REACTION OF BENZYL CHLORIDE WITH PROPYLENE AND TRIFLUOROPROPENE UNDER METALLOCOMPLEX INITIATION CONDITIONS

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The reactions of benzyl chloride with propylene and 3,3,3-trifluoropropene in the presence of $Fe(CO)_5$ + DMF were studied. With propylene, the reaction stops at the addition stage with the simultaneous formation of dibenzyl. In the case of 3,3,3-trifluoropropene, a telomerization takes place, whereby the second growing radical $C_6H_5CH_2CH_2CH(CF_3)CH_2\dot{C}HCF_3$ practically completely isomerizes with a 1,5-migration into the radical $C_6H_5\dot{C}HCH_2CH(CF_3)CH_2CH_2CF_3$. To confirm the structure of the isolated compounds, chromato-mass-spectrometry and ^{13}C NMR were used.

The use of metallocomplex initiation in the radical telomerization with the participation of benzyl chloride (BC) makes it possible to carry out the reaction selectively at the C—Cl bond [1, 2]. The use of BC as a telogen is of particular interest, since during the cleavage of the C—Cl bond, a relatively nucleophilic benzyl radical is formed, while most of the examples of radical telomerization studied until now were carried out with telogens giving electrophilic radicals at the initiation stage [3]. We have previously studied the telomerization of ethylene and vinyl chloride with BC [1, 2].

To study the influence of the nature of the monomer on the course of telomerization, in the present work we used propylene and trifluoropropene as monomers.

The reaction of propylene and trifluoropropene with BC was initiated by the $Fe(CO)_5$ + DMF system at 140-145°C in the range of the monomer/BC ratios from 1 to 5.

The reaction of propylene with BC stopped at the stage of addition with the formation of the $C_6H_5CH_2CH_2CHClCH_3$ (I) adduct and dibenzyl (II) (Table 1)

$$C_6H_5CH_2Cl \xrightarrow[DMF]{Fe(CO)_5} C_6H_5\dot{C}H_2$$

$$C_6H_5\dot{C}H_2 + CH_2 = CHCH_3 \rightarrow C_6H_5CH_2CH_2\dot{C}HCH_3 \quad (A)$$

$$A + C_6H_5CH_2Cl \xrightarrow{Fe(CO)_5,\ DMF} \underset{(I)}{C_6H_5CH_2CH_2CHClCH_3} + C_6H_5\dot{C}H_2$$

$$2C_6H_5\dot{C}H_2 \rightarrow (C_6H_5CH_2)_2 \quad (II)$$

The conversion of BC was 25-30% and the overall yield of (I) and (II) per reacted BC ≈ 70%. The data in Table 1 show that with increase in the M/S from 1 to 5, the ratio (I)/(II) changes in favor of the adduct, but they nevertheless are formed in comparable amounts. The absence of higher telomers, confirmed by GLC and chromato-mass spectrometric methods, indicate that the growing radical $C_6H_5CH_2CH_2\dot{C}HCH_3$ is most effective at the chain transfer stage and practically does not participate in the chain propagation stage with propylene. The results obtained indicate a relatively low efficiency of the addition of a benzyl radical to propylene, as a result of which the competing process of its dimerization into (II) proceeds actively.

Another pattern was observed in the case of trifluoropropene. In the same M/S range, its telomerization with BC takes place with the formation of the first two telomers. The characteristic feature of this process is the practically complete isomerization of the second growing radical C with a 1,5-migration of hydrogen to radical D, which precludes its participation in the chain propagation and transfer reactions. The high degree of rearrange-

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TABLE 1. Reaction of Benzyl Chloride (S) with Propylene (M) in the Presence of a $Fe(CO)_5$ (10 mole %) + DMF (30 mole %) System, 140°C, 4 h

M/S	Content in the reaction mixture, %			
	BC	(I)	(II)	(I)/(II)
1	71,0	13.5(46) *	9,7(33)	1,4
2	73,0	14.7(54)	6.8(25)	2,18
5	71,0	16,5(37)	4.6(16)	3,6
1	74 †	(41)	(26)	1,6

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*The yield per reacted BC is given in brackets.

†Yield per isolated products.

ment of radical C is due to the formation of a stable rearranged benzyl radical and a favorable combination of polar factors at the stage of the intermolecular chain transfer.

From the reaction mixture $C_6H_5CH_2CH_2CHClCF_3$ (III), $C_6H_5CH{=}CHCH(CF_3)CH_2CH_2CF_3$ (V) and $C_6H_5CHClCH_2CH(CF_3)CH_2CH_2CF_3$ (IV) were obtained. Using chromato-mass spectrometry the formation of $C_6H_5CH_2CH_2CH_2CF_3$ (VI) was also shown, the yield of which increases with increse in the concentration of the monomer (Table 2). The content of compounds (III)-(VI) amounts to 90% of the sum of the reaction products.

The formation of (III)-(VI) can be represented by the following scheme:

$$C_6H_5CH_2Cl \xrightarrow{Fe(CO)_5,\ DMF} C_6H_5\dot{C}H_2$$

$$C_6H_5\dot{C}H_2 + CH_2{=}CHCF_3 \rightarrow C_6H_5CH_2CH_2\dot{C}HCF_3 \qquad (B)$$

$$(B) + C_6H_5CH_2Cl \xrightarrow{Fe(CO)_5,\ DMF} \underset{(III)}{C_6H_5CH_2CH_2CHClCF_3} + C_6H_5\dot{C}H_2$$

$$(B) + CH_2{=}CHCF_3 \rightarrow C_6H_5CH_2CH_2CH(CF_3)CH_2\dot{C}HCF_3 \qquad (C)$$

$$(C) \xrightarrow{1,5\text{-}H} C_6H_5\dot{C}HCH_2CH(CF_3)CH_2CH_2CF_3 \qquad (D)$$

$$(D) + C_6H_5CH_2Cl \xrightarrow{Fe(CO)_5,\ DMF} \underset{(IV)}{C_6H_5CHClCH_2CH(CF_3)CH_2CH_2CF_3} + C_6H_5\dot{C}H_2$$

$$(IV) \xrightarrow{-HCl} C_6H_5CH{=}CHCH(CF_3)CH_2CH_2CF_3. \qquad (V)$$

$$B + DH \rightarrow C_6H_5CH_2CH_2CH_2CF_3 \qquad (VI)$$

It should be noted that in this reaction compound (II) is virtually not formed, while (IV) having a benzyl chlorine atom converts under the synthesis conditions and during the purification into (V) (cf. [4]).

The nucleophilic benzyl radical adds to the electrophilic trifluoropropene considerably more effectively than to the relatively nucleophilic propylene, as can be seen from the substantial difference in the ratio of the yields of the telomers and dibenzyl for these monomers. A noticeable difference is also observed on comparing the reaction products of BC with trifluoropropene and vinyl chloride. In both cases the formation of telomers takes place, but in the case of the easy polymerization of vinyl chloride, the second growing radical $C_6H_5CH_2CH_2CHClCH_2\dot{C}HCl$ does not rearrange, but effectively participates in the chain propagation and transfer processes, which leads to the formation of higher telomers. In the case of trifluoropropene, the reaction virtually stops at the formation of (IV) due to a highly efficient rearrangement of the intermediate radical. The ^{13}C NMR spectra of compounds (I), (III)-(V) (Table 3) agree with the proposed structure of the obtained products. For compounds (I), (III), (V) the spectra of individual compounds are given, while for (IV) – in a mixture with (V). Replacement of CH_3 by CF_3 in compound (III) does not substantially influence the chemical shift of ^{13}C of the neighboring CHCl group. At the same time the presence of this fragment in (III) is confirmed by the value $\delta_{CF_3} = 123.9$ ppm and $^3J_{C-C-F} = 34$ Hz for the $CHClCF_3$ group [4]. The data in Table 3 show that signals of the $CHClCF_3$ fragment are absent in compounds (IV) and (V). According to the ^{13}C and ^1H NMR data, compound (V) exists as practically only one E-isomer ($^3J_{CH=CH} = 15.6$ Hz. In the spectrum of the mixture of (IV) + (V) only two pairs of new signals appear, one of which belongs to the CHCl group ($\delta = 60$ ppm)

TABLE 2. Reaction of Benzyl Chloride (S) with 3,3,3-Trifluoropropene (M) in the Presence of a $Fe(CO)_5$ (5 mole %) + DMF (15 mole %) System, 140°C, 4 h

M/S	Content in the reaction mixture					
	BC	(II)	(III)	(IV)	(V)	(VI)
2	89	0,2	4,5 (41)	2,5 (23)	3,1 (29)	0,7 (6) *
3	92	0,4	3,0 (37)	1,4 (17)	1,0 (12)	1,7 (21)
5	87	–	2,0 (15)	7,4 (57)	0,7 (5)	2,7 (21)

*The yield per reacted BC is given in brackets.

TABLE 3. ^{13}C NMR Spectra of Isolated Compounds, δ, ppm with Reference to TMS ($^1J_{C-F}$ or $^2J_{C-C-F}$, Hz)

Formula	C_1	C_2	C_3	C_4	C_5	C_6	C_7	Ph
$C_6H_5\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}HCl\overset{4}{C}F_3$ (III)	31,2	32,4	56,2 (34)	123,9 (278)				136,7: 128,5; 128,1: 126,4
$C_6H_5CH{=}CH\underset{\overset{7}{C}F_3}{CH}\overset{5}{C}H_2\overset{6}{C}F_3$ (V)	137,2	120,5	46,9 (28)	20,8	31,0 (28)	126,3 (279)	126,6 (276)	135,5: 128,4: 126,4
$C_6H_5CHClCH_2\underset{CF_3}{CH}CH_2CH_2CF_3$ (IV)	59,2 60,8	38,1 39,0	39,6 39,8 (27; 25)	21,1 19,9	30,9 (28)	126,0 (280)	127,4 (280)	140,0; 140,2; 128,8: 128,6 126,6: 126,4
$C_6H_5CH_2CH_2CHClCH_3$ (I)	32,7	41,7	57,5	25,2				140,8: 128,3 125,8

and the other to CH_2 neighboring with CHCl (δ = 38.5 ppm), moreover signals appear which are characteristic for the $-CH(CF_3)CH_2CH_2CF_3$ fragment. The entire set of data obtained indicates the absence of a telomer with a normal structure $C_6H_5CH_2CH_2CH(CF_3)CH_2CHClCF_3$ among the compounds isolated.*

EXPERIMENTAL

The GLC analysis was carried out on a steel column (1300 × 3 mm) with 15% SKTFT-50X on Chromaton N-AW (0.16-0.20 mm), carrier gas – helium (60 ml/min), katharometer, 100-250°C (65 deg/min). Preparative GLC: steel column (1300 × 9 mm) with 20% SKTFT-50X on Chromaton N-AW. The ^{13}C NMR spectra were run in $CHCl_3$ in a "Jmodecho" regime, the ^1H NMR spectra – in CCl_4 (with reference to TMS) on a "Bruker WP 200" spectrometer. The chromato-mass spectral investigation was carried out on a HP 5971A mass selective detector, ionic source, 180°C, 70 eV. Quartz capillary column OV-1, 50 m × 0.25 mm, thickness of stationary phase 0.3 μ, 50°C (5 min), 4 deg/min-200°C-8 deg/min-285°C (20 min).

Reaction of Benzyl Chloride with Propylene. A 63-g portion (0.5 mole) of BC, 9.74 g (0.05 mole) of $Fe(CO)_5$, and 12.3 g (0.15 mole) of DMF were charged into a glass-lined autoclave, and then 42 g (1.0 mole) of preliminarily condensed propylene was added with cooling. The autoclave was filled with nitrogen (10 atm) and was heated for 4 h at 140°C. The conversion of BC was 26% (GLC). The reaction mixture was washed with HCl (1:1), 2 × 30 ml, and with H_2O to a neutral reaction (to remove the iron salts and DMF). The product was dried over $CaCl_2$; the wash waters were extracted with CCl_4, the extract was dried over $CaCl_2$ and was combined with the main reaction product. After evaporation of CCl_4 and BC, the residue was distilled under vacuum. Yield, 7.14 g (41%) of (I), bp 66°C (2 mm), n_D^{20} 1.5140, d_4^{20} 1.0146. Found, %: C 71.38; H 7.84; Cl 20.78; MR 49.92. $C_{10}H_{13}Cl$. Calculated, %: C 71.20; H 7.77; Cl 21.02; MR 49.64; and 2.48 g of dibenzyl (mp 52°C), yield 26% per reacted BC.

Reaction of Benzyl Chloride with 3,3,3-Trifluoropropene. Ten experiments were carried out using glass ampuls. The total amount of the charged reagents was: BC, 45.5 g (0.36

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mole); $Fe(CO)_5$ 3.38 g (0.018 mole); DMF, 3.68 g (0.054 mole); trifluoropropene, 69 g (0.72 mole).

Benzyl chloride, $Fe(CO)_5$, and DMF were charged into each ampul, the mixtures were frozen, the ampuls were evacuated, and the calculated amount of the olefin was condensed therein (filling to the extent of 25-30%). The mixture was heated for 2 h at 140°C, the reaction product was dissolved in CCl_4, the solution was passed through a layer of silica gel to separate the resins and iron salts, and CCl_4 and BC were distilled off. According to the GLC data, 40 g of BC did not react (conversion 13%). The residue (6.7 g) was distilled in vacuo. From the fraction bp 32-68°C (2 mm) compound (III) was isolated by preparative GLC (150°C, helium, 5 liters/h), n_D^{20} 1.4643; d_4^{20} 1.2445. Found, %: C 53.85; H 4.55; Cl 16.06; F 25.31; MR 49.39. $C_{10}H_{10}ClF_3$. Calculated, %: C 53.94; H 4.58; Cl 15.93; F 40.39; MR 49.34. From the fraction bp 68-85°C (2 mm), compound (V) was isolated (180°C, helium, 5 liters/h). Found, %: C 55.07; H 4.26; F 39.74. $C_{13}H_{12}F_6$. Calculated, %: C 55.32; H 4.29; F 40.39. PMR spectrum (δ, ppm, J, Hz): 7.12 (Ph), 6.48 d (=CHPh, $^3J_{CH=CH}$ = 15.6), 5.82 d.d (=CHCH, $^3J_{CHCH}$ = 9.1); 2.59 (CH), 1.85 (CH_2), 1.71 (CH_2CF_3). From the fraction bp 85-130°C (2 mm) compound (IV) was isolated (180°C, helium, 5 liters/h). Found, %: C 49.27; H 3.94; F 36.16. $C_{13}H_{13}ClF_6$. Calculated, %: C 48.99; H 4.11; F 35.77; undistillable residue 0.5 g.

Chromoto-mass spectrometry data: The ion masses (m/z) are given for the ^{35}Cl isotope. Given are: compound, type of ion, m/z (in brackets – the relative intensity with respect to the maximal signal, in %), number of chlorine atoms.

(I), $M^{+\cdot}$ 168(100), 1Cl, $M - HCl^+$ 132(36.3), $M - HCl - CH_3^+$ 117(68.3), $C_6H_5CH_2CH_2^+$ 105(12.2), $C_6H_5CH_2^+$ 91(73.2).

(III), $M^{+\cdot}$ 222(11.5), 1Cl, CF_3CHCl^+ 117(6.1), 1Cl, $C_6H_5CH_2CH_2^+$ 105(6.9), $C_6H_5CH_2^+$ 91(100), CF_3^+ 69(26.9).

(IV), $M^{+\cdot}$ 318(9.6), 1Cl, $M - Cl^+$ 283(100), $C_6H_5CHCl^+$ 125(80.8), 1Cl, $C_6H_5CH{=}CH^+$ 103(36.5), $C_6H_5CH_2^+$ 91(83.1), $C_6H_5^+$ 77(80.8), CF_3^+ 69(53.8).

(IVa), [stereoisomer of (IV)].

(V), $M^{+\cdot}$ 282(71.5), $M - CF_3^+$ 213(38.5), $M - CF_3CH_2CH_2^+$ 185(40.4), $M - CF_3CH_2CH_2 - HF^+$ 165(78.8), $C_6H_5CH{=}C{=}CH^+$ 115(83.8), $C_6H_5CH_2^+$ 91(16.5), $C_6H_5^+$ 77(63.0), CF_3^+ 69(100).

(VI), $M^{+\cdot}$ 188(7.7), $C_6H_5CH_2^+$ 91(100), CF_3^+ 69(17.3).

(II), $M^{+\cdot}$ 182(43.7), $C_6H_5CH_2^+$ 91(100), $C_6H_5^+$ 77(12.7).

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