CONCLUSIONS

1. 1. 1,2-Dithiolen-3-ones are attacked by phosphines at the sulfur atom in the 2 position to give reactive thioacylketenes, whereas the 1,2-dithiolan-3-ones under analogous conditions form β-thiolactones as the result of attack on the sulfur atom in the 1 position.

2. A new method was found for obtaining the esters of β-mercapto-α,β-unsaturated acids via the reaction of 1,2-dithiolen-3-ones with phosphines in the presence of alcohols.

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RADICAL TRANSFORMATIONS OF 1,1,1,3-TETRACHLORONONANE CAUSED BY INITIATING SYSTEMS BASED ON Fe(CO)$_5$ AND CONTAINING VARIOUS HYDROGEN DONORS

N. A. Rybakova and L. N. Kiseleva

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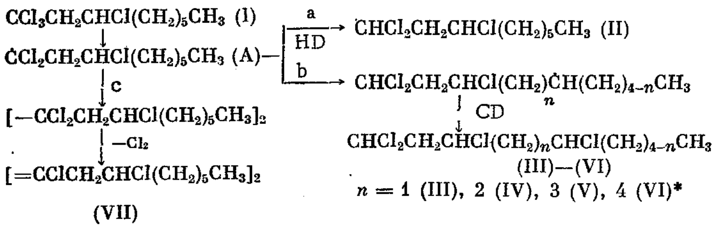
It is known [1, 2] that radicals (A) are generated when tetrachloroalkanes are treated with systems that contain Fe(CO)$_5$ in combination with a hydrogen donor (HD), which radicals can then take part in three competing reactions: a) reduction of the HD; b) rearrangement with the corresponding migration of hydrogen and subsequent cleavage of chlorine from the chlorine donor (CD); c) dimerization and subsequent dechlorination. When 1,1,1,3-tetrachlorononane is treated with systems that contain Fe(CO)$_5$ and HMPA, it was observed that, besides rearrangements with 1,5- and 1,6-migrations of hydrogen, rearrangements also occur in the intermediate radical with 1,7- and 1,8-migrations of hydrogen [2].

Only solitary examples are known of rearrangements with the migration of hydrogen or of other atoms and groups to a distant radical center [3-5], and consequently we made a more detailed study of reactions of this type. On the example of 1,1,1,3-tetrachlorononane (I) the transformations can be depicted by the following scheme:



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[*] The indicated values of n correspond to the 1,5-, 1,6, 1,7-, and 1,8-migration of hydrogen.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow.
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TABLE 1*

$Fe(CO)_5$, in mole % of (I)	Conversion of (I), %	Yield of reaction products, %		
		(II)	Σ(III)—(VI)	(VII)
10	66	22	18	0,6
15	80	27	33	4,1
20	84	24	34	4,0
30	95	34	36	3,6
40	100	20	25	5,1

*130°C, 3 h, 40 mole % of HMPA when based on (I), open reactor.

TABLE 2*

Expt. No.	Hydrogen donor	Amount of HD, in mole % of (I)	Conversion of (I), %	Yields of reaction products, %						
				(II)	(III)	(IV)	(V)	(VI)	Σ(III)—(VI)	(VII)
1	—	–	52	5	8	7	2	1,5	18,5	2,5
2	HMPA	40	80	27	15	15	1,8	1,4	33,4	4,1
3	»	100	98	61	16	12	1,4	1,1	30,5	3,8
4	DMF	40	76	18	12	10	1,4	1,3	24,7	1,2
5	»	100	72	28	16	14	1,6	1,3	32,9	2,6
6	Isopentanol	40	52	9	10	9	1,5	1,2	21,7	4,0
7	»	100	56	10	7	5	0,6	0,5	13,1	4,5
8	Cyclohexanol	40	59	10	8	7	1,2	0,9	17,1	None
9	»	100	82	29	10	9	1,1	0,9	21,0	»
10	»	300	93	52	10	9	0,9	0,7	20,6	»
11	HMPA	40	97	33	18	17	2,0	1,7	38,7	4,0
12	»	100	98	60	15	12	1,3	1,0	28,3	3,6
13	Isopropanol	40	100	19	3	3	None		6,0	None
14	»	300	79	40	13	10	Σ=1		24,0	14
15	Triethylsilane	100	100	54	9	10	1,4	1,6	22,0	6
16	»	300	100	72	4	4	Σ=1		9,0	3

*130°, 3 h, 15 mole % of $Fe(CO)_5$ when based on (I). Expts. 1-10 were run in an open reactor in a nitrogen atmosphere, while Expts. 11-16 were run in sealed rotated ampuls.

In the present paper we studied the effect of the $Fe(CO)_5$ concentration (Table 1), and the nature and concentration of the HD on the yields of the products (Table 2) obtained by the enumerated reactions (a)-(c) from 1,1,1,3-tetrachlorononane.

From the data in Table 1 it follows that an increase in the $Fe(CO)_5$ concentration in the initiating system from 10 to 15 mole % leads to an increase in the yield of the reduction (II), rearrangement Σ (III)-(VI), and dimerization (VI) products of the intermediate radicals (A). An increase in the $Fe(CO)_5$ concentration up to 30 mole % hardly changes the yields of (II), Σ (III)-(VI), and (VII). With further increase in the $Fe(CO)_5$ concentration the yields of (II) and Σ (III)-(VI) decrease, while the yield of (VII) remains practically unchanged.

As the HD we investigated HMPA, DMF, the isopropyl, isoamyl, and cyclohexyl alcohols, and triethylsilane (see Table 2). A high conversion of the starting tetrachlorononane (I) under the selected conditions is characteristic for the initiating systems containing these HD. In the absence of the HD the sum of the yields of the rearranged products is 3.5 times greater than the yield of (II) that is obtained by the reduction of radical (A). With increase in the HD concentration an increase in the yield of product (II) is observed in all cases. The highest yields of (II) were obtained in the experiments with HMPA (see Table 2, Expts. 3 and 12), cyclohexanol (Expt. 10), and triethylsilane (Expts. 15 and 16).

Rearrangements with 1,5-, 1,6-, 1,7-, and 1,8-migrations of hydrogen were observed in the reactions with all of the investigated HD, in which connection with triethylsilane the yield of the rearranged products was 22% (Expt. 15), whereas in the analogous reaction of 1,1,1,7-tetrachloroheptane they were obtained in a yield of only 1% [1]. The rearrangement of the radicals is greatest when the reaction is initiated by systems that contain HMPA and DMF (Expts. 2-5, 11, 12). Compounds, obtained as the result of the 1,5- and 1,6-migration of hydrogen, predominate in the rearranged products. Rearrangements with the migration of hydrogen to the more distant radical centers (1,7- and 1,8-) were detected in all of the experiments, except Expt. 13. The total yield of compounds (V) and (VI) does not exceed 3.7% (Expt. 11). The yield of dimer (VII), obtained by reaction (c), varies from 1 to 5%, and only when a 3-fold excess of isopropanol with respect to (I) is used does it reach 14% (Expt. 14).

It should be mentioned that in the experiments, run with HMPA in sealed ampuls and in an open vessel, the same results were obtained (Expts. 2 and 3, 11 and 12).

EXPERIMENTAL

The experimental procedure in the case of the open reactor is described in [2]. The reaction mixtures were analyzed by GLC on an LKhM-8MD5 instrument equipped with a katharometer, in a helium stream, with programming of the temperature from 150 to 270°, on two columns: 1) 1 m × 3 mm, packed with 20% SKTF T-50 deposited on Chromaton N-AW, 0.16-0.20, and 2) 1 m × 3 mm, packed with 15% Carbowax 20M deposited on Chromaton N-AW-HMDS, 0.16-0.20; the internal standard was 1,1,1,3-tetrachloroheptane. The reaction products were identified by GLC by comparing with authentic samples [2] on phases of different polarity (columns 1 and 2).

CONCLUSIONS

1. 1,1,1,3-Tetrachlorononane when treated with systems that contain $Fe(CO)_5$ and HMPA, DMF, isopropanol, isopentanol, cyclohexanol or triethylsilane, is reduced to 1,1,3-trichlorononane and rearranged to 1,1,3,5-, 1,1,3,6-, 1,1,3,7-, and 1,1,3,8-tetrachlorononanes via isomerization of the intermediate radicals with 1,5-, 1,6-, 1,7-, and 1,8-migrations of the hydrogen atom.

2. Systems containing triethylsilane, HMPA, or cyclohexanol are the most efficient in the reduction, and systems containing HMPA or DMF are the most efficient in the rearrangement.

3. The rearrangement of a substantial portion of the radicals, generated by the action of the system $Fe(CO)_5 + (C_2H_5)_3SiH$ on 1,1,1,3-tetrachlorononane, was observed for the first time.

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