired product $Me_3SiTePh$. Praefcke and Weichsel [4], however, observed that 4-methylphenyl trimethylsilyl telluride was formed, albeit in only 27% yield, on reaction of 4-methylphenyltelluromagnesium bromide in THF. The compound $(Me_3Si)_2Te$ has also been prepared from the reaction of Me_3SiCl with Li_2Te [2].

We have explored the reaction of Me_3SiCl with PhTeMgBr in THF in some detail and have observed that three products can be isolated: $(Me_3Si)_2Te$, 10% yield; $Me_3SiTePh$, 40%; and $Me_3SiO(CH_2)_4TePh$, 45%.

The third product, 4-(phenyltelluro)butyl trimethylsilyl ether, is evidently formed following cleavage of the THF by Me_3SiCl to yield $Me_3SiO(CH_2)_4Cl$ and then a subsequent reaction with PhTeMgBr. This reaction pathway is not a minor one but rather leads to a substantial yield of the tellurium-containing ether. Such ring-opening and cleavage of ethers by trimethylsilyl halides has been studied by a number of workers [5–7], and Friedrich and DeLucca [8] have recently reported the interhalogen-catalysed cleavage of ethers and esters by trimethyl-bromo- and -chloro-silane.

The purpose of the present paper is to report on the characterisation of the products of this reaction by high resolution ^{29}Si and ^{125}Te NMR spectroscopy. This technique, and in particular the coupling patterns observed for the two and three-bond coupling of ^{29}Si and ^{125}Te to the methyl protons, proved to be a very powerful one in identifying the products.

Experimental

Tellurium powder (0.30 mol) was added under dry oxygen-free nitrogen to a solution of PhMgBr (0.25 mol) in 500 ml of THF, the latter freshly distilled from sodium benzophenone ketyl. The solution of PhTeMgBr so obtained was cooled to 0°C and freshly distilled Me_3SiCl was then added dropwise. The reaction mixture was stirred overnight at room temperature and filtered. THF was removed from the filtrate under vacuum at 0°C and the resulting deep red liquid was fractionally distilled under vacuum (0.1 mmHg) to give first $(Me_3Si)_2Te$ as a colourless liquid at 25°C and, later, fractions at 70 and 85°C corresponding to $Me_3SiTePh$ and $Me_3SiO(CH_2)_4TePh$, respectively.

The NMR spectra were obtained on a Bruker WM 400 spectrometer at 126.24 MHz (^{125}Te) and at 79.49 MHz (^{29}Si) operating at ambient temperature. For ^{125}Te the resonances were found by utilising 166 kHz sweep widths, 10 μs (25°C) pulse widths and a 0.01 s delay between acquisitions. Final spectra were obtained at the appropriate frequency generally using a 5 kHz sweep width and 90° pulse widths with no delay. No broadband decoupling was employed. Data acquisition consisted of 16 k data points which were zero filled to 32 k data points for the Fourier transform. Similar procedures were used for ^{29}Si. Linewidths for ^{125}Te were 6 to 12 Hz and for ^{29}Si 1 to 2 Hz.

Mass spectra were recorded on a Hewlett–Packard 5985B mass spectrometer.

Characterisation of the products

The first fraction from the fractional distillation was identified as bis(trimethylsilyl) telluride. The ^{125}Te high resolution NMR spectrum is shown in Fig. 1a. The tellurium–silicon coupling can be discerned. The tellurium–proton couplings exhibit the characteristic pattern expected for coupling to an even number of protons in the two trimethylsilyl groups. The ^{29}Si high resolution NMR spectrum is shown in Fig. 2a and the symmetry of the spectrum reflects the coupling to the odd number of protons in each Me_3Si group. The NMR parameters abstracted from these spectra are given in Table 1.

Du Mont [9] has previously reported a ^{125}Te NMR chemical shift of -460 ppm for $(Me_3Si)_2Te$ with respect to $(MeC_6H_4)_2Te_2$ (-43 ppm with respect to Me_2Te). The present data yield a value of -858.3 ppm relative to neat Me_2Te. To confirm the present results we have prepared $(Me_3Si)_2Te$ by the reaction of lithium telluride with trimethylchlorosilane [2] and the product of that reaction gave an NMR spectrum identical to that of Fig. 1a and a ^{125}Te chemical shift of -858 ppm. The compound is difficult to characterise by chemical analysis because of its susceptibility to decomposition. The mass spectrum however yielded a parent ion peak of *m/e* (^{130}Te) of 276 in agreement with the formulation as $(Me_3Si)_2Te$.

The second fraction from the distillation, containing $Me_3SiTePh$, yielded the

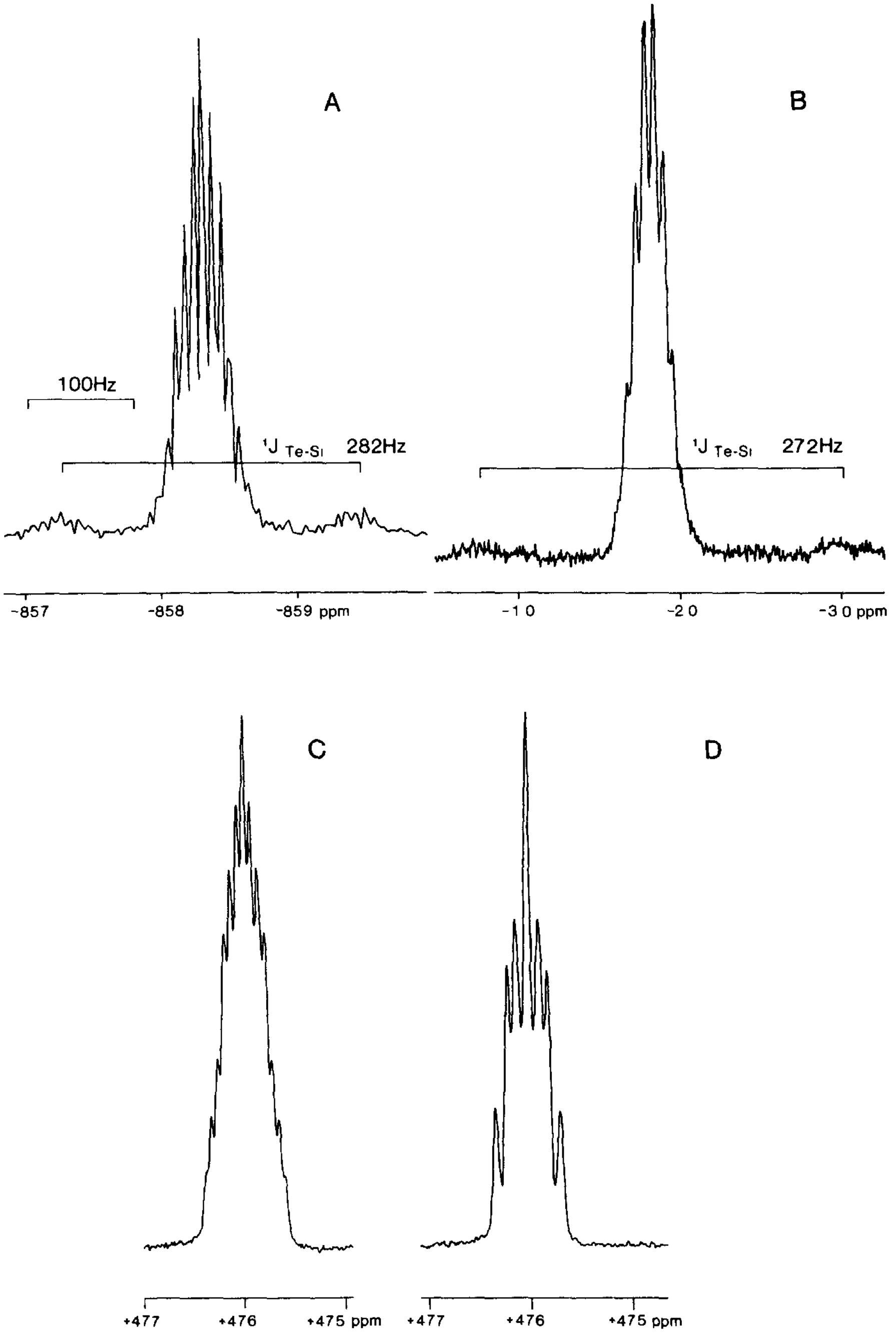

Fig. 1. The ^{125}Te NMR spectrum of (a) $(Me_3Si)_2Te$, (b) $Me_3SiTePh$ with phenyl protons decoupled, (c) $Me_3SiO(CH_2)_4TePh$ and (d) $Me_3SiO(CH_2)_4TePh$ with the phenyl protons decoupled.

NMR spectra shown in Fig. 1b and 2b. The ^{125}Te spectrum shows the coupling to the alkyl protons with the phenyl protons decoupled and the coupling pattern is characteristic of that for an odd number of protons. The ^{125}Te chemical shift of

TABLE 1

^{29}Si AND ^{125}Te NMR PARAMETERS (Solvent $C_6H_6 + C_6D_6$; $\delta(^{29}Si)$ are with reference to Me_4Si in C_6H_6; $\delta(^{125}Te)$ are with reference to neat Me_2Te)

Compound	$\delta(^{29}Si)$ (ppm)	$\delta(^{125}Te)$ (ppm)	$J(^{125}Te-^{29}Si)$ (Hz)	$^2J(^{29}Si-H)$ (Hz)	$^3J(^{125}Te-H)$ (Hz)
$(Me_3Si)_2Te$	−3.81	−858.3	282	6.99	7.0
$Me_3SiTePh$	+1.83	−1.8	272	6.98	7.0
					$^2J(^{125}Te-H)$
$Me_3SiO(CH_2)_4TePh$	+17.64	+475.9	–	6.60	14.4

$Me_3SiTePh$ is −1.8 ppm. Noting that the chemical shifts of $(Me_3Si)_2Te$ and Ph_2Te are −858.3 ppm and +688 ppm respectively, it can be seen that the tellurium nucleus becomes increasingly deshielded as the silyl groups are replaced by phenyl groups.

The ^{29}Si chemical shift of $Me_3SiTePh$ (+1.83 ppm) is very similar to that of $(Me_3Si)_2Te$ (−3.81 ppm). In general silicon shifts range from −170 to +150 ppm relative to Me_4Si [10]. These two compounds also have comparable $^1J(^{125}Te-^{29}Si)$ coupling constants. The only other tellurium-silicon compound which has previously been studied by NMR is $(H_3Si)_2Te$ where a ^{29}Si chemical shift of −88.90 ppm was reported but no tellurium–silicon coupling was observed [11].

The mass spectrum of $Me_3SiTePh$ yielded a parent ion peak with *m/e* (^{130}Te) of 280.

The third product of the reaction, $Me_3SiO(CH_2)_4TePh$, was somewhat more difficult to identify than the other two described above. The ^{125}Te spectra are shown in Fig. 1c and 1d. No silicon–tellurium coupling was observed suggesting the

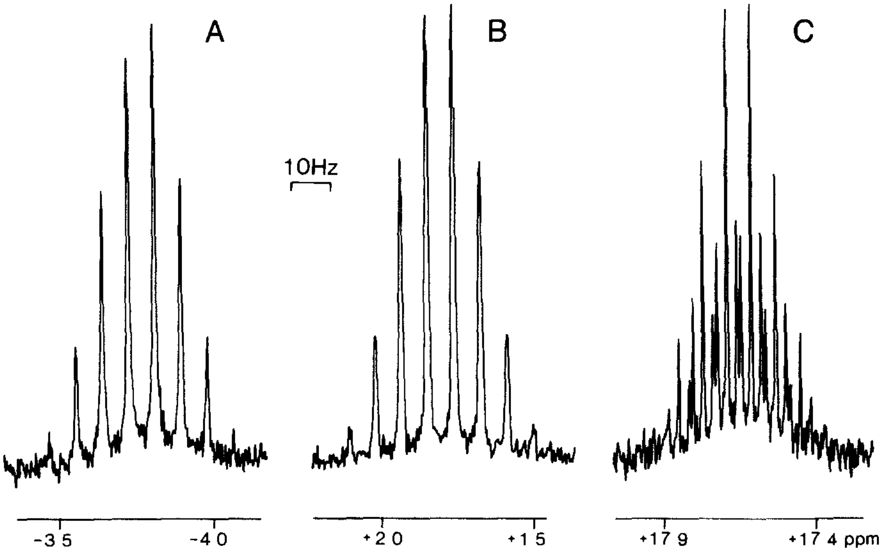

Fig. 2. The ^{29}Si proton-coupled NMR spectrum of (a) $(Me_3Si)_2Te$, (b) $Me_3SiTePh$ and (c) $Me_3SiO(CH_2)_4TePh$.

absence of a silicon–tellurium bond. When the phenyl protons were decoupled the ^{125}Te spectrum sharpened up considerably, evidence that a phenyl group was attached to tellurium (Fig. 1d). The symmetry of the phenyl-decoupled spectrum indicated that the tellurium was coupled to an even number of alkyl protons, i.e., a methylene group, and that this coupling appeared to be split further by a next nearest neighbour methylene group. The ^{125}Te chemical shift of +475.9 ppm is similar to that of other alkylphenyl tellurides reported in the literature, e.g., n-BuTePh (468 ppm), n-PrTePh (460 ppm) [12]. The above data are consistent with the presence of a $CH_2CH_2CH_2CH_2TePh$ moiety in this compound.

The ^{29}Si spectrum is shown in Fig. 2c. This spectrum was complex showing the presence of silicon coupled to an odd number of protons as in the Me_3Si group, but with further splitting into a set of triplets, presumably by a distant methylene group. This spectrum is consistent with the presence of the Me_3SiOCH_2 moiety while the ^{29}Si chemical shift of +17.64 ppm is similar to that of $Me_3SiOCH_2CH_2CH_2OCH_3$ (+15.3) [11]. Consistent with the formulation of this compound as $Me_3SiO(CH_2)_4TePh$, the ^{13}C and proton NMR spectra clearly showed the presence of four methylene groups. In the proton-decoupled ^{13}C spectrum evidence was also obtained for the coupling of one methylene carbon to tellurium. The ^{13}C and proton spectra also confirmed that the Me_3Si group had remained intact. The mass spectrum of this compound yielded a parent ion peak with *m/e* (^{130}Te) of 352 in agreement with its formulation as $Me_3SiO(CH_2)_4TePh$.

The ^{29}Si spectra could be used to monitor the separation of the products in the fractional distillation and this is illustrated in Fig. 3. A small amount of $(Me_3Si)_2O$ was also present in the distillate and this was used as a convenient internal standard.

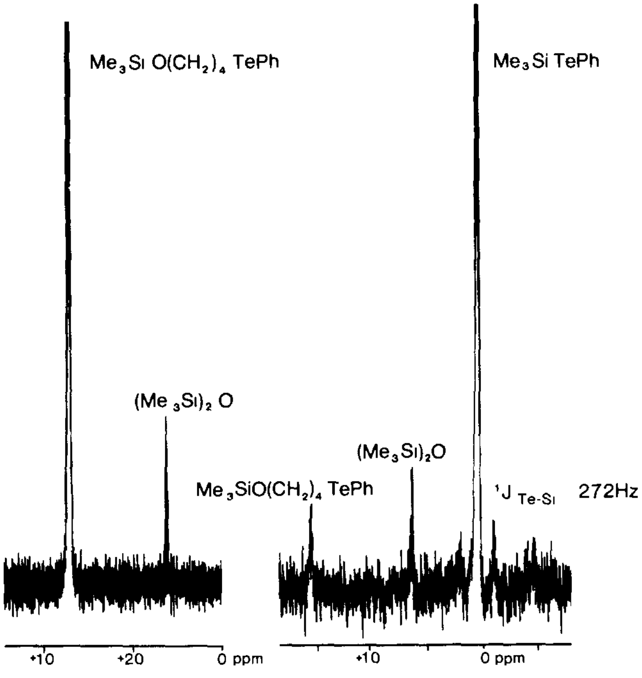

Fig. 3. The ^{29}Si NMR spectrum of the $Me_3SiO(CH_2)_4TePh$ and $Me_3SiTePh$ fractions. A small amount of $(Me_3Si)_2O$ was present in each fraction.

Acknowledgement

The authors wish to gratefully acknowledge a grant in support of this research from the Natural Sciences and Engineering Research Council of Canada.

References

1 J.E. Drake and R.T. Hemmings, Inorg. Chem., 19 (1980) 1879.
2 M.R. Detty and M.D. Seidler, J. Org. Chem., 47 (1982) 1354.
3 K.A. Hooton and A.L. Allred, Inorg. Chem., 4 (1965) 671.
4 K. Praefcke and C. Weichsel, Synthesis, (1980) 216.
5 K.C. Brinkman and J.A. Gladysz, J. Chem. Soc. Chem. Comm., (1980) 1260.
6 M.E. Jung and M.A. Lyster, J. Am. Chem. Soc., 99 (1977) 968.
7 M.E. Jung and M.A. Lyster, J. Org. Chem., 42 (1977) 3761.
8 E.C. Friedrich and D. DeLucca, J. Org. Chem., 48 (1983) 1678.
9 W.-F. du Mont and H.-J. Kroth, Z. Naturforsch. B, 36 (1981) 332.
10 H. Marsmann in P. Diehl, E. Fluck and R. Kosfeld (Eds.), NMR, Basic Principles and Progress, Vol. 17, Springer-Verlag, Berlin, New York, 1981, p. 151.
11 E.A.V. Ebsworth, J.M Edward and D.W.H. Rankin, J. Chem. Soc. Dalton Trans., (1976) 1667.
12 D.H. O'Brien, N. Dereu, C.-K. Huang, K.J. Irgolic and F.F Knapp, Jr., Organometallics, 2 (1983) 305.