STEP-BY-STEP TELOMERIZATION OF PROPYLENE AND 1-HEXENE BY

CARBON TETRABROMIDE

T. T. Vasil'eva, L. F. Germanova, V. I. Dostovalova, B. V. Nelyubin, and R. Kh. Freidlina UDC 66.095.2:(547.313.3+547. 313.6):547.412.134

Because of the high effectiveness of CBr_4 as a reaction chain carrier, the radical reactions of this compound with α -olefins lead, in general, to the formation of monomeric adducts [1]. In the case of vinyl chloride only, the formation of telomers has been recorded [2].

In the present work, we studied the reaction of CBr_4 with propylene and 1-hexene initiated by both azoisobutyronitrile (AIBN) and the $Fe(CO)_5 + DMFA$ system (IC). While in the presence of AIBN, the main products in the reactions studied are adducts (Ia, b), during initiation by IC we observed a step-by-step telomerization proceeding by the following scheme

 $CBr_{4} \xrightarrow{AIBN \text{ or IC}} CBr_{3}$ $\dot{C}Br_{3} + CH_{2} = CHR \rightarrow CBr_{3}CH_{2}\dot{C}HR$ $CBr_{3}CH_{2}\dot{C}HR + CBr_{4} \rightarrow CBr_{3}CH_{2}CHBrR$ (I^{a}, b) $CBr_{3}CH_{2}CHBrR \xrightarrow{IC} \dot{C}Br_{2}CH_{2}CHBrR$ $r_{2}CH_{2}CHBrR \rightarrow B\dot{C}HCH_{2}CHBrR$

 $CBr_2CH_2CHBrR + CH_2 = CHR \rightarrow RCHCH_2CBr_2CH_2CHBrR$ RCHCH_2CBr_2CH_2CHBrR + CBr₄ \rightarrow RCHBrCH_2CBr_2CH_2CHBrR (IIa, b)

In all the reactions, $R = CH_3$ (a), $CH_2CH_2CH_2CH_3$ (b).

In the known examples [3] the step-by-step telomerization proceeds together with the usual chain propagation, so that two telomers are formed with different structures and with two monomeric units in the molecule.

The characteristic feature of the reaction studied is that because of the high effectiveness of the telogen (CBr₄) and relatively low rate of propagation of the selected monomers, the usual reaction stops at the formation of an adduct. With its accumulation, the step-bystep telomerization begins, and thus only one step-by-step telomer with two monomeric units in the molecule is formed.

In the AIBN-initiated reaction of CBr4 with propylene (Table 1), the main product is 1.1.1.3-tetrabromobutane (Ia). Besides (Ia), small amounts of CHBr₃ and 1,1,3-tribromobutane (IIIa), the reduction products of CBr4 and (Ia), respectively, are also formed, as well as 2,4,4,6-tetrabromoheptane (IIa), the product of step-by-step telomerization. The application is known in the patent literature for compound (Ia) [4], but its method of synthesis has not yet been described. We found that the reaction of CBr4 with propylene is very sensitive to the temperature regime. As the result of rapid increase in the temperature, the process becomes uncontrolled. Therefore, the experiments shown in Table 1 were carried out at a temperature not higher than 80°C, with slow emergence into the temperature regime. This reaction is also sensitive to the material of the reactor and the method of initiation. At a ratio of $CBr_4:C_3H_6$ = 1:1, in a stainless steel autoclave (see Table 1, expt. 1) an adduct is mainly formed. When the reaction is carried out in hexane solution (see Table 1, expts. 2, 3), the yield of (Ia) increases and the reaction is more easily controlled. A different situation occurs when the reaction is carried out in an excess of propylene. While in an autoclave with a glass insert (Table 1, expts. 4, 5) compound (Ia) is, as before, the main product; in a stainless steel autoclave (expt. 6) the product of the step-by-step telomeriza-

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. 2759-2765, December, 1983. Original article submitted January 4, 1983. tion (IIa) is formed in an 85% yield. The same effect is also observed when the reaction is carried out in an autoclave with a glass insert, but with initiation by IC (expt. 8). It is interesting to note that while the formation of telomer (IIa) is not observed after 1 h (expt. 7), after 4 h (IIa) becomes the main reaction product. This is one of the proofs for the step-by-step character of the reaction, i.e., first adduct (Ia) is accumulated, and then it enters the secondary process with the formation of (IIa). Thus, under appropriate conditions, either (Ia) or the step-by-step telomer (IIa) can be obtained in one stage.

To reveal the general character of the step-by-step telomerization, we carried out a series of similar experiments with 1-hexene also (Table 2). The addition of CBr4 to 1-hexene by the action of γ -irridiation has already been described in the literature [5]. The experiments listed in Table 2 were carried out in either glass ampuls or autoclaves with a glass insert. In the presence of AIBN, CBr4 adds to hexene with the formation of 1,1,1,3-tetrabromoheptane (Ib) as the main product; the reduction products, CHBr3 and 1,1,3-tribromoheptane (IIIb), and the product of step-by-step telomerization, 5,7,7,9-tetrabromotridecane (IIb) are formed in a low yield. A change in the CBr4:1-hexene ratio from 1:2 to 1:5 leads to an increase in the yield of adduct (Ib) (see Table 2, expts. 1-3). A further change in the CBr4: 1-hexene ratio to 1:10 (see Table 2, expt. 4) leads to a decrease in the yield of (Ib), because of increase in the content of products (IIb) and (IIIb). In an IC-initiated reaction, the yield of the step-by-step telomerization product (IIb) reaches 27.5% after 1 h (see Table 2, expt. 5) and 47.6% after 4 h (see Table 2, expt. 6). The reduction also begins to play a more important role: the yield of (IIIb) increases. Increase in the temperature of the reaction to 100°C favors the formation of (IIIb) more (see Table 2, expt. 7). Iron pentacarbonyl can also initiate the formation of adduct (Ib) at ~20°C, and in this case the yield of (Ib) reaches 61.3% after 24 h (see Table 2, expt. 8).

The possible occurrence the step-by-step telomerization with the participation of (Ia) and (Ib) under the conditions studied was shown in a special series of experiments, in which actual samples of (Ia) and (Ib) were added to propylene or 1-hexene (Table 3). When the reaction is initiated by AIBN at 80°C, the reaction of (Ia) with propylene and 1-hexene (see Table 3, expts. 1, 5), and also that of (Ib) with 1-hexene (see Table 3, expt. 9) practically do not proceed. Increase in the reaction temperature to 140°C, and use of tert-butyl peroxide (TBP) with (Ia) and propylene leads to the formation of (IIa) in a yield of up to 47% (see Table 3, expt. 3). In the reaction of (Ia) and (Ib) with 1-hexene under comparable conditions (see Table 3, expts. 6 and 10), the reduction products are mainly formed, i.e., 1,1,3-tribromobutane (IIIa) from (Ia) and (IIIb) from (Ib). Thus, at 140°C, with propylene, addition is prevalent, and with 1-hexene, it is reduction, probably as the result of the higher ability of 1-hexene to appear as the hydrogen donor.

By using IC in the reactions of (Ia) and (Ib) with propylene and 1-hexene, the products of step-by-step telomerization (IIa), (IIb), and also 2,4,4,6-tetrabromodecane (IV) can be obtained in a yield of up to 50% (see Table 3, expts. 4, 7, 8, 12, 13). It should be noted that under these conditions, the reduction always proceeds to an appreciable extent.

The structure of compounds (Ib)-(IV) was studied by the ¹³C NMR method, and the parameters of the spectra are listed in Table 4. To confirm the structure of the compounds, we used the additive scheme of the influence of the halogens on the chemical shifts (CS) of ¹³C NMR in normal alkanes with a correction for a two-particle interaction of halogen atoms [6]. The calculated values of CS are given in brackets under the experimental ones. For all the signals of ¹³C atoms of these compounds, the calculated results satisfactorily agree with the experimental. It can be assumed that the one-particle contributions of the Br atoms and the two-particle corrections to them determine approximately, within 1 ppm the main part of the change in the CS of ¹³C NMR in alkanes during polybromo substitution. The signal of the methylene group of the CBr₃CH₂CHBr fragment of compound (Ib), which deviates from the experimental results by 2.5 ppm, is an exception. It is probable that in the presence of such a large number of Br atoms within the two C-C bonds, the role of the three-particle interactions increases.

Table 4 includes compound (IIa) which we have already described in [7]. This compound, together with compound (IIb), models two different terminal sections of the skeleton of compound (IV). The spectrum of this compound does in fact contain signals present in the spectra of compounds (IIb) and (IIa).

		Notes	eel autoclave	in hexane	e = 1:2 e = 1:4		same	eel autoclave		e same
			Stainless st	Glass insert Experiment	CBr ₄ :hexane CBr ₄ : hexan	Glass insert	The	Stainless ste	Glass insert	The
111111	. de	CBr ₂ (CH ₂ CHBrCH ₃) ₂ (IIa)	1	4,3	1,1	I	1	85,0	1	84,5
	f reaction mixture	CBr ₃ CH ₂ CHBrCH ₃ (Ia)	78,1	85,9	91,4	71,0	87,5	10,2	88,0	14,6
	Composition o	CHBr ₂ CH ₂ CHBrCH ₃ (IIIa)	2,5	2,4	2,0	4,8	1	3,0	2,0	1
		CBr4	16,9	9,2	1,6	11,0	11,0	0,8	6,0	I
		CHBr ₃	2,5	1,3	3,9	5,7	1,0	1,0	4,0	1
	Duration	of exper- iment, h	7	4	4	-	4	4	Ŧ	4
	C.H.	moles	1,0	0,25	0,25	1,25	1,25	2,5	1,25	1,25
	CBr.	moles	1,0	0,25	0,25	0,125	0,125	0,25	0,125	0,125
	+ - 	No.	4	2	ۍ <i>י</i>	4	5	9	* 2	* ∞

TABLE 1. Reaction of CBr4 with Propylene at 80° C in the Presence of AIBN

*Experiment with initiation by 10 mole % of Fe(CO) $_{5}$ + 30 mole % of DMFA.

TABLE 2. Reaction of CBr4 with 1-Hexene at 80°C in the Presence of AIBN

16	,H ₉ CBr ₂ (CH ₂ CHBrC,H ₃) ₂ (IIb)	2,42 4,56 4,56 4,56 4,5 6,9 1,5 1,5 1,5 1,5 1,5 1,5 1,5 1,5 1,5 1,5
action mixture, 9	CBr ₃ CH ₂ CHBrC	70,0 75,1 76,1 76,1 70,0 70,0 74,3 37,5 84,3 84,3 84,3 84,3 7,5 84,3 84,3 84,3 84,3 84,3 84,3 84,3 84,3
Composition of rea	CBr ₂ HCH ₂ CHBrC ₄ H ₅ (IIIb)	28,12 28,12 28,33 28,33 28,33 28,33 28,00 1,22 28,33 28,00 1,22 28,33 28,33 28,33 28,33 28,33 28,55 1,22 28,55 1,22 28,55 1,22 28,555 28,555 28,555 28,555 28,555 28,555 28,555 28,555 28,555 28,555 2
	CBr4	18,5 14,2 3,7 3,7 38,7 38,7
	CHBr ₃	ດີດ 20 20 20 20 20 20 20 20 20 20 20 20 20
Duration of	experiment, h	****
:	1-Hexene, mmoles	80,0 90,0 125,0 62,5 62,5 62,5 62,5 62,5
	mmoles	40,0 30,0 125,0 125,0 122,5 122,5 122,5 122,5 122,5 122,5
	Expt. No.	イクログラクトの * *+- ++

*Initiation by 10 mole % of Fe(CO)₅ + 30 mole % of DMFA. [†]The same at 100°C. [†]The same at 20°C.

Expt.	Compound	Olefin,		Reacti condi	Reaction conditions		Reaction prod-		
No.	(I), mmoles	mmoles	Initiator, mole %	т., °С	time, h	uct	3, 70		
1 2 3 4	(Ia), 125	C ₃ H ₆ 1250 300 500 1250	AIBN (2) TBP (1) TBP (2) $Fe(CO)_{5}(10) +$ +DMFA (30)	80 140 140 80	4 1 2 4	(IIIa) 0,6 1,2 9,3 1,2	(Ia) 99,0 94,5 36,7 34,6	(IIa) 4,3 46,7 52,6	
5 6 7	(Ia), 10	$\begin{array}{c} C_{6}H_{12} \\ 50 \\ 25 \\ 50 \end{array}$	ALBN (2) TBP (5) Fe (CO) $(10) +$	80 140 80	4 2 4	(IIIa) 38,8 14,6	(Ia) 99,4 42,9 10,2	(IV) - 54,6	
8 9 10	» 10 (Ib), 10	50 C ₆ H ₁₂ 50	AIBN (2)	80 80	4	13,9 (IIIb) 6,4 36.0	8,3 (Ib) 90,1 46.0	50,1 (IIb) 2,5	
11	» 10 » 10	50	$Fe(CO)_{5}(10) + + DMFA (30)$	80		12,5	50,5	32,2	
12	» 10 » 10	50	»	80	44	3, 6	^{22,1} 17,6	45,0 50,6	

TABLE 3. Reaction of Compounds Containing CBr_3 Group with $\alpha-$ Olefins

EXPERIMENTAL

The purity of the initial compounds and the products obtained was verified by the GLC method using a metallic column (1300 \times 3 mm) with 15% SKTFT-50kh on N-AW Chromaton 0.16-0.2 mm, carrier-gas He (60 ml/min), katharometer, and in a temperature programming regime (4 deg/min). The ¹³C NMR spectra were run for 50-70% solutions in CHCl₃ with reference to TMS on the Bruker WP-200 apparatus.

In experiments carried out with iron pentacarbonyl and dimethylformamide, at the end of the reaction, the reaction mixtures were diluted with CCl_4 (1:1), and were passed through a layer of silica gel (1 × 1 cm) to remove iron compounds, and then were chromatographed.

<u>Reaction of CBr4 with Propylene in the Presence of AIBN (Table 1, expt. 2).</u> The experiment was carried out in a rotating autoclave with a 300-ml glass insert. A solution of 83 g (0.25 mole) of CBr4 and 0.3 g of AIBN in 65 ml (0.5 mole) of hexane was placed in the glass insert. The insert was cooled with liquid N₂, and 65 ml (0.5 mole) of propylene previously condensed in a trap were added. Nitrogen was pumped into the autoclave to produce a pressure of 10 atm, and the autoclave was heated for 4 h at 80°C. After distillation of hexane, 94.0 g of a residue were obtained. The composition of the reaction mixture according to GLC data is given in Table 1. By fractional distillation, 79.3 g of 1,1,1,3-tetrabromobutane (Ia), bp 85°C (2 mm), $n_D^{2^\circ}$ 1.5915, $d_4^{2^\circ}$ 2.4298 were isolated (see [4]).

Reaction of CBr₄ with Propylene in the Presence of Iron Pentacarbonyl and Dimethylformamide (Table 1, expt 8). A mixture of 83 g (0.25 mole) of CBr₄, 4.9 g (10 mole %) of Fe-(CO)₅, and 5.5 g (30 mole %) of DMFA was placed in the glass insert. The mixture was cooled with liquid N₂, and 165 ml (2.5 moles) of propylene were added. Nitrogen was pumped into the autoclave to produce a 10-atm pressure, and the autoclave was heated for 4 h at 80°C. After treatment of the reaction mixture and distillation of the solvent, 71.2 g of a mixture were obtained, from which 59.8 g of a compound, bp 126-129°C (3 mm) were isolated. By repeated distillation, 55.4 g of 2,4,4,6-tetrabromoheptane (IIa), bp 106°C (2 mm), np^{2°} 1.5660, $d_4^{2°}$ 2.0728 were isolated (see [7]).

<u>Reaction of CBr4 with 1-Hexene in the Presence of AIBN (Table 2, expt. 4).</u> A 41.5-g portion (0.125 mole) of CBr4, 105.2 g (1.25 mole) of 1-hexene, and 0.4 g (2 mole %) of AIBN were charged into the glass insert of the autoclave. The autoclave was heated for 4 h at 80°C. The yield of 1,1,1,3-tetrabromoheptane (Ib) was 37.9 g (70.0%), mp 135°C (2 mm), $n_{D}^{2°}$ 1.5620. $d_4^{2°}$ 2.0552 (see [5]).

Reaction of CBr₄ with 1-Hexene in the Presence of $Fe(CO)_5 + DMFA$ (Table 2, expts. 6, 7). A mixture of 4.1 g (12.5 mmoles) of CBr₄, 5.3 g (62.5 mmoles) of 1-hexene, 0.24 g (10 mole %) of Fe(CO)₅ and 0.3 g (30 mole %) of DMFA was heated for 4 h at 80°C in a glass ampul, placed

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		δ;	, mqq	with r	eferenc	te to T	SM				J	с-н, ^г	Iz		
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1 2 3 4 5 6 7 cHBrcHacHacHacHacHacHa	^خ (طً	3,5	53,3 (53,1)	54,1 (54;3)	38,0 (38,6)	29,2 (30,2)	21,9 (22,6)	13,9 (13,7)	176	137	156	126	126	126	122
1 2 3 4 5 6 7 CBrcHachachachacha	(qr	6,5 (1,2)	66,8 (69,2)	51,7 (52,7)	39,2 (38,6)	29,5 (30,2)	21,8 (22,6)	14,1 (13,7)	1	137	156	126	126	126	122
2 3 4 5 6 7 CH4CHBrCH4CH4CH4CH4 CBr4 CBr4 5 6 7 CBr4 5 6 7 CBr4 5 6 7 CBr4 5 6 7	(dI (dI	8,5) (1) (2,8) (2,8)	59,8 58,1)	52,0 52,1 (52,9)	39,8 40,0 (39,0)	29,3 (30,2)	21,3 (22,6)	13,9 (13,7)	1	131	153	126	127	123	124
CHARTEN CHARTEN CHARTEN		9,1	59,3	52,0 (52,0)	39,8 30,8	29,3	21,8	13,9	I	131	146	123	126	122	125
CBr ₂ 2, 4, (I GBr ₂ 2, 3, 4, (I	<u>.</u>	9,2	60,2 60,2	45,5 45,6	28,9 27,9 28,1	(30,2)	(22,6)	(13,7)	1	134	155	126	I	ł	I
	9	9,2)	(61,5)	(46,4)	(26,8)						,				
2 3 4 CH5CHBrCHa 1 CH5CHBrCHa (I	(a)	8,5	59,9 60,0	45,3 45,4 1,6,4	27,9 28,1	,			1	140	151	132	1	I	ł
\2_3_4 CH4CHBrCHs		 9 (9 (9	6,10	(1,01)	(0,02)				<u></u>						
	-	-	-	•			•	•	•	•		-	•		

*In brackets values are given which were calculated according to [6].

 $^{\rm 1\,\,3}\,{\rm C}$ NMR Spectra of Compounds Obtained TABLE 4. in a metallic jacket. After appropriate treatment, the solvent was distilled, the contents of three ampuls were combined, and distilled to yield 1.0 g of 1,1,3-tribromoheptane (IIIb), bp 86°C (1 mm), $n_D^{2°}$ 1.5282, $d_4^{2°}$ 1.8043. Found: C 24.93; H 3.88; Br 70.82%. MR 57.52. C₇H₁₃Br₃. Calculated: C 24.95; H 3.89; Br 71.16%. MR 57.82. In addition, 5.3 g of 1,1,1,3-tetrabromoneptane and 7.0 g of 5,7,7,9-tetrabromotridecane (IIb), bp 170-175°C (2 mm), $n_D^{2°}$ 1.5342, $d_4^{2°}$ 1.6711 were isolated. Found: C 31.94; H 4.92; Br 63.45%. MR 93.03. C₁₃H₂₄Br₄. Calculated: C 31.23; H 4.84; Br 63.93%. MR 93.29.

Reaction of 1,1,1,3-Tetrabromobutane with 1-Hexene in the Presence of $Fe(CO)_5$ and DMFA (Table 3, expts. 7, 8). A mixture of 3.7 g (0.01 mole) of 1,1,1,3-tetrabromobutane, 4.2 g (0.05 mole) of 1-hexene, 0.2 g of (10 mole %) of $Fe(CO)_5$, and 0.2 g (30 mole %) of DMFA was placed in a glass ampul. The ampul was sealed and heated for 4 n at 80°C. The contents of the ampuls were combined, and the solvent was distilled. Distillation of the residue (5.9 g) gave 3.9 g of 2,4,4,6-tetrabromodecane (IV) (47.2% based on reacted 1,1,1,3-tetrabromobutane), mp 155°C (2 mm), $n_{\tilde{D}}^{2^\circ}$ 1.5479, $d_4^{2^\circ}$ 1.8237. Found: C 26.09; h 4.01; Br. 69.69%. MR 79.73, $C_{10}H_{18}Br_4$. Calculated: C 26.22; H 3.96; Br 69.80%. MR 79.49.

CONCLUSIONS

1. The reaction of CBr₄ with propylene and 1-hexene can be carried out depending on the method of initiation, as an addition reaction with the formation of $CBr_3CH_2CHBrCH_3$ and CBr_3CH_2 -CHBr(CH_2)₃Cu₃ or as a step-by-step telomerization with the formation of $CBr_2(CH_2CHBrCH_3)_2$ and $CBr_2(CH_2CHBrCH_2CH_2CH_2CH_3)_2$.

2. The addition of compounds containing a CBr_3 group to unsaturated compounds proceeded by cleavage of the C-Br bond during initiation by Fe(CO)₅ + DMFA.

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