a mixture of benzene and petroleum ether. The white crystals have mp 164 °C and yield 65%.

All the hydroxamic acids could be prepared by following the above procedure.

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Synthesis of $CHCl_2I$, CCl_3I, $CHBr_2I$, and CBr_3I

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The synthesis of $CHCl_2I$, CCl_3I, $CHBr_2I$, and CBr_3I has been reinvestigated. $CHCl_2I$ and CCl_3I were synthesized by reacting $CHCl_3$ with NaOI, $CHBr_2I$ was synthesized by reacting $CHBr_3$ with NaOI, and CBr_3I was synthesized by reacting $CHBr_3$ with NaI in acetone. The carbon-13 NMR spectra of $CHCl_2I$, CCl_3I, and $CHBr_2I$ were recorded. The chemical shifts were $CHCl_2I$ 11.2 ppm, CCl_3I 4.2 ppm, and $CHBr_2I$ −45.7 ppm all in reference to Me_4Si.

Introduction

Recently, the trigonal additivity procedure developed by Somayajulu and Zwolinski for correlating and estimating thermodynamic properties of organic substances,[1] such as standard enthalpies of formation, enthalpies of vaporization, and other thermodynamic properties, was found to be equally effective in correlating and estimating carbon-13 chemical shifts[2,3] of halomethanes of the general formula $CH_nF_mCl_pBr_qI_{4-n-m-p-q}$. To complement available literature information on carbon-13 chemical shifts, information was needed on the following key halogen compounds, viz., CCl_pI_u and CBr_qI_u or the corresponding $CH_nCl_pI_u$ and $CH_nBr_qI_u$. Synthetic procedures were sought to prepare these key halomethanes. Particular attention was directed to synthesis of chloroiodomethanes and bromoiodomethanes by using NaOI and NaI as iodating agents.

The original study of NaOI as an iodating agent was conducted by Dehn in 1909.[4] Dehn prepared NaOI in situ by reacting I_2 with aqueous NaOH or by the reaction of KI with NaOCl. When NaOI in aqueous NaOH solution was reacted with $CHCl_3$, CCl_3I was reported as the major product with CCl_2I_2 as a minor product. In turn, when NaOI in aqueous NaOH solution was reacted with $CHBr_3$, CBr_3I was reported as the major product with no evidence of CBr_2I_2.

As a result of these studies Dehn concluded that (1) NaOX reacting with hydrogen containing methanes would replace the hydrogen atom with an X atom and (2) that hypohalites are useful synthetic reagents for the preparation of methane tetrahalides.

Synthesis of $CHCl_2I$ and CCl_3I

(*a*) ***$CHCl_3$* as a Reactant.** In an attempt to repeat Dehn's synthesis of CCl_3I, 0.4 mol of I_2 was gradually added to a mixture of 300 cm^3 of 6.25 M NaOH and 26 cm^3 of $CHCl_3$ (source: Curtin; purity 99%) in a Morton flask. The reaction was kept in an ice bath and was stirred vigorously for about 15 h. Product analysis for this reaction and the other reactions described in this paper was performed by a Hewlett Packard 5982 A GC/MS data system. Separation was accomplished by a 10 in. × $^1/_8$ in. stainless steel column packed with 3% Apiezon L on 100/120 Suplecoport. The major product was found to be dichloroiodomethane, $CHCl_2I$, with a small amount of trichloroiodomethane, CCl_3I, as a minor product. The ratio between the two products being approximately 10 to 1 with chlorine being displaced preferentially to hydrogen. Some tetrachloroethane (decomposition product) was also observed. The overall yield of $CHCl_2I$ was ca. 10 mol %.

(*b*) ***Carbon Tetrachloride as a Reactant.*** Twenty-five cubic centimeters of carbon tetrachloride (source: Fisher Scientific; purity 99%) was reacted by the same procedure used above for chloroform except that 3 mol excess of I_2 was added and the reaction was allowed to proceed for over 5 days. The yield of CCl_3I was small, less than 5 mol %. Analysis of the products by GC/MS showed the principal products to be trichloroiodomethane and dichlorodiiodomethane with some hexachloroethane. The mole ratio of CCl_3I to CCl_2I_2 was 3.5 to 1.

Synthesis of $CHBr_2I$ and CBr_3I

(*a*) ***Bromoform as a Reactant.*** For the reaction between NaOI and $CHBr_3$, Dehn[4] stated that he obtained higher yields of CBr_3I by reacting KI solution with a mixture of NaOCl or NaOBr solution and bromoform than by reacting bromoform with a NaOI solution prepared by reacting I_2 with NaOH solution. Following Dehn's procedure the NaOI was generated by the gradual addition of 0.21 mol of KI (source: Baker; purity 99.5%) to a mixture of 150 cm^3 of 5.25% NaOCl solution with 23 g of NaOH and 1.8 mol of bromoform (source: Mallinckrodt; purity 99%). The reaction time was 24 h. Product analysis revealed that dibromoiodomethane was the major product (ca. 10 mol %) with trace amounts of bromodiiodomethane and tribromoiodomethane. The mole ratio of $CHBr_2I$ to $CHBrI_2$ to CBr_3I was 100:1:1. Here again our results contradicted Dehn's findings. We found that iodine displaces the halogen preferentially to hydrogen.

(*b*) ***Carbon Tetrabromide as a Reactant.*** Carbon tetra-

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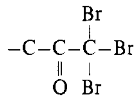
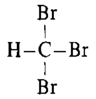
Table I. Summary of Experimental Results

reactant	reagent[a]	reaction time	products	yield, mol %	comments
$CHCl_3$	A	15 h	$CHCl_2I$	10	
			CCl_3I	1	
			CCl_2HCCl_2I	trace	dec product
CCl_4	A	5 days	CCl_3I	5	$CCl_3I:CCl_2I_2$ 3.5:1
			CCl_2I_2	*b*	
$CHBr_3$	A′	24 h	$CHBr_2I$	10	$CHBr_2I:CHBrI_2:CBr_3I$ 100:1.1
			$CHBrI_2$	*b*	
			CBr_3I	*b*	
CBr_4	A	6 days	CBr_3I	1	
			CBr_2HCBr_2I	trace	dec product
CBr_4	B	5 min	CBr_3I	30	
			$CBrI_3$	trace	CBr_2I_2 may have been formed, but was not detected
			 $-C(=O)-CBr_3$	substanl amts	product of free bromine and solvent
			 $HCBr_3$	substanl amts	dec product of tribromoacetone

[a] Key: A, NaOH + I_2, source of NaOI reagent; A′, KI + NaOCl, source of NaOI reagent; B, NaI in acetone. [b] See last column.

bromide (source: J. T. Baker; purity 99%) was allowed to react with NaOI in the method described previously for the $CHCl_3$ and CCl_4 reactions with 0.53 mol of I_2 being added and the reaction proceeding for 6 days. The only mixed halogenated methane identified for this reaction was tribromoiodomethane, although some tetrabromoethane was also detected. The overall yield of this reaction was very low (<1 mol %).

An effort was made to increase the yield of CBr_3I by dissolving the CBr_4 in CS_2 before reacting with NaOI. The reaction was carried out essentially as described previously. No increase in yield of CBr_3I was observed.

(*c*) *NaI/Acetone Procedure with Bromoform as a Reagent*. Sodium iodide in acetone is a well-known synthetic reagent for displacing chlorine or bromine in hydrocarbons with an iodine atom.[5] Shriner and Curtin[6] state that $CHBr_3$ and CBr_4 are the only common halogenated methanes that react with this reagent. The reagent's utility for the synthesis of bromoiodomethanes has not been previously investigated. Twenty-three cubic centimeters of NaI/acetone [prepared from 15 g of NaI (source: Fisher Scientific; purity 99.5%) and 100 cm^3 of acetone (source: Fisher Scientific; purity 99.5%)] were reacted with 0.02 mol of CBr_4 (source: J. T. Baker; purity not known) for 5 min. Analysis of the halogen containing products revealed CBr_3I and trace amounts of $CBrI_3$ along with brominated acetone and bromoform. Although dibromodiiodomethane may also have been formed, it was not detected. The overall yield of CBr_3I was over 30 mol %. A summary of the experimental results described above is given in Table I.

Properties of the Compounds Synthesized and Their ^{13}C Chemical Shifts

All of the chloroiodomethanes and bromoiodomethanes were found to be extremely sensitive to light, heat, and air, especially after they were separated from the aqueous NaOI/NaOH solutions. Due to the rapid decomposition of these compounds, it is necessary to keep them under an inert atmosphere (N_2 or Ar), below 0 °C and to rigorously exclude all light while recording the ^{13}C spectra. All spectra were recorded by using a JEOL PFT-100. The chemical shifts were $CHCl_2I$ 11.2 ppm, CCl_3I 4.2 ppm, and $CHBr_2I$ −45.7 ppm all in reference to Me_4Si.

Conclusions

As stated previously Dehn had apparently found that NaOI supplies an iodine atom which will displace hydrogen preferentially to chlorine or bromine. In the current study we have found that the halogens are displaced preferentially to hydrogen. It should be pointed out that Dehn used high-temperature distillation to separate the products and the Carius method to identify the products while GC/MS was used for separation and identification in this study. When $CHCl_3$ reacts with NaOI/NaOH reagent, iodine displaces chlorine about 3 times more readily than it does hydrogen. When $CHBr_3$ is reacted with the same reagent, the bromine atom is displaced about 30 times more readily than the hydrogen atom.

We have observed that when NaOI/NaOH reagent is reacted with either CCl_4 or CBr_4 almost no product is formed. This is essentially in agreement with Dehn's observations that hypohalites did not react with tetrahalogenated methanes. However, it should be noted that even though the NaOI reagent displaces halogens more readily than hydrogen, the hydrogen atom plays a significant role in the reaction mechanism.

NaI is no doubt present in the NaOI/NaOH reaction mixture. In an effort to increase product yield and to test how NaI behaves in the absence of NaOI, NaI in acetone was tested as an iodating reagent. It was found that this reagent displays a very different behavior from the NaOI/NaOH reagent. CBr_4 which essentially does not react with NaOI/NaOH reacts readily with NaI in acetone. $CHCl_3$ which reacts relatively easily with NaOI/NaOH does not react with NaI in acetone. $CHBr_3$ reacts with both reagents while CCl_4 reacts with neither reagent. Because of the different behavior of the NaOI/NaOH reagent and NaI in acetone, it seems reasonable that NaI is not responsible for the products found in the reactions of $CHCl_3$ and $CHBr_3$ with NaOI/NaOH reagent.

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