2. N. A. Kuz'mina, E. Ts. Chukovskaya, and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR, 254, 890 (1980).
3. T. T. Vasil'eva, L. N. Goncharova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 2373 (1976).
4. T. T. Vasil'eva, L. N. Goncharova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1182 (1977).
5. N. A. Rybakova and L. N. Kiseleva, Izv. Akad. Nauk SSSR, Ser. Khim., 1636 (1981).
6. B. L. Booth and B. L. Shaw, J. Organomet. Chem., 43, 369 (1972).
7. V. I. Dostovalova, F. K. Velichko, T. T. Vasil'eva, N. V. Kruglova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 213 (1981).
8. L. N. Kiseleva, N. A. Rybakova, N. A. Kuz'mina, T. T. Vasil'eva, and V. I. Dostovalova, Izv. Akad. Nauk SSSR, Ser. Khim., 2095 (1981).
9. R. Kh. Freidlina, F. K. Velichko, et al., Methods of Heteroorganic Chemistry. Chlorine. Aliphatic Compounds [in Russian], Nauka, Moscow (1973), pp. 152, 513.
10. E. Ts. Chukovskaya, A. A. Kamyshova, and R. Kh. Freidlina, Zh. Org. Khim., 3, 1358 (1967).

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# HYDROGEN MIGRATION IN 1,1-DICHLOROALKYL RADICALS

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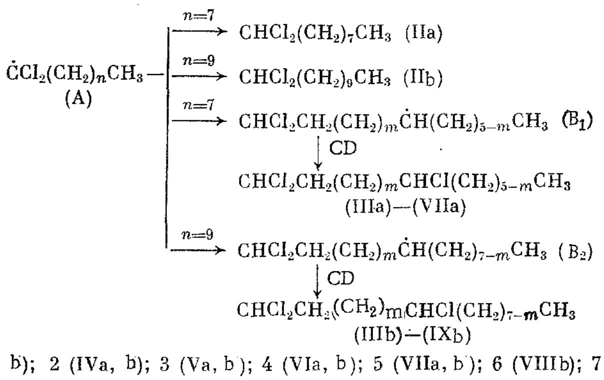
In compounds containing a $CCl_3$ group, rearrangement with 1,5- and 1,6-migration of hydrogen occurs under the action of systems based on $Fe(CO)_5$ in addition to reduction to $CH_2Cl$ [1]. In the case of 1,1,1,3-tetrachlorononane in addition to the products of these rearrangements and reduction of the $CCl_3$ group to $CHCl_2$ there are formed 1,1,3,7- and 1,1,3,8-tetrachlorononanes hypothetically as a result of rearrangement in the intermediate radical with 1,7- and 1,8-migration of hydrogen [2, 3].

In continuation of these investigations, in the present work the action of systems based on $Fe(CO)_5$ in combination with hexamethylphosphoramide (HMPA) or isopropanol on 1,1,1-trichlorononane (Ia) and 1,1,1-trichloroundecane (Ib) has been studied. As in [1-3] it is proposed that 1,1-dichloroalkyl radicals (A) are first generated in these reactions. By removal of hydrogen from a hydrogen donor these radicals are converted into 1,1-dichloroalkanes (IIa, b).

Migration of hydrogen in radicals A leads to the formation of the isomeric radicals ($B_1$, $B_2$), the reaction of which with a chlorine donor (CD) form trichloroalkanes (IIIa)-(VIIIa), (IIIb)-(Xb) (Table 1).



$m = 0$ (IIIa, b); 2 (IVa, b); 3 (Va, b); 4 (VIa, b); 5 (VIIa, b); 6 (VIIIb); 7 (IXb).

Under the selected conditions (130-140°C, 3 h) conversion of the initial trichloroalkanes (Ia, b) was closely similar (75-83%), but the yield of 1,1-dichloroalkanes (IIa, b) varied from 44 to 58% and did not in

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TABLE 1. Conversion of 1,1,1-Trichlorononane (Ia) and 1,1,1-Trichloroundecane (Ib) under the Action of Systems Based on $Fe(CO)_5$

| Trichloro-alkane (TCA) | $Fe(CO)_5$, mole % of TCA | Cocatalyst, mole % of TCA | Conversion, TCA, % | Yield of reaction products, % of theory | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | (II) | (III) | (IV)+(V) | (VI)+(VII) | (VIII) | isomeric TCA |
| (Ia) | 15 | HMPA, 40 | 82 | 44 | 1,5 | 26 | 4 | 1,5 | 33 |
| (IIa) | 10 | *i*-PrOH, 300 | 83 | 58 | 0,5 | 21 | 2 | 0,6 | 24 |
| (Ib) | 15 | HMPA, 40 | 82 | 46 | | 26 | 5 * | | 31 |
| (IIb) | 10 | *i*-PrOH, 300 | 75 | 47 | | 18 | 5 * | | 23 |

* Overall yield of trichloroundecanes (IIIb), (VIb)-(Xb).

TABLE 2. Data of $^{13}C$ NMR Spectra of Trichlorononanes

| Compound | δ, ppm from TMS | | | | | | |
|---|---|---|---|---|---|---|---|
| | $C^3$ | $C^4$ | $C^5$ | $C^6$ | $C^7$ | $C^8$ | $C^9$ |
| (IVa) | 22,3 | 38,2 | 63,0 | 38,2 | 28,6 | 23,0 | 14,0 |
| (Va) | 25,5 | 25,5 | 38,2 | 63,0 | 40,7 | 19,7 | 13,6 |
| (VIa) | 25,9 | 29,1 | 26,4 | 37,9 | 65,0 | 31,5 | 10,9 |
| (VIIa) | 25,9 * | 29,1 | 29,3 | 26,4 | 40,2 | 58,1 | 25,5 |
| | 25,4 † | 29,4 | 29,6 | 26,2 | 40,6 | 57,7 | 25,5 |

* Experiment.

† Calculated.

TABLE 3. Data of $^{13}C$ NMR Spectra of Trichloroundecanes

| Compound | δ, ppm from TMS* | | | | | |
|---|---|---|---|---|---|---|
| | $C^3$ | $C^4$ | $C^5$ | $C^6$ | $C^7$ | $C^8$ |
| (IVb) | 22,3 | 38,2 | 61,8 | 38,4 | 26,5 | 29,4 |
| (Vb) | 25,4 | 26,3 | 38,4 | 62,8 | 38,4 | 26,3 |

* For (IVb) and (Vb) signals for $C^1$ were found in the 73.0-73.2 ppm region, for $C^2$ at 43.4 ppm, for $C^9$ in the 31.1-31.6 ppm region, for $C^{10}$ in the 22.5-23.0 region, and for $C^{11}$ at 13.9 ppm.

practice depend on the system used. However, the overall yield of isomeric trichloroalkanes was greater when using $Fe(CO)_5$ + HMPA. Amongthe isomeric trichloroalkanes, 1,1,5- (IVa) and 1,1,6-trichlorononanes (Va) and undecanes (IVb) and (Vb) predominated.

The 1,1,3- (IIIa) and 1,1,9-trichlorononanes (VIIIa) that were probably formed as a result of 1,3- and 1,9-migration of hydrogen were identified by GLC from the appropriate evidence obtained by the reduction of 1,1,1,3- [2] and 1,1,1,9-tetrachlorononanes. The similar migration of hydrogen in polychloroalkanes is reported for the first time.

From the reaction mixture obtained from 1,1,1-trichlorononane (Ia) after distillation of (IIa) a fraction was isolated consisting, according to GLC and elemental analysis data, of trichlorononanes (IVa)-(VIIa), predominantly (80%) 1,1,5- (IVa) and 1,1,6-trichlorononanes (Va). The mixture of (IVa) and (Va) was separated by preparative GLC. The $^{13}C$ NMR spectra were recorded for the mixture and for the indicated fraction. The assignment of signals obtained in the $^{13}C$ NMR spectra to the appropriate isomer was made on the basis of calculating chemical shifts (CS) by the additive scheme [4, 5] for all isomeric trichloronomanes, taking the spectrum of n-nonane as a base [6]. The good agreement of the calculated and experimentally found CS in trichlorononanes should be noted. This is illustrated by the example of 1,1,8-trichlorononane (VIIa) Table 2.

Signals of the nucleus of $C^1$ compounds (IVa)-(VIIa) were found in the narrow region 73.0-73.4 ppm and for $C^2$ in the region 43.1-43.5 ppm. The spectrum of each trichlorononane (IVa)-(VIIa) had in it $^{13}C$ signals which made it possible to conform the structure of the isomers named above. Thus, the CS of $C^7$ was characteristic of isomer (IVa), $C^8$ of (Va), $C^7$ and $C^9$ of (VIa), and $C^8$ of (VIIa).

After distilling off 1,1-dichloroundecane from the reaction mixture obtained from 1,1,1-trichloroundecane a fraction was isolated containing 80% (IVb) + (Vb) and 20% other isomers. The elemental composition of this fraction corresponded with that calculated for isomers of overall formula $C_{11}H_{21}Cl_3$. Proposals on the structure of the compounds contained in this fraction were made on the basis of analysis of $^{13}C$ NMR spectra.

In the spectrum of this fraction there were two main (80%) collections of lines corresponding to the spectra of isomers (IVb) and (Vb) (Table 3) which were confirmed by calculations similar to those made above for trichlorononanes. In addition, the spectrum contained a series of lines which may probably be assigned to signals of other isomeric trichloroundecanes. Thus, according to the calculations, the signals at 47.9 and 55.1 ppm may be assigned to $C^2$ and $C^3$, respectively, in (IIIb), at 19.5 ppm to $C^{10}$ in (VIIb), at 10.8 ppm to $C^{11}$ in (VIIb), and 40.2 and 58.5 ppm to $C^9$ and $C^{10}$ in (IXb). It was impossible to exclude in the reaction mixture the presence of 1,1,4-trichloroalkanes, and in the case of (Ib) 1,1,7- and 1,1,11-trichloroundecanes as well, all the signals of which according to calculation practically coincide with the signals of other isomers. It is possible that all the isomeric 1,1,X-trichlorononanes are formed as a result of the investigated reaction, where X is the position of the third halogen in the hydrocarbon chain of the trichlorononane. However, the important isomers were the 1,1,5- and 1,1,6-trichloroalkanes.

## EXPERIMENTAL

GLC analysis was carried out on an LKhM-8MD5 instrument with a katharometer and programming of temperature from 160 to 260°C on the following columns: 1) 1 m × 3 mm with 20% SKTFT-50 on Chromaton N-AW (0.16-0.20 mm); 2) 1 m × 3 mm with 15% Carbowax 20M on Chromaton N-AW-HMDS (0.16-0.20 mm). In the case of (Ia) yields of reaction products were determined on 1,1,1,7-tetrachloroheptane, and for (Ib) on 1,1,1,3-tetrachloroheptane. The initial (Ia) and (Ib) were purified by redistillation. Preparative GLC was carried out on a column 1 m × 9 mm with 15% Carbowax 20M on Chromaton N-AW-HMDS (0.20-0.25 mm). Compounds (IIIa) and (VIIIa) were identified with known samples on phases of different polarity (columns 1 and 2).

$^{13}C$ NMR spectra were obtained for 50-80% solutions in $CCl_4$ on a Bruker HX-90 instrument.

Experiments with HMPA were carried out in an open vessel at 140°C (3 h) in a stream of nitrogen and experiments with i-PrOH in ampuls at 130°C (3 h). Reaction mixtures were processed, analyzed, and their products separated according to [2].

Reduction and Rearrangement of 1,1,1-Trichlorononane (Ia). The reaction product from (Ia) (10.2 g, 50 mmole) was distilled in vacuum. Three fractions were obtained: 1) bp 77-80°C (10 mm) 2.5 g; 2) bp 62-70°C (1 mm) 2.4 g; 3) bp 78-80°C (1 mm) 5 g.

1,1-Dichlorononane (IIa) was isolated from fraction 1 by a repeated distillation and had bp 59° (2 mm), $n_D^{20}$ 1.4514, $d_4^{20}$ 1.1212 (cf. [7]). $^{13}C$ NMR spectrum ($\delta$, ppm): 73.5 ($C^1$), 44.0 ($C^2$), 28.8 ($C^3$), 26.2 ($C^4$), 29.6 ($C^5$), 29.4 ($C^6$), 32.1 ($C^7$), 22.8 ($C^8$), 14.1 ($C^9$).

A mixture of isomers was isolated from fraction 2 by preparative GLC and consisted of 88% 1,1,5- (IVa) and 1,1,6- (Va) and 12% 1,1,7- (VIa) and 1,1,8-trichlorononane (VIIa). Found: C 46.77; H 7.29; Cl 45.66%. $C_9H_{17}Cl_3$. Calculated: C 46.65; H 7.34; Cl 46.00%.

A mixture of various amounts of 1,1,5- (IVa) and 1,1,6-trichlorononanes (Va) was isolated from fraction 3 by preparative GLC. Found: C 46.78; H 7.34; Cl 45.62%. $C_9H_{17}Cl_3$. Calculated: C 46.65; H 7.34; Cl 46.00%.

Synthesis of 1,1,9-Trichlorononane (VIIIa). 1,1,1-9-Tetrachlorononane was reduced with a system consisting of $Fe(CO)_5$ (15 mole %) and HMPA (100 mole %) at 140°C for 3 h in a stream of nitrogen. The reaction mixture was processed as in [2], distilled, and from the fraction of bp 78-80°C (10 mm) containing 95% (VIIIa) and 5% 1,1,1,9-tetrachlorononane compound (VIIIa) was isolated by preparative GLC, $n_D^{20}$ 1.4720, $d_4^{20}$ 1.1212. Found: C 46.86; H 7.20; Cl 46.13%. $C_9H_{17}Cl_3$. Calculated: C 46.65; H 7.34; Cl 46.00%. $^{13}C$ NMR spectrum ($\delta$, ppm): 73.7 ($C^1$), 43.7 ($C^2$), 25.9 ($C^3$), 29.3 ($C^4$), 28.8 ($C^5$), 28.5 ($C^6$), 26.9 ($C^7$), 32.7 ($C^8$), 44.8 ($C^9$).

Reduction and Rearrangement of 1,1,1-Trichloroundecane (Ib). The reaction product from (Ib) (9.5 g, 40 mmole) was fractionated in vacuum. Fractions obtained were: 1) bp 68-70°C (1.5 mm) (1.7 g); 2) bp 80-85°C (1 mm) (3.1 g); 3) bp 85-89°C (1 mm) (4 g).

From fraction 1, consisting of 95% (IIb) and 5% (Ib) according to GLC data, a repeat distillation gave 1,1-dichloroundecane (IIb) bp 98°C (1.5 mm), $n_D^{20}$ 1.4535, $d_4^{20}$ 0.9784. Found: C 58.38; H 9.76; Cl 31.68%. $C_{11}H_{22}Cl_2$. Calculated: C 58.66; H 9.85; Cl 31.49%. $^{13}C$ NMR spectrum ($\delta$, ppm): 73.2 ($C^1$), 43.7 ($C^2$), 30.1 ($C^3$), 26.3 ($C^4$), 29.0 ($C^5$), 29.3 ($C^6$), 29.5 ($C^7$), 26.0 ($C^8$), 31.9 ($C^9$), 22.6 ($C^{10}$), 13.9 ($C^{11}$).

Compounds (Ib), (IIIb)-(Xb) were present in fraction 2.

Fraction 3 contained, according to GLC, 80% 1,1,5- (IVb) and 1,1,6-trichloroundecane (Vb) and 20% other isomers (IIIb), (VIb)-(Xb). Found: C 50.79; H 8.21; Cl 41.36%. $C_{11}H_{21}Cl_3$. Calculated: C 50.88; H 8.15; Cl 40.97%.

## CONCLUSIONS

1,1,1-Trichlorononane and 1,1,1-trichloroundecane were reduced under the action of systems based on $Fe(CO)_5$ in combination with HMPA or isopropanol to the corresponding 1,1-dichloroalkanes and were rearranged into the isomeric trichlorononanes and trichloroundecanes with the predominance of 1,1,5- and 1,1,6-isomers. The formation of trichloroalkanes indicated rearrangements in the intermediate radicals $\dot{C}Cl_2(CH_2)_nCH_3$ as a result of hydrogen migration.

## LITERATURE CITED

1. T. T. Vasil'eva, N. V. Kruglova, V. I. Dostovalova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1856 (1978).
2. R. Kh. Freidlina, N. A. Rybakova, V. I. Dostovalova, and L. N. Kiseleva, Dokl. Akad. Nauk SSSR, 255, 887 (1980).
3. N. A. Rybakova and L. N. Kiseleva, Izv. Akad. Nauk SSSR, Ser. Khim., 1636 (1981).
4. J. T. Clerk, E. Pretsch, and S. Sternhell, $^{13}C$ Kernresonanz Spectroskopie, Frankfurt am Main (1973).
5. V. I. Dostovalova, F. K. Velichko, T. T. Vasil'eva, N. V. Kruglova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 213 (1981).
6. L. P. Lindenman and J. G. Adams, Anal. Chem., 43, 1245 (1971).
7. R. Kh. Freidlina, F. K. Velichko, et al., Methods of Heteroorganic Chemistry. Chlorine. Aliphatic Compounds [in Russian], Nauka, Moscow (1973), p. 513.