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The Jacobsen Rearrengement of Tribromobenzenes

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The Jacobsen rearrangement of tribromobenzenes was investigated at 110—180 °C in concentrated sulfuric acid. The reaction proceeds exclusively *via* the intramolecular 1,2-migration of the bromine atom, which is accelerated by the steric repulsion of the neighboring group. Sulfonation of both the reactant and the products occurs simultaneously with the rearrangement. The migration of bromine atoms in the sulfonic acids proceeds far more slowly, the rearranged products not being formed to any considerable extent by sulfonic acids.

The migration of alkyl groups and/or halogen atoms in alkylhalobenzenes and polyhalobenzenes, assumed to be modifications of the Jacobsen rearrangement, occurs under similar conditions. Alkyl migration has been extensively studied and its mechanism elucidated in detail.[1-3] On the other hand, only a few investigation have been reported on the migration of halogen atoms on the aromatic nuclei.[4-8]

At least in cases of alkyl migration, the rearrangements are supposed to be acid-catalyzed reactions, proceeding *via* protonated or SO_3H^+-added benzene derivatives, *i.e.* benzenium cations. However, no details of the halogen-migration have been confirmed so far.

During the course of investigations on the reactions, spectroscopic and chromatographic properties of polyhalogenated aromatic hydrocarbons,[9-11] we have studied the sulfuric acid-catalyzed rearrangements of polybromobenzenes as discussed the mechanism of the reaction.

Experimental

Materials. 1,2,3-Tribromobenzene was prepared by the method previously reported by Furuyama and Fukushi.[12] Dibromochloro- and bromodichloro-benzenes were prepared by the Sandmeyer reaction from the corresponding dihaloanilines. Other compounds were used after purification of the commercially available materials. All the polyhalobenzenes were identified by means of their melting and boiling points and spectral properties.

Reactions. The reactants polyhalobenzene (1.0×10^{-4} mol) and concentrated sulfuric acid (0.2 ml, special grade) were sealed in Pyrex tubes (6 mm dia. × 50 mm length). A number of the sealed tubes thus prepared were heated in a thermostatic oil bath under efficient mixing with a magnetic vibrator. The polyhalobenzenes are sparingly soluble in sulfuric acid at room temperature, and are not completely miscible under the reaction conditions (at 110—180 °C). Thus, sufficient mixing should be carried out to avoid the effect of diffusion on the reaction rates. Absence of such effects under experimental conditions was confirmed by the fact that approximately the same apparent rate constants were observed for the decrease of the amount of reactant polyhalobenzenes in preliminary runs carried out with varying efficiency of mixing.

The reactions were carried out at 110—180 °C for 10—24 h. Each sealed tube was taken out at appropriate intervals of time, cooled immediately and quenched by pouring into an excess of water. The halogenated hydrocarbon component was extracted by cyclohexane and analyzed by gas chromatography.

Spectral and Chromatographic Measurements. The ^1H-NMR spectra were recorded on a JEOL JNM-C60H spectrometer operating at 60 MHz, the chemical shifts being given in terms of parts per million (ppm) upfield from the signal of internal $^1H_2SO_4$ reference. The infrared and mass spectra were measured with JASCO DS-402G and Hitachi RMU-6L spectrometers, respectively. Gas chromatographic analyses were carried out on a Shimadzu GC-6A apparatus equipped with a polyethylene glycol 20M column (3 mm × 2 m).

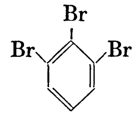
Results and Discussion

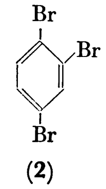
Formation of the Rearranged Products. Isomeric tribromobenzenes and their sulfonated products were obtained by the action of concentrated sulfuric acid on tribromobenzenes. However, the rates of reaction for the isomeric tribromobenzenes differ remarkably. The decrease in the reactant apparently shows first-order rate in each case (Table 1), 1,2,3-tribromobenzene (**1**) being most reactive. The amounts and proportions of tribromobenzene isomers present in the reaction system changed during the course of reaction. The relative amounts of three isomers **1**—**3** are given as a function of the reaction period in Fig. 1.

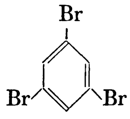
Table 1. Apparent first order rate constants for the decrease of tribromobenzenes

CH_3Br_3	Temp/°C	k_1/s^{-1}
1,2,3	160	2.94×10^{-4}
	180	9.00×10^{-4}
1,2,4	160	3.55×10^{-5}
	180	2.17×10^{-4}
1,3,5	160	—[a)]
	180	4.4×10^{-6}

a) The reaction is very slow under these conditions.


(**1**)


(**2**)


(**3**)

Formation of the sulfonic acids in the reaction medium causes loss in the total amount of tribromobenzenes. In the runs employing 1,2,3-tribromobenzene (**1**), the amount of the 1,2,4-isomer (**2**) produced increases

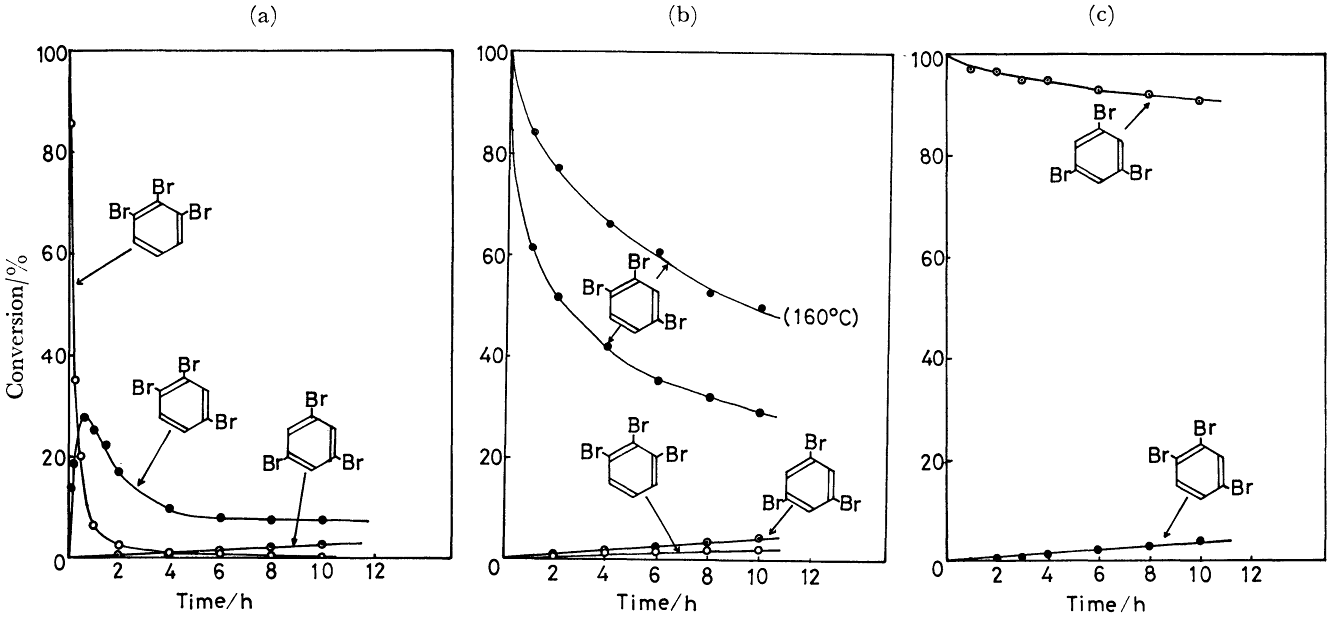


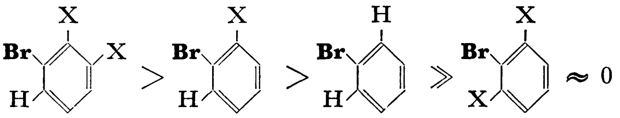
Fig. 1. Amounts of consumed and produced tribromobenzenes relative to the starting material (=100%) are plotted as a function of time with the runs starting from (a) 1,2,3-tribromobenzene (**1**), (b) 1,2,4-tribromobenzene (**2**), and (c) 1,3,5-tribromobenzene (**3**) and carried out at 180 °C (except the cases otherwise stated).

steeply in the earlier stage of the reaction process, decreasing gradually later (Fig. 1a). We see that very fast rearrangement from **1** to **2** is succeeded by considerably slower sulfonation of **2**.

In order to examine whether the rearrangement is intramolecular or intermolecular, crossover experiments with toluene, *m*-dichlorobenzene, trichlorobenzene, and naphthalene were carried out. No cross-products were obtained. This strongly suggests the intramolecular nature of the rearrangement. Another evidence in favor of intramolecularity of the rearrangement comes from the fact that the rate for consumption of the reactant, as well as that for the increases in the products, is linearly dependent on the initial concentration of the reactant. A quadratic relation is expected if the rearrangement is intermolecular.

1,2-Migration of the bromine substituent was found to occur exclusively in the rearrangement by the runs on bromodichloro- and dichlorobromo-benzenes (Table 2). No rearranged products were detected after 48 h reaction of 2,6-dichlorobromobenzene (**6**) at 180 °C. In contrast, 2,6-dibromochlorobenzene (**4**) rearranged nearly as fast as **1**, producing 2,5-dibromo- and 3,5-dibromo-chlorobenzenes. The proportion of products is similar to the case of **1**. The only reasonable explanation for the different behavior between **4** and **6** is that the migration of the chlorine substituent is negligible under the experimental conditions and that the migration of the bromine substituent in **6** is blocked by the chlorine atoms on the neighbor carbon atoms. In the case of 2,3-dichlorobromobenzene (**5**), the rearrangement to form 3,4-dichlorobromobenzene occurred with a rate slightly lower than that of **1**. However, the decrease in the rate of **5** is not remarkable, probably because the migration occurs considerably faster in bromobenzenes of 1,2,3-trihalosubstituted type than in that of 1,2-dihalo-substituted type. Migration of the chlorine substituent is not evident throughout the polyhalobenzenes (Table 2). This is also true in the case of 1,2,3-trichlorobenzene under similar conditions.

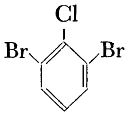
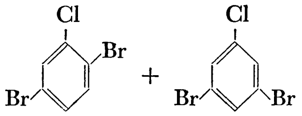
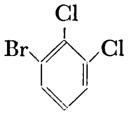
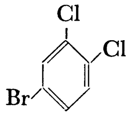
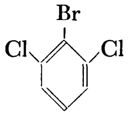
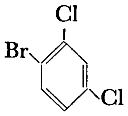
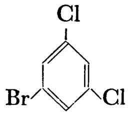
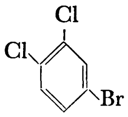
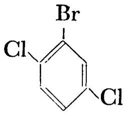
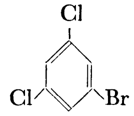
In conclusion, the rates of bromine migration decrease in the following order, the 1,2-migration being the only detectable pathway of the rearrangement.



Under more drastic conditions (above 250 °C in concentrated or fuming sulfuric acid), the intermolecular halogen migration to produce dibromo- and tetrabromobenzenes proceeds to a considerable extent.[7] However, the mechanism of these reactions evidently differs from that of the intramolecular rearrangement under discussion. In the runs carried out in phosphoric acid, polyphosphoric acid, selenic acid, concentrated hydrochloric acid, and fluorosulfuric acid[13] at temperatures 110—200 °C for 1—10 h, no rearranged products were detected. The results suggest the important role of sulfuric acid in the rearrangement.

Sulfonic Acids Formed During the Reaction and Their Possibility as Intermediates of the Rearrangement. In the reaction medium, considerable amounts of both the starting and the produced tribromobenzenes were sulfonated, resulting in a decrease in the total amount of tribromobenzene with the elapse of reaction period (Fig. 1). The sulfonic acids produced during the course of reaction were pursued by means of NMR and infrared spectroscopic methods. Figure 2a shows the NMR spectrum of a mixture of the produced sulfonic acids in the sulfuric acid layer of the reaction system separated from the organic layer after 1 h duration

Table 2. The rearrangements of bromodichloro- and dibromochloro-benzenes[a)]

Reactant	Product(s)
 **(4)**	
 **(5)**	
 **(6)**	b)
 **(7)**	
 **(8)**	b)
 **(9)**	b)
 **(10)**	b)

a) The reaction was carried out at 180 °C, the products being separated after 5—10 h. b) The starting trihalobenzene was recovered nearly quantitatively after digestion.

of the reaction at 165 °C. This is a typical example of the NMR spectra of the sulfonic acids in sulfuric acid, the signals being assigned by comparing them with those (Figs. 2b and 2c) of authentic tribromobenzenesulfonic acids. All the spectra (Figs. 2 and 3) were measured at 120 °C to avoid the crystallization of sulfonic acids. The NMR spectrum of 2,3,4-tribromobenzenesulfonic acid (**11**) shows an AB quartet (J=6.9 Hz) which can be assigned to the two hydrogen atoms on the adjacent carbon atoms. However, only a singlet was observed at 4.50 ppm upfield from the acidic ^{1}H signal of sulfuric acid when the spectrum of the same sulfonic acid was measured in concentrated sulfuric acid at 120 °C immediately after dissolution. This signal, corresponding to signal a in Fig. 2a, is assigned to **11**. The NMR spectrum of 2,4,5-tribromobenzenesulfonic acid (**13**) shows two signals at 4.08 and 3.87 ppm from the ^{1}H signal of H_2SO_4 (Fig. 2c), which correspond to signals b and c, respectively, in Fig. 2a.

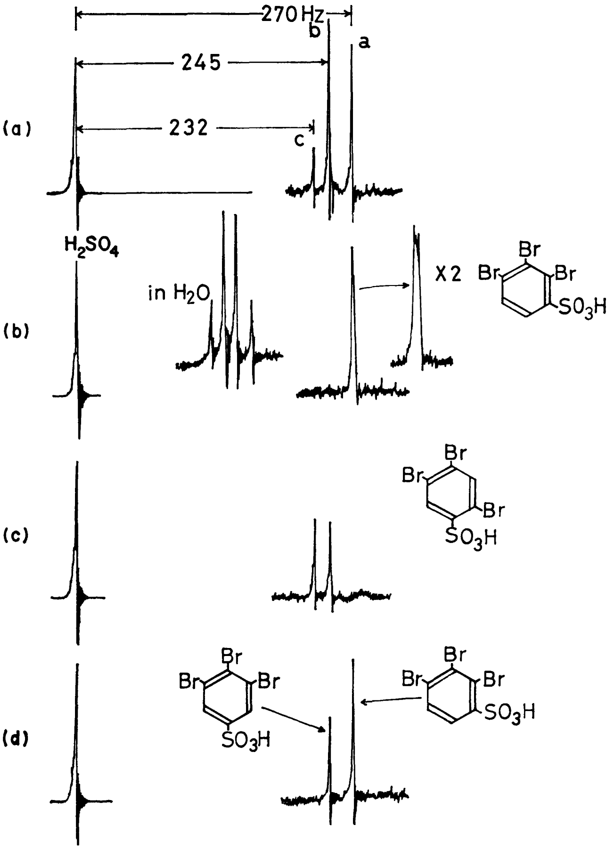


Fig. 2. NMR spectra of sulfonic acids in the reaction mixture. (a) Sulfuric acid layer of the reaction mixture starting from 1,2,3-tribromobenzene (**1**) and separated after 1 h's reaction at 165 °C. The organic layer was separated off after the reaction period. (b) 2,3,4-Tribromobenzenesulfonic acid (**11**) in water and sulfuric acid. (c) 2,4,5-Tribromobenzenesulfonic acid (**13**) in sulfuric acid. (d) Spectrum measured after heating 2,3,4-tribromobenzenesulfonic acid (**11**) in sulfuric acid without the contact of the organic layer (tribromobenzenes). Isomerization to produce 3,4,5-tribromobenzenesulfonic acid alone was observed.

Signals observed in Fig. 2a were thus assigned to the sulfonic acids. However, much higher intensity of signal b than that of c indicates the overlap of another signal at 4.08 ppm. Prolonged heating (at 165 °C) of the sulfuric acid solution of **11** resulted in the appearance of a signal at 4.08 ppm in addition to signal a in its NMR spectrum. The new signal is located at 4.08 ppm, approximately the same frequency as the higher frequency signal of **13**, and assigned to 3,4,5-tribromobenzenesulfonic acid (**12**) for the following reasons. (i) Electrophilic substitution on 1,2,3-tribromobenzene usually occurs predominantly on the 4-carbon atom, when the reaction is kinetically controlled, to form **11** in the case of sulfonation. However, sulfonation at higher temperature is often reversible and the more stable isomer **12** is expected to become the major product gradually. (ii) Under the reaction conditions, formation of 1,2,4-tribromobenzene (**2**) after quenching and digestion of the reaction mixture was shown to be negligible, no measurable amount of sulfonated 1,2,4-tribromobenzene being expected to be present in the

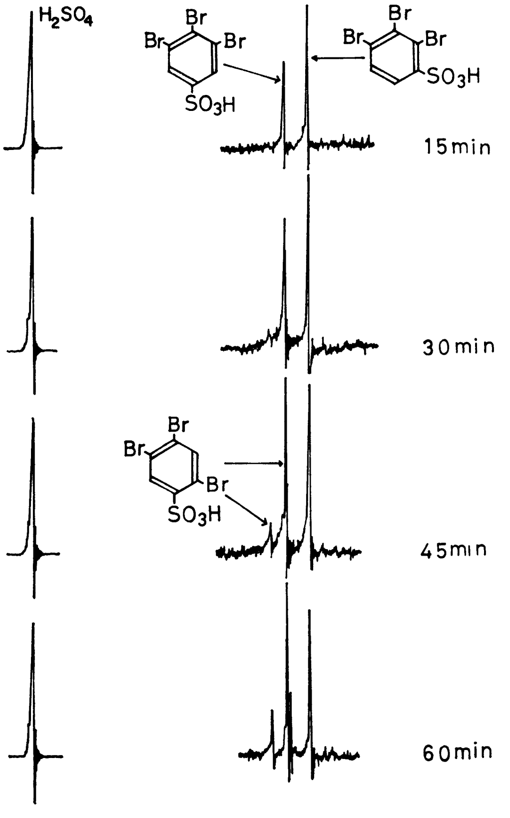


Fig. 3. Changes in NMR spectrum of the sulfuric acid layer during the process of the rearrangement of 1,2,3-tribromobenzene (**1**).

reaction mixture. No 2,4,6-tribromobenzenesulfonic acid was detected in either runs, and its formation from **1** is supposed to be a slow reaction.

The quantitative changes of these sulfonic acids during the course of reaction were determined by means of ^{1}H-NMR spectrometry.[14] When the reaction of **1** was carried out at 165 °C, the NMR spectrum of the sulfuric acid layer changed as a function of the reaction period (Fig. 3). As expected, sulfonic acid **11** was produced from **1** initially, amounts of sulfonic acids **12** and **13** increasing gradually. In the presence of tribromobenzenes, formation of **13** proceeds considerably faster than the isomerization to form **13** from the mixture of sulfonic acids **11** and **12**, which takes several hours to produce a detectable amount of **13** at the same reaction temperature. Thus, most of sulfonic acid **13** in the sulfuric acid layer is derived by sulfonation of the rearranged product **2**. Isomerization starting from 2,4,5-tribromobenzenesulfonic acid (**13**) also gave a mixture of sulfonic acids (**12**, **13**, and a small amount of 2,4,6-tribromobenzenesulfonic acid)[15] after heating for a longer period, the products being in slow equilibria in sulfuric acid solutions. Thus the migration of bromine atoms also proceeds with sulfonic acids, the rate being considerably lower than that of the runs in the presence of tribromobenzenes.

Actually the sulfonation to form **11**, **12**, and **13** proceeds simultaneously and/or successively with the rearrangement to form **2** and **3**, when **1** is treated with sulfuric acid. Thus the reaction of **1** at 180 °C was

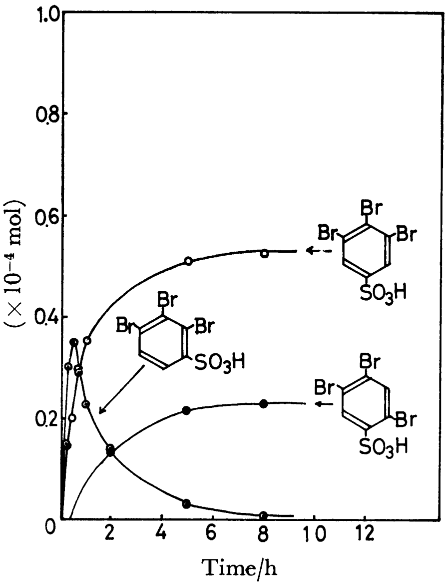


Fig. 4. Amounts of the produced sulfonic acids contained in the sulfuric acid layer are plotted as a function of time with the run starting from 1,2,3-tribromobenzene and carried out at 180 °C.

carefully reproduced and the sulfuric acid layer analyzed. The amounts of the sulfonic acids formed are plotted against the reaction period in Fig. 4. By comparing Fig. 4 with Fig. 1a, reactant **1** is supposed to undergo both sulfonation to **11** and isomerization to **2** and, to a less extent, to **3** initially, even if it is not certain whether compounds **1** and **11** are formed *via* a common intermediate or not.

The compositions of the sulfonic acids produced were determined also from the infrared spectra of the products in the sulfuric acid layer measured after their transformation into sodium salts. An example of the infrared spectra is shown in Fig. 5 together with the assignment of the bands to each sulfonic acid. Approximately the same results as in Fig. 4 were obtained from the changes in the infrared absorption intensities, leading to the same conclusion as obtained from the NMR spectra.

Mechanism of the Rearrangement. The rearrangement does not proceed in the presence of Brönsted acids other than sulfuric acid, and is not general-acid-catalyzed. Sulfonic acids **11**—**13** cannot be inter-

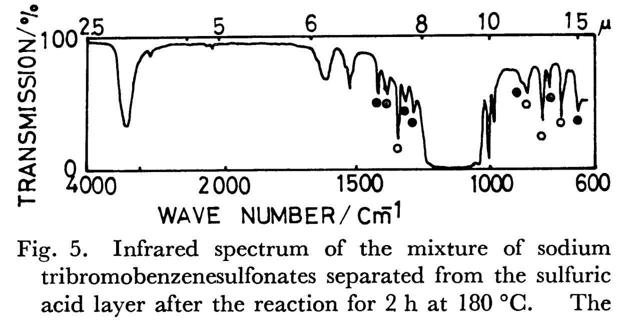


Fig. 5. Infrared spectrum of the mixture of sodium tribromobenzenesulfonates separated from the sulfuric acid layer after the reaction for 2 h at 180 °C. The absorption bands are assigned to 2,3,4-tribromobenzenesulfonate (◎), 3,4,5-tribromobenzenesulfonate(○), and 2,4,5-tribromobenzenesulfonate (●) by comparing with the spectra of authentic samples.

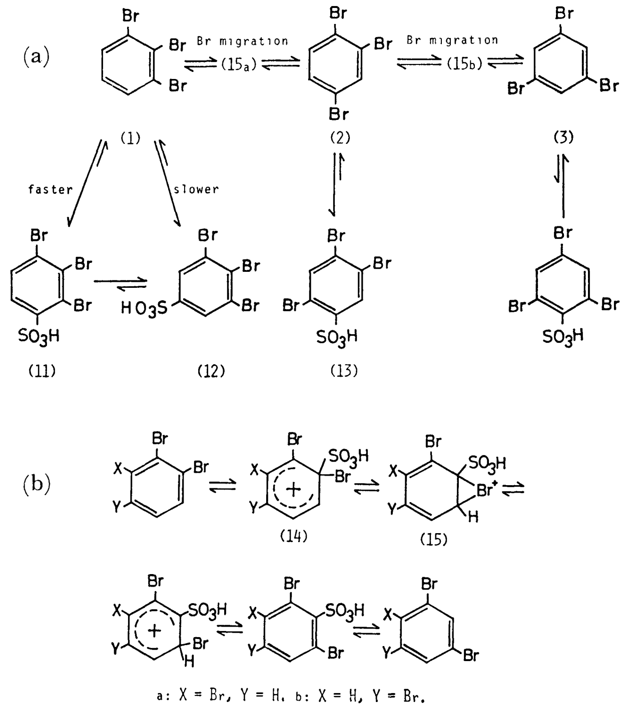


Fig. 6. (a) The whole reaction scheme including both isomerization and sulfonation. (b) Reaction mechanism for the bromine migration.

mediates of this rearrangement, since the isomerization to form bromine-migrated sulfonic acids is by far slower than the rearrangement itself. Moreover, the formation of tribromobenzenes from the sulfonic acids does not proceed to a considerable extent, probably because the equilibria among tribromobenzenes and the sulfonic acids are more favorable to the latter. Thus the possible intermediate or transition state for the reaction is a sulfonated benzenium cation (**14**) which is produced by the *ipso* attack of SO_3H^+, or more probably SO_3, and the subsequent formation of the three-membered ring containing bromine atom. The 1,2-shift proceeds more easily when the migrating bromine atom is sterically crowded. The formation of the bromonium cation might be assisted by the repulsion caused by the neighboring halogen atom. The repulsive force operating is of steric as well as electrostatic nature. The whole reaction is explained by the following scheme (Fig. 6). The desulfonation after rearrangement is expected to be a prompt reaction, since the sulfonic acid group is repelled sterically by the two bromine atoms on the neighboring carbon atoms. This is in line with the fact that it is difficult for 1,3,5-triboromobenzene to transform into the corresponding sulfonic acid and that 2,4,6-tribromobenzenesulfonic acid undergoes very fast desulfonation in sulfuric acid.

The rearrangement from **2** proceeds more slowly than that from **1**, giving **1** and **3**. The interconversion among the isomeric tribromobenzenes is reversible, thermodynamically controlled products being obtained after a very long period of reaction. Original Jacobsen rearrangements of polyalkylbenzenes tend to vicinal orientation, contrary to the rearrangements of polyhalobenzenes, and seem to proceed through a different mechanism.

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13) When **1** was treated in fluorosulfuric acid medium under almost the same conditions, several products were isolated by gas chromatography from the hexane soluble part, neither of them being identical with $C_6H_{6-n}Br_n$'s. A run carried out at 100 °C in fluorosulfuric acid gave a slight but detectable amount of **2** after a longer period of reaction. From the time-conversion curve of this reaction, the formation of **2** is concluded to occur secondarily probably catalyzed by sulfuric acid produced in the process of reaction.

14) The amounts of sulfonic acids **11**, **12**, and **13** are easily estimated by the following equations, where I_a, I_b, I_c are the intensities of the NMR signals at 4.50, 4.08, and 3.87 ppm upfield from $^1H_2SO_4$ signal, respectively. [**11**]$=k\cdot I_a$, [**12**]$=k(I_b-I_c)$, and [**13**]$=2k\cdot I_c$.

15) Since sulfonation is a reversible reaction, the bromine migration in the sulfonic acids is supposed to proceed through tribromobenzenes formed *in situ* by reverse desulfonation of the sulfonic acids in sulfuric acid. The electron withdrawing SO_3H group of the sulfonic acid might prevent the formation of benzenium cation (**14**) and subsequent bromonium cation (**15**) in Fig. 6. An evidence in favor of this hypothesis was obtained from the runs starting from mono- and di-bromonitrobenzenes. These compounds gave no rearranged products after being heated at 165 °C in sulfuric acid for several hours. The reactions at 180 °C and higher temperature caused decomposition of the starting materials, giving no rearranged products.