ACTIVATION OF TRANSFER OF HYDROGEN FROM THE Si-H BOND BY Mn AND Re CARBONYLS IN REACTIONS WITH ACRYLIC MONOMERS

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Radical telomerization of ethylene of triethylsilane (TES) initiated by binuclear carbonyls $M_2(CO)_{10}$ (M = Mn, Re) basically results in the formation of an Et₄Si adduct. Higher telomeric homologs, formed in similar conditions in peroxide initiation [1], are almost absent, which can be attributed to homolytic activation of H transfer in the TES $M_2(CO)_{10}$ system [2].

Acrylic compounds: methyl acrylate (MA), methyl methacrylate (MMA), and acrylonitrile (AN), were used as the monomers for studying homolytic activation of the Si-H bond, and it was shown that the nature of the monomer significantly and differently affects the activating capacity of Mn and Re carbonyls. The event of activation of transfer of H from the Si-H bond is manifested by the fact that highly selective radical addition of TES to the monomer can take place in the presence of $M_2(CO)_{10}$ and the degree of polymerization of the acrylic compounds, characteristic of reactions using peroxides, can decrease.

The selected ratio of reagents (1:1) permitted observing not only addition but also telomerization (Table 1, No. 2 and 4). The formation of three compounds was observed in almost all of the experiments, together with adducts: siloxanes, whose quantity was essentially a function of the occurrence of the basic reaction. A comparison of the data obtained (see Table 1) shows that in the case of $Mn_2(CO)_{10}$, the yield of the adduct decreases in the sequence MA-MMA. In conditions of a radical process, the decrease in the efficiency of the reaction in going from MA to MMA is totally explainable, since a relatively stable tertiary adduct radical $Et_3SiCH_2\dot{C}(Me)CO_2Me$ is formed from MMA and is less active in the stage of chain transfer than the adduct radical $Et_3SiCH_2CHCO_2Me$, which leads the chain in the reaction with MA. However, these reactions take place totally differently in initiation with Re carbonyl. The significantly lower efficiency of the Re₂(CO)₁₀-TES system, in comparison to $Mn_2(CO)_{10}$, as an H carrier in the reaction with MA is also manifested by the fact that

FABLE 1		Addition	of	TES	to	Unsaturated	Compounds	(M)	×
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y portion	Initiator	т., °С	Cor s	nver- ion	M/TES (init	identified cts for ed TES, %	T1, %	Ratio of th consi their	o of pr e reac dered sum,	roducts tion for %	Ratio telome for $\Sigma T_1 +$ mole,	of ers T ₂ ,
No. b			W	TES		Σ of produ react	Yield	T ₁	s,	$\Sigma S_{2,3}$	T ₁	T_2
CH ₂ =CHCO ₂ Me												
1 2 3 4	$\begin{array}{c} Mn_2(CO)_{10} \\ Mn_2(CO)_{10} \\ Mn_2(CO)_{10} \\ Re_2(CO)_{10} \end{array}$	140 140 140 160	40 50 70 80	50 65 30 95	0,5 1 2 1	$\begin{array}{c} 66,0\\96,2\\53,0\\98,2\end{array}$	$36,8 \\ 30,8 \\ 5,3 \\ 4,1$	95,1 86,1 77,8 6,4	4,9 6,5 9,8 67,1	-7,4 12,4 26,5	100 99,5 100 81,9	0,5 18,1
$CH_2 = C(Me)CO_2Me$												
5 6	$\begin{array}{ c c c } Mn_2(CO)_{10} \\ Re_2(CO)_{10} \\ \hline \end{array}$	140 160	$\begin{array}{c} 25\\80 \end{array}$	50 100	1 1	70,7 91,8	8,1 39,5	40,9 79,9	36,0 18,1	23,1 2,0	100 100	
*Test experiments conducted in optimum conditions obtained after variation of the conditions for all parameters (38												

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experiments) are reported.

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	20	;	rouna/ca	uculated, /	0							
Compound	<i>d</i> _n	d_{4} ²⁹	υ	н	Si	spectrum	CO2	CH ₃ O	CH ₃ CH ₂	CH2	CH2	H0-
$Et_3SiCH_3CH_2CO_2Me$ (T_1)	1,4436	1	59,61 59,41	$\frac{10,84}{10,89}$	13,80 13,86	H'1 DEI	173,3	3,8 50,7	1,2 7,2	2,4 28,0	$\begin{array}{c} 0.7\\ 3.0;\ 6.3\end{array}$	
${ m Et_{3}Si(CH_{2}CHCO_{2}Me)_{2}H}$ (T_{2})	I	ſ				H,	171,6 175,2	3,6 50,8	$^{1,7}_{7,3}$	$\begin{array}{c} 1.7; \ 2.2\\ 30.5; \ 31.4 \end{array}$	$\begin{array}{c} 0.8\\ 3,3; \ 14,6 \end{array}$	$^{2,3}_{39,7}$
Et _s SiCH ₂ CHCO ₂ Me Me	1,4444	0,8599	$\frac{61,17}{61,10}$	$\frac{11.05}{11,10}$	12,48 12,96	D ^{E3}	176,1	56,7	$^{20,7}_{7,1}$		3,4; 16,3	34,9
$Et_{s}Si-O-SiEt_{3} *$ (S ₁)	1,4332	0,8475	58,49 58,50	$\frac{12,11}{12,20}$	21,49	H ¹			0,8 6,5		6,1	
*S ₂ , S ₃ : siloxane	es of ur	determine	ed structi	ure; ¹ H M	AR(ô, ppm): 0.8 m	(CH ₃), 0	.4 q (CH ₂	Si).	-		

TABLE 2. Characteristics of the Compounds Separated

formation of a significant amount of telomer T_2 with two monomeric units is only observed in the case of $\text{Re}_2(\text{CO})_{10}$ (Table 1, No. 4).

The results obtained show that the essence of the effect of binuclear carbonyls does not simply consist of facilitating homolytic cleavage of the Si-H bond in TES but also consists of the different character of the intermediately formed complexes or particles which participate in H transfer.

In consideration of the analogies in the literature in the occurrence of the individual stages and our data, the scheme of the reaction in the presence of $Mn_2(CO)_{10}$ can be represented as follows:

$$Mn_2(CO)_{10} \rightarrow 2Mn(CO)_5$$

$$\begin{split} \dot{\mathrm{Mn}}(\mathrm{CO})_5 & \longrightarrow [\mathrm{HMn}(\mathrm{CO})_5] + \mathrm{Et}_3 \dot{\mathrm{Si}} \\ [\mathrm{HMn}(\mathrm{CO})_5 & \to \mathrm{HCOMn}(\mathrm{CO})_4] \\ [\mathrm{HCOMn}(\mathrm{CO})_4] + \mathrm{M} & \to [\mathrm{HCOMn}(\mathrm{CO})_4 \mathrm{M}] \\ \mathrm{B} & \xrightarrow{\mathrm{-CO}} [\mathrm{Mn}(\mathrm{CO})_4 \mathrm{CH}_2 \mathrm{CH}_2 \mathrm{CO}_2 \mathrm{Me}] \\ \mathrm{C} & \xrightarrow{\mathrm{+Et}_3 \mathrm{Si}} \mathrm{Et}_3 \mathrm{SiCH}_2 \mathrm{CH}_2 \mathrm{CO}_2 \mathrm{Me} \end{split}$$

In contrast to Mn hydride, migration of H to $HRe(CO)_5$ is considered less probable [3]. It is known that in the usual conditions of initiation of telomerization, when the initiator does not interfere in the chain transfer stage, the distribution of the telomeric homologs is determined by the monomer-telogen ratio. However, when $Mn_2(CO)_{10}$ is used as the initiator, the change in M/TES from 0.5 to 2 does not result in the appearance of higher telomers (see Table 1, No. 1-3), i.e., a deviation from the usual mechanism of the reaction is observed. The process of transfer of H to the monomer apparently takes place in complex B, whose composition also determines the real M/TES ratio.

EXPERIMENTAL

The ¹H NMR spectra were made on a Hitachi-Perkin-Elmer R-20 spectrometer, and the ¹³C NMR spectra were made on a Bruker WR-200 spectrometer (CCl₄ and CHCl₃ internal standards with suppression of the reaction with H, and in the DERT technique). The GLC analysis was performed on a LKhM-8MD-5 chromatograph with a katharometer in a current of helium with temperature programming from 60 to 250°C (6°C/min) and in a steady-state mode at 115°C in a 3000 × 3 mm column with 20% SKTFT-50 on Chromosorb W (0.10-0.20 mm); preparative GLC was performed on a Tsvet chromatograph at 150, 165, and 185°C in a 1700 × 9 mm column with 15% SKTFT-50 on Chromaton N-AW (0.20-0.25 mm). The weight concentration of the products of the reaction was calculated with the areas of the peaks using a standard, succinic acid dimethyl ester.

Experimental Method. The experiments with the acrylic monomers were conducted in sealed glass ampuls previously evacuated and filled with nitrogen.

<u>Addition of TES to MA. a) $Mn_2(CO)_{10}$ Initiator.</u> Here 6.5 mmole of TES, 3.7 mmole of MA, 4 mole % (of TES) of $Mn_2(CO)_{10}$ were used, 140°C, time of 2 h. The adduct $Et_3SiCH_2CH_2CO_3Me$ (I) (37% according to GLC) and siloxane S_2 were separated (Table 2).

<u>b) $\operatorname{Re}_2(\operatorname{CO})_{10}$ initiator</u>. Here 32.5 mmole of TES, 19 mmole of MA, and 0.4 mole % (of TES) of $\operatorname{Re}_2(\operatorname{CO})_{10}$ were used, 160°C, 2 h. Separated: (I) (4% of theoretical according to GLC), hexaethyldisiloxane S₁ (35% according to GLC), siloxane S₃, and telomer T₂ Et₃Si(CH₂-CHCO₂Me)₂H (see Table 2). The conditions of conducting the analytical experiments are reported in Table 1, No. 1-4.

<u>Addition of TES to MMA. a) $Mn_2(CO)_{10}$ Initiator.</u> Here 6.5 mole of TES, 3.7 mmole of MMA, and 4 mole % (of TES) of $Mn_2(CO)_{10}$ were used, 140°C, 2 h. Adduct $Et_3SiCH_2CH(Me)CO_2Me$ was separated (10% according to GLC) (see Table 2).

b) In initiation of the reaction with $\text{Re}_2(\text{CO})_{10}$ (0.4 mole % of TES), the yield of the adduct was 39.5% according to GLC (see Table 1, No. 6). The conditions of conducting the analytical tests are reported in Table 1, No. 5-6. The siloxanes were identified by GLC with known samples (S_{1-3}).

CONCLUSIONS

The nature of the monomer has a significant effect on the capacity of Mn and Re carbonyls to activate transfer of hydrogen from the Si-H bond in the reaction of triethylsilane with acrylic monomers due to the intermediate formation of complexes which include the monomer.

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REACTION OF CHLORO- AND BROMO-ALKYL SUBSTITUTED

SILANES CC1₂XCH₂CHXSi(CH₃)₃ WITH ZINC

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Silylcyclopropanes (SP) are highly reactive compounds and can be widely employed in organic synthesis. Known methods for their preparation are the addition of silyl carbenes to olefins or of carbene fragments to vinylsilanes [1].

We have examined the possibility of preparing SP by intramolecular reductive cyclization of $\alpha, \gamma, \gamma, \gamma, \gamma$, tetrahaloalkylsilanes by a method developed in [2]. The preparation of the haloalkylsilane starting materials CC1, BrCH, CHBrSiMe, (I) and CC1, CH, CHClSiMe, (II) has been described previously [3, 4]. It is of interest to compare reductive cyclization with the participation of single Br or Cl atoms and also the competition between Br and Cl in gemtrihaloalkyl groups.

The reaction of (I) and (II) with zinc proceeds at bp in methanol or ethanol, or at 78-80°C in DMF. In methanol and DMF 100% conversion of the starting materials is achieved in 1-2 h. Depending on the structure of the polyhaloalkylsilane and on the reaction conditions, three reaction routes are possible (see reaction scheme below): reductive cyclization (route a), hydrogenolysis (route b), and reductive dimerization (route c). For (I)

Scheme

 $\begin{array}{c|c} & a & CI \\ \hline & & CHCl_2CH_2CHBrSiMe_3 + CHCl_2CH_2CH_2SiMe_3 + \\ \hline & & (VI) \\ \hline & & CHCl_2CH_2CHBrSiMe_3 + CHCl_2CH_2CH_2SiMe_3 + \\ \hline & & (VI) \\ \hline & & (VII) \\ \hline & & + C_2H_5CHCISiMe_3 \\ \hline & & (VIII) \\ \hline & & C \\ \hline \end{array}$ \rightarrow (Me₃SiCHBrCH₂CCl₂)₂ + (Me₃SiCH₂CH₂CCl=)₂

all these reactions are realized but for (II) only a and b. From (I) and (II) route a leads to the cyclopropanes (III) and (IV) and the allyltrimethylsilane (V). As was demonstrated in [5, 6], a feature of the opening of the SP ring is the formation of allylsilanes, in contrast to the carbon analogs from which branched hydrocarbons are obtained. The formation of chlorine - substituted cyclopropanes on reductive cyclization has been observed previously *Deceased.

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