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Initiators

Reactions of Dialkoxicarbenium Ions with Styrene and 1.1-Diphenyl Ethene

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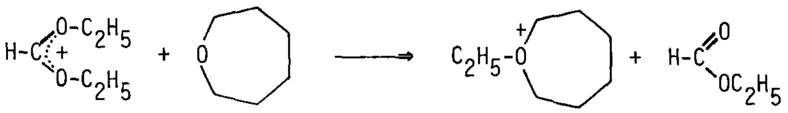
Summary

Several dialkoxicarbenium ions have proved to initiate the cationic polymerization of styrene. In order to elucidate the mechanism of initiation, some of these dialkoxicarbenium ions were reacted with 1.1-diphenyl ethene and the reaction products are described.

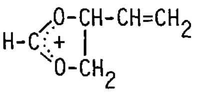
Introduction

Since a number of years now it is known that dialkoxicarbenium ions are effective initiators for the cationically propagating polymerization of cyclic ethers and cyclic acetals, respectively (1, 2,3). This holds for acyclic dialkoxicarbenium ions after the classical work by MEERWEIN (4) as well as for those cyclic ions which derive from 1.3-dioxolane. REICHERT et al. (1) were the first to show the polymerization of oxacycloheptane (oxepane) initiated by diethoxicarbenium-hexachloroantimonate and they showed that on the initiation step in the reaction an alkyl group is transferred from the initiator to the monomer:



Only recently, JEDLINSKI (5) and LUKASZCZYK (6) presented papers which again deal with initiation of polymerization of cyclic acetals by 1.3-dioxolane-2-ylium ions.

Dialkoxicarbenium ions are known to be strong alkylating agents and 4-vinyl-1.3-dioxolane-2-ylium ions 1 and 4-phenyl-1.3-dioxolane-2-ylium ions 2 are as reactive to undergo alkylation of aromatic compounds (7). Because of the high reactivity of the leaving



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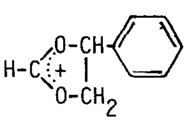

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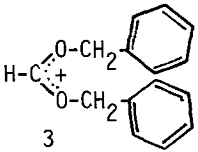

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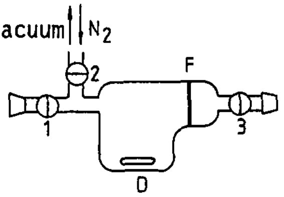
alkylating group one has failed up todate to synthesize compound 3 in pure form; as a result of self-alkylation poly(benzyl) is formed.

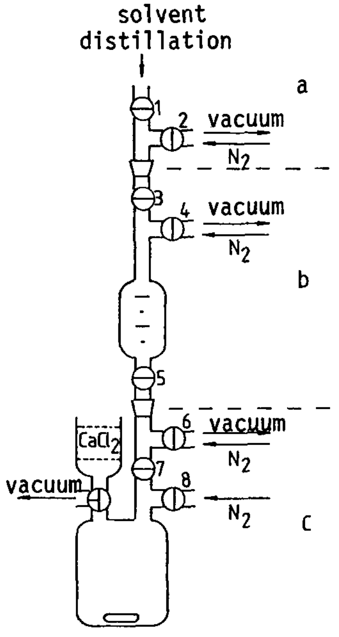
For all these reasons we were interested to investigate the reaction of dialkoxicarbenium ions with vinyl compounds.

Experimental

All dialkoxicarbenium ions 4 - 8 used in these experiments were freshly prepared under a blanket of pure and dry nitrogen according to the description given by BORCH (8) immediately prior to use. Apparatus I was used for these preparations. The reactants were injected by means of a syringe in a stream of nitrogen through stopcock 1. 0.01 mole of HBF_4 (1.6 cc of 50% wt/wt in diethyl ether) dissolved in 20 cc CH_2Cl_2 were injected, followed slowly by adding 0.005 mole of the corresponding orthoester. The solution was stirred at 195K for 15 min after which the dialkoxicarbenium ion salt crystallizes. It was filtered under nitrogen through filter F and was washed twice with 10 cc portions of CH_2Cl_2/Et_2O 1:1 at 195K. The salts were dried in the apparatus in vacuo at 253K. The yields were 4 73%, 5 65%, 6 85%, 7 80%, 8 78%.



apparatus I



apparatus II

To carry out reactions of the salts 4 - 8 having BF_4^- as the counter anion with vinyl compounds, the vinyl compounds were dissolved in 100 cc CH_2Cl_2 in apparatus II and after removal of IIa and IIb, apparatus I was connected to II, and after the olefin solution had been cooled down to the reaction temperature, the salts dissolved in 100 cc CH_2Cl_2 were rinsed into the reaction vessel. Polymeric reaction products were separated as usual and low molecular weight reaction products were identified by GC and ^{1}H-nmr, respectively.

Results

Dialkoxicarbenium-tetrafluoroborate 4 and 1.3-dioxolane-2-ylium-tetrafluoroborate 6 polymerize vinyl compounds like styrene, α-methyl styrene, and s-butylvinylether quite readily at low temperatures, whereas α-methyl styrene undergoes side reactions at higher temperatures. The results of these experiments are compiled in Table 1.

Table 1: Reaction of some vinyl compounds with dialkoxicarbenium salts

monomer/initiator system	ratio	T (K)	time (min)	conversion to polymer (%)
styrene / 4	10:1	293	120	91
	100:1	293	120	68
styrene / 6	100:1	293	120	43
α-methyl styrene/4	1:1	293	60	-a)
	10:1	293	120	11b)
s-butylvinylether/4	100:1	195	60	94

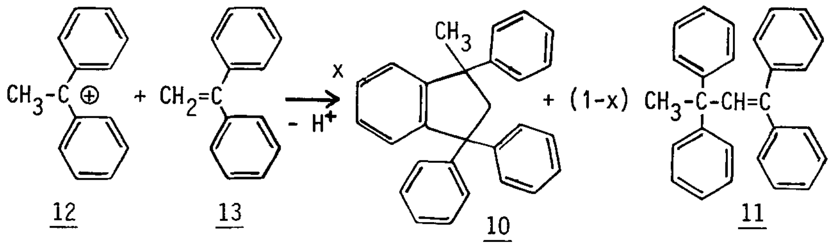
solvent: CH_2Cl_2 ; monomer approx. $4x10^{-3}$ mole/l depending on initiator yield in preparation
a) 27% 1.1.3-trimethyl-3-phenylindane 9
b) plus 18% 9

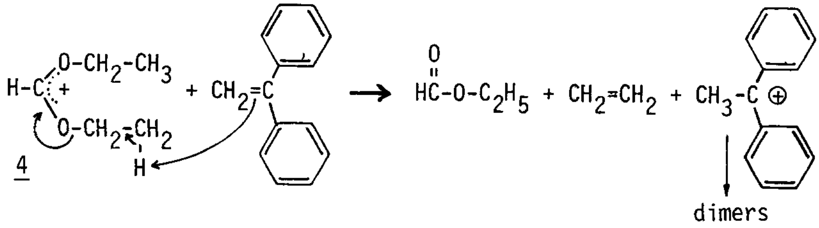
Table 1 shows that the reaction of α-methyl styrene with the initiator salt 4 yields considerable quantities of 1.1.3-trimethyl-3-phenylindane 9 which is known to be formed on proton initiation of α-methyl styrene polymerization (9). It is the predominant reaction over the formation of polymer. Obviously dialkoxicarbenium ions can initiate the cationic polymerization of some vinyl compounds as given in Table 1. But these experiments tell us nothing about the initiation step. From the formation of 9 on reaction with α-methyl styrene one may suggest that protons play the role of being the active initiator.

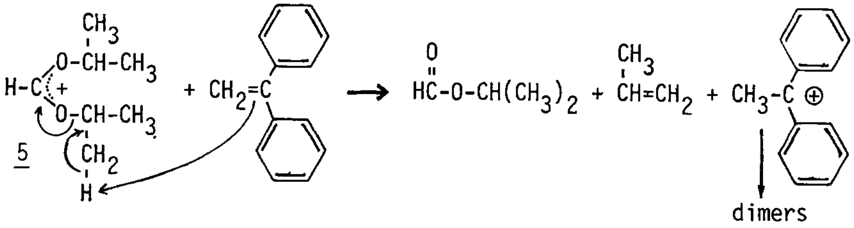
The olefin 1.1-diphenyl ethene has been used in many cases to elucidate the initiation step in cationic processes since this compound does not undergo propagation reactions and by this enables the investigator to look at the chemistry of initiation (10, 11,12).

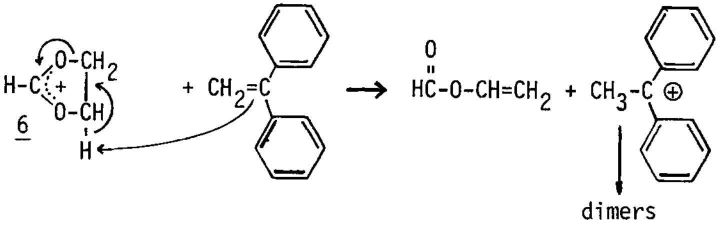
All the dialkoxicarbenium salts 4 - 8 transfer a proton to the β-carbon atom of 1.1-diphenyl ethene in the course of which the dimers 10 and 11 are formed. All the reaction products were identified by melting points, GC, and ^{1}H-nmr, respectively. In all cases no alkyl transfer from the salt to the vinyl compound was observed. Since dimerization of 12 with 13 to 10 and 11, respectively, sets free a proton, this cascade of reactions pushes forward the overall reaction towards formation of reaction products from esters and protons.

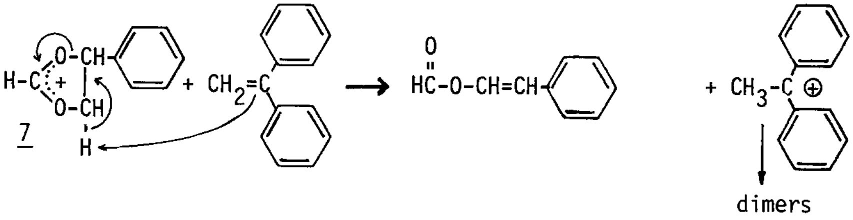
The findings indicate that dialkoxicarbenium ions as well as 1.3-dioxolane-2-ylium salts initiate vinyl compound cationic polymerization by proton transfer.











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