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The Reactions of Tellurium Tetrachloride with Aliphatic Monoketones

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ABSTRACT

The reactions of 13 aliphatic ketones with tellurium tetrachloride has been studied with proton, carbon-13, and tellurium-125 NMR. Tellurium tetrachloride adds electrophilically to the α-carbon of the enol to form ketonyl tellurium trichlorides. Unsymmetric ketones gave mixtures of isomeric ketonyl tellurium trichlorides. Steric hindrance determines which ketonyl tellurium trichlorides form. Except for the ketonyl tellurium trichloride from 2-butanone, tellurium reacts preferentially with the least substituted α-carbon. Six methyl alkyl ketones also yielded appreciable amounts of diketonyl tellurium dichlorides. In all diketonyl tellurium dichlorides, tellurium is bonded to less hindered methylene carbons.

INTRODUCTION

The reactions of tellurium tetrachloride with ketones in refluxing chloroform were investigated by Morgan and co-workers in the 1920's [1]. Although all of these reactions were carried out under exactly the same conditions with a 2 : 1 molar ratio of ketone to tellurium tetrachloride, only one of the possible products was isolated from most of the reaction mixtures [2]. 2-Butanone, 3-pentanone, and 4-heptanone produced only ketonyl tellurium trichlorides in 75%–85% yield even though enough ketone was present to give diketonyl tellurium dichlorides. The reaction with acetone led to the isolation of diacetonyl tellurium dichloride in 16% yield. Methyl alkyl ketones (2-pentanone, 3-methyl-2-butanone, 2-hexanone, 4-methyl-2-pentanone but not 2-butanone) yielded diketonyl tellurium dichlorides. Morgan succeeded in isolating a ketonyl tellurium trichloride and a diketonyl tellurium dichloride only from the reaction mixture obtained by refluxing 3,3-dimethyl-2-butanone and tellurium tetrachloride. 2,4-Dimethyl-3-pentanone did not react. Morgan [2] mentioned that the reaction mixture obtained from an unsymmetric ketone could contain two ketonyl tellurium trichlorides with the $TeCl_3$-group bonded to one or the other of the two carbon atoms adjacent to the carbonyl group. However, he was unable to prove the presence of isomeric ketonyl tellurium trichlorides. Nuclear magnetic resonance (NMR) spectroscopy (proton, carbon-13, Te-125) may be used to determine the distribution of products formed in these reactions without the necessity of isolating the organic tellurium compounds. Tellurium-125 magnetic resonance spectroscopy should be especially useful because of the expected large shift difference between organyl tellurium trichlorides [3] and diorganyl tellurium dichlorides [4], and the sensitivity of tellurium shifts to the structure of the carbon skeleton of alkyl groups [5, 6].

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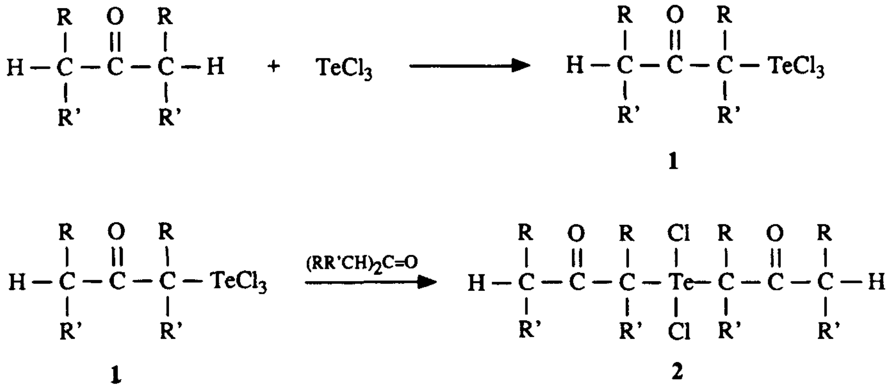

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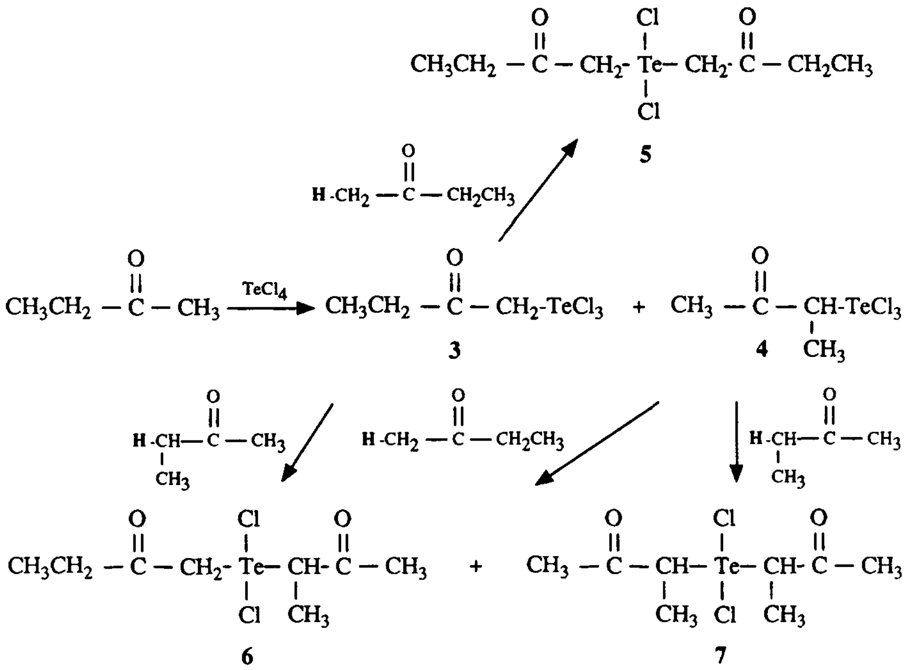

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RESULTS AND DISCUSSION

The reactions of 13 aliphatic monoketones with tellurium tetrachloride in molar ratios of 1 : 1 or 2 : 1 in refluxing chloroform were reinvestigated. The reactions mixtures were refluxed for 45 min and then examined by proton, carbon-13, and tellurium-125 magnetic resonance spectroscopy. The spectra showed that in almost all cases at least two products had formed.

Symmetric ketones may form ketonyl tellurium trichlorides **1** and diketonyl tellurium dichlorides **2** (Equation 1). Unsymmetric ketones with at least one hydrogen atom on each of the carbon atoms bonded to the carbonyl group have the potential of producing two ketonyl tellurium trichlorides (**3**, **4**), and three diketonyl tellurium dichlorides (**5**, **6**, **7**) as shown for methyl ethyl ketone (Equation 2). Steric and electronic factors determine which of these products form.

Proton and Carbon-13 Chemical Shifts

The presence of several products in the reaction mixtures made the proton NMR spectra rather complex. Not all the proton resonances were well separated. Overlapping resonances were the rule in the spectra of reaction mixtures from unsymmetric ketones that formed two isomeric tellurium trichlorides. However, the downfield resonances caused by the hydrogens on the tellurium-bearing carbon atoms could always be easily assigned. These assignments were verified by comparison with the shifts of purified tellurium trichlorides and dichlorides. Several of the solutions were studied at 200

MHz to resolve close-lying proton resonances. The proton, carbon-13, and tellurium-125 chemical shifts for ketonyl tellurium trichlorides and diketonyl tellurium dichlorides are summarized in Tables 1–4.

For ketonyl tellurium trichlorides the proton resonances for the hydrogens on the tellurium-bearing carbon appear between 5.20 and 5.70 δ (Table 1, H_a). These shifts show that the trichlorotelluro group deshields these protons by approximately 3.1 ppm with respect to the ketone precursors. The deshielding effect is strong enough to be felt by the hydrogens on the carbon adjacent to the tellurium-bearing carbon. These hydrogens resonate about 1.4 ppm further downfield in the trichlorides than in the ketones (Table 1, H_b).

The trichlorotelluro group has a deshielding effect on the carbon atoms similar to the effect observed for protons. The resonances for the carbons attached to tellurium are found between 79 and 95 δ, approximately 50 ppm downfield from the corresponding resonances in the ketones (Table 2, C_a) [7]. The exact carbon-13 shift of a tellurium-bearing carbon atom depends on the degree of alkyl substitution at this carbon. Unsubstituted methylene carbons resonate at approximately 79 δ. The signals for carbons with one methyl group are consistently at about 88 δ. More substituted carbons have shifts between 92 and 95 δ. The resonances of the carbonyl carbons are located between 209 and 225 δ, approximately 10 ppm downfield from the resonances of the corresponding carbonyls in the ketones [8]. These shifts are also dependent on the degree of alkyl substitution.

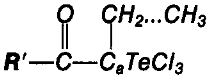
Six methyl alkyl ketones yielded appreciable amounts of diketonyl tellurium dichlorides. The spectra of the dichlorides are characterized by proton singlets between 4.61 and 4.80 δ and carbon-13

TABLE 1 Proton Chemical Shifts for Ketonyl Tellurium Trichlorides

Ketonyl Structure *R—TeCl₃* *R*	$R'\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{TeCl_3}{\mid}}{CH_a}{}^{a}CH^{b}\text{—}$			*R′*		
	H_a	H_b	$-CH_3$	$-CO-CH-$	$-CH_2-$	$-CH_3$
$CH_3-CO-CH_2—$	5.32			2.52		
$CH_3CH_2-CO-CH-CH_3$	5.43	2.46		2.75		1.22
$CH_3CH_2CH_2-CO-CH-CH_2CH_3$	5.20^a	3.00	1.37	2.70	1.76	1.00
$(CH_3)_2CH-CO-C(CH_3)_2$		2.49		3.00		1.29
$CH_3CH_2-CO-CH_2—$	5.27			2.82		1.10
$CH_3-CO-CH-CH_3$	5.47	2.46		2.50		
$CH_3CH_2CH_2-CO-CH_2—$	5.26			2.74	1.72	1.00
$CH_3-CO-CH-CH_2CH_3$	5.42^a	—^{b}	—^{b}	2.72		
$(CH_3)_2CH-CO-CH_2—$	5.37			2.88		1.28
$CH_3-CO-C(CH_3)_2$		2.46		2.49		
$CH_3CH_2CH_2-CO-CH-CH_3$	5.44	2.30		2.63	1.78	0.85
$CH_3CH_2-CO-CH-CH_2CH_3$	5.20^a	—^{b}	—^{b}	—^{b}		—^{b}
$(CH_3)_2CH-CO-CH-CH_3$	5.70	2.45		3.08		1.33, 1.21^c
$CH_3CH_2-CO-C(CH_3)_2$		2.47		2.56		1.05
$CH_3CH_2CH_2CH_2-CO-CH-CH_3$	5.46	2.32		2.65	1.52, 1.27	0.85
$CH_3CH_2-CO-CH-CH_2CH_2CH_3$	5.26^a	—^{b}	—^{b}	—^{b}	—^{b}	
$(CH_3)_2CHCH_2-CO-CH_2—$	5.33			2.71	2.22^d	1.02
$(CH_3)_2CHCH_2-CO-CH-CH_3$	5.53	2.43		2.64	2.30^d	1.02
$(CH_3)_3C-CO-CH_2—$	5.42					1.32

[a] Doublet of doublets because of nonequivalent diastereotopic H_b protons.
[b] Not observed due to overlapping resonances or to low intensity.
[c] Nonequivalent diastereotopic methyl groups.
[d] Methine protons.

TABLE 2 Carbon-13 Chemical Shifts for Ketonyl Tellurium Trichlorides

Ketonyl Structure *R—TeCl$_3$*	 $R'{-}C(=O){-}C_\alpha(CH_2...CH_3)TeCl_3$			*R'*		
R	**C=O**	**C$_\alpha$**	*-CH$_2$, -CH$_3$*	*-CO-CH-*	*-CH$_2$-*	*-CH$_3$*
$CH_3\text{-}CO\text{-}CH_2\text{—}$	209.0	79.8		30.1		
$CH_3CH_2\text{-}CO\text{-}CH\text{-}CH_3$	217.7	87.2	11.3	33.7		7.7
$CH_3CH_2CH_2\text{-}CO\text{-}CH\text{-}CH_2CH_3$	218.8	94.5	21.3, 14.4[a]	42.7	16.6[a]	13.2[a]
$(CH_3)_2CH\text{-}CO\text{-}C(CH_3)_2$	224.6	91.7	22.5	36.6		18.9
$CH_3CH_2\text{-}CO\text{-}CH_2\text{—}$	211.9	79.7		36.1		7.4
$CH_3\text{-}CO\text{-}CH\text{-}CH_3$	214.8	88.0	11.4	27.5		
$CH_3CH_2CH_2\text{-}CO\text{-}CH_2\text{—}$	212.3	79.5		44.2	17.1	13.2
$CH_3\text{-}CO\text{-}CH\text{-}CH_2CH_3$	216.4	94.5	21.0	28.5		14.3
$(CH_3)_2CH\text{-}CO\text{-}CH_2\text{—}$	216.1	78.5		41.1		17.5
$CH_3\text{-}CO\text{-}C(CH_3)_2$	218.9	91.7	22.8	27.7		
$CH_3CH_2CH_2\text{-}CO\text{-}CH\text{-}CH_3$	217.6	87.4	11.2	41.6	16.4	13.1
$CH_3CH_2\text{-}CO\text{-}CH\text{-}CH_2CH_3$	218.4	93.6	21.3	34.6		14.3
$(CH_3)_2CH\text{-}CO\text{-}CH\text{-}CH_3$	221.0	87.3	11.5	38.4		18.2, 16.6[b]
$CH_3CH_2\text{-}CO\text{-}C(CH_3)_2$	—[c]	91.2	9.8[d]	31.6		7.0[d]
$CH_3CH_2CH_2CH_2\text{-}CO\text{-}CH\text{-}CH_3$	217.7	87.6	11.2	39.6	24.7 21.7	13.4
$CH_3CH_2\text{-}CO\text{-}CH\text{-}CH_2CH_2CH_3$	218.7	91.8	29.3, 22.6, 13.6	34.6		7.0
$(CH_3)_2CHCH_2\text{-}CO\text{-}CH_2\text{—}$	209.0	81.3		52.6	25.6	22.4
$(CH_3)_2CHCH_2\text{-}CO\text{-}CH\text{-}CH_3$	217.4	88.3	11.3	48.4	24.7	22.3, 22.1[b]
$(CH_3)_3C\text{-}CO\text{-}CH_2\text{—}$	218.8	78.7		27.7		22.8

[a,d] These chemical shift assignments may be interchanged.
[b] Nonequivalent diastereotopic methyl carbons.
[c] Not observed because of low intensity.

resonances between 57 and 59 δ for the carbons attached to tellurium (Table 4). These shifts show that the deshielding effect of the dichlorotelluro group is not as pronounced as the effect of the trichlorotelluro group.

Tellurium-125 Chemical Shifts

Tellurium-125 magnetic resonance proved to be a convenient method for detecting and identifying tellurium-containing ketones in the reaction mixtures. This method was especially useful for the identification of products derived from isopropyl ketones that do not have hydrogen atoms on the carbon atoms bonded to tellurium. The resonances of protons on carbon atoms not bonded to tellurium in the tellurium trichlorides and dichlorides were not well separated. The tellurium-125 chemical shifts for the ketonyl tellurium trichlorides and diketonyl tellurium dichlorides are collected in Tables 3 and 4.

The difference in tellurium-125 shifts between ketonyl tellurium trichlorides (1372–1632 δ) and diketonyl tellurium dichlorides (735–745 δ) is at least 627 ppm, showing the powerful deshielding effect of the additional chlorine in the trichlorides. Table 3 is arranged to reveal the effect of alkyl substitution on the tellurium-125 shifts of the trichlorides. All the trichlorides in which tellurium is bonded to a methylene group have tellurium-125 resonances in the narrow range of 1364–1376 δ. Structural changes in the alkyl group on the other side of the carbonyl group have little effect on the tellurium-125 shifts. Methyl substitution at the tellurium-bearing carbon ($COCH_2Te$ to $COCH[CH_3]Te$) causes the tellurium resonance to move downfield by approximately +111 ppm. This change is similar in direction but smaller in magni-

TABLE 3 Tellurium-125 Chemical Shifts for Ketonyl Tellurium Trichlorides

Ketonyl Structure *R—TeCl₃* *R*	*δ, Te-125*	*Ketonyl Structure* *R—TeCl₃* *R*	*δ, Te-125*
$CH_3\text{-}CO\text{-}CH_2\text{—}$	1372	$CH_3\text{-}CO\text{-}\underset{\mid}{C}H\text{-}CH_2CH_3$	1488
$CH_3CH_2\text{-}CO\text{-}CH_2\text{—}$	1374	$CH_3CH_2\text{-}CO\text{-}\underset{\mid}{C}H\text{-}CH_2CH_3$	1488
$CH_3CH_2CH_2\text{-}CO\text{-}CH_2\text{—}$	1376	$CH_3CH_2CH_2\text{-}CO\text{-}\underset{\mid}{C}H\text{-}CH_2CH_3$	1490
$(CH_3)_2CH\text{-}CO\text{-}CH_2\text{—}$	1373	$CH_3\text{-}CO\text{-}\underset{\mid}{C}H\text{-}CH_3$	1483
$(CH_3)_2CHCH_2\text{-}CO\text{-}CH_2\text{—}$	1373	$CH_3CH_2\text{-}CO\text{-}\underset{\mid}{C}H\text{-}CH_3$	1485
$(CH_3)_3C\text{-}CO\text{-}CH_2\text{—}$	1364	$CH_3CH_2CH_2\text{-}CO\text{-}\underset{\mid}{C}H\text{-}CH_3$	1484
$CH_3\text{-}CO\text{-}\underset{\mid}{C}(CH_3)_2$	1632	$(CH_3)_2CH\text{-}CO\text{-}\underset{\mid}{C}H\text{-}CH_3$	1482
$CH_3CH_2\text{-}CO\text{-}\underset{\mid}{C}(CH_3)_2$	1621	$(CH_3)_2CHCH_2\text{-}CO\text{-}\underset{\mid}{C}H\text{-}CH_3$	1489
$(CH_3)_2CH\text{-}CO\text{-}\underset{\mid}{C}(CH_3)_2$	1625		

tude when compared to the changes of +189 and +215 ppm for α-methyl substitution in dialkyl tellurides [6] and dialkyl ditellurides [5]. The introduction of an additional methyl group [$COCH(CH_3)Te$ to $COC(CH_3)_2Te$] causes a large downfield shift change of +143 ppm. Methyl substitution on the carbon β to the tellurium [$COCH(CH_3)Te$ to $COCH(CH_2CH_3)Te$] causes a change in shift of only a few ppm. These small changes are much different than the large upfield shift changes upon β-methyl substitution in dialkyl ditellurides [5] and dialkyl tellurides [6].

All diketonyl tellurium dichlorides observed in this study have the tellurium attached to a methylene carbon. Tellurium-125 shifts are within a narrow range of 10 ppm (735–745 δ) (Table 4). As observed for the trichlorides, the tellurium shifts of the dichlorides are not influenced by the structure of the alkyl group on the other side of the carbonyl group.

Isomeric Ketonyl Tellurium Trichlorides

Among the 13 ketones that were reacted with tellurium tetrachloride in refluxing chloroform in the presence of sodium hydrogen carbonate eight had the potential of forming two isomeric ketonyl tellurium trichlorides (Equation 2). Isomeric pairs of trichlorides were formed by 2-butanone, 2-pentanone, 3-methyl-2-butanone, 3-hexanone, 2-methyl-3-pentanone, and 3-heptanone. The isomer ratios (Table 5) were determined using the tellurium-125 integrals and the proton integrals of the resonances for the CH_2Te and $CHTe$ groups. A slight excess of tellurium tetrachloride (12 mmol) was reacted with each ketone (11 mmol) to simplify the proton spectra by limiting the amount of diketonyl tellurium dichloride formed. An example of a tellurium-125 spectrum of a reaction mixture containing two isomeric tellurium trichlorides is presented in Figure 1.

TABLE 4 Proton, Carbon-13, and Tellurium-125 Chemical Shifts for Diketonyl Tellurium Dichlorides, $(R\text{—}CO\text{-}CH_2)_2TeCl_2$

	-CH₂-Te		*C═O*	*R*			*R*			
R—	*H-1*	*C-13*	*C-13*	*H-1*			*C-13*			*δ, Te-125*
$CH_3\text{—}$	4.62	58.9	200.3	2.42			30.2			735
$CH_3CH_2\text{—}$	4.69	57.2	204.7	2.68	1.18		36.3	7.4		—[a]
$CH_3CH_2CH_2\text{—}$	4.61	58.2	202.9	2.65	1.72	1.02	44.7	17.1	13.3	741
$(CH_3)_2CH\text{—}$	4.73	57.2	206.6	2.80	1.20		40.7	17.7		745
$(CH_3)_2CHCH_2\text{—}$	4.61	59.1	202.5	2.52	2.20	1.00	51.5	25.0	22.3	734
$(CH_3)_3C\text{—}$	4.80	57.4	208.5		1.32		44.0	26.4		742

[a] Not observed because of low intensity.

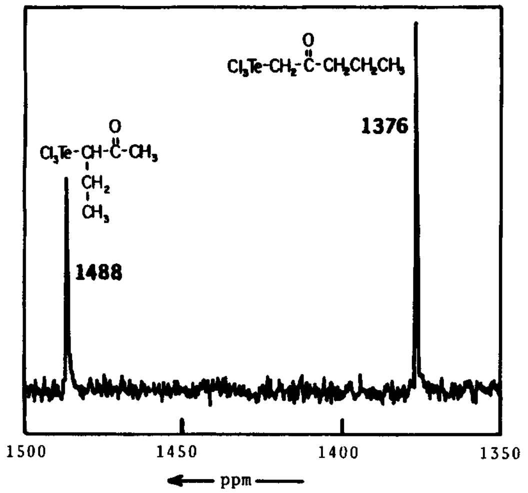


FIGURE 1 Te-125 NMR spectrum of the mixture obtained by refluxing 12 mmol tellurium tetrachloride and 11 mmol 2-pentanone in 30 mL of $CDCl_3$ for 45 min. Varian FT 80 spectrometer at 25.104 MHz, 5624 scans, 0.5 sec repetition rate, sweep width 8 KHz. Intensity ratio: δ 1376/δ 1488 = 67/33.

The reaction of tellurium tetrachloride with ketones may be viewed as an electrophilic addition of tellurium tetrachloride to the carbon-carbon double bond of the enol. Unsymmetric ketones may have two enols. Attack of tellurium tetrachloride is influenced by two opposing effects: the electron density at the C=C-OH carbon that increases with successive alkyl substitution and promotes bond formation with tellurium, and steric hindrance that also increases with alkyl substitution but impedes bond formation with tellurium. 2-Butanone is the only ketone in which electron density is more influential than steric hindrance. Hence, the reaction mixture contains 5 times more ketonyl tellurium trichloride with tellurium bonded to the methyl-substituted carbon than ketonyl tellurium trichloride with tellurium attached to the methylene carbon (Table 5). Methyl substitution at the β-carbon (2-butanone to 2-pentanone) or additional methyl substitution at the α-carbon (2-butanone to 3-methyl-2-butanone) tips the balance in favor of tellurium-carbon bond formation at the less hindered methyl (CH_3CO) carbon. 4-Methyl-2-pentanone produced only one tellurium trichloride with tellurium bonded to the methyl (CH_3CO) carbon. In unsymmetric ethyl ketones, C_2H_5COR (R > C_2H_5), the electronic and steric effects favor the reaction of tellurium tetrachloride with the methylene hydrogens of the ethyl group by a large margin (Table 5). These results imply that it is quite difficult to force tellurium to bond to an α-carbon substituted with two alkyl groups when another less sterically hindered carbon is available. When a less sterically hindered carbon is not present in the molecule, tellurium tetrachloride will react with methine carbons. For instance, 2,4-dimethyl-3-pentanone and tellurium tetrachloride yields 2,4-dimethyl-3-oxo-2-pentyl tellurium trichloride in refluxing chloroform in 78% yield. Morgan reported this ketone to be unreactive toward tellurium tetrachloride [2].

The tellurium trichloride isolated by Morgan [2] in 75% yield from the reaction of 2-butanone and tellurium tetrachloride was proposed to be 2-oxo-1-butyl tellurium trichloride (eqs. 2, 3). When this reaction was repeated by refluxing a chloroform solution of 2-butanone with tellurium tetrachloride for 45 minutes, the same white solid reported by Morgan was isolated in 66% yield. The proton NMR spectrum of this solid has a one-hydrogen quartet at 5.47 δ, a three-hydrogen doublet at 2.46 δ, and a three-hydrogen singlet at 2.50 δ. This spectrum is consistent with a structure in which the trichloro tellurium group is attached to the α-carbon of an ethyl group rather than to a methyl carbon. This trichloride is, therefore, 2-oxo-3-butyl tellurium trichloride, **4**, and not the compound claimed by Morgan. However, the reaction mixture does contain a small amount of 2-oxo-1-butyl tellurium trichloride. The spectrum (Figure

TABLE 5 Ratio of Isomeric Ketonyl Tellurium Trichlorides[a]

Ketone	% Cl_3Te at		Ketone	% Cl_3Te at	
CH_3-CO-R	CH_3	R	CH_3CH_2-CO-R	CH_3CH_2	R
Methyl ketones			Ethyl ketones		
CH_3-CO-CH_3	50	50	CH_3CH_2-CO-CH_2CH_3	50	50
CH_3-CO-CH_2CH_3	16	84	CH_3CH_2-CO-$CH_2CH_2CH_3$	91	9
CH_3-CO-$CH_2CH_2CH_3$	67	33	CH_3CH_2-CO-$CH(CH_3)_2$	85	15
CH_3-CO-$CH(CH_3)_2$	71	29	CH_3CH_2-CO-$CH_2CH_2CH_2CH_3$	92	8
CH_3-CO-$CH_2CH(CH_3)_2$	100	0	CH_3CH_2-CO-$CH_2CH(CH_3)_2$	100	0

[a] Tellurium tetrachloride (12 mmol), ketone (11 mmol) in chloroform in the presence of sodium hydrogen carbonate. The ratios from Te-125 spectra reported in this table are in good agreement with the ratios from H-1 spectra.

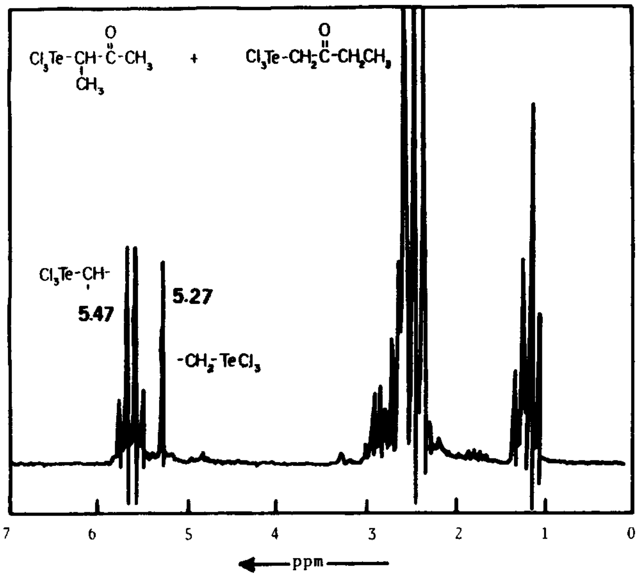


FIGURE 2 Proton NMR spectrum of the mixture obtained by refluxing 12 mmol tellurium tetrachloride and 11 mmol 2-butanone in 30 mL of $CDCl_3$ for 45 min. Intensity ratio: δ 5.47/δ 5.27 = 84/16.

2) of the solution taken at the end of the reflux period has a singlet at 5.27 δ characteristic of hydrogens on a methylene carbon attached to a trichlorotelluro group (Table 1) and the resonances of an ethyl group. The Te-125 shifts (Table 3) support the conclusions drawn from the proton spectra. Recrystallization of the reaction mixture from carbon tetrachloride cleanly separated these two isomeric tellurium trichlorides.

Diketonyl Tellurium Dichlorides

Diketonyl tellurium dichlorides were formed only from methyl alkyl ketones. Tellurium in these compounds is always bonded to two methylene carbons (Table 4). Unsymmetric methyl ketones could form three diketonyl tellurium dichlorides (eq. 2). However, no spectroscopic evidence was found for dichlorides in which tellurium is bonded to one methylene carbon and to one methine carbon. A trichlorotelluro group bonded to an alkyl-substituted α-carbon did not react under the conditions of these experiments with another molecule of the ketone that formed the tellurium trichloride, even if it is a methyl ketone. Steric hindrance appears to be responsible for this lack of reactivity. Whereas methyl alkyl ketones (2-oxo-alkanes), with exception of 2-butanone, form *bis*(2-oxo-1-alkyl) tellurium dichlorides and ketonyl tellurium trichlorides in roughly equal amounts, ethyl alkyl ketones produce only small quantities of the dichlorides (Table 6) even when the molar ratio of ketone to tellurium tetrachloride is 2 : 1. Steric arguments explain the low yields of these dichlorides. The ratios for the isomeric trichlorides given in Table 6 (ketone/$TeCl_4$ 2 : 1) are close to but not the same as the ratios in Table 5 (ketone/$TeCl_4$ 1 : 1).

EXPERIMENTAL

Materials

Tellurium tetrachloride (99%) and isobutylmagnesium chloride (1.96 M in diethyl ether) were purchased from Alpha Products. Acetone (Omnisorb, glass distilled), chloroform, and petroleum ether (bp 35–60°C) were supplied by MCB Manufacturing Chemists, Inc. 2-Butanone, 4-methyl-2-pentanone, carbon tetrachloride, and sodium hydrogen carbonate were obtained from Fisher Scientific Co. 3-Pentanone, 4-heptanone, 2-pentanone, 3-methyl-2-butanone, 3-heptanone, and propionaldehyde were obtained from Eastman Kodak Co. 2,4-Dimethyl-3-pentanone, 3,3-dimethyl-2-butanone, 3-hexanone, and 2-methyl-3-pentanol were purchased from Al-

TABLE 6 Ratios of Isomeric Ketonyl Tellurium Trichlorides and Diketonyl Tellurium Dichlorides

R_1-CO-R_2	$TeCl_4$ (mmol)	Molar Ratio Ketone/$TeCl_4$	% Cl_3Te at		% R_2TeCl_2
R_1 R_2			R_1	R_2	
CH_3-CO-CH_2CH_3	15	1.7	18	78	4
CH_3-CO-$CH_2CH_2CH_3$	30	2.0	32	15	53
CH_3-CO-$CH(CH_3)_2$	30	2.3	64	10	26
CH_3-CO-$CH_2CH(CH_3)_2$	7.5	2.0	55	0	45
CH_3-CO-$C(CH_3)_3$	38	2.0	59	0	41
CH_3CH_2-CO-CH_2CH_3	30	2.0	47	47	6
CH_3CH_2-CO-$CH_2CH_2CH_3$	12	0.9	88	9	3
CH_3CH_2-CO-$CH_2CH_2CH_2CH_3$	30	2.0	92	8	Trace
$CH_3CH_2CH_2$-CO-$CH_2CH_2CH_2CH_3$	30	2.0	50	50	0

drich Chemical Co. All ketones were purified by distillation before use. 2-Methyl-3-pentanone and 5-methyl-3-hexanone were prepared by the chromic acid oxidation of 2-methyl-3-pentanol and 5-methyl-3-hexanol, respectively. 5-Methyl-3-hexanol was synthesized from isobutylmagnesium chloride and propionaldehyde. Chloroform-*d* (99.8%) was purchased from Merck, Sharp and Dohme.

Nuclear Magnetic Resonance

Proton spectra were recorded on Varian Associates EM 390 and XL 200 spectrometers. Carbon-13 spectra were recorded with JEOL PFT 100/Nicolet 1080 and Varian Associates FT 80 Fourier transform spectrometers. Proton and carbon-13 chemical shifts are reported in ppm relative to internal TMS. All proton resonances had the expected multiplicities and integrated intensities. The shifts were assigned on the basis of multiplicities and intensities obtained from spectra of isolated and purified ketonyl tellurium trichlorides and diketonyl tellurium dichlorides. An additional feature aided in the assignments of proton shifts. The trichlorotelluro group attached to the α-carbon of a propyl or butyl ketone makes the α-carbon chiral and the adjacent methylene protons diastereotopic. Resonances for the individual diastereotopic β-protons (Table 1, H_b) and other diastereotopic protons were not observed at 90 MHz either due to complex proton coupling or to interference from overlapping resonances. However, the chiral α-protons were doublets of doublets because of coupling to the nonequivalent β-protons. In a few cases, nonequivalent diastereotopic carbons were observed in the carbon-13 spectra (Table 2).

Tellurium-125 spectra were recorded on a Varian Associates FT 80 spectrometer equipped with a broad-band probe tuned to 25.104 MHz. About 3,000–23,000 average transients at a pulse repetition rate of 0.5 sec with proton-noise decoupling were required to obtain satisfactory signal-to-noise ratios using a sweep width of 8 KHz stored in 8K data points. Tellurium-125 chemical shifts are referenced to dimethyl telluride with external diphenyl ditelluride [$\delta(Me_2Te) = \delta(Ph_2Te_2) + 688$] in $CDCl_3$ as standard.

Determination of Isomer Ratios for Ketonyl Tellurium Trichlorides

For the determination of the ratios of the isomeric ketonyl tellurium trichlorides, a slight excess of tellurium tetrachloride (3.26 g, 12 mmol) was refluxed for 45 min with the ketone (11 mmol) in chloroform-*d* (3 mL) in the presence of sodium hydrogen carbonate (1.0 g, 12 mmol). After the reaction mixture had cooled to room temperature, aliquots were withdrawn for proton and tellurium-125 NMR spectroscopy. The ratios (Table 5) of the isomeric tellurium trichlorides were obtained from the proton and the tellurium integrals.

Determination of the Ketonyl Tellurium Trichloride/Diketonyl Tellurium Dichloride Ratios

Tellurium tetrachloride, the ketone, and sodium hydrogen carbonate were added to chloroform (50 mL/30 mmol $TeCl_4$). The mixture was refluxed for 45 min, then cooled to room temperature, and filtered. The solvent was removed from the filtrate under vacuum. Portions of the crude product were dissolved in $CDCl_3$ to obtain proton, C-13, and Te-125 spectra. The ratios of the tellurium compounds were obtained from the proton and tellurium integrals (Table 6).

Isolation of Ketonyl Tellurium Trichlorides and Diketonyl Tellurium Dichlorides

To assist in the assignment of NMR signals, several ketonyl tellurium trichlorides and dichlorides were isolated from the crude reaction products and purified. The purified compounds (white crystals) were found to contain no impurities by proton, C-13, and Te-125 NMR spectroscopy. The reported yields are based on tellurium tetrachloride.

2-Oxo-3-butyl Tellurium Trichloride

2-Butanone (1.90 g, 26 mmol) and tellurium tetrachloride (4.00 g, 15 mmol) were refluxed in 28 mL of chloroform for 30 min. The solvent was evaporated under vacuum and the crude product was recrystallized from 100 mL of carbon tetrachloride to give 2-oxo-3-butyl tellurium trichloride (mp 91–92°C, 3.17 g, 9.9 mmol, 66% yield).

4-Oxo-3-heptyl Tellurium Trichloride

4-Heptanone (6.85 g, 60 mmol), tellurium tetrachloride (8.08 g, 30 mmol) and 5 g of sodium hydrogen carbonate were refluxed in 60 mL of chloroform for 40 min. The reaction mixture was filtered, the filtrate concentrated to about 10 mL, and 50 mL of petroleum ether was added. Upon cooling in the refrigerator, white crystals of 4-oxo-3-heptyl tellurium trichloride formed (5.25 g, 15 mmol, 50% yield).

3,3-Dimethyl-2-oxo-1-butyl Tellurium Trichloride and bis*(3,3-Dimethyl-2-oxo-1-butyl) Tellurium Dichloride*

3,3-Dimethyl-2-butanone (7.50 g, 75 mmol) and tellurium tetrachloride (10.20 g, 38 mmol) were refluxed in 75 mL of chloroform for 40 min. Evaporation of the solvent under vacuum gave 9.0 g of crude solid. The crude product was dissolved in 300 mL of warm petroleum ether. On cooling and filtration, crystals of 3,3-dimethyl-2-oxo-1-butyl tellurium trichloride were obtained (4.67 g, 14 mmol, 37% yield). Concentration of the filtrate gave the dichloride (3.39 g, 10 mmol, 26% yield).

bis(*2-Oxo-1-pentyl*) *Tellurium Dichloride*

2-Pentanone (5.16 g, 60 mL), tellurium tetrachloride (8.02 g, 30 mmol) and 5 g of sodium hydrogen carbonate were refluxed in 50 mL of chloroform for 45 min. After filtration and evaporation of the solvent, a light yellow oily residue (8.81 g) was obtained. Proton NMR showed this oil to be a mixture of 47% trichlorides and 53% *bis*(2-oxo-1-pentyl) tellurium dichloride. The oil was triturated with 45 mL of carbon tetrachloride. The carbon tetrachloride solution was concentrated to 10 mL. On cooling in the refrigerator the concentrate deposited white crystals of *bis*(2-oxo-1-pentyl) tellurium dichloride (0.93 g, 2.8 mmol, 9% yield).

Bis(*4-methyl-2-oxo-1-pentyl*) *Tellurium Dichloride*

The crude white solid (1.50 g) from the reaction of 4-methyl-2-pentanone (1.50 g, 15 mmol) and tellurium tetrachloride (2.02 g, 8 mmol) was triturated with petroleum ether (50 mL). On cooling of the solution in the refrigerator, a small amount of white crystalline dichloride precipitated.

2,4-Dimethyl-3-oxo-2-pentyl Tellurium Trichloride

2,4-Dimethyl-3-pentanone (1.38 g, 12 mmol) and tellurium tetrachloride (3.26 g, 12 mmol) were dissolved in 30 mL of chloroform. After addition of sodium hydrogen carbonate (1.0 g, 12 mmol), the mixture was refluxed for 1 h. The mixture was cooled to room temperature and then filtered to remove a small amount of tellurium and residual sodium hydrogen carbonate. The filtrate was evaporated under vacuum. The residue (4.29 g) was recrystallized from 30 mL of petroleum ether to give 2,3-dimethyl-3-oxo-2-pentyl tellurium trichloride (3.3 g, 9 mmol, 78% yield). Analysis for $C_7H_{13}Cl_3OTe$ (347.1) calcd. (found): C 24.22 (24.14), H 3.78 (3.86).

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