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STRUCTURE ELUCIDATION OF A ZWITTERIONIC 2-OXAZOLINE OBTAINED BY CYCLOFUNCTIONALIZATION OF N-ACETYLDIALLYLAMINE WITH TELLURIUM TETRACHLORIDE

JAN BERGMAN* and JAN SIDÉN
Royal Institute of Technology, Department of Organic Chemistry S-100 44 Stockholm, Sweden

and

KNUT MAARTMANN-MOE
Department of Chemistry, University of Bergen N-5014 Bergen, Norway

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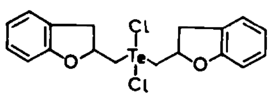
Abstract—Interaction of tellurium tetrachloride with N-acetyldiallylamine in CH_3CN gave a zwitterionic 2-oxazoline **8a**, whose structure was determined by X-ray crystallography. The 2-oxazoline was found to react readily with nucleophilic reagents; water caused cleavage of the oxazoline ring and deacetylation to yield a compound with an intact tetrachlorotellurate(IV) function.

Cyclofunctionalizations of suitably substituted alkenes induced by Se- or Te-containing reagents have been studied rather intensely during recent years. The formation[1] of compound **1** by heating 2-allylphenol with TeO_2 in HOAc containing LiCl and the conversion[2] of N-carbethoxy-4-pentenylamine into compound **2** by treatment with C_6H_5SeCl are representative examples. The field has also recently briefly been reviewed.[3] In this paper we report the synthesis and structural elucidation of some 2-oxazolines formed by cyclization (induced by $TeCl_4$ or $TeBr_4$) of N-acetylated allylamines (notably **3b**) via the oxygen atom.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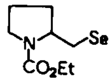
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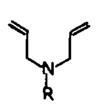
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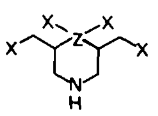
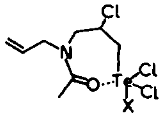
b R=COCH3
c R=COCF3


4a X=Cl Z=Te
b X=Br Z=Te
c X=Cl Z=Se
d X=Br Z=Se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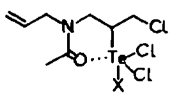
b X=C6H4-4-OEt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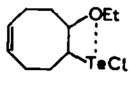
b X=C6H4-4-OEt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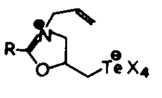

8a R=CH3 X=Cl
b R=C6H5 X=Cl
c R=C2H5 X=Cl
d R=C(CH3)3 X=Cl
e R=CH3 X=Br

Cyclofunctionalizations

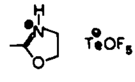
We and others[2,4] are interested in the cyclofunctionalization of unsaturated amines due to the general importance of alkaloid synthesis. As a first simple model we decided to study the reaction between diallylamine (protected as well as unprotected) and $TeCl_4$. Migalina and coworkers[5] have already briefly studied the interaction of the reagents ($TeO_2 + HCl_{aq}$) and ($TeO_2 + HBr_{aq}$) with diallylamine and reported the formation of the tellurazine derivatives[6] **4a** and **4b**, clearly interesting candidates for coupling[7,8] as well as carbonylation–detelluration reactions.[9] We anticipated, however, that under different conditions and with appropriate N-protection, other types of cyclofunctionalizations might occur, such as formation of pyrroles and/or pyridines.

Compound **3b** reacted rapidly with $TeCl_4$ in acetonitrile to yield crystals in high yield of the composition $C_8H_{13}Cl_4NOTe$. NMR data immediately revealed that only one of the allyl groups in **3b** had been attacked. The salient feature of the IR spectrum was a shift of the band[10] at 1650 cm^{-1} (C=O) in **3b** to a new band at 1668 cm^{-1} in the product. From these data, the structures **5a** and **6a** were suggested.

In order to distinguish between the assumed structures **5** and **6** and to learn more about the nature of the interaction between oxygen and tellurium, a feature which earlier has been recognized[11-13] in various types of organotellurium compounds (e.g. in compound **7**), the new product was studied by X-ray crystallography, which gave conclusive evidence for the admittedly unexpected structure **8a**. A somewhat related reaction had earlier been discovered by Fraser and Meikle,[14] who found that interaction of $CH_3CONHCH_2CH_2OH$ with TeF_6 in CH_3CN for 7 days at room temperature in the presence of NaF (as HF scavenger) yielded the oxazolinium salt **9**.

In hindsight the transformation (**3b**→**8a**) is not, after all, so surprising as it is already known[15] that certain phenylselenating agents, will react with suitable alkenyl substituted ketones to afford cyclized products. Thus ethyl 2-(2-propenyl)acetoacetate afforded the 2,3-dihydrofurane derivative **10**.[15] Furthermore treatment of certain N-(allyl) amides with concentrated H_2SO_4 at below 25° will give rise to 2-oxazolines. Thus addition H_2SO_4 to N-allyl-p-toluamide gave 2-(p-tolyl)-5-methyl-2-oxazoline in 50% yield.[16]

Although many routes[17] to 2-oxazolines are known, the transformation (**3b**→**8a**) now reported seems to be the first example of a direct metal-induced conversion of a derivative of an alkenyl amine into a 2-oxazoline. Schmitz[18–19] has studied the reaction of $PdCl_2$ and $RhCl_3$ with **3b** and obtained complex mixtures containing **11** and **12** but apparently no 2-oxazolines. Similar unattractive mixtures were obtained with various Hg^{2+}, Tl^{3+} and Pb^{4+} reagents in this laboratory. Not even $SeCl_4$, $SeBr_4$, C_6H_5SeCl, or $4\text{-}OEtC_6H_4TeCl_3$ yielded, according to preliminary studies,[20] oxazolines. The product from **3b** and 4-ethoxyphenyl tellurium trichloride showed a strong band in the IR spectrum at 1748 cm^{-1} and ^{13}C NMR data indicated that only one of the allyl groups had been attacked. On the basis of these data the adduct has been tentatively assigned structure **5b** or **6b**, both of which featuring Te–O coordination. Actually the only reagent found to behave analogously with $TeCl_4$ was $TeBr_4$, which with **3b** slowly (compared to $TeCl_4$) yielded yellow crystals of **8e**. After 3 h at 40° in CH_3CN the yield was almost quantitative.



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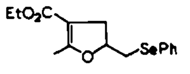

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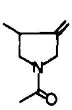

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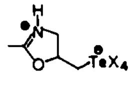
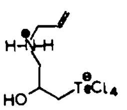


13 a X = Cl
b X = Br



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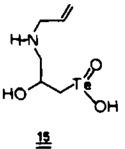

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Several other N-acylderivatives of diallylamine (but not[21] **3c**) did also (with $TeCl_4$) yield products of type **8** (e.g. **8b** and **8c**). N-acetylmonoallylamine yielded compound **13a**.

Structure determination of **8a**

The compound **8a**, $C_8H_{13}Cl_4NOTe$, crystallizes in the tetragonal system $a = b = 10.542(1)$ Å, $c = 25.817(2)$ Å; $V = 2869.4(9)$ Å^3 at $t = 19 \pm 1°$; $M = 408.6$; $Z = 8$; $F(000) = 1568$; $\mu(\text{Mo}K\alpha) = 28.6$ cm; space group $P4_12_12$ (No. 92). 2236 unique reflections with $I > 2\sigma(I)$ were recorded using monochromated Mo-radiation ($\lambda = 0.71073$ Å) and the ω-scan technique. An ENRAF–NONIUS CAD4 goniometer was used.

The structure was determined by Patterson methods followed by Fourier syntheses. Full matrix least square refinements converged to a conventional R-factor of 4.9% and an E.S.D., of an observation of unit weight equal to 1.23. No absorption of extinction corrections were applied to the data, considering the quality of the crystal. Refinement of the enantiomorph structure lead to inferior R-factors and positional errors.

An ORTEP drawings of the molecule is shown in Fig. 1, including the numbering of the atoms. The Cl1*-atom belongs to a molecule related by symmetry. The atoms belonging to the five-membered ring and the carbon atoms C5 and C6 are strictly coplanar.

An X-ray structure analysis at low temperature is intended. The present atomic coordinates etc., are available from K. M.-M. and are deposited at the Cambridge Crystallographic Data Centre, Cambridge (UK).

Chemical reactions and properties of compound **8**

Compound (**8a**) readily dissolved in water at room temperature to give a clear solution, which upon concentration (after 1 h) deposited crystals of the ring-opened and deacetylated product (**14**). The first steps in this sequence, e.g. formation of a pseudobase followed by ring-opening should be expected[22] to be fast under the given conditions. On the other hand the fast deacetylation makes it tempting to suggest neighbouring group participation of the tellurium atom (Scheme 1).

The fact that the tetrachlorotellurate(IV) function is unaffected by water under these conditions is in harmony with results reported[23] by Petragnani *et al*, who found that tetrahaloaryltellurates(IV) are stable in water. Treatment of **8a** with boiling water, however, resulted in complete hydrolysis, yielding the tellurinic acid (**15**).

2-Oxazolines are of current interest[24–26] for the synthesis of ketones and many other important types of compounds (not the least optically active compounds) and in a preliminary experiment we have found that **8b** in THF readily reacted with phenyllithium to yield an adduct, which could be readily hydrolysed to benzophenone.

EXPERIMENTAL

Melting points were determined on a micro hot stage melting point apparatus. All the tellurium compounds described in this paper did melt with decomposition (formation of elemental tellurium). At room temperature the compounds are completely stable and seems to be rather insensitive to light, air and moisture.

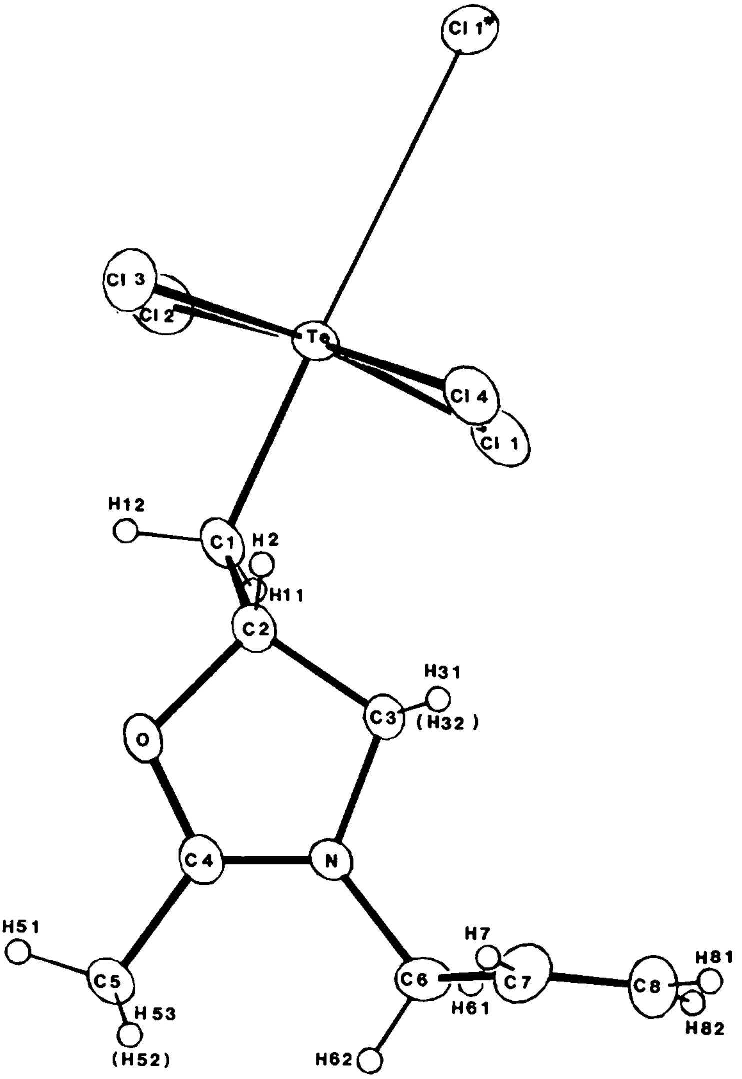
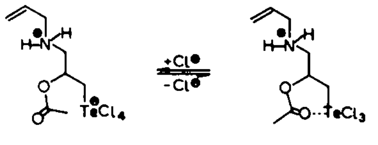


Fig. 1. ORTEP drawing of **8a**. O, C2 and C3 are in the plane of the paper.



Scheme 1.

IR spectra were recorded on a Perkin-Elmer 421 infrared spectrophotometer as KBr discs. ^{13}C-NMR spectra were recorded on a Bruker WP 200 instrument.

Preparation of the oxazoline **8a**

Tellurium tetrachloride (26.7 g, 0.1 mol) was added to a stirred soln of N-acetyldiallylamine (13.9 g, 0.1 mol) in acetonitrile (60 ml) at 25°. The added reagent dissolved rapidly and soon (1–3 min) the product precipitated. After 1 h the product was collected, washed with acetonitrile and dried. Yield; 40.0 g (98%), m.p. 181° dec. IR: 3008, 2945, 1668, 1460, 1423, 1404, 1370, 1268, 1107, 998, 957 cm^{-1}.

The sample for the X-ray investigation was obtained by recrystallization from acetonitrile. In this connection it was noted that prolonged reflux of **8a** in this solvent caused decomposition (formation of elemental Te). Fast decomposition was observed in boiling acetic acid or acetic anhydride.

Preparation of compounds **8b**, **8c**, **8d** and **8e**

These compounds were prepared following the procedure for **8a**, except that the temperature was kept at 40° and the reaction time prolonged to 3 h. **8b**; Yield: 96%, m.p. 224° dec. IR: 3060, 3010, 2990, 2955, 1641, 1452, 1429, 1259, 988, 942, 866, 774, 708 cm^{-1}. **8c**; Yield: 95%, m.p. 208° dec. IR: 2990 2950, 1665, 1645, 1475, 1450, 1270, 950. **8d**; Yield: 90%, m.p. 268° dec. IR: 3000, 2960, 1660, 1630, 1490, 1440, 1430, 1280, 1215, 950. **8e**; Yield: 99%, m.p. 166° dec. IR: 3008, 2944, 1669, 1460, 1422, 1368, 1269, 1106, 996, 953 cm^{-1}.

Hydrolysis of the oxazoline **8a**

Compound **8a** (4.08 g, 0.01 mol) in water (25 ml) was stirred at 25° until (~1 h) a clear soln was obtained. After concentration to *ca* 10 ml, crystals of the ring-opened and hydrolysed product **14** was obtained. Yield: 65% m.p. 150° dec. IR: 3500(br), 3160(br), 3090(br), 1563, 1408, 1293, 1255, 1090, 1046, 991, 953 cm^{-1}.

Reaction of N-acetyldiallylamine with p-ethoxyphenyl tellurium trichloride

p-Ethoxyphenyl tellurium trichloride (3.55 g, 0.01 mol)[27] was added to a stirred solution of N-acetyldiallylamine (1.39 g, 0.01 mol) in CH$_3$CN (15 ml) at 50°. After 5 h the clear solution was allowed to cool. After 2 days the solid formed was collected and recrystallized from acetonitrile.

Yield: 80%, m.p. 162° dec. IR: 2910, 2780, 1748, 1589, 1495, 1240, 1185 cm^{-1}.

Preparation of the oxazoline **13a**

The procedure given for **8a** was used on the 0.01 mol scale. Yield: 96%, m.p. 240° dec. IR: 3260, 1670, 1490, 1390, 1260, 1000 cm^{-1}.

Reaction of **8a** *with phenyllithium*

Compound **8a** (4.08 g, 0.01 mol) was suspended in THF (40 ml) under N_2. Addition of phenyllithium (0.01 mol) to the stirred soln at 10° caused rapid dissolution of **8a**. After 1 h at 10° the reaction mixture was quenched by addition of water (10 ml), whereupon more water (400 ml) and ether (100 ml) was added. The ether phase was washed with water, dried and evaporated whereupon benzophenone 1.60 g (88%) was obtained. The water phase was concentrated to a small volume which resulted in the precipitation of compound **14**, 1.51 g (44%).

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[20] In some of these cases, crystalline compounds quite different from **8** were isolated. The structures will be reported in future communications.

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