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Hydride Transfer to Stable Carbenium Salts

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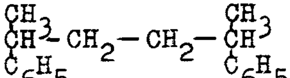
SUMMARY

The interaction between $(C_6H_5)_3CSbCl_6$, $(C_6H_5)_2CHSbCl_6$, $(ClC_6H_4)_3CSbCl_6$ and poly(ε-caprolactone), dimers of α-methylstyrene and of 1,1-diphenylethylene is investigated. By the use of ^{1}H-NMR spectroscopy it is found that hydride transfer proceeds to the stable salts.

INTRODUCTION

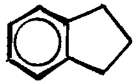
The stable carbenium salts can initiate polymerization of vinyl and heterocyclic monomers by different mechanisms: addition to the monomer, hydride transfer to the initiator and electron transfer (BAWN et al., 1971). The usual proof for hydride transfer initiation mechanism is the presence of the product of hydride transfer to the initiator in the reaction mixture. But the stable carbenium salts are strong hydride acceptors (OLAH and SCHLEYER, 1972) and they may be expected to abstract a hydride ion from the polymer chain as well.

In the present work the possibility of proceeding of this side reaction to the initiators $(C_6H_5)_3CSbCl_6$, $(C_6H_5)_2CHSbCl_6$ and $(ClC_6H_4)_3CSbCl_6$ is investigated. The following model compounds are used: 2,5-diphenylhexane (I) - for the polymer chain of styrene and its derivatives, indan (II) - for one of the possible types of end groups of these polymers, 1,1,4,4-tetraphenylbutane (III) - for vinyl polymers with a higher content of aromatic groups as well as a polymer - poly(ε-caprolactone) (IV).

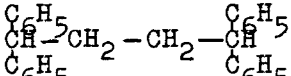


$CH_3-CH(C_6H_5)-CH_2-CH_2-CH(C_6H_5)-CH_3$

(I)



(II)



$(C_6H_5)_2CH-CH_2-CH_2-CH(C_6H_5)_2$

(III)

$-\!\!\!\!\![O\!-\!(CH_2)_5CO]\!\!-_n$

(IV)

EXPERIMENTAL

$(C_6H_5)_3CSbCl_6$ and $(C_6H_5)_2CHSbCl_6$ were synthesized under vacuum from the corresponding chlorides and $SbCl_5$; $(C_6H_5)_3CSbCl_6$ mp 230°C decomp., $(C_6H_5)_2CHSbCl_6$ mp 97°C decomp.i.vac. (I) and (III) were obtained by anionic dimerization of α-methylstyrene and of 1,1-diphenylethylene under vacuum (SZWARC 1971). (I) was purified by thin layer chromatography (n_D^{20} 1.5440). III was recrystalized from ethanol (mp 121°C). Poly(ε-caprolactone) with molecular mass 200000 was prepared as described elsewhere (RASHKOV et al., 1983). Indan was dried over CaH_2 and sodium mirror.

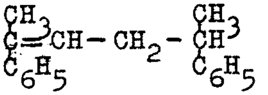
The experiments were performed under vacuum at initial concentrations of the stable salts 10^{-2}–10^{-4} mol.dm^{-3} and at concentrations of the model compounds 1 mol.dm^{-3} at 25°C and at -20°C.

The ^{1}H-NMR spectra of the reaction mixtures after evaporation of the solvent were measured on a Bruker 250 MHz spectrometer in $CDCl_3$ with HMDSO as internal standard. The consumption of the trityl salt in the reactions with poly(ε-caprolactone) and with indan was determined from the decrease in the absorption maximum at 430 nm in the visible spectra of the reaction mixtures.

RESULTS AND DISCUSSION

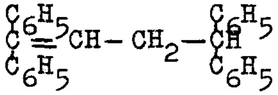
At 25°C hydride transfer proceeds from all the compounds studied. In the ^{1}H-NMR spectra of the reaction mixtures of $(C_6H_5)_2CHSbCl_6$ and I-IV a signal due to the protons of the methylene group of diphenylmethane appears at 3.97 ppm. In the case of $(C_6H_5)_3CSbCl_6$ and $(ClC_6H_4)_3CSbCl_6$ signals due to the methine groups of the corresponding arylmethanes appear at 5.55 ppm and 5.50 ppm.

The stable salts react with the dimers of α-methylstyrene and of 1,1-diphenylethylene at different rates. In the reaction mixtures of the diphenylmethyl salt diphenylmethane is detected after 3 hours reaction time. $(ClC_6H_4)_3CH$ is formed 5 hours after the beginning of the reaction. The reactions of $(C_6H_5)_3CSbCl_6$ with I and with III proceed at the lowest rate - triphenylmethane is found after 5 days. These differences in the rates of interaction of the salts are in accordance with our previous results (PANAYOTOV et al., 1981) for different rates of hydride transfer to stable salts with electrophilic different cations. The NMR spectra of the reaction mixtures of I and III show signals at 5.70 ppm and 5.99 ppm respectively. Probably the cations formed from these compounds as a result of a hydride abstraction are converted into



$C(CH_3)(C_6H_5){=}CH{-}CH_2{-}CH(CH_3)(C_6H_5)$

and



$C(C_6H_5)(C_6H_5){=}CH{-}CH_2{-}CH(C_6H_5)(C_6H_5)$

and the signals at 5.70 and 5.99 ppm are due to the protons of the corresponding methine groups adjacent to the double bonds.

The kinetic curves of the interaction between $(C_6H_5)_3CSbCl_6$ and poly(ε-caprolactone) and indan are S-shaped. In the reaction with poly(ε-caprolactone) 14% of the salt convert into triphenylmethane for 2 hours; the conversion is 75% for 8 hours. The hydride transfer from indan proceeds at the highest rate - the conversion is 64% for 2 hours. The R_{max} of the consumption of $(C_6H_5)_3CSbCl_6$ in the reaction with poly(ε-caprolactone) is 1.83×10^{-8} mol.dm^{-3}.s^{-1} and with indan- 1.22×10^{-7} mol.dm^{-3}.s^{-1}. These results are proved by the NMR spectra of the reaction mixtures.

At -20°C the hydride transfer to the salts is impeded. No signal of $(C_6H_5)_3CH$ is found in the NMR spectra of the reaction mixtures of poly(ε-caprolactone) and $(C_6H_5)_3CSbCl_6$ after 2 hours and after 8 hours reaction time.

The results obtained show that the presence of products of hydride transfer to the initiator in the reaction mixture is not a sufficient proof for hydride transfer initiation mechanism.

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