PREPARATION OF FLUOROTOLUENE BY REACTION OF METHYLCYCLOPENTADIENE WITH DIFLUOROCARBENE GENERATED FROM DIFLUOROCHLOROMETHANE UNDER CONDITIONS OF PULSED GAS COMPRESSION*

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Copyrolysis of difluorochloromethane with methylcyclopentadiene under conditions of pulsed gas compression at 924-1157 K takes place with the participation of difluorocarbene and a mixture of isometric fluorotoluenes with a total yield of 66-68% is formed. In the absence of $CHClF_2$, methylcyclopentadiene under conditions of pulsed compression at 1019-1190 K undergoes partial transformation into benzene and cyclopentadiene.

One of the most convenient methods for preparing fluorobenzene and its derivatives is the high-temperature reaction of cyclopentadiene and its homologs with sources of difluoroor fluorochlorocarbene [2, 3].

In this work we studied the reaction of methylcyclopentadiene (MCPD) and dichlorofluoromethane (DFCM) as the source of difluorocarbene under conditions of pulsed gas compression with a characteristic time of 10^{-3} sec.

EXPERIMENTAL

A mixture of DFCM and MCPD was placed in an evacuated metal flask in the required volume ratio (controlled by partial pressure) and argon was added until the Ar concentration was 97-99% by volume. This provided a nearly adiabatic pulsed compression process.

The experiments were carried out in a free piston single compression-expansion cycle apparatus [4]. The operating cylinder of the apparatus was washed three times beforehand with the starting mixture at 20°C and the cylinder then filled to a pressure of 1 atm. The maximum degree of pulsed compression was determined as described in [4]. The maximum temperature at the time of the pulsed compression-expansion was calculated from the Poisson equation $T_{max} = T_0 \varepsilon^{\gamma-1}$, where T_0 is the initial temperature, K; ε is the maximum degree of compression; $\gamma = C_p/C_V$ is the adiabatic index; and C_p and C_V are the heat capacities of the mixture at constant pressure and volume, respectively.

The initial reagents and reaction products were analyzed by gas-liquid chromatography on an LKhM-72 chromatograph with a flame ionization detector on a 200 \times 0.2 cm column with 10% SKTFT \times 50 on Chromosorb R, and He carrier gas (30 ml/min), 90°C. Quantitative measurements were carried out with calibration curves obtained by absolute normalization. The chromatograph was calibrated before every series of experiments.

¹⁹F NMR spectra were obtained on an RS-56M spectrometer. Basic experimental data are summarized in Tables 1-4.

RESULTS AND DISCUSSION

Reaction of MCPD with DFCM under conditions of pulsed gas compression is observed at a degree of compression corresponding to a temperature of 924 K. Conversion of the starting substances increases as the temperature increases and reaches 90% at 1157 K. The reaction leads to formation of a mixture of isomeric fluorotoluenes (FT), fluorobenzene (FB), benzene, as well as methane, ethane, tetrafluoroethylene, and other products.

*For previous communication, see [1].

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TABLE 1. Composition of Reaction Products^{*} of MCPD and DFCM for Various Degrees of Compression (initial mixture MCPD:CPD:DFCM: Ar = 0.88:0.12:1.00:98.00 by volume)

^e max	T	Reaction mixture comp., vol. %					Conversion,		Yield of FT based	Selectivity of FT forma tion, %		
	K	DFCM	MCPD	CPD	C ₆ H ₆	FB	FT _	DFCM	MCPD	tial MCPD, %	with resp. to DFCM	with resp. to MCPD
8,22 8,69 9,10 9,56 10,10 10,96 11,40 12,45	924 952 970 1003 1033 1080 1103 1157	0,88 0,82 0,77 0,57 0,57 0,40 0,25 0,20 0,10	0,76 0,70 0,64 0,44 0,33 0,20 0,14 0,07	0,120 0,120 0,110 0,075 0,060 0,030 0,028 0,014	0,004 0,020 0,025 0,040 0,060 0,080 0,080	0,008 0,028 0,030 0,040 0,060 0,090 0,140 0,250	0,10 0,15 0,19 0,38 0,48 0,58 0,48 0,48	12,0 18,0 23,0 43,0 60,0 75,0 80,0 90,0	13.6 20,5 29,5 50,0 62,5 77,3 84,1 92,0	11,4 17,0 21,6 43,2 54,5 65,9 54,5 40,8	83.3 83.3 89,6 88,3 80.0 77.3 60,0 40.0	83,3 83,3 79,2 86,4 87,3 85,3 64,9 44,4

*Calculated on the hydrocarbon portion.

TABLE 2. Composition of Reaction Products^{*} of MCPD and DFCM at Various Degrees of Compression (initial mixture MCPD:CPD:DFCM: Ar = 0.95:0.05:2.00:97.00 by volume)

	T _{max} , K	Reaction mixture comp., vol.%					Conversion,		Yield of FT based on ini-	Selectivity of FT forma- tion, %		
e max		DFCM	MCPD	CPD	C.H.	FB	FI	DFCM	MCPD	tial MCPD, %	with resp. to DFCM	with resp. to MCPD
8,93 10,07 11,42 12,10 13,04 13,17 13,70	917 976 1042 1090 1116 1121 1149	2,00 1,82 1,20 0,80 0,62 0,60 0,30	0,95 0,75 0,38 0,15 0,11 0,11 0,04	0,050 0,030 0,015 0,004 0,003 0,003 0,001	0 0,010 0,040 0,080 0,110 0,110 0,130	0 0,010 0,040 0,090 0,130 0,140 0,200	0 0,18 0,47 0,65 0.59 0,55 0,38	0 9,0 40,0 60,0 69,0 70,0 85,0	0 21,0 60,0 84,2 88,4 88,5 95,8	0 19,0 49,5 68,4 62,1 57,9 40,0	0 100.0 58,8 54.2 47,1 39,3 22,4	0 90,0 82,5 81,2 70,2 65,5 41,8

*Calculated on the hydrocarbon portion.

TABLE 3. Composition of Reaction Products* of Pyrolysis of MCPD at Various Degrees of Compression (initial mixture MCPD: CPD:Ar = 0.95:0.05:99.00 by volume)

		Reaction	Conversion		
^e max	T _{max} , K	MCPD	CPD	C ₆ H ₆	of MCPD, %
8,84 9,56 9,74 10,10 10,15 10,30 11,58	1019 1065 1071 1093 1102 1113 1190	0.935 0.890 0.880 0.863 0.830 0.723 0.457	0,056 0,059 0,062 0,075 0,079 0,100 0,137	0,009 0,014 0,020 0,033 0,042 0,063 0,142	1,6 6,3 7,4 9,2 12,6 23,6 51,9

*Calculated on the hydrocarbon portion.

TABLE 4. Composition of Reaction Products* of DFCM and FT at Various Degrees of Compression (initial mixture DFCM:FT:Ar = 0.78:0.48:98.74)

_	T _{max} , K	Reaction	mixture com	Conversion, %		
^e max		DFCM	FT	FB	DFCM	FT
9,30 10,30 10,67 10,73 10,96	1081 1163 1175 1179 1194	0,32 0,17 0,15 0,14 0,06	$\begin{array}{c} 0,467\\ 0.462\\ 0,457\\ 0,454\\ 0.442\end{array}$	0,013 0,018 0,023 0,026 0,038	59,0 78,2 80,7 82,3 92,0	$ \begin{array}{c c} 2,7 \\ 3,8 \\ 4,8 \\ 5,4 \\ 7,9 \\ \end{array} $

*Calculated on the hydrocarbon portion.

Formation of FT under conditions of pulsed gas compression indicates that pyrolysis of DFCM, just as in a continuous reactor [2, 3], leads to formation of difluorocarbene which is joined to MCPD



As the temperature increases, the total amount of isomeric FT in the reaction products increases, at first reaching a maximum at 1080-1090 K and then gradually decreasing. Under optimal conditions and equimolar ratios of the starting materials, the FT yield is 66%. A twofold molar excess of DFCM insignificantly increases the yield (to 68%). The ratio of isomeric FT does not depend on the maximum temperature in the compression pulse and is ortho: meta:para 2:1.3:1.

From the data of Table 1 it follows that selectivity is maintained at a level of 80-85% up to conversion of materials of about 75%, which is reached at 1080 K. At conversions greater than 80% selectivity decreases sharply (~40% at 90% conversion).

FB and benzene yields increase with increase in temperature so that the FB content in the products exceeds the CPD content in the initial MCPD. In order to explain their formation pathway the thermal stability of FT and MCPD was studied. It appeared that pure FT are stable up to 1200 K. Pyrolysis of MCPD under pulse conditions at a maximum pulse temperature of 1019-1190 K leads to formation of two main compounds, cyclopentadiene (CPD) and benzene, as well as methane, ethane, and other products. As the temperature goes from 1019 to 1190 K, the CPD: C_6H_6 ratio changes from 6:1 to 1:1. Experimental results are given in Table 3.

Thus, the formation of benzene during pyrolysis of MCPD is most of all a result of isomerization of the latter with expansion of the ring (cf. [5]) followed by dehydrogenation, while CPD is a dealkylation product of MCPD. Reaction of difluorocarbene with CPD, which appears as a contaminant in the initial MCPD and is formed during pyrolysis of MCPD, also leads to formation of FB.



The decrease of FT yield as temperature increases while at the same time FB yield increases may be related to partial dealkylation of FT in the presence of HCl that is formed during decomposition of DFCM at 924-1160 K. In particular, according to [4], dealkylation of toluene to benzene is the principal reaction under conditions of pulsed gas compression in a toluene-HCl mixture. By using special experiments it was shown that pyrolysis of a mixture of FT and DFCM leads to an insignificant decrease in the quantity of FT (~8% at 1194 K) and to formation of FB (Table 4).

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1-TRIFLUOROMETHYL-2-CHLOROETHYLTHIOLATED CARBONYL COMPOUNDS: SYNTHESIS AND PROPERTIES

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1-Trifluoromethyl-2-chloroethylsulfenyl chloride thiolates enolizible ketones, forming products of mono- and disubstitution. The properties of the resultant sulfides are determined by the presence in the molecule of two acidic CH centers. Thus, bromination proceeds at the ambident center and reaction with bases leads to (1-trifluoromethylvinyl) sulfides which are able to undergo intramolecular cyclizations and Diels-Alder reactions.

l-Trifluoromethyl-2-chloroethylsulfenyl chloride (I), like trifluoromethanesulfenyl chloride [1, 2], reacts under mild conditions (-50°C) with carbonyl compounds (acetone, acetophenone, acetylacetone, acetoacetic and methylacetoacetic esters), giving products of monothiolation of (II)-(VI) in yields up to 90%.



With excess (I) under more rigid conditions (20°C) the bis-substitution product (VII) is also formed (see scheme at the top of following page).

The obtained sulfides of β -dicarbonyl compounds (IV) and (V), unlike (II), (III), and (VII, exist mostly in the enol form (IR, PMR). Their PMR spectra have a signal at 13-18 ppm (OH) and in the IR spectra the OH absorption band lies in the region of 2990-3000 cm⁻¹.

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