EXPERIMENTAL

The epoxidation of (I) was carried out in a nonseparated electrolytic cell with two 2×3 -cm platinum electrodes separated by 2 cm. The cell was filled with a solution of (I) in 100 ml 10:5:4 MeCN-THF-H₂O (volume ratio) containing 0.2 g NaBr and a current was passed with control of the electrode current and potential by means of a P-5827 potentiostat. The consumption of (I) was monitored by thin-layer chromatography. The amount of NaBr was varied by $\pm 10-15\%$ in order to provide the required current strength at a given potential. After the electrolysis, the mixture was evaporated and the residue was extracted with ether. The extract was washed with aqueous NaHCO3 and aqueous Na2SO4 and dried over Na2SO4. The extract was evaporated to give an oily product containing both (I) and (III) as indicated by thinlayer chromatography. Cleavage of (III) through diol (IV) to aldehydoester (II) and the separation of (II) as the chromatographic separation of (II) and (VI) were carried out as described in our previous work [3].

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CONCLUSIONS

The anodic ω -epoxidation of the ethyl ester of Z,Z-farnesylic acid proceeds regioselectively when the electrolysis is carried out under rigorously controlled conditions with I = 10-12 mA and V = 2-2.5 V.

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EXCHANGE OF BROMINE AND CHLORINE BY IODINE IN ALIPHATIC HALIDES CATALYZED

BY IRON PENTACARBONYL

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The exchange of halogen by iodine is one of the most important methods for the synthesis of organoiodine compounds [1]. The most common modification of this reaction is the exchange of Cl and Br by I according to Finkelstein [2]. In light of the limitations to the methods for the synthesis of organoiodine compounds, the search for new modifications of the exchange of halogens by iodine holds clear interest.

In our previous work [3], we reported the capacity of $Fe(CO)_5$ to participate in the transfer of halogen atoms from polyhalomethanes to growing radicals in homolytic telomerization reactions. It was of interest to study the possibility of using Fe(CO); as an initiator for the exchange of Br and Cl by I. I_2 and CHI_3 were used as the iodination agents. The halogen exchange was studied for normal bromoalkanes and chloroalkanes and allyl bromide.

At 75-130°C, Fe(CO), initiates the exchange of halogen by I at the primary carbon atom in an aliphatic chain.

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TABLE 1. Exchange of Br by I in 1-Bromopentane (60 mmoles)

Experi- ment no.	Iodination agent (IA), mmoles	Fe(CO)₅, mmoles	T., °C	Time, h.	Yield of n- C ₅ H ₁₁ I, % (rel. to IA)
1* 2* 3 4 5 6 7 8 9 10 11	$\begin{array}{c} I_{2,} 20 \\ CHI_{3,} 20 \\ I_{2,} 10 \\ I_{2,} 10 \\ I_{2,} 10 \\ CHI_{3,} 10 \\ CHI_{3,} 10 \\ I_{2,} 20 \\ CHI_{3,} 20 \\ I_{2,} 10 \\ I_{2,} 10 \end{array}$	$ \begin{array}{c} - \\ - \\ 6 \\ 12 \\ 3 \\ 6 \\ 3 \\ 6 \\ 6 \\ 3 \\ 3 \\ 3 \end{array} $	$\begin{array}{c} 140\\ 140\\ 130\\ 125-130\\ 130\\ 130\\ 130\\ 80-85\\ 80-85\\ 125\\ 128\\ \end{array}$	1,5 1,5 1,5 1,5 1,5 1,5 1,5 1,5 1,5 1,5	4 1 80 51 77 91 47 22 3 62 78

*The exchange does not proceed at 90°C.

TABLE 2. Exchange of Halogen by I in Alkyl Halides and Allyl Bromide (60 mmoles) in the Presence of Fe(CO)₅ (6 mmoles)

Experi- ment no.	Starting compound	lodination agent (IA), 10 mmoles	T ., °C	Time, h	Iodide yield, % (rel. IA)
1 2 3 4 5 6 7 * 8 9 10 [†]	$\begin{array}{c} n-C_4H_9Br\\ n-C_4H_9Br\\ n-C_4H_9Cl\\ n-C_4H_9Cl\\ n-C_5H_{14}Cl\\ n-C_5H_{14}Cl\\ r-C_5H_{14}Cl\\ cH_2=CHCH_2Br\\ cH_2=CHCH_2Br\\ cH_2=CHCH_2Br\\ cH_2=CHCH_2Br\\ cH_2=CHCH_2Br\\ \end{array}$	$\begin{matrix} I_2 \\ CHI_3 \\ I_1 \\ I_2 $	$\begin{array}{c} 105\\ 105\\ 85-90\\ 85\\ 117\\ 115-120\\ 75-80\\ 75-80\\ 75-80\\ 75-80\\ 75-80\\ 75-80\\ 75-80\\ 78\end{array}$	1,5 1,5 1,5 1,5 1,5 1,5 1,5 15 min 0,5 1 0,5	83 40 73 39 73 76 85 55 55 59 28

*Fe(CO)₅ 3 mmoles

+Experiment without Fe(CO),

$$\begin{array}{rcl} \mathrm{R}-\mathrm{Br}(\mathrm{Cl}) \xrightarrow{\mathrm{I}_{\mathfrak{s}}, \ (\mathrm{CHI}_{\mathfrak{s}})} \mathrm{R}-\mathrm{I} \\ \mathrm{R} &= n - \mathrm{C}_{\mathfrak{s}}\mathrm{H}_{11}, \ n - \mathrm{C}_{4}\mathrm{H}_{\mathfrak{s}}, \ \mathrm{CH}_{2} = \mathrm{CH} - \mathrm{CH}_{2} \end{array}$$

Tables 1 and 2 show that I_2 and CHI_3 may serve as iodination agents in the presence of $Fe(CO)_3$.

The exchange of bromine by iodine in 1-bromopentane proceeds rapidly at $125-130^{\circ}$ C and the reaction is largely complete after 1-2 h (see Table 1, experiments 3, 10, and 11). When using I₂, as increase in the Fe(CO)₅ concentration leads to a decrease in the yield of 1iodopentane (experiments 3 and 4), while in the case of CHI₃, the yield of 1-iodopentane increases with an increase in the Fe(CO)₅ concentration (experiments 6 and 7). At 80-85°C, CHI₃ is not effective (experiment 9), while I₂ gives 1-iodopentane in 22% yield (experiment 8). At 130°C, I₂ and CHI₃ are comparable in effectiveness. At 90-140°C, the exchange of Br by I virtually does not proceed without Fe(CO)₅.

The data for the exchange of Cl in 1-chlorobutane and 1-chloropentane and of Br in 1bromobutane and allyl bromide by iodine are given in Table 2. At 85-105°C, I_z gives better iodide yields than CHI_3 for 1-bromo- and 1-chlorobutanes (experiments 1-4). At 117-130°C, there are no marked differences in reactivity of 1-bromo- and 1-chloropentanes, which both give 1-iodopentane in identical yield (compare experiment 5 in Table 1 with experiment 5 in Table 2).

In the case of allyl bromide, the exchange occurs rapidly; the reaction with I_2 takes 15 min at 75-80°C (experiment 7). The reaction with CHI₃ gives allyl iodide in 55-59% yield in 0.5-1 h (experiments 8 and 9). Allyl bromide is capable of exchanging bromine for iodime in the absence of Fe(CO)₅. The yield of allyl iodide does not reach 30% in the absence of Fe(CO)₅.

 CHI_2Br , CH_2I_2 and traces of $CHIBr_2$ were found among the products of the reaction of 1bromopentane with CHI_3 in the presence of $Fe(CO)_5$. These results and the analogy with numerous examples of the homolysis of the C-Hal bond in the C-Hal₃ group [3] (Hal = Cl and Br) by the action of $Fe(CO)_5$ indicate a radical mechanism for the exchange reaction.

 $\begin{aligned} & \operatorname{Fe}(\operatorname{CO})_5 \to \operatorname{Fe}(\operatorname{CO})_4 + \operatorname{CO} \\ & \operatorname{CHI}_3 + \operatorname{Fe}(\operatorname{CO})_4 \to \operatorname{CHI}_2 + \operatorname{Fe}(\operatorname{CO})_4 \mathrm{I} \\ & \operatorname{CHI}_2 + \operatorname{RBr} \to \operatorname{CHI}_2 \mathrm{Br} + \mathrm{R} \\ & \operatorname{R} + \operatorname{CHI}_3 \to \operatorname{RI} + \operatorname{CHI}_2 \\ & \operatorname{R} + \operatorname{Fe}(\operatorname{CO})_4 \mathrm{I} \to \operatorname{RI} + \operatorname{Fe}(\operatorname{CO})_4 \end{aligned}$

This scheme was also supported by the finding that the iodide yield is more than 1.7 mole per mole $Fe(CO)_{5}$.

In order to identify CHI_2Br , we carried out the reactions of CHI_3 with Br_2 and the disproportionation of CHI_3 with $CHBr_3$ initiated by $Fe(CO)_5$.

a)
$$\operatorname{CHI}_{3} + \operatorname{Br}_{2} \xrightarrow{\operatorname{Fe}(\operatorname{CO})_{5}} \operatorname{CHI}_{2}\operatorname{Br} + \operatorname{CHIBr}_{2}$$

b) $\operatorname{CHI}_{3} + \operatorname{CHBr}_{3} \xrightarrow{\operatorname{Fe}(\operatorname{CO})_{5}} \operatorname{CHI}_{2}\operatorname{Br} + \operatorname{CHIBr}_{2}$
(1)

In order to identify CHIBr2, we carried out the reaction of CHBr3 with I2.

Re(CO)

$$CHBr_3 + I_2 \xrightarrow{re(CO)_5} CHBr_2I + CHBrI_2 + CHI_3$$
(2)

The compounds obtained were identified by gas-liquid chromatography using their retention times on phases differing in polarity.

EXPERIMENTAL

The gas-liquid chromatographic analysis was carried out on an LKhM-8MD-5 chromatograph using a katharometer detector and 1000×3 -mm stainless stell columns packed with 5% XE-60 on Chromatone N-AW-DMCS (0.16-0.20 mm) and 5% SE-30 on Chromatone N-AW-HMDS (0.16-0.20 mm). The helium gas carrier flow rate was 1.5-2 liters/h and the column temperature was 50-100°C. Preparative gas-liquid chromatography was carried out on a Tsvet 4-67 chromatograph with a preparative attachment on a 1000 × 8-mm stainless stell column packed with 15% XE-30 on Celite 545 at 110°C. The experiments in Tables 1 and 2 were carried out without isolation of the pure compounds and identification on the two columns with phases of differing polarity relative to authentic samples. The iodide yields were determined by gas-liquid chromatography using methyl dichloroacetate, 1-bromopentane, and 1-iodopentane as internal standards. A preparative experiment was carried out in order to isolate 1-iodopentane.

Reaction of 1-Bromopentane with I_2 in the Presence of $Fe(CO)_5$. A sample of 4 ml (0.03 mole) $Fe(CO)_5$ was added dropwise with stirring over 20 min to a mixture of 72 ml (0.6 mole) 1-bromopentane and 25 g (0.1 mole) I_2 at 130°C. Heating was continued for an additional 100 min at 130°C. Then, the mixture was passed through a layer of silica gel (10 mm) on a filter. The filtrate was shaken with metallic Hg and separated from Hg₂I₂. Distillation and additional purification by preparative gas-liquid chromatography gave 7 g 1-iodopentane (35% relative to I_2) with physical constants corresponding to literature values [4]. ¹³C NMR spectrum in CCl₄ (δ , ppm): 6.18 (CH₂I), 13.95 (Me), 21.63, 32.60, 33.24 ((CH₂)₃).

CONCLUSIONS

Indine and indoform in the presence of $Fe(CO)_5$ are effective reagents for the exchange of Br and Cl by indine at the primary carbon atom of an aliphatic chain.

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