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METHODS IN CHALCOGEN CHEMISTRY

V*. A NEW REAGENT FOR THE SYNTHESIS OF AROMATIC TELLURIUM COMPOUNDS

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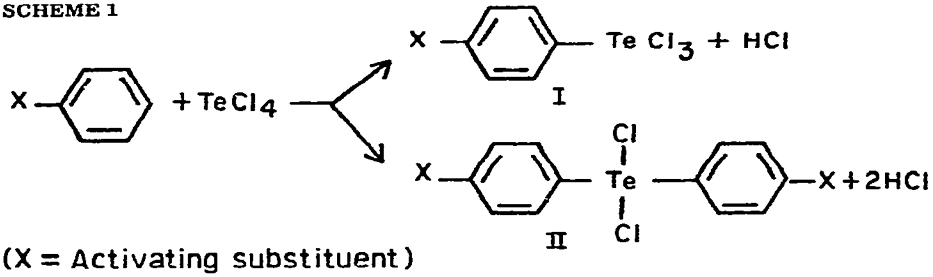
Summary

It has been discovered that the combination of tellurium tetrachloride with more than one molar equivalent of aluminum chloride constitutes an efficient reagent for the introduction of tellurium into aromatic molecules. Kinetic control of the reaction with benzene (a substance inert to $TeCl_4$ alone) selectively yielded the products of successive substitution on tellurium as follows: diphenyl ditelluride (via reductive workup from phenyltellurium trichloride), diphenyltellurium dichloride and triphenyltelluronium chloride after evolution of 1,2 and 3 equivalents HCl, respectively.

Extension of this simple reaction to the preparation of numerous other aromatic tellurium compounds appears feasible.

It has been known for many years [2] that tellurium tetrachloride reacts with aromatic compounds only when these contain activating substituents, e.g. RO, HO, R_2N, RS, to give mixtures of aryltellurium thrichlorides (I) and bis(aryl)tellurium dichlorides (II) as illustrated in Scheme 1.

SCHEME 1



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[*] For Part IV of this series see ref. 1.

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Less reactive species, such as benzene or toluene, were considered inert under these conditions. While the joint occurrence of an aryltellurium trichloride and a bis(aryl)tellurium dichloride indicates a sequential substitution at tellurium, little is known regarding the selective formation of species I or II, nor has an extension to replacement of an additional chlorine atom by a third aromatic substituent been achieved by the indicated route.

Recently, Bergman [3] reported that a moderate rate of reaction (12—24 h at reflux) could be achieved when Lewis acid catalysts were added to the mixture of $TeCl_4$ and non-activated aromatic compounds. Using benzene as a model reagent, we have confirmed Bergman's findings at ratios of $AlCl_3/TeCl_4$ smaller than one. However, the picture changes very dramatically when more than one molar equivalent of $AlCl_3$ is present. Figure 1 shows the measured rates for preparative scale reactions based upon the stoichiometry of evolved HCl for 2, 3 and 4 equivalents of $AlCl_3$ per mole equivalent of $TeCl_4$ in benzene solution at reflux temperature. It is readily seen that the first equivalent of HCl requires only a 5—10 min reaction time, that in the 2 equivalent $AlCl_3$ case the curve asymptotically approaches a 2 equivalent HCl evolution and that both 3 and 4 equivalents of $AlCl_3$ give very similar curves leading to just over 3 equivalents of HCl produced at reaction times on the order of one hour. By comparison, the HCl evolution at 1 equivalent $AlCl_3$ is so slow that no meaningful curve can be depicted on the scale of Fig. 1.

The above kinetic picture is nicely confirmed by isolation of the organotellurium compounds present at the various stages of this multistep electrophilic substitution reaction. Reactions were quenched by addition of ice and water. The product at the 1 equivalent HCl stage was then reduced by addition of

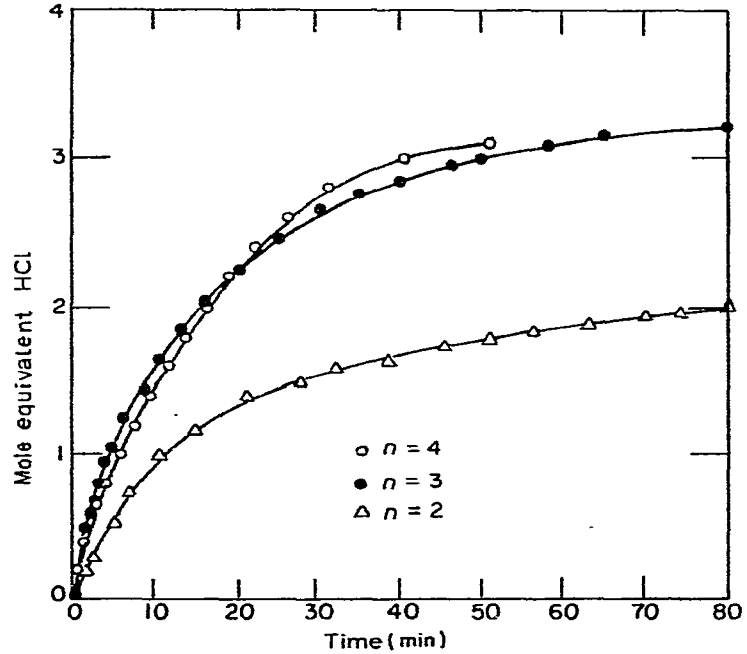


Fig. 1. Reaction of $TeCl_4$ with benzene in the presence of n $AlCl_3$.

TABLE 1

REACTION OF $TeCl_4$ WITH BENZENE[a] IN THE PRESENCE OF $AlCl_3$

Reactants		Products				M.p. (°C)
$TeCl_4$ (mol)	$AlCl_3$ (mol)	HCl (mol)	$C_6H_5TeCl_3$[b] Yield (%)	$(C_6H_5)_2TeCl_2$ Yield (%)	$(C_6H_5)_3TeCl$ Yield (%)	
0.1	0.2	0.1	53.3			65[c]
0.1	0.2	0.2	17	45.4		157—158[d]
0.1	0.3	0.2		58.5		157—158[d]
0.1	0.3	0.3			60.6	249—250[e]

[a] Used as the reaction medium. [b] Isolated as its reduction product: $C_6H_5TeTeC_6H_5$. [c] Lit. [4] m.p. 66°. [d] Lit. [5] m.p. 158°. [e] Lit. [6] m.p. 244—245°.

sodium disulfite (known to give a quantitative reduction of phenyltellurium trichlorides) to give diphenyl ditelluride.

Products at the 2 and 3 equivalent HCl stage were isolated from the benzene layer and the aqueous phase, respectively, by crystallization. Table 1 summarizes these results of preparative runs. No attempts were made to optimize yields, nor was a complete workup for minor products attempted.

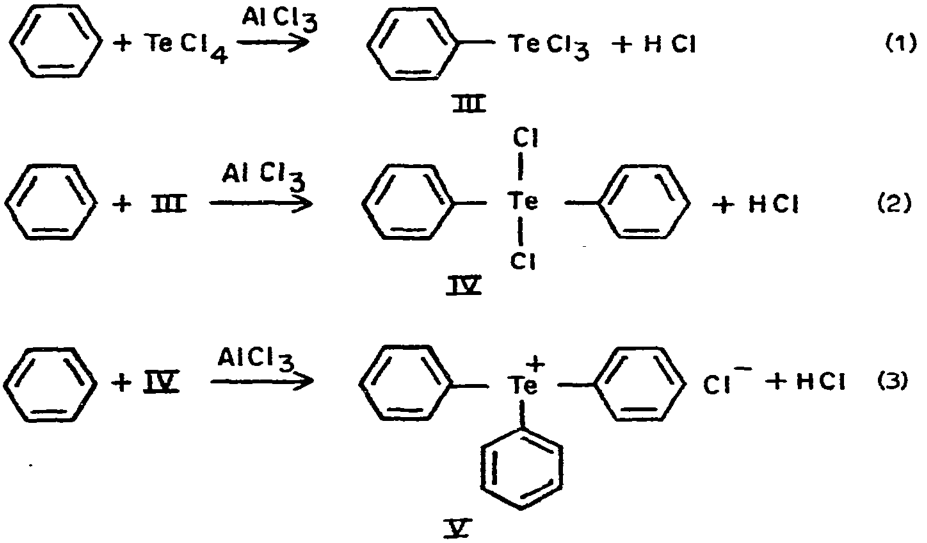
The preparative results, coupled with the preliminary kinetic data permit some statements on the possible operating mechanisms:

(a). From the isolated products it appears that the overall reaction progresses as a sequence of three electrophilic substitution reactions on benzene as depicted in Scheme 2. Each step in the series is optimally catalyzed by the presence of $AlCl_3$ in a given minimum concentration.

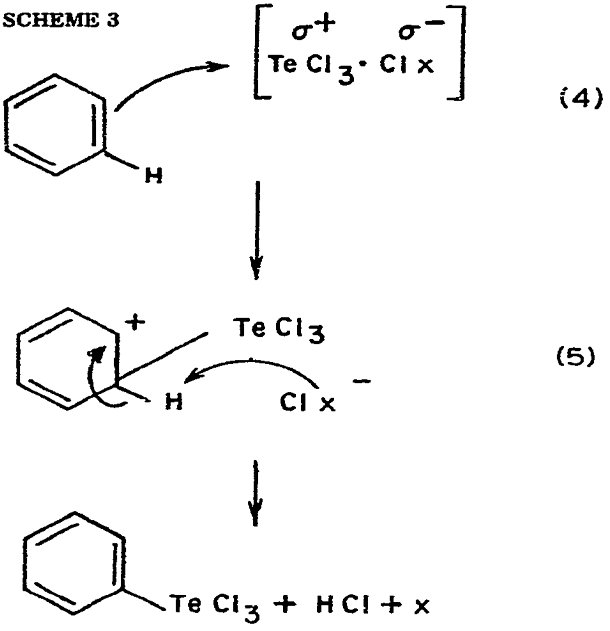
(b). The large molar excess of benzene in the reaction mixtures ($TeCl_4$/$AlCl_3$/C_6H_5 $1/n/34$; $n = 1,2,3,4$) appears to preclude involvement of an $AlCl_3$—benzene complex as the rate-determining factor.

(c). The extremely slow reaction rate for step 1, Scheme 2 with a 1/1 ratio

SCHEME 2



SCHEME 3



of $TeCl_4/AlCl_3$ appears to exclude the known 1/1 complex [7,8] from significant participation in either steps 1, 2 or 3.

(d). The very similar, fast reaction rates for reaction 1, Scheme 2 with $TeCl_4/n\ AlCl_3$ ($n = 2$, 3 or 4) implicate a common species (x) in the rate-determining step of this reaction. The precise rate may then be dependent either on the speed of the electrophilic attack 4 or the rearomatization reaction 5 as depicted in Scheme 3.

(e). The extremely slow rate for reaction 3, Scheme 2 when $TeCl_4 + 2\ AlCl_3$ is used, indicates that species x is ineffective either in promoting an electrophilic attack by compound IV on benzene or now lacks the ability to withdraw a proton in the rearomatization reaction analogous to step 5, Scheme 3.

Any inhibition of the latter step appears unlikely, thus we may conclude that the complex (IV : x) is insufficiently activated for the initial electrophilic attack.

(f). The ready conversion of IV to V when $TeCl_3 + 3\ AlCl_3$ is present, implicates another species y in the electrophilic attack or aromatization steps leading to V. The lack of a further rate acceleration for this step with $TeCl_4 + 4\ AlCl_3$ speaks against a simple dependence on the $AlCl_3$ concentration and tends to substantiate the need to invoke a catalytically active species y. Otherwise, the arguments for the properties of y are similar to those presented for x.

Much more detailed studies are, of course, required to make definitive statements regarding the precise nature of x and y. As already stated, the complex $TeCl_4 \cdot AlCl_3$ is known [7,8] and presumably is inactive in the present system. Equally, the complex $TeCl_4 \cdot 2\ AlCl_3$ has been described [9] and might be involved in the present reaction by dissociating to an electrophilic tellurium cation and a strong Lewis acid counterion.

Experimental

All melting points are uncorrected. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

General procedure

Benzene, tellurium tetrachloride and aluminum chloride were placed into a 500 ml two-necked, round-bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a reflux condenser. The reflux condenser was connected with Tygon tubing to a gas dispersion tube immersed in water containing phenolphthalein indicator. The reaction mixture was heated to reflux with stirring under nitrogen. Vigorous hydrogen chloride evolution occurred immediately. The hydrogen chloride was swept through the condenser into phenolphthalein solution by nitrogen and titrated with NaOH solution. The reaction was quenched with ice and water when a desired amount of HCl had been evolved as depicted in Fig. 1.

Diphenyl ditelluride

A mixture of 26.8 g (0.1 mol) of tellurium tetrachloride, 26.6 g (0.2 mol) of aluminum chloride and 300 ml of dry benzene was treated in the manner described in the general procedure. The reaction mixture was poured into 300 ml of ice water when one equivalent of HCl had been generated (10—12 min). The resulting slurry containing phenyltellurium trichloride was reduced by addition of 30 g sodium disulfite in 100 ml water and vigorous stirring to provide for extraction of the desired reaction product into the organic phase. The benzene layer was then separated, washed with H_2O, dried over anhydrous sodium sulfate and evaporated to dryness in vacuo. The resulting solid was recrystallized from ethanol to give 21.8 g (53.3%) of diphenyl ditelluride as an orange-red crystalline solid, m.p. 65° (lit. [4] m.p. 66°).

Diphenyltellurium dichloride

A mixture of 26.8 g (0.1 mol) of tellurium tetrachloride, 39.9 g (0.3 mol) of aluminum chloride and 300 ml of dry benzene was treated in the manner described in the general procedure. The reaction mixture was poured into 400 ml of ice water when two equivalents of HCl had evolved. The benzene layer was separated, washed with H_2O, dried over anhydrous sodium sulfate and evaporated to dryness in vacuo. The resulting solid was recrystallized from ethanol to yield 20.6 g (58.5%) of diphenyltellurium dichloride as a white crystalline solid, m.p. 157—158° (lit. [5] m.p. 158°).

Triphenyltelluronium chloride

A mixture of 26.8 g (0.1 mol) of $TeCl_4$, 39.9 g (0.3 mol) of $AlCl_3$ and 300 ml of dry benzene was treated in the manner described in the general procedure. The reaction mixture was poured into 400 ml of ice and water when three equivalents of HCl had evolved. A dark colored solid was separated by filtration of the quenched reaction mixture and dissolved in the minimum amount of boiling water. The hot mixture was then quickly filtered to give a clear colorless solution. On cooling the filtrate, crystallization of the product started immediately, yielding 23.9 g (60.6%) of triphenyltelluronium chloride as a white crystalline solid, m.p. 249—250° (lit. [6] m.p. 244—245°). (Analysis found: C, 54.98; H, 3.86; Cl, 9.13; Te, 32.10. $C_{18}H_{15}ClTe$ calcd.: C, 54.82; H, 3.83; Cl, 8.99; Te, 32.35%.)

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