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# Reaction of Alkylbenzene. IX.[1] A Study of the Reaction of Methylbenzenes under the Influence of Aluminum Chloride-Hydrogen Chloride by Means of NMR

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The $^1H$ and $^{13}C$ NMR spectra of the complex layers obtained by the reaction of several methylbenzenes with aluminum chloride were measured at room temperature, and the proton exchanges were investigated. The ring $^1H$ signal shifted to a higher field as a result of fusion with the signal of the aliphatic $CH_2$ group of the methylbenzenonium ion, which resulted from the protonation to ring carbons. Thus, the proton exchange is considered to proceed among the ring carbons of aromatic hydrocarbon and its benzenonium ion in the complex layer intermolecularly as well as intramolecularly. This finding agrees with the results obtained from the $^{13}C$ NMR spectra of the complexes. The $^{13}C$ spectral data showed that the ease of the protonation to ring carbons depends upon the differences in the chemical shifts between the complex layer and the starting aromatic hydrocarbon, and some facts concerning the isomerization of methylbenzenes were discussed.

Investigations concerning benzenonium ions have been reported by many workers.[2–5] The presence of the benzenonium ion was supported first by measurements of vapor pressure and conductivity. The addition of the proton to an aromatic carbon atom, thus forming an "aliphatic" $CH_2$ group, was confirmed by observations of electronic[6] and infrared[7] spectra. More direct evidence for the structure of benzenonium ions was mainly obtained from the $^1H$ NMR spectra.

The $^1H$ NMR spectra of some methylbenzenonium ions were obtained by using $HF–BF_3$,[8,9] $HFSO_3$[10] or $HF–SbF_5$.[11] In all these experiments the spectra of benzenonium ions were measured at a low temperature in order to obtain well-resolved signals, since proton exchange occurred at higher temperatures.

Recently, Koptyug and his co-workers[12] measured the $^{13}C$ NMR spectrum of the mesitylenonium ion at room temperature by using aluminum chloride with hydrogen chloride and discussed how the positive charges on the ring-carbon atoms of the ion can be calculated on the basis of the relative shift differences between the mesitylenonium ion and mesitylene.

In the present work the $^1H$ and $^{13}C$ NMR spectra of the complex layers obtained by the reaction of several methylbenzenes with aluminum chloride were measured at room temperature in order to clarify the behavior of the methylbenzenonium ion under the influence of proton exchange.

## Experimental

*Preparation of the Complexes.* The reaction was carried out in a long necked flask with a long side tube, as is shown in Fig. 1. About 3 g of aromatic hydrocarbon was placed in the reaction vessel (3) and about the same amount of pulverized aluminum chloride in the side tube (4). After the open end of the side tube had been sealed, the aluminum chloride was sublimed slowly under the reduced pressure of 3 mmHg by means of a ribbon heater. One-third to one-half of the aluminum chloride in the side tube was transferred into the reaction vessel, which contained the aromatic hydrocarbon which had been held at 2 °C with stirring by means of a magnetic stirrer. During the sublimation, the hydrogen chloride produced by the reaction of aluminum chloride with the moisture which existed in the system was absorbed in the aromatic hydrocarbon. Then the reaction mixture is gradually turned from a light yellow to a light vermilion as a result of the dissolving of the aluminum chloride. When the reaction mixture was left standing for a while, a colored complex of a

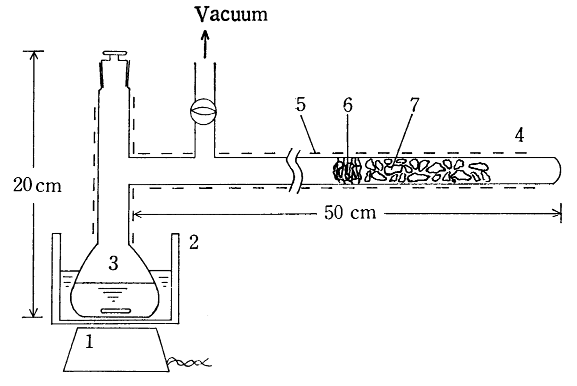

Fig. 1. Reaction flask
1. magnetic stirrer, 2. ice bath, 3. reaction vessel,
4. side tube, 5. ribbon heater, 6. glass wool,
7. $AlCl_3$.

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Table 1. THE CONSTITUENTS OF THE COMPLEXES OF METHYLBENZENES WITH ALUMINUM CHLORIDE–HYDROGEN CHLORIDE
(Reaction temp.: 2 °C, Reaction time: 70 min)

| Compound | Reaction products (wt%) | Al[a] (wt%) | Cl[a] (wt%) | Cl/Al (ratio) | ArH/Al (ratio) |
|---|---|---|---|---|---|
| Toluene | — | 6.2 | 27.3 | 3.34 | 3.14 |
| *p*-Xylene | *m*-Xylene (13.4) | 6.3 | 28.0 | 3.39 | 2.66 |
| *m*-Xylene | — | 6.0 | 28.5 | 3.62 | 2.78 |
| Mesitylene | — | 6.4 | 29.7 | 3.53 | 2.24 |
| Pseudocumene | mesitylene (1.2) | 6.5 | 26.9 | 3.15 | 2.30 |
| Hemimellitene | pseudocumene(3.0) | 5.2 | 23.0 | 3.95 | 2.92 |

a) Al: ±0.3 wt%, Cl: ±1.0 wt%.

high viscosity was separated as a lower layer, leaving colorless hydrocarbon as the upper layer. The lower complex layer was examined by NMR and then quenched with water before submitting it to the vpc analysis for hydrocarbons.

*Measurements.* The $^1H$ NMR spectra were measured at 22.5 °C on a JEOL JNM-3H-60 spectrometer with 60 MHz, using a neat liquid. Tetramethylsilane was used as the external standard.

The $^{13}C$ NMR spectra were measured at 26 °C on a JEOL C-60HL spectrometer with a 15.09 MHz RF unit. The $^1H$-decoupled $^{13}C$ spectra were obtained by means of a single scan. The chemical shifts were measured relative to $CS_2$.

*Analyses of Hydrocarbons.* The hydrocarbons in the complex layer were analyzed by means of vpc after the complex had been decomposed with water. The analyses were made at 100—130 °C by employing a vapor-phase chromatograph (Shimadzu Model GC-3AF) with a flame ionization detector and a 3 mm × 3 m column packed with Benton-34 or Ucon-LB-550X; nitrogen was used as the carrier gas.

*Analyses of Aluminum and Chlorine.* The aluminum and chlorine in the complex layer were determined by the oxine- and the mercurimetric-titration methods,[13] respectively.

## Results and Discussion

It is well known that, in the presence of hydrogen chloride, aluminum chloride dissolves in aromatic hydrocarbon by forming a benzenonium ion. In the present work, when aluminum chloride was heated, a certain amount of hydrogen chloride which was produced from the reaction of aluminum chloride with moisture evolved and was absorbed in the aromatic hydrocarbon. As more hydrogen chloride was not added in the reaction system, the amount of the complex layer seems to be proportional to that of the evolved hydrogen chloride. When both the reactants had been dehydrated extremely, aluminum chloride did not dissolve at all in aromatic hydrocarbon. Therefore, it seems that the dissolved aluminum chloride may form a certain protonic acid by reacting with hydrogen chloride or other proton donors. In each run, about a half of the aluminum chloride in the side tube dissolved in the aromatic hydrocarbon, but the excess aluminum chloride did not dissolve. Therefore, the complex layer seems to have similar constituents in each preparation under the given reaction conditions.

*Analyses of Complex Layers.* The constituents of the complex layers obtained by the reaction at 2 °C are shown in Table 1. Some methylbenzenes isomerized to the most stable isomer in a small amount. The ratio of Cl/Al is about 3.5. This value means that the protonic acid produced from aluminum chloride in the complex layer is not only $H^+AlCl_4^-$ but also some other acids, such as $H^+\ AlCl_3OH^-$ and $H^+\ Al_2Cl_7^-$.

On the other hand, the ArH/Al ratio for each complex is estimated to be between 2.24 and 3.14. This indicates that the aromatic hydrocarbon which exists in the complex layer is represented by the following equation:

$$\alpha ArH + HB + AlCl_3 \longrightarrow (\alpha - 1)ArH + ArH_2^+\cdot AlCl_3\cdot B^-$$

where HB is HCl or $H_2O$ and where $\alpha$ is not necessarily an integer. Accordingly, the excess aromatic hydrocarbon which does not form benzenonium ions is considered to react as a solvent. The fluctuation of

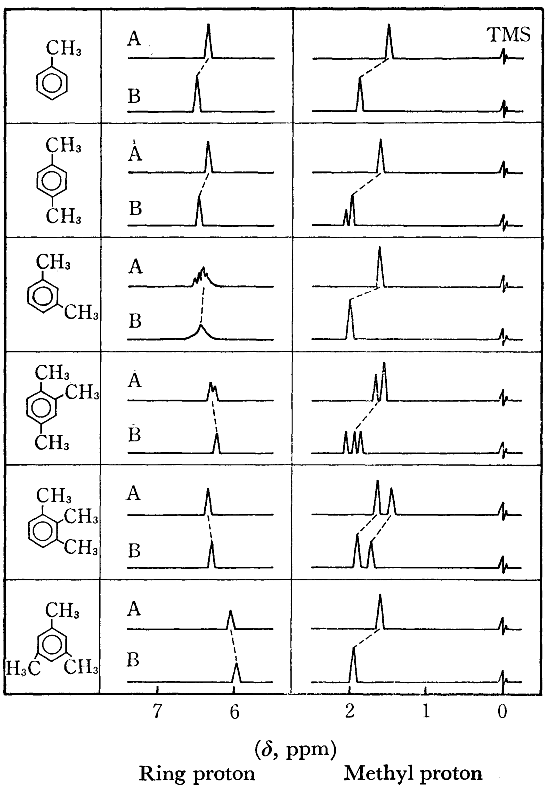

Fig. 2. The $^1H$ NMR spectra of the starting aromatic hydrocarbons (A) and the complexes (B).

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TABLE 2. THE $^1$H CHEMICAL SHIFT VALUES OF THE COMPLEXES OF METHYLBENZENES WITH ALUMINUM CHLORIDE–HYDROGEN CHLORIDE.[a,b]

| Compound | Methyl protons | | | Ring protons | | |
|---|---|---|---|---|---|---|
| | Aromatic hydrocarbon ($\delta$, ppm) | Complex ($\delta$, ppm) | Difference ($\Delta\nu$, Hz) | Aromatic hydrocarbon ($\delta$, ppm) | Complex ($\delta$, ppm) | Difference ($\Delta\nu$, Hz) |
| Toluene | 1.50 | 1.85 | −21.0 | 6.35 | 6.50 | −9.0 |
| *p*-Xylene | 1.60 | 1.96 | −21.6 | 6.35 | 6.44 | −5.4 |
| | | 2.04[c] | | | | |
| *m*-Xylene | 1.62 | 1.99 | −22.2 | 6.32 | 6.40 | −4.8 |
| Pseudocumene | 1.65[d] | 2.02 | −22.2 | 6.31 | 6.26 | +3.0 |
| | | 1.93 | −16.8 | | | |
| | 1.53 | 1.87 | −19.2 | | | |
| Hemimellitene | 1.63 | 1.91 | −16.8 | 6.36 | 6.31 | +3.0 |
| | 1.46 | 1.72 | −15.6 | | | |
| Mesitylene | 1.60 | 1.92 | −21.0 | 6.06 | 5.96 | +6.0 |

a) All the chemical shifts are referred to tetramethylsilane as an external standard.
b) The differences in chemical shifts between aromatic hydrocarbons and complexes are shown by Hz (positive; higher field shift, negative; lower field shift).
c) The intensity of the signal was about half of that of the signal at 1.96 ppm, and the signal could not be assigned.
d) This signal was assigned to the 1-$CH_3$ and 2-$CH_3$ groups, but it split into a doublet with an equal intensity in the complex.

the amount of such an aromatic hydrocarbon could not be interpreted.

*$^1$H NMR Spectra.* The $^1$H NMR spectra of the starting aromatic hydrocarbons (A) and the complexes (B) are shown in Fig. 2. Each $^1$H chemical shift ($\delta$) of the complexes, and the difference ($\Delta\nu$) of each chemical shift between the aromatic hydrocarbon and its complex, are given in Table 2.

The proton signals of methyl groups in all of the complexes shifted about 20 Hz to a lower field. However, when cyclohexane was used as an internal reference in the complex layer, the proton signal of cyclohexane also shifted about 20 Hz to a field lower relative to the external reference. Therefore, the differences in the shifts of the methyl groups are considered to result mainly from the use of an external reference; thus, it seems that the methyl protons are not significantly affected by the formation of methylbenzenonium ions.[14]

On the other hand, the shifts of ring protons given in Table 2 are apparently up-field shifts, considering the influence of the external reference. MacLean and his co-workers,[9] who measured the NMR spectra of a mixture of aromatic hydrocarbon and its benzenonium ion in $HF$–$BF_3$, using excess HF as the solvent at various temperatures, found that signals of the ring and the methylene protons fused into a single signal at temperatures above −30 °C; this fused signal was observed between both the resolved signals.

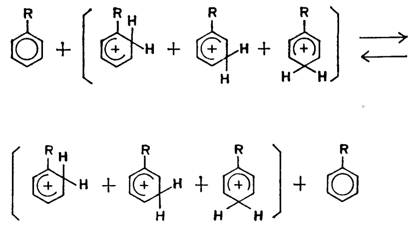
In the present observation, the up-field shift of ring protons seems to be caused by the fusing of the signals of the ring and methylene protons.[15]

The up-field shifts of the ring protons of each complex are in the following order:

Mesitylene>Hemimellitene>Pseudocumene>
*m*-Xylene>*p*-Xylene>Toluene

This order is proportional to the basicity of methylbenzenes.[2] Consequently, the proton signals of more basic benzene rings are shifted to a higher field by the fusion with the methylene signal.

The fusion of signals may result from the proton exchange. As the observed signal of the ring protons in the complex layer is a singlet, the proton exchange is considered to occur not only among the ring carbons of the same benzenonium ion intramolecularly, but also among the ring carbons of aromatic hydrocarbon and those of its benzenonium ion intermolecularly as follows:



*$^{13}$C NMR Spectra.* Figure 3 shows diagrams of the $^{13}$C NMR spectra of the starting aromatic hydrocarbons (A) and the complexes (B). Their chemical shift values are listed in Table 3. The assignments of the $^{13}$C signals of each starting aromatic hydrocarbon were determined by reference to the literature.[16–18] The assignments of signals for the ring carbons of

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[14] The lowerings of the chemical shift based on the external reference are considered to be caused by some physical factors. The volume magnetic susceptibility of aluminum chloride, considered to be one of the physical factors, was determined to be $(0.70\pm0.05)\times10^{-6}$ cgs unit (measured at 100 MHz), by using hexamethyldisilane as the reference. The magnitude of the susceptibility corresponds to a lowering of the chemical shift of about 6 Hz.

[15] M. Strohmeyer and C. Witte (*Ann. Chem.*, **729**, 21 (1969)) reported that aromatic hydrocarbon, which forms a stable methylbenzenonium ion in $AlCl_3$–$HCl$ at −30 °C, must possess at least three methyl groups at the 1,3,5-positions.

[16] P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 1838 (1961).

[17] P. C. Lauterbur, *ibid.*, **83**, 1846 (1961).

[18] W. R. Woolfenden and D. M. Grant, *ibid.*, **88**, 1496 (1966).

TABLE 3. THE $^{13}$C CHEMICAL SHIFT VALUES (ppm)$^{a)}$ OF PURE METHYLBENZENES AND THE COMPLEXES OF METHYLBENZENES WITH ALUMINUM CHLORIDE–HYDROGEN CHLORIDE

| Compound | Ring carbon position | Aromatic hydrocarbon observed value (w) | Calculated value$^{b)}$ (s) | Difference (w−s) | Complex (x) | Difference (w−x) | Methyl carbon position | Aromatic hydrocarbon observed value (y) | Complex (z) | Difference (y−z) |
|---|---|---|---|---|---|---|---|---|---|---|
| Toluene | C-1 | 55.9$^{c)}$ | 55.7 | 0.2 | 46.5 | 9.4 | 1-CH$_3$ | 172.2$^{c)}$ | 170.3 | 1.9 |
| | CH-3,5 | 64.3 | 64.3 | 0.0 | 57.8 | 6.5 | — | — | — | — |
| | CH-2,6 | 64.9 | 65.0 | −0.1 | 64.0 | 0.9 | — | — | — | — |
| | CH-4 | 67.7 | 67.8 | −0.1 | 74.2 | −6.5 | — | — | — | — |
| *p*-Xylene | C-1,4 | 58.0$^{c)}$ | 58.5 | −0.5 | 57.9 | 0.1 | 1,4-CH$_3$ | 172.1$^{b)}$ | 171.4 | 0.7 |
| | CH-2,3,5,6 | 64.5 | 64.3 | 0.2 | 63.5 | −1.0 | — | — | (168.0)$^{d)}$ | — |
| *m*-Xylene | C-1,3 | 59.6$^{c)}$ | 55.0 | 4.6 | 45.1 | 14.5 | 1,3-CH$_3$ | 172.3$^{c)}$ | 169.9 | 2.4 |
| | CH-5 | 63.2 | 63.6 | −0.4 | 56.1 | 7.1 | — | — | — | — |
| | CH-2 | 65.0 | 65.0 | 0.0 | 63.0 | 2.0 | — | — | — | — |
| | CH-4,6 | 66.9 | 67.8 | −0.9 | 71.9 | −5.0 | — | — | — | — |
| Mesitylene | C-1,3,5 | 56.4$^{c)}$ | 54.3 | 2.1 | 44.1 | 12.3 | 1,3,5-CH$_3$ | 172.2$^{c)}$ | 170.1 | 2.1 |
| | CH-2,4,6 | 66.1 | 67.8 | −1.7 | 69.8 | −3.7 | — | — | — | — |
| Pseudocumene | C-2 | 57.4 | 55.0 | 2.4 | 45.4 | 12.0 | 2-CH$_3$ | 173.5 | 171.5 | 2.0 |
| | C-4 | 58.4 | 57.8 | 0.6 | 46.0 | 12.4 | 4-CH$_3$ | 172.1 | 170.4 | 1.7 |
| | C-1 | 60.3 | 58.5 | 1.8 | 55.4 | 4.9 | 1-CH$_3$ | 173.8 | 173.3 | 0.5 |
| | CH-6 | 62.7 | 63.6 | −0.9 | 57.8 | 4.9 | — | — | — | — |
| | CH-3 | 63.8 | 64.3 | −0.5 | 64.0 | −0.2 | — | — | — | — |
| | CH-5 | 66.6 | 67.1 | −0.5 | 77.8 | −11.2 | — | — | — | — |
| Hemimellitene | C-1,3 | 57.3 | 55.0 | 2.3 | 47.6 | 9.7 | 1,3-CH$_3$ | 172.6 | 171.1 | 1.5 |
| | C-2 | 58.7 | 55.7 | 3.0 | 56.6 | 2.1 | 2-CH$_3$ | 177.8 | 177.8 | 0.0 |
| | CH-4,6 | 65.4 | 66.4 | −1.0 | 70.4 | −5.0 | — | — | — | — |
| | CH-5 | 67.8 | 67.1 | 0.7 | 60.7 | −7.1 | — | — | — | — |

a) Referred to $^{13}$CS$_2$.
b) The calculated values of the chemical shifts were based on the additivity relations reported by Savitsky[19] and by Lauterbur.[17]
c) These data were assigned with Refs. 16 and 17.
d) See footnote c, Table 2.

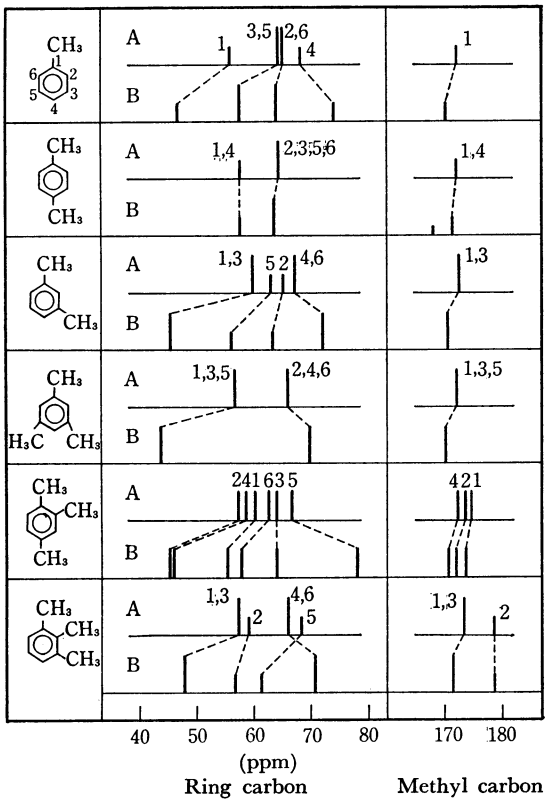

Fig. 3. The diagrams of the $^{13}$C NMR spectra of the starting aromatic hydrocarbons (A) and the complexes (B).

pseudocumene and hemimellitene, the chemical shifts of which have not been reported, were performed on the basis of the peak intensities and then by using the additivity relations of chemical shifts postulated for disubstituted benzenes by Savitsky[19] and by Lauterbur.[17] The calculated values of the chemical shifts of ring carbons based on the additivity relations are also listed in Table 3. As can be seen in Table 3, the small differences between the calculated values and the observed values indicate that the above assignments of chemical shifts are acceptable.

Each ring $^{13}$C signal of the complexes was also assigned by considering the peak intensities and the basicity of each ring carbon. The signals of each ring carbon were observed in the same order as those of the starting aromatic hydrocarbons, except for the signals of hemimellitene, which were ascertained by means of the peak intensities. On the other hand, the signals of the methyl groups were easily assigned by examining the peak intensities.

The mesitylenonium ion was independently prepared by introducing HCl gas into a mixture of mesitylene and two times as many moles of aluminum chloride in a stream of nitrogen. Figure 4 shows the diagrams of the $^{13}$C NMR spectra of mesitylene (a), the mesitylenonium ion (b), and the complex of mesitylene (c). From the spectrum of the mesitylenonium ion (b), it

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19) G. B. Savitsky, *J. Phsy. Chem.*, **67**, 2723 (1963).

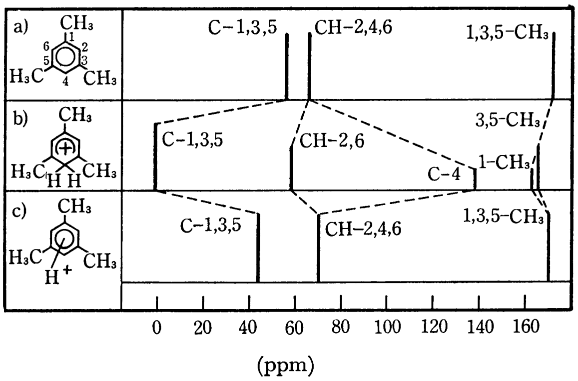


Fig. 4. The diagrams of the $^{13}C$ NMR spectra of mesitylene, the mesitylenonium ion and the complex of mesitylene.
a) mesitylene b) mesitylenonium ion ($ArH^+_2$, measured at −20 °C) c) complex ($ArH$: $ArH_2^+$)

was found that the $^{13}C$ signal of the methylene group resulted from the protonation to the C-4 ring carbon shifted to a higher field, similar to that of the alicyclic $CH_2$ group of cyclohexane (165 ppm), while the signals of the other ring carbons and of the methyl ones shifted to a lower field because of the decrease in the electron density caused by the protonation. These facts well agreed with Koptyug's findings concerning the $^{13}C$ NMR spectrum of the mesitylenonium ion. On the other hand, as is shown in Fig. 4 (c), the CH-2,6 and CH-4 signals of the complex were fused into a single signal, and all three signals of the complex shifted less than did the resolved signals of the mesitylenonium ion. These relations hold generally on the fused spectra of other complexes.

The following results were drawn from the data of the fused spectra in Fig. 3:

a) The protonation occurred more easily on the more basic ring carbon. Then the ring carbon signal shifted to a higher field.

b) The signals of the ring carbons with less basicity are shifted to a lower field by the decrease in electron density. Of course, such carbons also have a chance to be protonated, but the contribution of the protonation is less than that of the more basic carbon.

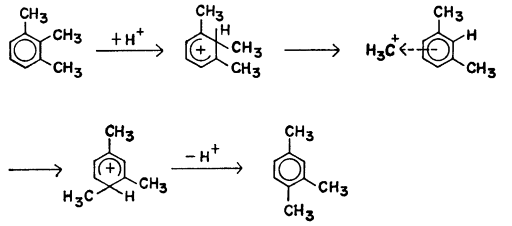
c) The methyl-substituted ring carbons are considered to be protonated to a small extent. Thus, their signals are shifted to a much lower field.

d) The signals of the methyl groups are shifted to a lower field, since the methyl groups are charged somewhat positively because of the decrease in the electron density through I- and H-effects.

*Isomerization Mechanism.* As is shown in Table 1, the complexes of some methylbenzenes, such as *p*-xylene, pseudocumene, and hemimellitene, gave small amounts of isomerized products after decomposition with water. The isomerization of methylbenzenes is known to proceed usually by means of the intramolecular 1,2-shift of methyl group;[20,21] the ease of the isomerization depends upon the ease of the protonation to the methyl-substituted carbons.

In the above three methylbenzenes, the signals of the methyl-substituted carbons showed an interesting behavior. The signals of the ring carbons, such as the C-1,4 of *p*-xylene, the C-1 of pseudocumene, and the C-2 of hemimellitene, showed small differences (w−x) compared with those of other methyl-substituted carbons. The small differences mean that such carbon atoms were protonated to a substantial extent and that then the methyl groups substituted for these atoms might have been easily rearranged to other positions. Moreover, the signals of the methyl groups attached to the above-mentioned carbons, such as the 1,4-$CH_3$ of *p*-xylene, the 1-$CH_3$ of pseudocumene, and the 2-$CH_3$ of hemimellitene, also shifted very slightly to a lower field compared with those of other methyl carbons. This finding indicates that the above methyl groups are charged less positively than the others and that, therefore, they may rearrange more easily.

The isomerization of hemimellitene is generally considered to proceed by means of the 1,2-shift of 1-$CH_3$ or 3-$CH_3$ groups. However, the above results suggest that hemimellitene may be isomerized by the rearrangement of the 2-$CH_3$ group according to the following scheme:



We are currently investigating this reaction further in an attempt to elucidate this mechanism.

The authors wish to thank Dr. Koichi Hatada of the University of Osaka for helpful discussions. The authors also wish to thank Mr. Hiroshi Okuda and Mr. Yoshio Terawaki of the University of Osaka for the measurements of the NMR spectra.

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