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$TeCl_4$ AS A CATALYST IN CATIONIC OLIGOMERISATIONS AND POLYMERISATIONS

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Summary

$TeCl_4$ catalyses the oligomerisation and polymerisation of certain substituted phenylethylenes and substituted benzyl chlorides. The catalysis is cationic, $TeCl_4$ acting as a Lewis acid. The termination of polymerisation of the substituted ethylenes is by an internal Friedel-Crafts reaction, whereas that of the substituted benzyl chlorides is by reaction with chloride ions. Contrary to the usual reactivity sequence, stilbene was found to be more reactive than α-methylstyrene in the $TeCl_4$-catalysed polymerisations.

Introduction

The reactions of $TeCl_4$ with unsaturated organic substrates have been extensively studied. Mechanisms involving the $TeCl_3^+$ ion as an electrophile were suggested for many of the addition and substitution reactions [1]. The reaction path depends on reaction conditions as well as on the nature of substituents in the neighborhood of the reacting site. For example, cyclohexene reacts with $TeCl_4$ to yield the pure addition product, 2-chlorocyclohexyltelluriumtrichloride [2—4]. Unidentified chlorination products were formed in the reaction between styrene and $TeCl_4$ alone [2,5], but in ether the addition of the $TeCl_3^+$ moiety to the styrene was observed [6]. The reaction of $TeCl_4$ with 1,1-diarylethylenes was reported to yield the chlorination product 1,1-diaryl-2-chloroethylene as well as a π complex between $TeCl_2$ and two molecules of 1,1-diarylethylene [6].

Tellurium tetrahalides and alkyl tellurium trihalides are known to act as Lewis acids towards Lewis bases such as pyridine and its derivatives [7,8], derivatives of ethylenediamine [9], thiourea [7,10], ether [11] and X^- [12].

In this paper we report the reactions of $TeCl_4$ with selected olefins and with benzyl type chlorides under conditions leading to oligomerisation and polymerisation.

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Experimental

Materials. $TeCl_4$ (C.P.-Merck, W. Germany), α-methylstyrene (purum, Fluka, Switzerland), *trans*-stilbene (puriss, Fluka, Switzerland), *cis*-stilbene (C.P., Sigma, USA), benzyl chloride (A.R., Merck, W. Germany), 1-hydroxyethylbenzene (C.P., Aldrich, USA), benzhydrol (C.P., Merck, W. Germany) were not further purified before use. Benzhydryl chloride and 1-chloroethylbenzene were synthesized from the corresponding alcohols by the reaction with thionyl chloride, drying with anhydrous Na_2SO_4 and distillation (at 130°C/3 mmHg for benzhydryl chloride and 74—76°C/20 mmHg for 1-chloroethylbenzene).

Instrumentation. PMR-Varian-HA-100; ^{13}C NMR-Varian CFT-20; MS-Hitachi Perkin—Elmer RMU-6; Elemental analysis and molecular weight determinations were carried out at Alfred Bernhardt Analytische Laboratorium (W. Germany).

Polymerisations. All polymerisations were carried out by dissolving 0.01 mol of the monomer and 0.01 mol $TeCl_4$ in 50 ml CH_2Cl_2 or CH_3CN and keeping the mixture at room temperature for 5—8 h. The mixtures were filtered to remove inorganic residues and the solvent distilled from the filtrate to leave the oligomers, which were recrystalized from methanol.

Spectroscopic data. Polystilbene: PMR ($CDCl_3$) δ 7.28 (10H, m); 3.30 (2H, m) ppm. ^{13}C NMR ($CDCl_3$) δ 129.34—125.95; 52.81; 36.12 ppm. Dimer of α-methylstyrene: MS: M^+ 236; PMR ($CDCl_3$) δ 7.18 (9H); 2.30 (2H, m); 1.70 (3H, s); 1.35 (3H, s); 1.03 (3H, s) ppm. ^{13}C NMR ($CDCl_3$) δ 152.10; 150.98; 148.68; 127.93; 127.19; 126.61; 125.43; 124.94; 122.47; 59.32; 50.78; 42.78; 30.86; 30.71; 30.36 ppm.

Polymer from benzyl chloride: PMR ($CDCl_3$) δ 7.20 (4H, m); 3.83 (2H, s) ppm. ^{13}C NMR ($CDCl_3$) δ 144.26; 142.56; 140.70; 136.44; 136.19; 128.78; 128.44; 128.13; 45.48; 42.96; 42.56 ppm.

Oligomer from benzhydryl chloride: PMR ($CDCl_3$) δ 7.21 (10H, m); 5.40 (1H, s) ppm. ^{13}CMR ($CDCl_3$) δ 143.96; 141.85; 129.41; 129.29; 128.40; 126.20; 56.56; 56.23 ppm.

Analysis

Polymer from benzyl chloride: M.W. for $C_6H_5CH_2(C_6H_4CH_2)_{21}C_6H_4CH_2Cl$: Found (osmometrically) 2100; calcd.: 2075.
Found: C, 91.19; H, 6.83; Cl, 1.77; calcd.: C, 90.78; H, 5.68; Cl, 1.71%.

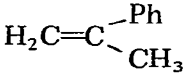
Oligomer from benzhydryl chloride: M.W. for $(C_6H_5)_2CH(C_6H_4CHC_6H_5)_5$-$C_6H_4CHClC_6H_5$: Found (osmometrically) 1210; calcd.: 1202.
Found: C, 89.08; H, 5.34; Cl, 2.79; calcd.: C, 90.69; H, 5.20, Cl, 2.89%.

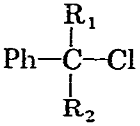
Oligomer from 1-chloroethylbenzene: M.W. for $C_6H_5CH(CH_3)(C_6H_4CH(CH_3))_6$-$C_6H_4CH(CH_3)Cl$: Found (osmometrically) 878; calcd.: 869.
Found: C, 86.98; H, 8.39; Cl, 3.95; calcd.: C, 88.38; H, 7.48; Cl, 4.09%.

Polymer from *trans*-stilbene: M.W. for $CH_2Ph(CHPhCHPh)_8CH(\underline{C_6H_4)CHPhC}HPh$
Found (osmometrically) 1787; calcd.: 1800.
Found: C, 92.56; H, 6.65; calcd.: C, 93.33; H, 6.66%.

Results and discussion

The monomers which were polymerised with $TeCl_4$ can be divided into two groups.

I Substituted ethylenes: PhCH=CHPh and 
$H_2C{=}C(Ph)(CH_3)$

II Substituted benzyl chlorides: 
$Ph{-}C(R_1)(R_2){-}Cl$

where $R_1 = R_2 = H$; $R_1 = H$, $R_2 = CH_3$; $R_1 = H$, $R_2 = C_6H_5$.

The results are summarized in Table 1.

The yields of the polymers obtained based on the monomer consumed were quantitative.

trans-Stilbene is known to be inactive in polymerisations and only a few cases are known in which the dimer or oligomers are obtained [13]. With $TiCl_4$ and CCl_3COOH as co-catalyst the pentamer of *cis*-stilbene was obtained [14]. In our experiments, with $TeCl_4$ as catalyst *trans*-stilbene was readily oligomerised to the decamer.

18-Crown-6 is known to inhibit electrophilic reactions of $TeCl_4$ and to enhance slightly its nucleophilic reactivity [15]. When a quantity of 18-Crown-6 equimolar to the $TeCl_4$ was added to the polymerisation mixture, no polymerisation took place with any of the monomers listed in Table 1. It seems therefore that the initiator in these reactions is the $TeCl_3^+$ [1] ion and the polymerisation is cationic. Phenylethylenes are well known to polymerise by cationic mechanisms [16]. The initiation and propagation can be formulated for *trans*-stilbene, for example, as follows:

$$\text{Initiation}\quad PhCH{=}CHPh + TeCl_4 \rightarrow TeCl_3\overset{+}{C}HPhCHPh + Cl^-$$

$$\text{Propagation}\quad TeCl_3\overset{+}{C}HPhCHPh + n\ CHPh{=}CHPh \rightarrow TeCl_3(CHPhCHPh)_nCHPh\overset{+}{C}HPh$$

TABLE 1

OLIGOMERISATION AND POLYMERISATION OF VINYL MONOMERS AND BENZYL CHLORIDES WITH $TeCl_4$ AS CATALYST (in 50 ml CH_2Cl_2, t 8 h, T 25°C. Initial concentration of monomers and $TeCl_4$ was 0.01 M)

Monomer	MW [a]	$\overline{DP}_N$	M.P. [b] (°C)
trans-stilbene [c]	1790	10	—
α-methylstyrene	354	3	—
benzyl chloride	2100	23	86—89
1-chloroethylbenzene	878	8	82—85
benzhydryl chloride	1210	7	75—80

[a] Determined osmometrically. [b] Softening point. [c] When *cis*-stilbene was used it isomerised rapidly to the *trans* isomer, which then polymerised.

A priori, three modes of termination can be considered. The termination also depends on the degree of polymerisation, n.

Termination (1) $TeCl_3(CHPhCHPh)_nCHPh\overset{+}{C}HPh$

$$\xrightarrow{-TeCl_3^+} CHPh{=}CPh(CHPhCHPh)_{n-1}CHPhCH_2Ph$$

or $TeCl_3(CHPhCHPh)_nCHPh\overset{+}{C}HPh$

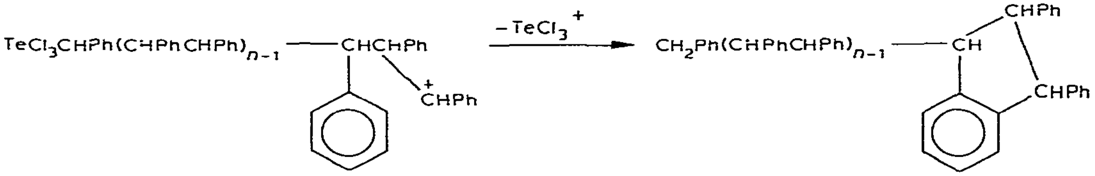
$$\xrightarrow{-H^+} TeCl_3(CHPhCHPh)_nCPh{=}CHPh$$

(2) $TeCl_3(CHPhCHPh)_nCHPh\overset{+}{C}HPh$

$$\xrightarrow{Cl^-} TeCl_3(CHPhCHPh)_nCHPhCHPhCl$$

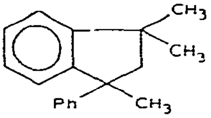
The $TeCl_3(CHPhCHPh)_nCHPhCHPhCl$ formed can be further polymerised by $TeCl_4$, as described for the substituted benzyl chlorides.

(3) Internal Friedel Crafts:



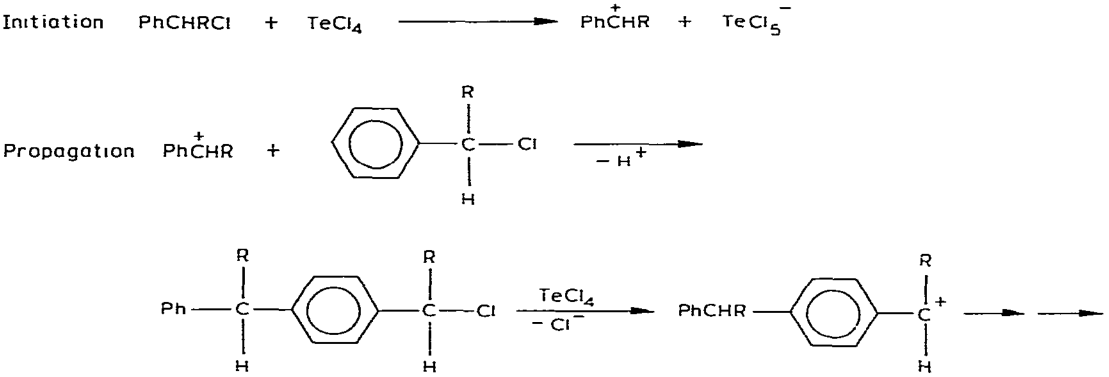
The internal Friedel Crafts termination produces a five membered ring by the electrophilic attack of the positive terminal carbon on the aromatic ring at carbon 3 and elimination of a proton. The Tellurium-free product may result from the electrophilic substitution of $TeCl_3^+$ by a proton. Chlorine can also be introduced into the product by the addition of HCl to a double bond formed by mode 1 termination.

In the oligomerisation of α-methylstyrene with $TeCl_4$ as catalyst, a mixture of dimer and trimer was obtained. The dimer, which was isolated from the reaction mixture by distillation (160—165° C/10 mmHg), was found to be



The formation of this product is evidence for the operation of the internal Friedel-Crafts mode of termination followed by displacement of $TeCl_3^+$ (eq. 3 above). It is to be noted that the action of HCl on α-methylstyrene was not found to yield this dimer. In the case of the polymerisation of *trans*-stilbene the decamer obtained did not contain tellurium, chlorine or a double bond, which indicates that the termination was also by an internal Friedel-Crafts reaction.

Although the propagation in these polymerisations involves cationic attack on the ethylenic double bond to produce a stabilized carbonium ion, termination is the result of an electrophilic attack on the aromatic ring. In the polymerisation reactions of substituted benzyl chlorides with $TeCl_4$, the latter reacts as a Lewis acid in Friedel-Crafts reactions, the complex $TeCl_5^-$ and the benzyl cation being formed. The formation of the benzyl cation is the initiation step of the polymerisation. The benzhydryl cation is more stable than the benzyl cation, which is in accordance with the fact that benzhydryl chloride polymerises very rapidly with $TeCl_4$. The polymerisation of substituted benzyl chlorides can be represented as follows:



$$\text{Termination: (1) } PhCHR(C_6H_4\overset{+}{C}HR) \xrightarrow{Cl^-} PhCHR(C_6H_4CHR)_{n-1}C_6H_4CHRCl,$$

the $PhCHR(C_6H_4CHR)_{n-1}C_6H_4CHRCl$ formed can be initiated again by reacting with $TeCl_4$

$$\text{or (2) } PhCHR(C_6H_4CHR)_{n-1}C_6H_4\overset{+}{C}HCH_3$$

$$\xrightarrow{-H^+} PhCHR(C_6H_4CHR)_{n-1}C_6H_4CH{=}CH_2$$

In the propagation reaction the substitution can be either at the *para* or the *ortho* positions. The consumed $TeCl_4$ in the reaction is regenerated from the $TeCl_5^-$ and H^+ is formed, so that only a catalytic amount of the $TeCl_4$ is needed for the reaction. The $TeCl_4$ is therefore a catalyst for the polymerisation and not an initiator which is introduced into the polymer chain. HCl is evolved during the reaction in equimolar amount to the benzyl chloride consumed. The alternative mode of bonding in the polymer through the methylene groups can be excluded, as is evident from the spectroscopic data for the oligomers obtained (see Experimental).

The oligomers from benzyl chloride and substituted benzyl chlorides contained chlorine, and did not contain double bonds, which suggests that the chloride ions are the termination species (mode 1 in the termination). Thus $TeCl_4$ is unique in its behaviour as a reagent for the oligomerisations of the above monomers. Styrene, which is readily polymerised by various Lewis acids, yields only the dimer containing a $TeCl_3$ terminal group [17]. α-Methylstyrene yields the trimer though in cationic polymerisations it is less reactive than styrene. *trans*-Stilbene which is known to be quite inactive in polymerisations [13], on treatment with $TeCl_4$ gave an oligomer with a significantly higher degree of polymerisation than α-methylstyrene or styrene.

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