LITERATURE CITED

1. G. M. Nazin and G. V. Manelis, Izv. Akad. Nauk SSSR, Ser. Khim., 811 (1972).
2. V. V. Dubikhin and G. M. Nazin, Izv. Akad. Nauk SSSR, Ser. Khim., 923 (1974).
3. G. K. Klimenko, Proceedings of the Fourth All-Union Symposium on Combustion and Explosion [in Russian], Nauka, Moscow (1977), p. 585.
4. V. A. Pal'm, Fundamentals of the Quantitative Theory of Organic Chemistry [in Russian], Izd. Khimiya, Leningrad (1977), p. 319.
5. N. G. Yunda, I. Yu. Kozyreva, G. V. Lagodzinskaya, and G. B. Manelis, Izv. Akad. Nauk SSSR, Ser. Khim., 1772 (1983).

RADICAL TELOMERIZATION OF ETHYLENE BY TRIETHYLSILANE INITIATED BY $Mn_2(CO)_{10}$ OR BUTYL PEROXIDE

A. B. Terent'ev, M. A. Moskalenko,
and R. Kh. Fredilina

UDC 541.128:541.515:66.095.
2:547.313.2.547.245

The thermal radical telomerization of ethylene with triethylsilane (TES) [1] and the addition of TES to α-olefins in the presence of tert-butyl peroxide (TBP) [2] lead to the formation of tetraalkylsilanes $Et_3Si(CH_2CH_2)_nH$. When using $Fe(CO)_5$ as the initiator, triethylaklylsilanes and/or triethylalkenylsilanes are obtained depending on the reaction conditions [3]. The formation of TES radicals in the $Et_3SiH—Mn_2(CO)_{10}$ system was demonstrated by ESR spectroscopy using the spin trap method [4].

In order to elucidate the effect of the nature of the initiating system on the course of the telomerization, we studied the reaction of TES with ethylene in the presence of $Mn_2(CO)_{10}$ and compared the course of the telomerization in the presence of TBP, $Mn_2(CO)_{10}$, and $Fe(CO)_5$ (Table 1). The reaction proceeds by the scheme

$$Et_3SiH \xrightarrow{R^\cdot} Et_3Si^\cdot$$

($R^\cdot$ — initiating radical)

$$Et_3Si^\cdot + nCH_2 = CH_2 \rightarrow Et_3Si(CH_2CH_2)_n^\cdot$$

$$Et_3Si(CH_2CH_2)_n^\cdot + \text{HD}^* \rightarrow Et_3Si(CH_2CH_2)_nH(T_n)$$

The first three members of the series (T_1–T_3) are formed predominantly in the presence of TBP. The distribution of these products (see Table 1) is close to that found in the case of thermal initiation [1]. In the presence of $Mn_2(CO)_{10}$ under analogous conditions, virtually only the adduct is formed. An increase in the carbonyl concentration leads to an increase in the conversion and, thus, of the adduct yield. The change in the nature of the telomer distribution in the presence of $Mn_2(CO)_{10}$ in favor of T_1 indicates that the system of TES with $Mn_2(CO)_{10}$ is an efficient hydrogen transfer agent, i.e., in the telomerization reaction, this system not only initiates the reaction but also participates in chain transfer at the Si—H bond (see scheme above). It is interesting that, in contrast to the reaction with $Fe(CO)_5$, in which a mixture of Et_4Si and $Et_3SiCH=CH_2$ is formed under these conditions (see Table 1, experiment 4) [3], only saturated compounds are formed when the reaction is initiated by $Mn_2(CO)_{10}$. In order to clarify the effect of the olefin/TES ratio on the yields of Et_4Si and $Et_3SiCH=CH_2$, the addition of TES to 1-hexane (M) was carried out in the presence of $Mn_2(CO)_{10}$ or $Fe(CO)_5$ for M/TES from 0.2 to 5; the yield of the unsaturated silane was found to remain in the range from 20 to 40% (Table 2).

EXPERIMENTAL

The ^{13}C NMR spectra were taken on a Bruker WP-200 spectrometer with CCl_4 as the internal standard and the PMR spectra were taken on a Perkin-Elmer R-20 spectrometer relative to TMS.

---

*The hydrogen donor is TES or the $TES—Mn_2(CO)_{10}$ system.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2825-2827, December, 1984. Original article submitted April 20, 1984.

TABLE 1. Telomerization of Ethylene (M) with Triethylsilane (S)

Experiment	Load, mmoles			Conversion, %		Telomer distribution, % of the sum of T_1-T_3*		
	M	S	initiator	M	S	T_1	T_2	T_3
1	9,3	13,0	TBP., 0,13	30	25	64	29	7
2	12,8	13,0	$Mn_2(CO)_{10}$, 0,05	30	40	98	1	1
3	12,1	12,0	$Mn_2(CO)_{10}$, 0,5	60	70	100	–	–
4	14,3	13,0	$Fe(CO)_5$, 1,0	40	50	100 †		

---

*The identified compounds comprise 75-90% of the sum of the reaction products.

†Gas–liquid chromatographic and ^{13}C NMR analysis indicates that the adduct is a mixture of 45% Et_4Si and 55% $Et_3SiCH{=}CH_2$.

TABLE 2. The Addition of Triethylsilane to 1-Hexene

Experiment	Initiator, mole %	Conversion, %		Initial M/TES ratio	$Et_3SiC_6H_{11}$, %
		TES	M		
1	$Mn_2(CO)_{10}$, 4	10	63	0,2	39
2	$Mn_2(CO)_{10}$, 4	28	20	5	32
3	$Fe(CO)_5$, 8	38	49	0,2	21
4	$Fe(CO)_5$, 8	24	12	5	22

Analytical gas–liquid chromatography was carried out on a 3000 × 3-mm column packed with 15% SKTFT-50 on Chromatone N-AW (column 1) and a 3000 × 3-mm column packed with 15% Carbowax on Chromatone N-AW (column 2) with helium gas carrier and a katharometer detector. The preparative gas–liquid chromatography was carried out an a 2400 × 9-mm column packed with 15% SKTFT-50 on Chromatone N-AW.

Telomerization of Ethylene with Triethylsilane. The experiments were carried out in a test autoclave with 6-cm^3 glass inserts. The starting compounds placed in the glass inserts were purified by the freeze–thaw technique and then ethylene was introduced. The unit was heated in a constant-temperature oil bath at 140°C for 1 h. The contents were stirred by rotation of the autoclave at 8 rpm. The experimental conditions and results of the gas–liquid chromatographic analysis are given in Table 1. The chromatograms were analyzed by the internal normalization method. A sample of Et_4Si was isolated by preparative gas–liquid chromatography from the reaction mixture of reaction 3. PMR spectrum (δ, ppm, from TMS): 0.45 t (CH_3), 0.85 q q (CH_2); ^{13}C NMR spectrum: 2.8 (CH_2), 7.2 (CH_3). Reaction mixture of experiment 4: ^{13}C NMR spectrum (δ, ppm, from TMS): 3.0, 2.8, 2.3 (CH_2Si), 7.6, 6.9, 6.8 (CH_3), 131.8, 135.9 ($CH_2{=}CH$), 210 ($C{=}O$).

Addition of Triethylsilane to 1-Hexene. These experiments were carried out in 4-ml glass ampules after prior evacuation at 140°C for 1 h. The results of the gas–liquid chromatographic analysis are given in Table 2.

CONCLUSIONS

Complexes of triethylsilane with $Mn_2(CO)_{10}$ are effective hydrogen transfer agents in the step involving chain transfer at the Si–H bond in radical telomerization.

LITERATURE CITED

1. A. N. Nesmeyanov, R. Kh. Freidlina, and E. Ts. Chukovskaya, Dokl. Akad. Nauk SSSR, 115, 734 (1957).
2. N. M. K. El-Durini and R. A. Iakson, J. Organomet. Chem., 232, 117 (1982).
3. R. Kh. Fredilina, E. Ts. Chukovskaya, I. Tsao, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 132, 374 (1960).
4. R. G. Gasanov and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1244 (1981).