RADICAL COTELOMERIZATION OF ETHYLENE AND PROPYLENE WITH CC14

N. A. Grigor'ev UDC 66.095.2:541.515:547.313.2:547.313.3:547.412.133 and R. Kh. Freidlina

Work on the radical cotelomerization of two monomers of very different polarities — propylene and vinyl chloride [1-3] and ethylene and vinyl chloride [4] — with CCl₄ has revealed the substantial influence of polar effects in the chain growth and transfer stages of these reactions. We decided to examine the extent to which polar effects influence the cotelomerization with CCl₄ of two nucleophilic monomers — ethylene and propylene — that are closer in polar properties. Since we have already examined the homotelomerization of each of these monomers with CCl₄ in detail [5, 6], we were able to simplify the identification of all the cotelomerization products to a considerable extent.

EXPERIMENTAL

The GLC analyses were carried out on an LKhM-8MD with a katharometer, 2000×3 mm steel column with 10% SKTFT-50 silicone rubber on Chromaton N-AW, He (6 liters/h), 135 and 150°C; preparative GLC was carried out on a Khrom-3 with a preparative attachment, 2400 ×6 mm steel column with 5% silicone SE-30 on Chromaton N-AW, He (12 liters/h), katharometer, 95 and 115°C. The PMR spectra were recorded on a Hitachi-Perkin-Elmer R-20 (60 MHz) and RYa-2309 (90 MHz) spectrometers. Runs were carried out in 10-ml stainless-steel autoclaves in the presence of benzoyl peroxide (BP) by the method described earlier [1]. The quantities of the reactants, reaction conditions, and results of GLC analyses of the reaction mixtures are summarized in Table 1.

We isolated the cotelomerization products by carrying out a series of runs under conditions like those of run 5 (Table 1). Unreacted CCl₄ was stripped off and the residue was fractionated by vacuum distillation. The cotelomerization products were isolated from the fractions by preparative GLC.

*Here and subsequently T_n^E , T_n^P , T_2^{EP} , and T_3^{EEP} , etc., denote the telomers and cotelomers with n monomer units in the chain; the superscript indicates the sequence of the monomer units in the cotelomer molecule.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 625-629, March, 1980. Original article submitted January 22, 1979.

			n>3	42867				
	osition of reaction products, mole%		TT.	53.862				
		، 	۹. ۴	91111				
			T ₃ PEP	\$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$				
		PEE	T ₃ +T ⁵ +T ⁵	10010 7,0010				
3P)			ш. Е	0,4 6,2 6,2 2,9				
03 g 1			۵. ۴	$\begin{array}{c} 42.4\\ 21.7\\ 21.7\\ 9.2\\ 9.2\\ 15,1\\ 15,1\end{array}$				
h, 0.(Comp	R	$^{1}_{\pm T_{2}^{\text{EP}}}$	26,9 24,3 26,2 26,2				
°, 3			щ Ч	1,3 4,1 17,6 17,6 10,9				
,06)	cc14 (90		_~ ਜ	14,8 24,9 22,2 28,3 28,3				
cc14		•	ш <u>г</u>	2,3,20 3,10 3,20 3,20 3,20 3,20 3,20 5,40 5,40 5,40 5,40 5,40 5,40 5,40 5,4				
He with	Conver-	sion of	CCI4, %	6,7 8,3 16,1 19,7 49,7				
and Cs.		C ₃ H ₆	C ₃ H,	8,64 2,63 1,37 1,00				
of CaH4		C ₃ H,	cci	0,89 1,15 0,97 0,88 0,88				
ation c		C ₃ H ₆	ccit	7,68 3,01 0,53 0,88				
lomeriz	tity, mmole		C,H,	9,6 9,6 30,0 41,1 71,4				
Cote			C,H,	82,9 62,0 71,3 71,3				
1.	Ougn	,	cci	10,8 20,6 31,0 80,8 80,8				
TABLE			uny	40040				

BP)	
60	
0.03	
3 h,	
•	
ວູ06)	
cc14	
with	
C ₃ H ₆	
and	
C₂H₄	
of	
Cotelomerization	
.	
ABLE	

*Run carried out in a 30-ml autoclave in the presence of 0.13 g BP for 5 h.

			s, ppm						
Com poun	Formula	Cı	C3	C3	C4	C•	2 CH3	4 CH-	6 С Н ,
(I) (II)	$\begin{array}{c} 1 & 2 & 3 & 4 \\ CCl_3CH_4CH_4CH_2CH_2CH_4CH & [6] \\ Ccl_4CH_2CHCH_4CHCl & [1] \\ & 1$	2,75 2,67	1,93	1,93 1,90	3,59 3,99		1,17	1,52	
(III)	CCl ₃ CH ₂ CHCH ₂ CH ₂ CI [7]	2,68	2,04	1,91	3,61		1,18		
(IV)	$CCl_{2}CH_{2}CH_{2}CH_{2}CH_{2}CI \qquad (T_{2})$	2,67	2,15	1,88	3,57		1,15		i
(V)	CH_3 $CCl_4CH_2CH_2CH_2CHCl$ (T_2^{EP})	2,64	1,88	1,88	4,02			1,53	
(VI)	$\begin{array}{c} 1 & 2 & 3 & 4 & 5 & 8 \\ CCl_{s}CH_{*}CHCH_{*}CHCH_{*}CHCl \qquad [3] \\ \vdots \\ $	2,64				4,04	1,12	0,93	1,52
(VII)	$CCl_{3}CH_{2}CH_$	2,70	}			3,54	1,18		
(VIII)	ĊH ₃ CCl ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CHCl (T ^{EEP})	2,70				4,03			1,54
(IX)	$\begin{array}{c} CH_3 \\ CCl_3CH_2CHCH_2CH_2CH_2CH_2CHCl (T^{PEP}) \\ 1 \\ CH_3 \\ CH_3 \\ CH_3 \\ \end{array}$	2,68	2,02			4,02	1,17		1,52

TABLE 2. PMR Parameters of Some Homotelomers and Cotelomers*

*Multiplet centers are quoted.

TABLE 3. Elemental Analyses of Isolated Cotelomers

Catalorna	Found Calculated, %						
Coleionier	С	н	Cl				
$\begin{array}{c} T_2^{PE} + T_2^{EP} \\ T_3^{PEE} + T_3^{EEP} \\ T_3^{PEP} \end{array}$	$ \begin{array}{r} 32,55 \\ \overline{32,17} \\ 38,45 \\ \overline{38,12} \\ 40,70 \\ \overline{40,63} \end{array} $	$ \begin{array}{r} 4,53 \\ \overline{4,50} \\ 5,68 \\ \overline{5,60} \\ \overline{5,60} \\ \overline{5,97} \\ \overline{6,06} \\ \end{array} $	62,98 63,33 55,99 56,28 52,83 53,31				

supported by the results of elemental analysis (Table 3). The results of PMR [Table 2, (IX)] and elemental analysis (Table 3) of the second compound, which appears between T_3^E and T_3^P , imply that it is a single cotelomer with the structure $CCl_3CH_2CH_2CH_2CH_2CH_2CHC1CH_3$ (T_3^{PEP}).

The GLC analysis of the reaction mixture revealed no other compounds apart from the homotelomers and cotelomers in the region up to T_3^P .

DISCUSSION

We can write the cotelomerization of ethylene and propylene with CCl4 as

In addition to the homotelomers we detected both possible cotelomers with two monomer units, T_2^{PE} and T_2^{EP} , in the reaction mixture (Table 1). Under the conditions of run 5 they were formed in the ratio 1.4:1, which we measured from the integrated intensities of the CH₃, CH₂Cl, and CHC1CH₃ groups in the PMR spectrum of the mixture of these cotelomers.

In the cotelomerization the stage leading to product formation, chain transfer by the growing radicals to CCl₄, competes with two others, addition to CH₂ =CH₂ and to CH₂ =CHCH₃. The formation of any particular homotelomers and cotelomers and their distribution can depend on the polar properties of all the reactants that are involved in these reactions. The formation of the T₂ cotelomers involves the radicals CCl₃CH₂CH₂CH₂CH₂CH₂(A) and CCl₃CH₂CH₂CH₂CH₂CH₄(B). Radicals (B) seems to be more nucleophilic than radical (A), since its CH₃ group is α to the radical center, and chain transfer by it to the electrophilic CCl₄ should proceed more easily than in the case of radical (A). This in turn should result in the preferential formation of T₂^{EP}. However, T₂^{PE} predominates in the mixture of T₂ cotelomers; i.e., the ratio of the T₂ cotelomers is not solely dependent on the polar effects in the chain transfer stage. The first stage leading to the formation of T₂^{EP} or T₂^{PE} is the addition of the electrophilic CCl₃ radical (σ = +0.454 [8]) to CH₂ =CH₂ or CH₂ =CHCH₃. Apparently the CCl₃ radical adds to the more nucleophilic CH₂ =CHCH₃ at a higher rate than to CH₂ =CH₂, which also results in the ultimate predominance of T₂^{PE} in the mixture of T₂ cotelomers.

In addition to the T₂ cotelomers, we identified three of the six possible cotelomers with three monomer units, T_3^{PEE} , T_3^{EEP} , and T_3^{PEP} , in the reaction mixture. The first two cotelomers were isolated as a mixture; comparison of the integrated intensities of the CH₂Cl and <u>CHClCH₃</u> groups gave a T_3^{PEE}/T_3^{EEP} ratio of 2:1 (under the conditions of run 5). Here, as in the case of the T₂ cotelomers, the cotelomer in which the first unit is propylene predominates, probably as a result of the same factors that were responsible for the experimental ratio of the T₂ cotelomers. We isolated the cotelomer T_3^{PEP} in the pure state. Its content depended only slightly on the reactant ratio and was higher than that of T_3^{EEP} and T_3^{PEE} in the runs with excess propylene (runs 1-3).

The chromatogram of the reaction mixture revealed several more peaks on the other side of the peak of T_3^P . Since with the experimental reactant ratios (runs 1-5, Table 1) T_3^P and T_3^E were present in small quantities, these peaks cannot belong to the homotelomers with n > 3. Consequently, the products whose retention times are higher than that of T_3^P should be the cotelomers containing more than three monomer units in the chain.

Variation of the reactant ratio revealed that when the $C_{3}H_{6}/C_{2}H_{4}$ ratio is reduced the content of T_{2}^{p} and higher products with n > 3 falls while that of the T_{2} and T_{3} cotelomers increases (runs 1-4, Table 1). The total content of the T_{2} and T_{3} cotelomers was 11.0% in run 1 but 37.7% in run 4. However, since the content of ethylene homotelomers increases simultaneously a $C_{3}H_{6}/C_{2}H_{4}$ ratio close to one is the optimum for the maximum yield of the T_{2} and T_{3} cotelomers. With this ratio (run 5, Table 1) the yield of the T_{2} and T_{3} cotelomers is reasonably high (38.5%) and the yield of higher products is small, while the content of the ethylene and propylene homotelomers remains roughly the same as in the runs with higher $C_{3}H_{6}/C_{2}H_{4}$ ratios (64.9% in run 1 and 59.5% in run 5).

CONCLUSIONS

2. The influence of the polar factors persists throughout all stages of the cotelomerization of CC14 with ethylene and propylene, two monomers that differ less in polar properties than the monomer pairs examined earlier.

LITERATURE CITED

- 1. R. Kh. Freidlina, T. A. Onishchenko, and B. L. Zhuk, Izv. Akad. Nauk SSSR, Ser. Khim., 2250 (1974).
- R. Kh. Freidlina, T. A. Onishchenko, and B. L. Zhuk, Dokl. Akad. Nauk SSSR, <u>220</u>, 135 (1975).
- 3. T. A. Onishchenko, B. L. Zhuk, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1374 (1975).
- 4. B. L. Zhuk, T. T. Miftakhov, T. A. Onishchenko, and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR, <u>226</u>, 581 (1976).
- 5. B. A. Englin and R. Kh. Freidlina, Zh. Fiz. Khim., 39, 2208 (1965).
- 6. B. N. Osipov, Dissertation, Moscow (1969).
- 7. R. Kh. Freidlina, T. A. Onishchenko, B. L. Zhuk, and O. A. Eletskaya, Dokl. Akad. Nauk SSSR, 227, 108 (1976).
- 8. V. Palm, Usp. Khim., <u>30</u>, 1069 (1961).