Heteroatom Chemistry
Volume 5, Number 5/6, 1994

The Reactions of Tellurium Tetrachloride with Acetone

Chang-Kai Huang

Institute of Chemistry, Academia Sinica, Beijing, China

Harold Marhold

Institut für Chemie, Montanuniversität Leoben, A-8700 Leoben, Austria

Daniel H. O'Brien*

Department of Chemistry, Texas A&M University, College Station, TX 77843

Kurt J. Irgolic

Institut für Analytische Chemie, Universität Graz, Universitätplatz 1, A-8010 Graz, Austria

Received 5 July 1994

ABSTRACT

The reactions of acetone with tellurium tetrachloride have been studied with the aid of proton, carbon-13, and tellurium-125 NMR spectroscopy. In the absence of a proton scavenger, such as sodium hydrogen carbonate, at ambient temperature, a 2:1 ratio of acetone to tellurium tetrachloride quickly forms mainly acetonyl tellurium trichloride. At higher temperatures and after longer periods, the initially formed acetonyl tellurium trichloride is converted to 2-methyl-4-oxo-2-penten-1-yl tellurium trichloride through an acid-catalyzed aldol condensation. In the presence of sodium hydrogen carbonate, the condensation reaction is prevented, and an equilibrium mixture of acetonyl tellurium trichloride and bis(acetonyl) tellurium dichloride is formed.

INTRODUCTION

The reaction of tellurium tetrachloride with suitable aromatic and aliphatic compounds is a convenient way to prepare organic tellurium compounds [1]. These reactions proceed in a satisfactory manner only when activated hydrogen atoms are present in the organic reagents. Examples of activating groups in aromatic hydrocarbons are alkoxy, phenoxy, thiophenoxy, hydroxy, dialkylamino, and acetamido [2]. Aliphatic compounds condense easily with tellurium tetrachloride when carbonyl groups activate neighboring methylene hydrogens. Whereas 1,3-diketones yield stable telluracyclohexane derivatives that are easy to isolate, purify, and handle, even in a humid atmosphere, monoketones produce ketonyl tellurium trichlorides and diketonyl tellurium dichlorides that are easily hydrolyzed and decompose with elimination of elemental tellurium [3,4]. The reactions of aliphatic ketones with tellurium tetrachloride were investigated by Morgan and co-workers in 1925 [4]. Because only one product, either a ketonyl tellurium trichloride or a diketonyl tellurium dichloride, was isolated in low yield from most of the reaction mixtures, the factors determining the reactivity of monoketones toward tellurium tetrachloride and governing the product distribution cannot be deduced from Morgan's data [4].

Earlier, we investigated the reactions of aliphatic monoketones with tellurium tetrachloride in the presence of a proton scavenger [5]. The re-

*To whom correspondence should be addressed.

1042-7163/94/$5.00 + .25

actions conducted by Morgan were carried out in the *absence* of a proton scavenger such as sodium hydrogen carbonate, and, under these conditions, the reaction is somewhat more complicated. To gain information about these reactions, identify all the products formed, and define the conditions required for the preparation of a particular ketonyl tellurium compound, we carried out and report here the reactions of tellurium tetrachloride with acetone using proton, carbon-13, and tellurium-125 NMR spectroscopy. Tellurium-125 nmr spectroscopy can easily differentiate between ketonyl tellurium trichlorides and diketonyl tellurium dichlorides. The Te-125 shift difference between these compounds was estimated to be very large on the basis of the Te-125 shifts reported for a few other aliphatic tellurium chlorides [6,7]. We have found this shift difference to be greater than 600 ppm [5].

EXPERIMENTAL

Materials

Tellurium tetrachloride (99%) was purchased from AlF. Chloroform, stabilized with a nonpolar hydrocarbon, acetone (Omnisorb™, glass distilled), and petroleum ether (bp 35–60°) were supplied by MCB Manufacturing Chemists, Inc. Carbon tetrachloride and sodium hydrogen carbonate were obtained from Fisher Scientific Co. (Pittsburgh, PA). Chloroform-*d* (99.8 atom %) was purchased from Merck, Sharp & Dohme. Mesityl oxide (practical) was supplied by Eastman Kodak. Acetone was purified by distillation. Chloroform was dried over molecular sieves.

Instrumentation

The H-1 and C-13 NMR spectra of the substances in $CDCl_3$ solution were recorded on EM-390 and JEOL PFT 100/Nicolet 1080 spectrometers, respectively, with TMS as internal standard. A Varian FT-80 spectrometer equipped with a broad-band probe tuned to 25.104 MHz was used to obtain the Te-125 NMR spectra. Tellurium-125 chemical shifts are referenced to neat dimethyl telluride at 25,094,885 Hz and are estimated to be accurate to ±1 ppm. Tellurium-125 spectra required approximately 3000 to 6000 average transients at a pulse repetition rate of 0.5 s with proton-noise decoupling to obtain satisfactory signal-to-noise ratios using a sweep width of 8 KHz stored in 8K data points. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

Acetonyl Tellurium Trichloride and Diacetonyl Tellurium Dichloride

Tellurium tetrachloride (9.40 g, 0.035 mole), distilled acetone (4.00 g, 0.69 mole), $NaHCO_3$ (5.79 g, 0.069 mole), and chloroform (60 mL) were placed into a 250-mL, one-necked flask equipped with a reflux condenser, a $CaCl_2$ drying tube, and a magnetic stirring bar. The stirred mixture was refluxed for 40 minutes. The yellow solution was separated from solid material by vacuum filtration. The filter cake was washed with three 20-mL portions of chloroform. The filtrate was combined with the washings and concentrated at room temperature in a rotary evaporator under an aspirator vacuum. The oily residue (5.7 g) was dissolved in carbon tetrachloride (10 mL). Petroleum ether (100 mL) was added to this solution. On cooling in the refrigerator, diacetonyl tellurium dichloride separated as colorless crystals. The crystals were filtered off and recrystallized from $CHCl_3/CCl_4$ (1:1 v/v). The dichloride (3.5 g, 32% yield) melted at 120–122° (Ref. 126-8°). Evaporation of the solvent from the filtrate under an aspirator vacuum at room temperature left impure acetonyl tellurium trichloride (2.2 g, 22% yield) as an oily residue. The trichloride was characterized by NMR spectroscopy.

2-Methyl-4-oxo-2-penten-1-yl Tellurium Trichloride from Acetone

Tellurium tetrachloride (9.40 g, 0.035 mole), distilled acetone (4.00 g, 0.069 mole), and dry chloroform (20 mL) were refluxed for 30 minutes. Then the reaction mixture was kept at 30° for 19 hours and at 50° for an additional 4 hours. The black solution was filtered (0.07 g solid), and the filtrate concentrated in a rotary evaporator at room temperature under an oil pump vacuum. The purple-black syrupy residue (9.3 g) was dissolved in $CHCl_3/CCl_4$ (1:1 v/v) at 60°. This solution was poured into petroleum ether (300 mL). The mixture was cooled in a refrigerator. The crystalline solid that had formed was recrystallized from carbon tetrachloride. The white product (4.9 g, 43% yield) melted at 105–106°.

2-Methyl-4-oxo-2-penten-1-yl Tellurium Trichloride from Mesityl Oxide

Mesityl oxide (2-methyl-4-oxo-2-pentene) (2.18 g, 0.022 mole) and tellurium tetrachloride (6.00 g, 0.022 mole) were dissolved in dry chloroform (35 mL). The mixture was refluxed for 25 minutes. The hot, black mixture was filtered to obtain a black solid (0.2 g). The filtrate was evaporated under vacuum in a rotary evaporator. The solid purple-black residue was dissolved in chloroform (50 mL). This solution was poured into petroleum ether (25 mL). On cooling in the refrigerator, crystals (7.1 g) separated. After recrystallization from carbon tetrachloride, white crystals with a melting point of 106° were obtained (96% yield). For $C_6H_9Cl_3OTe$,

TABLE 1 Proton, Carbon-13, and Tellurium-125 Shifts for the Reaction Products of Acetone and Mesityl Oxide with Tellurium Tetrachloride

Compound		*CH_2Te*	*$\underline{C}H_3CO$*	*C=O*	*$\underline{C}H_3C$=*	*HC=, –C=*	*Te-125*
$CH_3COCH_2TeCl_3$, **1**	H-1	5.32	2.52				1372
	C-13	79.8	30.9	209.0			
$(CH_3COCH_2)_2TeCl_2$, **2**	H-1	4.62	2.42				735
	C-13	58.9	30.2	200.3			
$CH_3COCH=C(CH_3)-CH_2TeCl_3$, **3**	H-1	4.58	2.50		2.23	6.45	
	C-13	63.0	30.8	207.7	29.3	124.0,158.2	1362

TABLE 2 Dependence of the Product Distribution in the Reaction of Acetone with Tellurium Tetrachloride on Temperature, Reaction Time, and Ratio of Reagents[a]

Entry	*Temperature °C*	*Time*	*$NaHCO_3$*	*$RTeCl_3$[b] 1*	*R_2TeCl_2[b] 2*	*$R'TeCl_3$[b] 3*
1	23[c]	20 min	no	100	0	0
2	30[c]	19 h	no	26	0	74
3	50[c]	4 h	no	20	0	80
4	61[c]	10 min	no	93	3	4
5	61°	40 min	no	75	9	16
6[c]	61[c]	40 min	no	0	0	100
7	23[c]	20 min	yes	93	7	0
8	61[c]	10 min	yes	68	32	0
9	61°	40 min	yes	67	33	0
10[d]	61°	40 min	yes	29	71	0

[a]All reactions were carried out in chloroform with 2 mole of acetone per mole of $TeCl_4$ unless otherwise stated. Entries 1, 4, and 5, entries 2 and 3, and entries 7, 8, and 9 are successive measurements on the same sample.
[b]*R* = Acetonyl; R' = 2-Methyl-4-oxo-pent-2-en-yl. Product amounts represent relative number of moles based upon integrated intensities of appropriate proton resonances.
[c]After 40 minutes reflux, the sample was kept at room temperature for 6 days.
[d]Three mole of acetone per mole of tellurium tetrachloride.

calcd. (found): C 21.76 (21.86); H 2.72 (2.77); Cl 32.13 (31.93).

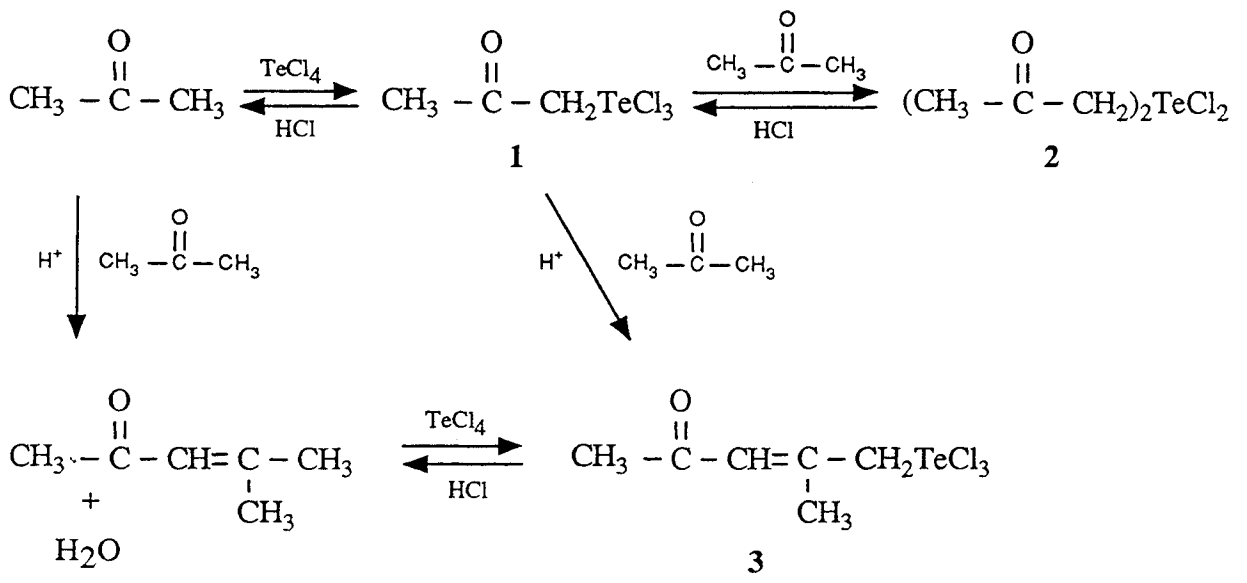
RESULTS AND DISCUSSION

The Reaction of Tellurium Tetrachloride with Acetone in the Absence of Sodium Hydrogen Carbonate

Morgan [4] refluxed redistilled acetone (2 mole) and tellurium tetrachloride (1 mole) in dry chloroform and isolated a tellurium-containing substance as colorless, nacreous plates in 17% yield. This product was the least soluble component of the reaction mixture and melted between 126–128°. The results of elemental analysis suggested that this substance was bis(acetonyl) tellurium dichloride. When Morgan's procedure was repeated, and the reaction mixture examined by proton NMR spectroscopy, a rather complex spectrum was obtained that indicated the presence of several tellurium-containing products.

A sample of bis(acetonyl) tellurium dichloride was prepared according to Morgan's procedure [4] and purified by several crystallizations from chloroform/carbon tetrachloride (1:1 v/v). The proton NMR spectrum of a solution of these white crystals in chloroform-*d* showed the expected two singlets (δ 2.42, CH_2; δ 4.62, CH_3) with the correct intensity ratio (Table 1). The Te-125 resonance (δ 735) identified the compound as a diorganyl tellurium dichloride [5]. The concentrated mother liquor from this preparation gave a proton spectrum with four resonances with intensity ratios that could not be interpreted as a mixture of diacetonyl tellurium dichloride and acetonyl tellurium trichloride.

When tellurium tetrachloride and acetone (1:2 molar ratio) were kept in chloroform for only 20 minutes, the reaction mixture gave a two-line proton spectrum (δ 2.52, 3H, δ 5.32, 2H) and a Te-125 resonance at δ 1372. The proton spectrum is in agreement with the formation of acetonyl tellurium trichloride. The downfield Te-125 resonance at δ 1372 compared to the resonance at δ 735 for



SCHEME

the dichloride confirms the presence of a trichloride. The $TeCl_3$ group is substantially more electron attracting than the $TeCl_2$ group. Similarly, the proton resonances of the hydrogens on the carbon attached to tellurium of acetonyl tellurium trichloride are downfield from the corresponding resonances of diacetonyl tellurium dichloride (Table 1).

When attempts were made to increase the yield of diacetonyl tellurium dichloride by allowing the reaction to proceed above room temperature for extended periods of time, no diacetonyl tellurium dichloride could be isolated. The proton NMR spectrum of the reaction mixture consisted of four signals in the intensity ration of 1:2:3:3 (Table 1). The Te-125 resonance at δ 1362 identified this new product as an organyl tellurium trichloride. A single crystal X-ray structural analysis of the white solid isolated from the reaction mixture in 43% yield identified the compound as 2-methyl-4-oxo-2-penten-1-yl tellurium trichloride, the product of the reaction of tellurium tetrachloride with mesityl oxide [8].

The system tellurium tetrachloride (1 mole)/acetone (2 mole) in chloroform was then investigated by proton NMR spectroscopy at various temperatures and reaction times in the presence and absence of sodium hydrogen carbonate (Table 2). The reaction sequence that describes the behavior of this system is shown in Scheme 1.

The reaction of tellurium tetrachloride with acetone is rapid at room temperature, initially producing only acetonyl tellurium trichloride, **1**. Comparing the integrals of the remaining acetone methyl hydrogens to the product methylene hydrogens showed that over 90% of the tellurium tetrachloride had reacted at 23° after *only* 20 minutes (Entry 1, Table 2). At this point, early in the reaction, the only product present is acetonyl tellurium trichloride. Similar integral comparisons showed that essentially all the tellurium tetrachloride had reacted after longer periods or at higher temperatures (Entries 2–10, Table 2). No diacetonyl tellurium dichloride, **2**, was detected in reaction mixtures that had been kept for several hours at temperatures as high as 50° (Entries 2 and 3). Small amounts of the dichloride **2** began to appear in reaction mixtures maintained at the reflux temperature of chloroform (Entries 4 and 5). With increasing reaction time and in the absence of an acid scavenger such as sodium hydrogen carbonate, acetonyl tellurium trichloride, **1**, and diacetonyl tellurium dichloride, **2**, were completely converted to 2-methyl-4-oxo-pent-2-en-1-yl tellurium trichloride, **3**. The reaction mixture that had been refluxed for 40 minutes and then kept at room temperature for 6 days contained only this pentenyl tellurium trichloride (Entry 6).

The conversion of diacetonyl tellurium dichloride to the pentenyl tellurium trichloride requires the cleavage of at least one carbon–tellurium bond (Scheme 1, **2** → **1**). Acetonyl tellurium trichloride could be converted to the pentenyl tellurium trichloride either directly (Scheme 1, **1** → **3**) or first through cleavage to acetone, condensation of acetone to form mesityl oxide, and then reaction of the mesityl oxide with tellurium tetrachloride to form **3**. It could not be ascertained which of these two pathways was being followed in the conversion of acetonyl tellurium trichloride to the pentenyl tellurium trichloride. It is well known that acetone condenses to mesityl oxide in an acid-cat-

alyzed aldol reaction [9]. Hydrogen chloride is always present in the reaction mixture, in the absence of a proton scavenger, as the product of the reaction of tellurium tetrachloride with acetone.

The Reaction of Tellurium Tetrachloride with Acetone in the Presence of Sodium Hydrogen Carbonate

The acid-catalyzed formation of mesityl oxide and the consequent formation of 2-methyl-4-oxo-2-penten-1-yl can be prevented by addition of sodium hydrogen carbonate as a hydrogen chloride scavenging agent (Entries 7–10, Table 2). Under these conditions, only acetonyl tellurium trichloride and diacetonyl tellurium dichloride are produced. After a few minutes at room temperature, acetonyl tellurium trichloride is the major product (Entry 7). Again, comparison of integrals shows that virtually all of the tellurium tetrachloride has reacted to form mainly acetonyl tellurium trichloride after this short period. Refluxing of the reaction mixture then produces an equilibrium mixture containing about a 2:1 ratio of acetonyl tellurium trichloride to diacetonyl tellurium dichloride (Entry 8). After further reflux and 6 days at room temperature, the molar ratio of dichloride to trichloride had not substantially changed (Entry 9). The reaction can be forced toward diacetonyl tellurium dichloride by using an excess of acetone. When acetone and tellurium tetrachloride in a 3:1 molar ratio were refluxed in chloroform for 40 minutes, the ratio of dichloride to trichloride was 71:29 (Entry 10).

ACKNOWLEDGMENTS

Financial support for this investigation by the Robert A. Welch Foundation of Houston, TX, and the Karl-Franzens-Universität Graz, Austria (travel funds), is gratefully acknowledged.

REFERENCES

[1] K. J. Irgolic: *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, p. 29 (1974).
[2] K. J. Irgolic: in D. Klamann (ed): *Organotellurium Compounds, Houben-Weyl Methods of Organic Chemistry*, GeorgThieme Verlag, Stuttgart, Germany, vol. 12b, p. 305 (1990).
[3] K. J. Irgolic: *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, pp. 67 and 77 (1974).
[4] G. T. Morgan, O. E. Elvins, *J. Chem. Soc.*, 1925, 2625.
[5] D. H. O'Brien, K. J. Irgolic, C.-K. Huang, *Heteroatom Chem.*, *1*, 1990, 215.
[6] H. C. E. McFarlane, W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1973, 2416.
[7] W. McFarlane, F. J. Berry, B. C. Smith, *J. Organometal. Chem.*, *113*, 1976, 139.
[8] C.-K. Huang, D. H. O'Brien, K. J. Irgolic, E. A. Meyers, *Cryst. Struct. Commun.*, *11*, 1982, 1593.
[9] J. March: *Advanced Organic Chemistry*, 3rd ed., John Wiley & Sons, New York, 1985, p. 834.