2. In the telomerization of vinyl acetate with methyl propionate, together with the $CH_3O_2CCH(CH_3)[CH_2-CH(O_2CCH_3)]_nH$ telomers, are also formed compounds of type $CH_3O_2CCR(CH_3)[CH_2CH(O_2CCH_3)]_2H$ due to rearrangement of the radicals with 1,5-H migration.

3. Characteristic signals were isolated in the PMR and 13 C NMR spectra that permitted reliably establishing the structure of this type of compounds.

LITERATURE CITED

1. C. M. Starks, Free Radical Telomerization, Academic Press, New York (1974), p. 179.

2. R. Kh. Freidlina and A. B. Terent'ev, Acc. Chem. Res., <u>10</u>, 9 (1977).

3. F. W. Mellows and M. Burton, J. Phys. Chem., <u>66</u>, 2164 (1962).

4. A. B. Terent'ev, N. S. Ikonnikov, and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR, 196, 1373 (1971).

5. A. B. Terent'ev, V. I. Dostovalova, and R. Kh. Freidlina, Org. Magn. Reson., 9, 301 (1977).

TELOMERIZATION AND COTELOMERIZATION OF VINYLIDENE CHLORIDE AND PROPYLENE WITH 1,1,1-TRICHLOROETHANE

IN PRESENCE OF COORDINATION INITIATORS BASED ON Fe(CO)5

N. A. Grigor'ev, N. A. Kuz'mina, E. Ts. Chukovskaya, A. L. Tumanskaya, and R. Kh. Freidlina

Vinylidene chloride (VDC) enters into telomerization with CCl_4 [1] and $CCl_3CH_2CH_2Cl$ [2] in the presence of coordination initiators based on iron compounds. Without isolating the pure products, the cotelomerization of CCl_4 with VDC and a number of other monomers, initiated by an analogous catalytic system, has been described [3]. It seemed of interest to study the telomerization of VDC with 1,1,1-trichloroethane (TCE), and also the cotelomerization of VDC and propylene with TCE, since these reactions can lead to compounds that contain several gem-poly(chloroalkyl) groupings.

EXPERIMENTAL

The GLC analysis was run on an LKhM-8MD instrument under the following conditions: 1) 1000×3 mm steel column packed with 5% Silicone SE-30, at 130°C, and using 1,1,1,5-tetrachloropentane as the internal standard; 2) 2000×3 mm steel column packed with 15% SKTPT-50, at 110 and 160°. The preparative GLC was run on a Tswett-2 instrument using the following steel columns: 1000×10 mm, packed with 15% Carbowax 20 M, at 130°; 4) 1000×10 mm, packed with 15% Silicone E-301, at 170°. Chromaton N-AW was the solid support for all of the columns, He was the carrier gas, and a katharometer was the detector. The PMR spectra were taken on a Hitachi-Perkin-Elmer R-20 spectrometer (60 MHz), using 50% CCl₄ solutions and HMDS as the internal standard.

<u>Telomerization of Vinylidene Chloride with 1,1,1-Trichloroethane in Presence of Fe(CO)₅ and i-PrOH.</u> Into an 0.5-liter enameled autoclave was loaded 3.9 g of Fe(CO)₅, 78.1 g of i-PrOH, 10.7 g of TCE, and 19.4 g of VDC (VDC/TCE = 0.25). The mixture was heated for 30 min at 130-140° and then treated with 10% HCl solution, washed with water, dried over MgSO₄, and the tars were precipitated with n-pentane. After distilling off the n-pentane and unreacted TCE the residue (10.8 g) was analyzed by GLC (column 1). The pure compounds were isolated from the residue by vacuum distillation and subsequent preparative GLC (columns 3 and 4).

Cotelomerization of Vinylidene Chloride and Propylene with 1,1,1-Trichloroethane in Presence of Fe-(CO)₅ and DMF. The reaction was run in rotated 7-ml sealed glass ampuls. The amount of the reactants, the experimental conditions, and the results of analyzing the reaction mixture by GLC (column 2) are given in Table 1. To isolate the cotelomerization products we ran a series of experiments in 25-ml sealed glass ampuls at 130° (4 h). Into the ampul was charged 0.22 g of Fe(CO)₅, 0.22 g of DMF, 6 g of TCE, and 1 g of VDC,

UDC 66.095.2:547.413.133.2

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1333-1336, June, 1980. Original article submitted May 18, 1979.

oles	2
mm	
1.7	i
0	
Fe(C	•
e of	
mole	
6 m	
3 (0 .	১
CCI	\$
CH	
with	
ICH ₃)
CH CH	
CH,	1
and (
C12	5)
0 II	= 0 . 2
CH	C13 -
on of	CH ₃ C
zati	C1₂∕C
meri	Ŭ
telo	CH_2
ы С	L30°,
Т Ц	ΙF,]
CABI	f Dì
	U U

Expt.	Taken j	for reaction	1, mmoles	с́н	С.Н. С.		Co	nversion, 9		Composit	ion of rea	ction prod	ucts, mole	d/0
No.	CH ₃ CCl ₃	CH ₂ =CCl ₂	C ₃ H ₆	CH ₃ GGl ₃	CH_=CCI	Tíme, h	CH3CCI3	CH2=CCI2	C ₃ H ₆	d.t.	√ ^T	TP 22	T ^{VP}	\mathbf{T}_2^{V}
<u>+0104100</u>	22256 22255 2255 2255 2255 2555 2555 25		887 77,2,5,8 2,2,2,7,0 2,2,2,7,0 2,2,2,7,0 2,2,2,7,0 2,2,2,7,0 2,2,2,7,0 2,2,2,7,0 2,2,2,7,0 2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,2	$\begin{array}{c} 0.83\\ 0.78\\ 0.78\\ 0.78\\ 0.78\\ 0.78\\ 0.25\\ 0.16\end{array}$	3,30 3,54 0,99 0,66 0,66	0404444 NRORNON	23,52,29 5,52,29 5,55,52,79	28,0 17,1 14,5 7,4 5,7	$\begin{array}{c} 0.00\\$	64,4 63,3 63,3 64,4 64,1 76,3 38,0 31,7 31,7	11, 6,1 7,4 30,6 41,2 8,1,2	4444,0440 6410,876,64	23,0 23,8 31,0 33,0 4,4 4,0 19,3 19,3	0,000,55 9,00,05 1,1 1,1 1,1 1,1 1,1 1,1 1,1 1,1 1,1 1,

TABLE 2. PMR Spectral Data for Isolated Polychloroalkanes

	C3	1,60d	4,40 m -
E	 5	4,31 m 6,00 t -	2,81 d 3,95 s
6, pp	ΰ	2,71d 3,17d 3,83s	3,43 s 3,59 s
	CH,CCl2	2,22 s 2,23 s 2,43 s	2,42 s
Compound		$\begin{array}{c} \mathrm{CH}_{s}\mathrm{COI}_{s}\mathrm{CH}_{s}\mathrm{CH}_{s}\mathrm{CH}_{\mathrm{CH}}^{2}\mathrm{CH}_{\mathrm{S}}^{2}\mathrm{CH}_{\mathrm{S}}^{2}\mathrm{CH}_{\mathrm{S}}^{2}\mathrm{H}_{\mathrm{S}}^{2}$	CH ₃ CCl ₂ CH ₂ CCl ₂ CH ₂ CCl ₂ CH ₂ CCl ₂ CH ₂ CCl ₃ * (T_2^{VP}) CH ₃ CCl ₂ CH ₂ CCl ₃ CH ₂ CCl ₃ (T_2^{V}) *C ₄ 1.61 ppm.

953

and the whole was recondensed with 1.7 g of C_3H_6 . The reaction mixture was worked up as described above to give 1.5 g of products, from which the pure compounds were isolated by preparative GLC (column 4). The cotelomerization of VDC and propylene with TCE gives ~35% of tar (based on the sum of identified products). Based on the elemental analysis data, the tar contains 56.54% of Cl and corresponds to the empirical formula $C_{12}H_{19}Cl_7$. The conversion of the reactants was based on the composition of the reaction products, including the tar.

DISCUSSION OF RESULTS

The telomerization of VDC with TCE proceeds with a low overall yield of the reaction products, which, based on the GLC analysis data, is ~15%, when based on VDC. The T_1^V and T_2^V telomers are formed by the usual scheme:

 $CH_{3}CCl_{3} + nCH_{2} = CCl_{2} \xrightarrow{Fe(CO)_{5}} CH_{3}CCl_{2}(CH_{2}CCl_{2})_{n}Cl (n = 1, 2)$

The yield of T_1^{V} is 8.2, and that of T_2^{V} is 2.7%. Chlorocyclohexane (II) is formed in the same way as that described previously for the transformations of VDC in the presence of AlCl₃ [4]. Tetrachlorobutane (I) is apparently obtained by the reduction of T_1^{V} in i-PrOH as the medium [8]. The secondary formation of propylene by the dehydration of i-PrOH during reaction [8] leads to the appearance of T_1^{P} and T_2^{VP} in the reaction mixture. The yields of the secondary products were: $T_2^{VP} - 1.3\%$, (I) -1%, (II) -1.7%. The yield of T_1^{P} (when based on TCE) was 1%. When the reaction is run under the same conditions, but replacing the i-PrOH by HMPA, T_1^{P} and T_2^{VP} are absent in the products. The T_2^{VP} cotelomer can be formed either by the addition of propylene to the growing CH₃CCl₂CH₂CCl₂ radical or by secondary reaction at the CCl₃ group in T_1^{V} .

It may be assumed that in the cotelomerization of propylene and VDC with TCE the yield of the cotelomers will be higher than in the telomerization of VDC with TCE in the presence of i-PrOH. A study of this cotelomerization in a broad range of reactant ratios and reaction times makes it possible to ascertain the mechanism for the formation of T_2^{VP} . It also seemed of interest to initiate for the first time the cotelomerization by coordination initiators based on Fe(CO)₅ and isolate the pure products. We used DMF instead of i-PrOH to exclude the secondary formation of propylene from i-PrOH.

The propylene (T_1^P, T_2^P) and VDC (T_1^V, T_2^V) homotelomers were identified in the cotelomerization product of VDC and propylene with TCE. Of the two possible cotelomers with two monomeric units, $CH_3CCl_2CH_2-CCl_2CH_2CHClCH_3$ (T_2^{VP}) and $CH_3CCl_2CH_2CH(CH_3)CH_2CCl_3$ (T_2^{PV}) , only the first was detected. It should be mentioned that the formation of both of the possible cotelomers, with two monomeric units in the chain, was always observed in the cotelomerization of various monomers with CCl_4 and $CHCl_3$ when initiated by peroxides [9]. The presence of only one T_2^{VP} cotelomer in the reaction mixture can be due to the fact that it is formed

	Fou Cal	nd culated	%
Compound	c	н	ĊÌ
CH ₃ CCl ₂ CH ₂ CCl ₂ CH ₂ CHClCH ₃	<u>31,38</u> 30.86	4,09	64,66
$CH_{3}CCl_{2}CH_{2}CCl_{2}CH_{2}CCl_{3}$	$\frac{22,40}{22,01}$	$\frac{2,23}{2,16}$	74,93

TABLE	3.	Elemental	Anal	lysis	Data	for
Isolated	Co	mpounds				

by the secondary reaction of T_1^V with propylene. Such reaction of T_1^V was described in [6] on the example of its reaction with 2-chloropropene.

Varying the ratios of the reactants disclosed that the amount of T_1^V that can enter into secondary reaction increases with decrease in the $C_3H_6/CH_2 = CCl_2$ ratio (see Table 1, expts. 4-7), while the amount of T_2VP increases at first, and then it decreases. The probability of secondary reaction at the CCl₃ group increases with increase in the yield of T_1V , but a simultaneous decrease in the initial propylene concentration, which is needed to form T_2^{VP} , leads in sum total to a decrease in its yield. The yields of the reaction products as a function of the time, with the initial concentrations of the reactants kept constant (see Table 1, expts. 1-3), reveals that T_1^V is consumed to form T_2^{VP} . The amount of T_1^V decreases with increase in the reaction time, while the amount of T_2^{VP} increases.

These facts, and also the rules observed when varying the ratios of the reactants and the reaction time, tend to indicate that T_2^{VP} can be formed via the stepwise addition of propylene to the CCl₃ group in T_1^{V} .

CONCLUSIONS

1. The telomerization of $CH_2 = CCl_2$ with CCl_3CH_3 , initiated by $Fe(CO)_5$ in combination with i-PrOH or HMPA, leads to the formation of the telomers $CH_3CCl_2(CH_2CCl_2)nCl$ (n = 1, 2).

2. In the cotelomerization of propylene and $CH_2 = CCl_2$ with CCl_3CH_3 , initiated by the $Fe(CO)_5 = DMF$ system, both of the homotelomers are formed and only one cotelomer with two monomeric units: CH3CCl2CH2CCl2-CH₂CHClCH₃.

LITERATURE CITED

- L. M. Bobinova, E. N. Zil'berman, V. L. Zvezdin, I. Ya. Slonim, and O. A. Mochalova, Zh. Org. Khim., 1. 5, 216 (1969).
- N. A. Kuz'mina, E. Ts. Chukovskaya, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1977, 921. 2.
- 3. D. Vofsi and M. Asscher, German Patent 1,916,489 (1969); Chem. Abstr., 72, 32708g (1970).
- A. E. Kulikova, E. N. Zil'berman, N. K. Taikova, and N. M. Pinchuk, Zh. Org. Khim., 4, 1899 (1968). 4.
- T. Sato, M. Seno, and T. Asahara, Mon. J. Inst. Ind. Sci. Univ. Tokyo, 24, 230 (1972). 5.
- A. A. Kamyshova, E. Ts. Chukovskaya, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 6. 1903.
- 7. A. A. Kamyshova, B. N. Osipov, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1972, 60.
- 8. E. Ts. Chukovskaya, N. A. Kuz'mina, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1970, 2343. B. L. Zhuk, Dissertation, Moscow (1975).
- 9.