the reaction was conducted for (*Z*)-1,2-diphenylpropene. In this case, only the cis epoxide **10** and starting material were detected by gas chromatographic analysis of the reaction mixture. The identities of both the trans and cis epoxides were established by comparison to authentic samples.[31]

Epoxidation of Cyclohexene, 1-Methylcyclohexene, and 1,2-Dimethylcyclohexene. Due to the volatility of these epoxides, the yields were determined by gas chromatography. These yields were determined at low conversion (10–40% reaction) to ensure that all of the peroxide had reacted (analysis of mixtures containing large amounts of hydroperoxide resulted in low yields, presumably due to decomposition upon injection into the GC). The yields are corrected for unreacted starting material. A typical procedure is described for cyclohexene. A 10-mL bomb was charged with 0.25 mL (2.47 mmol) of cyclohexene and 0.17 mL of mesitylene (0.62 mmol) as an internal standard. A drop of this mixture was removed and analyzed by gas chromatography to determine the ratio of olefin to mesitylene. To the remaining solution were added 0.018 g (0.062 mmol) of Cp^*MoO_2Cl in 1 mL of toluene and 0.23 mL (3 M, 0.62 mmol) of *tert*-butyl hydroperoxide in toluene. The mixture was allowed to react at room temperature for 1 h. Gas chromatographic analysis of the reaction mixture revealed that 9.5% of the olefin had been converted to cyclohexene epoxide in 85% yield. In the same manner, the yield of methylcyclohexene epoxide was found to be 93% and the yield of 1,2-dimethylcyclohexene epoxide was found to be 99%. The identities of the three epoxides were determined by comparison to authentic samples.

Relative Rate Studies. In a typical procedure, a stock solution of 0.05 mL of 1,2-dimethylcyclohexene (3.70 mmol) and 1.5 mL of cyclohexene (14.8 mmol) was prepared and analyzed by gas chromatography to determine the ratio of the two olefins. The samples for the relative rate determinations were prepared by charging a 10-mL bomb with 0.50 mL of the stock solution (3.70 mmol of cyclohexene, 0.925 mmol of 1,2-dimethylcyclohexene), 0.003 g (0.010 mmol) of Cp^*MoO_2Cl, and 0.015 mL (0.083 mmol) of 3-ethyl-3-hexyl hydroperoxide. The mixture was allowed to react for 1 h at room temperature and then analyzed by gas chromatography. The data were corrected for the relative concentrations of the olefins as well as the relative response of the flame ionization detector of the gas chromatograph. The response correction factor of the FID detector was measured by integration of the response of each analyte against an internal standard. This was calculated over a concentration regime corresponding to that used in these experiments, and the response factors were found to be nearly linearly dependent on the concentration in this range.

Similarly, the relative rates were measured with *tert*-butyl hydroperoxide (used as a 2.7 M solution in toluene) and *n*-hexyl hydroperoxide. As a check on the data obtained, the relative amount of the olefins was varied (29.62 mmol of cyclohexene and 3.7 mmol of 1,2-dimethylcyclohexene). This gave the same relative rates within 5%.

As an additional check, several runs were monitored by gas chromatography over a 4-h time span to ensure the products were stable to the reaction conditions. No significant change in the relative amounts of the two epoxides was detected in these experiments.

Acknowledgment. We acknowledge the National Institutes of Health for financial support of this work through Grant No. GM-25459 (to R.G.B.) and the National Science Foundation for a predoctoral fellowship (to M. K.T.). We are grateful to Professor R. Breslow for helpful discussions, and we thank Professors J. W. Faller and J. E. Bercaw for disclosure of results prior to publication.

Registry No. **5**, 119782-31-9; **6**, 125978-97-4; **7**, 132774-70-0; **8**, 62960-04-7; **9**, 23355-99-9; **10**, 10282-18-5; $Cp^*Mo(CO)_3Cl$, 63511-23-9; cyclooctene, 931-88-4; cyclooctene oxide, 286-62-4; 1,2,4,5-tetramethylcyclohexadiene, 26976-92-1; geraniol, 106-24-1; (*E*)-1,2-diphenylpropene, 833-81-8; (*Z*)-1,2-diphenylpropene, 1017-22-7; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 1,2-dimethylcyclohexene, 1674-10-8; cyclohexene epoxide, 286-20-4; methylcyclohexene epoxide, 1713-33-3; dimethylcyclohexene epoxide, 17612-36-1; *tert*-butyl hydroperoxide, 75-91-2; 3-ethyl-3-hexyl hydroperoxide, 90951-85-2; *n*-hexyl hydroperoxide, 4312-76-9.

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[31] These epoxides were prepared by reaction of the respective olefins with *p*-chloroperbenzoic acid. For a general description of the procedure see: Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 135.

Synthesis and Reactivity of α-(Dichloroorganyltelluro) Ketones

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The reaction of equimolar amounts of ketones or ketone trimethylsilylenol ethers with organyltellurium trichlorides in boiling benzene produces α-(dichloroorganyltelluro) ketones. The yields are good in the reaction of ketones and ketone silylenol ethers with (*p*-methoxyphenyl)tellurium trichloride; however, the reaction with aliphatic tellurium trichlorides gives good results only with ketone silyl enol ethers; reaction with ketones gives low yields of the α-(dichloroorganyltelluro) ketones. α-[Dichloro(*p*-methoxyphenyl)telluro]acetophenone and α-[dichloro(*p*-methoxyphenyl)telluro]pinacolone afford the corresponding α-chloro ketone in good yield on pyrolysis. Under similar conditions, the α-[dichloro(*p*-methoxyphenyl)telluro]cycloalkanones give low yields of the α-chloro ketones. Reaction of the α-(dichloroorganyltelluro) ketones with halogens (Cl_2, Br_2) gives the corresponding α-halo ketone even in the case of the cycloalkanones. The α-(dichloroorganyltelluro) ketones were characterized by ^1H and ^{13}C NMR and IR spectroscopies. X-ray analyses of α-[dichloro(*p*-methoxyphenyl)telluro]cyclohexanone showed that the intramolecular distance Te---O is shorter than the sum of the van der Waals radii of the Te and O, indicating an interaction between the tellurium atom and the carbonyl oxygen.

Introduction

Although α-thio- and α-selenocarbonyl compounds are well-known and are valuable synthetic tools, their tellurium counterparts have scarcely been investigated and only a few reports deal with the synthesis and reactivity of this class of organoelemental compounds.[1-13] The most complete study concerning this matter reports the synthesis

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of some bis(dichlorotelluro)acetophenones and α-(dichloroorganyltelluro)alkanones as well as their reduction to the corresponding tellurides.[12] The α-(dichloroorganyltelluro) ketones were obtained by reacting the ketones with tellurium tetrachloride in carbon tetrachloride under reflux. More recently Kambe and coworkers reported the synthesis of α-tellurocarbonyl compounds through the reaction of lithium enolates with arenetellurenyl halides.[11] Ho and co-workers prepared α-telluro esters by reacting benzenetellurenyl iodide with the corresponding organozinc compounds.[13]

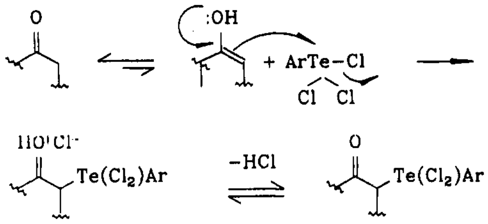
Several years ago Petragnani obtained α-(dichloroaryltelluro)acetone and -acetophenone compounds by reaction of an excess of the corresponding ketone with aryltellurium trichlorides.[5] Sadekow prepared α-(dichloroaryltelluro)acetophenones by reacting aryltellurium trichlorides with silyl enol ethers of acetophenones.[11] Although these two reactions are potentially good methods to introduce an organyltellurium moiety at the α-position of a ketone, the first suffers the limitation of using a great excess of the ketone and both are limited to methyl ketones. Recently, we reported preliminary results on the scope and limitations of these reactions, demonstrating that they could be performed in stoichiometric amounts and that cycloalkanones also react satisfactorily by both methods.[14] In view of the good results obtained, we extended the study investigating the reactivity of aliphatic tellurium trichlorides toward ketones and ketone silyl enol ethers, since alkyltellurium trichlorides are little investigated compounds and their reactivity toward organic substrates is unknown.[15] On the other hand, it was recently reported by Barton and co-workers that the tellurium extrusion from diorganyltellurides catalyzed by palladium leads to the formation of carbon–carbon bonds.[16] In this way, the availability of α-(organyltelluro) ketones bearing alkyl groups linked to tellurium is desirable for further studies.

In this paper, we give a full account of our findings on the reaction of alkyl- and aryltellurium trichlorides with ketones and ketone silyl enol ethers and report their transformation into α-halo ketones.

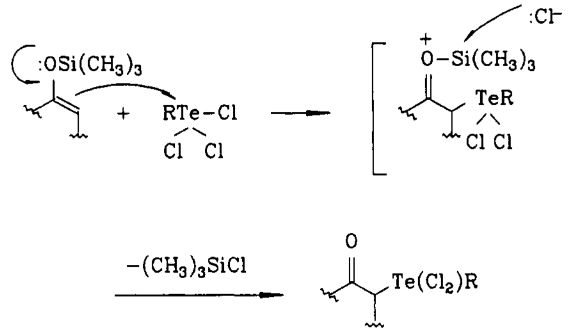
Results and Discussion

The aryltellurium trichloride employed was the (*p*-methoxyphenyl)tellurium trichloride in view of its ease of preparation. The reaction with ketones was performed in boiling benzene and occurred with hydrochloric acid gas evolution, requiring a prolongued reaction time (6–72 h). Stoichiometric amounts of the reagents were used, except in the reaction with acetone, when acetone was used as the solvent. The workup was made by adding methanol/water (1:1) to the reaction mixture to destroy the unreacted aryltellurium trichloride, which was transformed into the aryltellurium oxychloride, which is equally insoluble in the organic phase and in the aqueous phase. After the extraction, the residual oil was chromatographed on silica gel, eluting first with diethyl ether to remove the excess nonreacted ketone and then with chloroform. Some elemental tellurium was observed on the top of the chromatographic column. The products were recrystallized from chloroform/petroleum ether. In some cases, it was necessary to maintain the system in the refrigerator for some days in order to obtain crystalline material. The methyl ketones and cycloalkanones gave the desired products; however, diisopropyl ketone and 2,6-dimethylcyclohexanone failed to give the α-telluro ketone, probably due to steric hindrance. The reaction with 2-methylcyclohexanone showed pronounced regioselectivity, leading exclusively to the 2-[dichloro(*p*-methoxyphenyl)telluro]-6-methylcyclohexanone. Once more, the steric crowding at the 2-position of the substrate can account for this selectivity. The α-(dichloroaryltelluro) ketones are light-sensitive and decompose slowly, liberating tellurium when exposed to light for a long period (several days at ceiling light). Heating to high temperatures also causes their decomposition, as will be discussed later.

Scheme I



Scheme II



The reaction of the aryltellurium trichloride with ketones is presumed to occur via the enol form of the ketone as shown in Scheme I.

The reaction of ketones with alkyltellurium trichlorides gave very poor yields of the α-telluro ketones presumably due to the unstability of the alkyltellurium trichlorides, since a great amount of elemental tellurium could be detected in the reaction medium after the time indicated in Table I.

In view of the prolongued reaction time required in the reaction of ketones with the organyltellurium trichlorides and the highly acidic reaction medium resulting from the acid delivery in the last step of the reaction, we decided to react stoichiometric amounts of ketone silyl enol ethers and organyltellurium trichlorides to obtain the corresponding α-(dichloroorganyltelluro) ketones. With this methodology, the reaction times were shorter, the yields were higher in some cases, and the presence of acid in the reaction medium was avoided. These facts make this methodology attractive from a synthetic point of view. The workup and the purification of the products were performed as described before. Analogous to the results de-

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(13) Ho, Y.; Huang, Z.; Huan, X. *Synth. Commun.* **1989**, *19*, 1625.
(14) Stefani, H. A.; Comasseto, J. V.; Petragnani, N. *Synth. Commun.* **1987**, *17*, 443.
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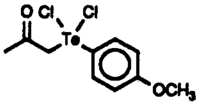
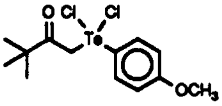
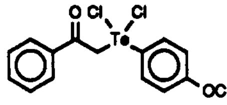
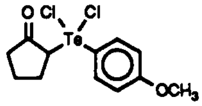
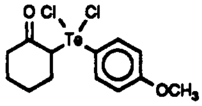
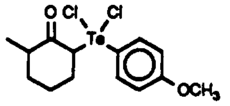
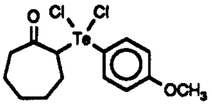
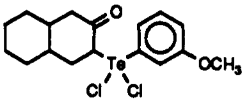
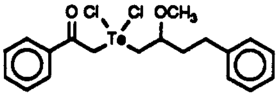
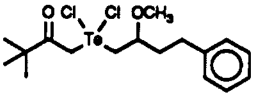
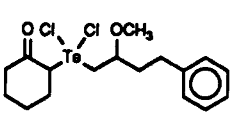
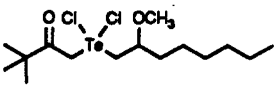
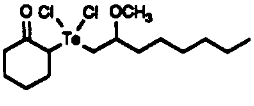
Table I. α-(Dichlorotelluro) Ketones Prepared

α-(dichlorotelluro) ketone[b]		reaction time, h	% yield[a]	mp, °C	anal. found (calcd)		IR ν(C═O),[c,g] cm^{-1}	^{1}H NMR (CDCl$_3$/TMS int) δ, ppm (*J*, Hz)	^{13}C NMR (CDCl$_3$/TMS int) δ, ppm
no.	structure				% C	% H			
1		1 (A) 11 (B)	75 48	137–138	33.21 (33.12)	3.49 (3.30)	1705 (1712)[d]	2.37 (s, 3 H), 3.85 (s, 3 H), 4.76 (s, 2 H), [7.03 (d, *J* = 8.75, 2 H), 8.07 (d, *J* = 8.75, 2 H) AA′BB′ system]	29.87, 55.62, 67.16, 115.92, 119.65, 135.52, 162.52, 199.71
2		72 (A) 10 (B)	73 94	90–92	38.37 (38.57)	4.38 (4.48)	1690 (1708)[d]	1.21 (s, 9 H), 3.81 (s, 3 H), 4.97 (s, 2 H), [7.0 (d, *J* = 8.88, 2 H), 8.04 (d, *J* = 8.88, 2 H) AA′BB′ system]	26.08, 43.68, 55.25, 65.86, 115.35, 118.32, 135.41, 161.91, 207.88
3		48 (A) 6 (B)	80 90	135–136	42.65 (42.41)	3.44 (3.33)	1653 (1683)[d]	3.82 (s, 3 H), 5.37 (s, 2 H), 7.44–8.08 (m, 5 H), [7.02 (d, *J* = 8.57, 2 H), 8.13 (d, *J* = 8.57, 2 H) AA′BB′ system]	55.49, 66.56, 115.74, 118.46, 128.95, 129.24, 134.41, 134.67, 135.65, 162.36, 191.84
4		14 (A) 7 (B)	82 70	104–106	37.25 (37.08)	3.71 (3.60)	1730 (1751)[d]	2.10–2.48 (m, 6 H), 3.82 (s, 3 H), 4.63 (t, *J* = 8.69, 1 H), [7.01 (d, *J* = 8.69, 2 H), 8.09 (d, *J* = 8.69, 2 H) AA′BB′ system]	22.52, 25.66, 37.09, 55.19, 68.22, 115.14, 119.12, 135.75, 161.95, 211.81
5		72 (A) 7 (B)	92 80	124–126	38.55 (38.76)	4.19 (4.00)	1698 (1715)[d]	1.65–2.73 (m, 8 H), 3.85 (s, 3 H), 4.78 (dd, *J* = 16.0, 8.0, 1 H), [7.03 (d, *J* = 9.03, 2 H), 8.10 (d, *J* = 9.03, 2 H) AA′BB′ system]	25.00, 25.45, 29.09, 41.26, 55.38, 78.58, 115.54, 115.89, 136.07, 162.18, 204.73
6		7 (A) 6 (B)	87 60	134–136	39.81 (40.34)	4.22 (4.35)	1687 (1713)[d]	1.14 (d, 3 H), 1.31–2.68 (m, 7 H), 3.84 (s, 3 H), 4.94 (dd, *J* = 16.0, 8.0, 1 H), [7.03 (d, *J* = 9.03, 2 H), 8.10 (d, *J* = 9.03, 2 H) AA′BB′ system]	30.10, 46.26, 55.49, 80.10, 115.71, 116.23, 136.16, 162.33, 206.38
7		7 (A)	85	*f*	40.62 (40.34)	4.48 (4.35)	1678 (1702)[d]	1.39–2.69 (m, 10 H), 3.80 (s, 3 H), 4.95 (m, 1 H), [7.01 (d, *J* = 8.33, 2 H), 8.56 (d, *J* = 8.33, 2 H) AA′BB′ system]	42.58, 55.37, 81.73, 115.53, 118.37, 136.89, 162.12, 209.07
8		10 (A) 2.3 (B)	81 86	148–150	44.63 (44.69)	4.78 (4.85)	1694 (1715)[d]	1.27–3.16 (m, 14 H), 3.84 (s, 3 H), 5.00 (dd, *J* = 16.0, 8.0, 1 H), 7.03 (d, *J* = 8.48, 2 H), 8.10 (d, *J* = 8.48, 2 H) AA′BB′ system]	55.41, 78.91, 115.59, 115.96, 136.13, 162.15, 205.07
9		4 (B)	86	108–110	47.47 (47.05)	4.57 (4.86)	1665 (1683)[e]	1.87–2.19 (m, 2 H), 2.58–2.71 (m, 2 H), 3.43 (s, 3 H), 3.68 (t, *J* = 12.5, 2 H), 3.97–4.08 (m, 1 H), 5.15 (AB quartet, 15 Hz), 7.15–7.98 (m, 10 H)	30.60, 34.53, 51.13, 57.15, 57.34, 74.61, 126.06, 128.13, 128.44, 129.07, 134.45, 134.58, 140.88, 192.11
10		36 (A) 24 (B)	4 85	78–90	44.32 (44.24)	5.64 (6.19)	1693 (1708)[e]	1.20 (s, 9 H), 1.96–2.14 (m, 2 H), 2.65 (t, *J* = 7.28, 2 H), 3.40 (s, 3 H), 3.59 (t, *J* = 11.55, 2 H), 3.91–4.04 (m, 1 H), 4.78 (AB quartet, 15 Hz), 7.16–7.31 (m, 5 H)	30.40, 34.40, 43.56, 56.80, 56.85, 57.95, 74.40, 125.82, 127.94, 128.21, 140.73, 208
11		28 (A) 22 (B)	23 89	120–122	44.51 (44.36)	5.23 (5.28)	1697 (1715)	1.63–2.76 (m, 12 H), 3.28 (t, *J* = 14.31, 1 H), 3.44 (s, 3 H), 3.65 (dd, 4.36, 1 H), 3.89–4.07 (m, 1 H), 4.68 (dd, *J* = 12.7, 6.8, 1 H), 7.17–7.33 (m, 5 H)	25.41, 29.10, 30.71, 34.74, 41.08, 41.17, 57.24, 57.33, 65.76, 74.89, 126.11, 128.28, 128.52, 205.03
12		8 (B)	38	*f*	40.88 (41.36)	6.81 (6.87)	1694 (1708)[e]	0.79–0.83 (m, 3 H), 1.17 (s, 9 H), 123–174 (m, 10 H), 3.38 (s, 3 H), 3.47 (t, *J* = 11.11, 2 H), 3.85–3.91 (m, 1 H), 4.71 (AB quartet *J* = 15.23)	13.86, 22.29, 24.28, 26.20, 31.45, 32.64, 50.51, 57.79, 59.13, 74.75, 208.14
13		4 (B)	76	*f*	41.16 (41.16)	6.17 (6.21)	1698 (1715)[e]	0.89 (t, *J* = 6.47, 1 H), 1.25–2.78 (m, 21 H), 3.21 (t, *J* = 10.91, 1 H), 3.44 (s, 3 H), 3.68 (dd, *J* = 12.39, 6.87, 1 H), 3.81–4.00 (m, 1 H)	13.88, 22.36, 24.39, 26.85, 29.15, 31.49, 33.00, 40.97, 41.79, 49.83, 57.11, 75.27, 204.85

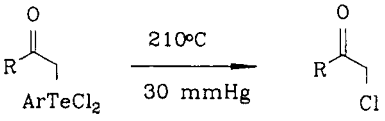
[a] Yield of the recrystallized product. [b] Recrystallized from CHCl$_3$/petroleum ether. [c] KBr pellets. [d] Spectra taken on a Perkin-Elmer 457-A spectrometer. [e] Spectra taken on a Perkin-Elmer 1750 FT spectrometer. [f] Oils at room temperature. [g] Values in parentheses refer to the nonsubstituted ketone. Method A: Reaction of organoyltellurium trichlorides with ketones in benzene under reflux. Method B: Reaction of organoyltellurium trichlorides with ketone silyl enol ethers in benzene under reflux.

scribed for (*p*-methoxyphenyl)tellurium trichloride with ketones, silyl enol ethers failed to react with diisopropyl ketone and 2,6-dimethylcyclohexanone. On the other hand, reaction of 2-methylcyclohexanone with (*p*-methoxyphenyl)tellurium trichloride gave exclusively 2-[dichloro(*p*-methoxyphenyl)telluro]-6-methylcyclohexanone. This fact is probably due to the steric crowding at the 2-position of the silyl enol ether, which hinders the reaction at this site. On the other hand, trace amounts of acid in the aryltellurium trichloride causes the decomposition of the silyl enol ether to the parent ketone, which then reacts with the aryltellurium trichloride via enol, leading to the less-substituted product.

A possible mechanism for the reaction of ketone silyl enol ethers with organyltellurium trichlorides is depicted in Scheme II.

Contrary to the results obtained when ketones were used, reaction of alkyltellurium trichlorides with ketone silyl enol ethers gave good yields of the desired products, which were isolated and purified in the same way as were the aryltellurium derivatives (for yields and spectral data, see Table I).

As mentioned before, the α-(dichloroorganyltelluro) ketones are thermally unstable, and at high temperature (210 °C) under vacuum (30 mmHg), they decompose, giving α-chloro ketones. However in only two cases was it possible to isolate the α-chloro ketone (α-chloropinacolone and α-chloroacetophenone) in syntheticaly useful yields. In the case of cycloalkanones, the α-chloro ketones were isolated in low yields contaminated with chlorinated aromatic products, elemental tellurium, and nonidentified tarry byproducts (eq 1).

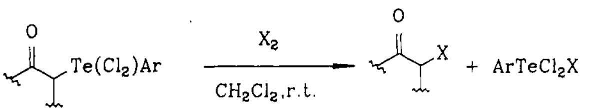


(1)

$Ar=p\text{-}CH_3OC_6H_4$; $R=C_6H_5$ 81%

$R=t\text{-}Bu$ 85%

In view of this lack of generality, we decided to investigate another route to α-halo ketones from α-(dichloroorganyltelluro) ketones. Reaction of α-(dichloroorganyltelluro) ketones with stoichiometric amounts of chlorine or bromine in methylene dichloride at room temperature led to the α-halo ketones in good yields. The reaction was very rapid (Table II) and a aryltellurium trihalide was formed as by-product, which was separated from the reaction mixture by filtration (eq 2).



(2)

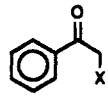
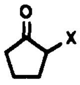
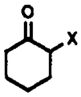
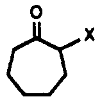
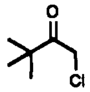
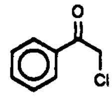
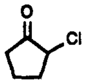
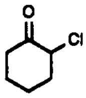
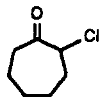
$Ar=p\text{-}CH_3OC_6H_4$

$X_2=Cl_2,Br_2$

When an excess of halogen was used, polyhalogenated ketones and halogenated aromatic byproducts were formed, the aryltellurium trichlorides acting as Lewis acids. In the reactions with bromine, mixtures of α-chloro and α-bromo ketones were formed.

The α-(dichloroorganyltelluro) ketones were characterized by infrared and ^1H and ^{13}C NMR spectroscopies and by an X-ray analysis of 2-[dichloro(*p*-methoxyphenyl)telluro]cyclohexanone. The introduction of a $RTeCl_2$ group in the α-position of a ketone reduces the ν(C=O) frequency (see Table I). This result is in accordance with published data for compounds containing a tellurium moiety in the vicinity of an electron-rich functionality,[15] suggesting an interaction of the tellurium atom with the carbonyl oxygen. A X-ray analyses for 2-[dichloro(*p*-methoxyphenyl)telluro]cyclohexanone showed that the intramolecular distance between the tellurium atom and the carbonyl oxygen (2.93, 2.94 Å) is shorter than the sum of the van der Waals radii of the Te and O of 3.60 Å,[17] and it is much shorter than the upper range of 3.3–3.4 Å found for weak bonds. Similar results were obtained for other tellurium compounds containing tellurium–halogen bonds in the neighborhood of carbon–oxygen bonds and has been interpreted in terms of three-center bonds between X, Te, and O.[18-20] Such an interaction should be possible also

Table II. α-Halo Ketones from α-(Dichlorotelluro) Ketones

α-halo ketone	reaction time, h	% yield	% chromatographic purity
	4	74	37 (X = Cl) 62 (X = Br)
	30	56	3 (X = Cl) 84 (X = Br)
	5	65	16 (X = Cl) 84 (X = Br)
	7	60	14 (X = Cl) 86 (X = Br)
	3	77	94
	2	78	68
	5	71	100
	5	65	91
	3	68	92

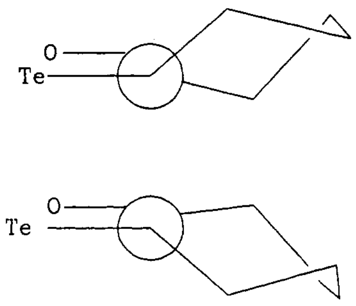


Figure 1. Newman projections for 2-[dichloro(*p*-methoxyphenyl)telluro]cyclohexanone.

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Table III. α-Effect for the $RTeCl_2$ Group in α-(Dichlorotelluro) Ketones

compd	chem shift of the α carbon,[a] ppm	Δδ, ppm	compd	chem shift of the α carbon,[a] ppm	Δδ, ppm
1	67.16 (30.2)[23]	36.96	8	78.91 (25.3)[24]	53.61
2	65.86 (24.4)[24]	41.46	9	57.34 (24.9)[23]	32.44
3	66.56 (24.9)[23]	41.66	10	57.95 (24.4)[24]	33.55
4	68.22 (37.0)[23]	31.22	11	65.76 (40.7)[23]	25.06
5	78.58 (40.7)[23]	37.88	12	59.13 (24.4)[24]	34.73
6	80.10 (40.9)[23]	39.2	13	57.11 (40.7)[23]	16.51
7	81.73 (42.7)[23]	39.03			

[a] Values in parentheses refer to the nonsubstituted ketones.

Table IV. Chemical Shifts of the Carbon in α-(Dichloroorganyltelluro) Ketones Compared with Those of the Nonsubstituted Ones ($\delta(RCOCHR^1Te(Cl_2)Ar) - \delta(RCOCH_2R^1)$)

compd	chem shift,[a] ppm	Δδ, ppm	compd	chem shift,[a] ppm	Δδ, ppm
1	199.71 (205.1)	−5.39	8	205.07 (212.4)	−7.33
2	207.88 (211.0)	−3.12	9	192.11 (196.0)	−3.89
3	191.84 (196.0)	−4.16	10	208.0 (211.0)	−3.0
4	211.81 (218.1)	−6.29	11	205.03 (208.8)	−3.77
5	204.73 (208.8)	−4.07	12	208.14 (211.0)	−2.86
6	206.38 (210.3)	−3.92	13	204.85 (208.8)	−3.95
7	209.07 (211.7)	−2.63			

[a] Values in parentheses refer to the nonsubstituted ketones.[23]

in 2-[dichloro(*p*-methoxyphenyl)telluro]cyclohexanone in view of the conformation of the cyclohexane ring shown in the Newman projection in Figure 1.[21] Concerning the ^1H NMR spectra of the α-(dichlorotelluro) ketones, it was observed that the $RTeCl_2$ groups greatly deshield the α-protons relative to the nonsubstituted ketone, probably due to the electron-attracting nature of the $RTeCl_2$ groups. The carbon atom directly bound to the tellurium moiety suffers a considerable downfield shift compared with the nonsubstituted ketone (Table III). This effect can also be attributed to the electron-attracting nature of the $RTeCl_2$ groups. The carbonyl carbon of the α-(dichloroorganyltelluro) ketones is shielded compared to the nonsubstituted ones (Table IV). This is consistent with the observation that electron-withdrawing substituents increase the shielding of the carbonyl carbon, instead of deshielding it.[22]

In conclusion, we demonstrated that the reaction of ketones and ketone silyl enol ethers with organoyltellurium trichlorides is general when the ketones are methyl ketones or α-unsubstituted cycloalkanones. The product α-(dichloroaryltellurium) ketones can be transformed into α-halo ketones.

Experimental Section

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-80 or on a Bruker AC-200 spectrometer. IR spectra were obtained with liquid films or KBr pellets of the compounds on a Perkin-Elmer 1750-FT spectrometer. Merck silica gel 60 (70–230 mesh or 230–400 mesh) was used for column chromatography, and prepared plates (silica gel 60F 254 on aluminium) were used for TLC.

α-(Dichloroorganyltelluro) Ketones from Organyltellurium Trichlorides and Ketones. The ketone (3 mmol) was added to a suspension of the organyltellurium trichloride (3 mmol) in benzene (10 mL) at room temperature. The mixture was heated under reflux, and the reaction was monitored by TLC using chloroform as solvent. After the time indicated in Table I, the reaction mixture was treated with methanol/water (3 × 50 mL, 1:1) and extracted with chloroform. The organic phase was dried with magnesium sulfate, and the solvents were evaporated under vacuum in a rotatory evaporator. The residual oil was filtered through a silica gel column, eluting first with ethyl ether and then with chloroform. The product was recrystalized from chloroform/petroleum ether (30–60). For yields and physical and spectral data, see Table I.

α-(Dichloroorganyltelluro) Ketones from Organyltellurium Trichlorides and Ketone Silyl Enol Ethers. The procedure described above was followed using equimolar amounts of the organyltellurium trichloride and the ketone silyl enol ether (for yields and physical and spectral data, see Table I).

α-Chloroacetophenone by Pyrolysis of α-[Dichloro(*p*-methoxyphenyl)telluro]acetophenone. α-[Dichloro(*p*-methoxyphenyl)telluro]acetophenone (0.85 g, 2 mmol) was placed in a round-bottomed flask connected to a receiver refrigerated with dry ice/acetone and introduced into a preheated Kugelrohroffen at 210 °C under a pressure of ~30 mmHg. After 5 min of heating, a colorless liquid was collected in the receiver. Column chromatography on silica gel eluting with chloroform afforded 0.25 g (81%) of α-chloroacetophenone.

α-Chloropinacolone by Pyrolysis of α-[Dichloro(*p*-methoxyphenyl)telluro]pinacolone. Following the procedure described above, 0.099 g (85%) of α-chloropinacolone was obtained, starting from 0.40 g (1 mmol) of α-[dichloro(*p*-methoxyphenyl)telluro]pinacolone.

Reaction of α-(Dichloroorganyltelluro) Ketones with Halogens—α-Halo Ketones. To a solution of the α-(dichloroorganyltelluro) ketone (2 mmol) in methylene dichloride (10 mL) was added a solution of chlorine or bromine (2 mmol) in the same solvent. The mixture was vigorously stirred until the precipitation of the aryltellurium trihalide occurred, which was then separated by filtration. The filtrate was washed three times with water (25 mL) and then with brine (2 × 30 mL). The organic phase was dried with magnesium sulfate, and the solvent was evaporated in a rotatory evaporator. The residue was purified by preparative thin-layer chromatography on silica gel eluting with petroleum ether (30–60). The yields are given in Table II.

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