ORGANIC CHEMISTRY

REARRANGEMENT OF POLYBROMOALKYL RADICAL WITH 1,5- AND 1,6-MIGRATION OF HYDROGEN IN THE REDUCTION OF 1,1,1,3-TETRABROMOHEPTANE

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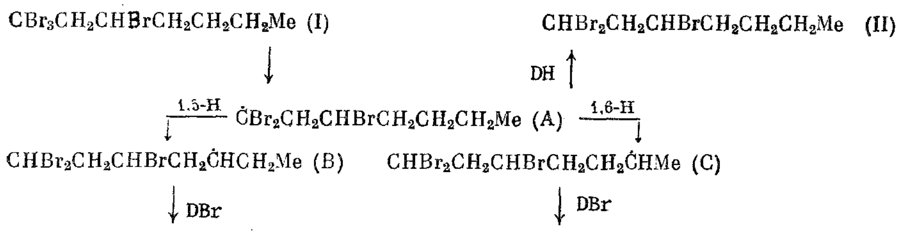
In the chemistry of polychloroorganic compounds it is known that reduction of compounds containing CCl_3 groups by isopropanol in the presence of $Fe(CO)_5$ is accompanied by rearrangement of the intermediate radicals with 1,5- and 1,6-migration of H [1, 2]. Similar rearrangements for polybromoalkyl radicals are not known. In the reduction of compounds containing CBr_3 groups with UV irradiation in THF [3] or in the system $Ni(CO)_4$ + THF [4], corresponding reduction products were identified containing a $CHBr_2$ group but no rearrangement was observed. Reduction of tribromomethylcarbinol [5] by the action of various alcohols in the presence of $RuCl_2 \cdot [P(C_6H_5)_3]_3$ has been reported and in [6] it was noted that in the reaction of CBr_4 and compounds containing CBr_3 groups with 1-alkenes (1-hexene, propene), under the action of $Fe(CO)_5$ + DMF side reactions led to the formation of $CHBr_3$ and compounds with a $CHBr_2$ group. The system $Fe(CO)_5$ + a hydrogen donor is widely used for the reduction of CCl_3 groups to $CHCl_2$ [7].

The work reported here was directed at a study of the reduction of 1,1,1,3-tetrabromoheptane (I) (TBH) under the action of a system including $Fe(CO)_5$ plus Et_3SiH or i-PrOH as hydrogen donors, together with an examination of the possibility that there may be rearrangement of the intermediate radicals. The experimental results on the reduction of (I) are set out in Table 1.

In the case of Et_3SiH + $Fe(CO)_5$ at 100°C, 1,1,3-tetrabromoheptane (II) was formed in quantitative yield from tetrabromoheptane. In the absence of $Fe(CO)_5$, or when this was replaced by benzoyl peroxide (BPO), there was little or no reaction. Further reduction of an actual sample of (II) under identical conditions was not observed.

In the case of i-PrOH at a ratio i-PrOH:(I) = 3:1 in the presence of $Fe(CO)_5$ at 100°C there was little or no reaction. Heating to 130°C led to the formation of the reduction product (II) in 22-46% yield and, in addition, a mixture of approximately equal quantities of 1,1,3,5-tetrabromoheptane (III) and the 1,1,3,6-isomer (IV) with an overall yield of up to 30%. With i-PrOH:(I) = 8:1, (II) was formed in 64% yield and the isomeric products (III) and (IV) in 15% yield.

Compounds (II) and (IV) were isolated individually by preparative GLC. Formation of the tetrabromoheptanes (III) and (IV) could occur by rearrangement of the radicals (A) with 1,5- and 1,6-migration of H:



DH = H donor, DBr = Br donor.

In the presence of the highly effective hydrogen donor Et_3SiH, the reaction proceeds with the formation of the reduction product (II) only, i.e., of the two competing reactions in which the radical (A) can participate – separation of H from Et_3SiH and isomerization – only the first occurs. In the presence of the less effective hydrogen donor i-PrOH, radicals (A) are partially isomerized to radicals (B) (1,5-H) and (C) (1,6-H) which capture Br and form the corresponding tetrabromoheptanes (III) and (IV). The structures of (I) to (IV) were

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TABLE 1. Reduction of 1,1,1,3-Tetrabromoheptane (I)

TBH (I)	Hydrogen donor	Initiator	T., °C	Time, hr	Conversion of (I)	Yield, %	
mmole						(II)	(III), (IV)
	Et_3SiH	$Fe(CO)_5$					
5	5,5	0,5	100	2	93	91	–
5	5,5	0,5	100	4	100	97	–
5	5,5	None	100	4	10	9	–
5	5,5	BPO 0,05	100	4	10	8	–
15	*i*-PrOH, 15	0,5	100	4	30	9	–
5	15	0,5	130	4	100	46	23
75	225	7,5	130	4	100	22 *	30
5	40	0,5	130	4	100	64	15
1,1,3-tribromoheptane (II)	Et_3SiH						
5	5,5	$Fe(CO)_5$ 0,5	100	4	No reaction		

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*Some resinous product formed.

TABLE 2. ^{13}C NMR Spectra of Tetrabromoheptanes

Compound	δ ^{13}C, ppm, from TMS						
	C^1	C^2	C^3	C^4	C^5	C^6	C^7
$CHBr_2CH_2CHBrCH_2CHBrCH_2Me$ (III)	42,3 42,6	53,4 52,9	52,6	45,6	56,3	32,1	11;8
$CHBr_2CH_2CHBrCH_2CH_2CHBrMe$ (IV)	42,8 42,8	53,4 53,2	53,4 52,8	36,7 36,1	38,6 38,1	50,0 49,6	26,4
$CBr_3CH_2CHBrCH_2CH_2CH_2Me$ (I)	36,5	66,8	51,7	39,2	29,5	21,8	14,1
$CHBr_2CH_2CHBrCH_2CH_2CH_2Me$ (II)	43,5	53,3	54,1	38,0	29,2	21,9	13,9

confirmed by their ^{13}C NMR spectra (Table 2). We have reported compounds (I) and (II) and their ^{13}C NMR spectra previously [6]. In the spectra of (III) and (IV) the signals of C^4 and C^7 are characteristic. In (III), the methylene carbon C^4 has two Br atoms in the β-position and hence lies ~10 ppm downfield from that in (IV) in which there is only one Br in the β-position. On the other hand, C^7 in (III) has Br in the γ-position and in (IV) in the β-position which produces a difference of some 15 ppm downfield in the chemical shift of the C^7 in (IV). In addition, for assignment of the signals spectra were run using the DERT* technique with different polarity for the groups CH_2, CH, and CH_3. Assignment of the signals of C^3 and C^5 was made on the following basis: since the presence of Br in the γ-position shifts the C signal upfield, then in (III) there are three Br atoms in the γ-position to C^3 to which is assigned the 52.64 ppm signal, and there is one Br γ to C^5 with a signal at 56.31 ppm. In (IV) the C^6 signal is upfield from C^3 and is determined by the chemical shift of these carbons in the isostructural hydrocarbon.

EXPERIMENTAL

The purity of the starting materials and of the products obtained was checked by GLC using a metal column, No. 1, 1300 × 3 mm with 15% SKTFT-50X on chromaton N-AW 0.16-0.20 mm, catharometer detector, helium carrier gas. Separation of compounds by preparative GLC was carried out on column No. 2, 1300 × 9 mm with 20% SKTFT-50X on the same carrier. The ^{13}C NMR spectra were run on a "Bruker WP-200" instrument using 50% solutions in CCl_4 and TMS.

Reduction of 1,1,1,3-tetrabromoheptane (I) by isopropanol in the presence of $Fe(CO)_5$. 31.2 g (75 mmole) (I), 13.5 g (225 mmole) i-PrOH, and 1.5 g (7.5 mmole) $Fe(CO)_5$ were heated in a sealed ampul enclosed in a metal sheath in an oil bath at 130°C for 4 h. A resinous reaction mixture was obtained. To free it from iron salts and tar, a solution in CCl_4 was passed through a layer of silca gel, the CCl_4 distilled off, and the residue distilled in vacuum. Products were 5.6 g (22%) 1,1,3-tetrabromoheptane, bp 84°C (2 mm), $n_D^{20} = 1.5280$, $d_4^{20} = 1.8037$ (compare [6]) and 9.3 g (30%) of a mixture of tetrabromoheptanes (III) and (IV) with bp 135-140°C (2 mm); nonvolatile residue, 4.5 g (III) and (IV) were separated by preparative GLC on column 2, 182°C, 4.6 liter/hr helium.

1,1,3,5-Tetrabromoheptane (III), $n_D^{20} = 1.5610$, $d_4^{20} = 2.0713$. Found, %: C 20.37; H 2.95; Br 76.65; MR 65.01. $C_7H_{12}Br_4$. Calculated, %: C 20.22; H 2.91; Br 76.87; MR 65.58.

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*Double-pulse — Translator.

1,1,3,6-Tetrabromoheptane(IV), $n_D^{20} = 1.5625$, $d_4^{20} = 2.0710$. Found, %: C 20.41; H 2.91; Br 76.54; MR 65.07. $C_7H_{12}Br_4$. Calculated, %: C 20.22; H 2.91; Br 76.87; MR 65.58. The ^{13}C NMR spectra are given in Table 2.

Reduction of 1,1,1,3-tetrabromoheptane (I) by triethylsilane in the presence of $Fe(CO)_5$. Into a glass ampul were placed 5 mmole (I), 5.5 mmole Et_3SiH, and 0.5 mmole $Fe(CO)_5$ and the whole heated in a metal sheath in an oil bath at 100°C (see Table 1). The product yield was determined by GLC against 1,1,1,3-tetrabromoheptane as reference using column 1.

SUMMARY

1. Rearrangement, with 1,5- and 1,6-migration of hydrogen, has been observed in radicals containing radical centers on the group CBr_2.

2. A method has been proposed for the selective reduction of a CBr_3 group to $CHBr_2$ under the action of $Fe(CO)_5$ + triethylsilane or isopropanol.

LITERATURE CITED

1. R. Kh. Freidlina and A. V. Terent'ev, Advances in Free Radical Chemistry, (ed. L. Heyden), Vol. 6, New York (1980), p. 11.
2. N. A. Rybakova and L. N. Kiseleva, Izv. Akad. Nauk SSSR, Ser. Khim., 1636 (1981).
3. N. Mitsuo, T. Kunieda, and T. Takizawa, J. Org. Chem., 38, No. 12, 2255 (1973).
4. T. Kunieda, T. Tamura, and T. Takizawa, J. Chem. Soc. Chem. Commun., 15, 885 (1972).
5. J. Blum, S. Shtelzer, and P. Albin, J. Mol. Catal., 16, 167 (1982).
6. T. T. Vasil'eva, L. F. Germanova, V. I. Dostovalova, B. V. Nelyubin, and R. Kh. Friedlina, Izv. Akad. Nauk SSSR, Ser. Khim., 2759 (1983).
7. E. G. Chukovskaya, R. Kh. Friedlina, and N. A. Kuzmina, Synthesis, 10, 773 (1983).

OXIDATIVE SPLITTING OF TERTIARY ALCOHOLS IN ALKALINE MEDIUM

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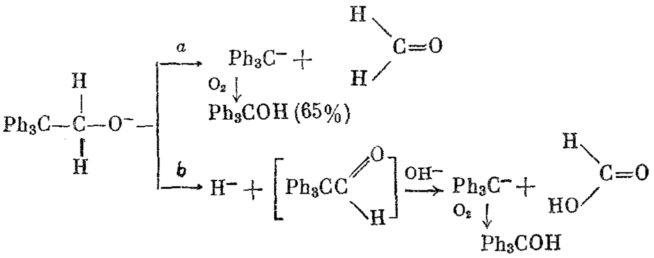
Alcoholates of primary and secondary alcohols are reducing agents, able to transfer a hydride ion to appropriate acceptors such as carbonyl compounds, nitro compounds, alcohols, etc. [1]. In these reactions the C—H bond is cleaved (dehydrogenation or oxidation of alcohols). However, with the presence in the alcohol of a radical R (corresponding to a carbanion that surpasses or is commensurable in its stability with the hydride ion), the cleavage of the C—C bond, i.e., splitting of the alcohol is possible. We thus showed that a primary alcohol 2,2,2-triphenylethanol, containing a trityl radical, is readily split in an alkaline medium



The stabilities of Ph_3C^- and H^- are similar [2], and therefore, the reaction may proceed in two directions. Unfortunately, it is impossible to establish the real path of the reaction, because in an alkaline medium, Ph_3CCHO splits to form Ph_3C^- [3].

Alcoholates of tertiary alcohols split naturally with cleavage of the C—C bond and the formation of most stable carbanion R^-

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