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The Reaction of Ethylbenzene with Methylbenzene–$AlCl_3$–HCl Complex

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Synopsis. Toluene, *m*-xylene, and mesitylene complexes prepared with $AlCl_3$ and HCl, were separated from the upper hydrocarbon layer and allowed to react with ethylbenzene at 2 and 30 °C. The proton exchange between methylbenzenium ions and ethylbenzene, and the transalkylation of ethylbenzene were investigated by ^{13}C NMR spectroscopy.

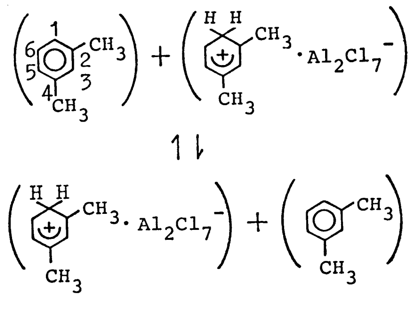
In a previous paper,[1] it was reported that methylbenzenes–$AlCl_3$–HCl complexes give fairly stable methylbenzenium ions even at room temperature due to the extraordinary stability of the methyl group for rearrangement. However, NMR spectroscopic studies[2] indicate that proton exchange between the methylbenzenium ions and their parent methylbenzenes takes place in these complex layers.

In order to clarify the behavior of the proton exchange in these complex layers, we have studied the reactions of the methylbenzenes complexes with ethylbenzene which is easily transalkylated in a strong acid.

Reaction with m*-Xylene Complex.* Equimolar ethylbenzene to *m*-xylene was added as an upper layer to a *m*-xylene complex layer prepared by the same procedure as reported.[1] The mixture was then agitated vigorously at 2 and 30 °C for 1 h. The reaction attained equilibrium. After the reaction was completed, the hydrocarbon and complex layers obtained were analyzed separately by VPC. The results are given in Table 1.

In the reaction at 2 °C no transalkylated products were obtained, no proton transfer from *m*-xylenium ion to ethylbenzene taking place in the complex layer. However, proton transfer proceeded in the reaction at 30 °C, giving di- and trisubstituted products. 5-Ethyl-*m*-xylene was obtained in a substantial amount in the complex layer. The complex layers were studied by ^{13}C NMR spectroscopy. The spectra measured at 2 and 30 °C are shown in Fig. 1.

The spectrum of the *m*-xylene complex layer (Fig. 1(a)) gave a set of fused ring signals[1] resulting from *m*-xylenium ion and *m*-xylene, indicating that fast proton exchange between *m*-xylenium ion and *m*-xylene takes place in the complex layer, as follows.[3]



The protonation of *m*-xylene probably occurs at 1- and 5-positions. The formation of 3-protonated *m*-xylene is also expected, but no evidence of the 3-protonated *m*-xylene was obtained in the spectrum.[4]

Figure 1(b) shows a spectrum of the *m*-xylene complex layer in the reaction with ethylbenzene at 2 °C. When ethylbenzene was added to the *m*-xylene complex layer, some parts of ethylbenzene were dissolved into the complex layer and some parts of unprotonated *m*-xylene were transferred to the upper hydrocarbon layer. However, no transalkylated products were obtained in the complex layer. The spectrum indicates that ethylbenzene dissolved is not protonated by proton exchanging with *m*-xylenium ion and that a set of fused ring signals of *m*-xylenium ion is found in a slightly broader range of field than that of Fig. 1(a), *viz.*, the signals of (1—1°, 5—5°) and (3—3°) are shifted to higher field, and the signals of (2—2°, 4—4°) and (6—6°) to lower field. This is because the content of unprotonated *m*-xylene in the complex layer is less than that of the initial complex layer and hence the relative intensity of ring signals of *m*-xylenium ion is enhanced in the fused signals.

On the other hand, the spectrum of the complex layer obtained at 30 °C (Fig. 1(c)) shows that the ring signals of the *m*-xylene complex have disappeared and a new set of ring signals is observed besides those of *m*-xylene and ethylbenzene.

In order to investigate the new signals, 5-ethyl-*m*-xylene was prepared with *m*-xylene and ethyl bromide by the Friedel-Crafts reaction and allowed to react with an equimolar amount of HAl_2Cl_7. The complex thus obtained consists of only 5-ethyl-*m*-xylenium ion. The NMR spectra of 5-ethyl-*m*-xylene and its complex are shown in Figs. 1(d) and (e), respectively. All the signals of 5-ethyl-*m*-xylenium ion in Fig. 1(c) show almost the same chemical shifts as those in Fig. 1(e) except for the ring methylene signal (1··) which broadens, becoming obscure (Fig. 1(c)). This indicates that no proton exchange between 5-ethyl-*m*-xylenium ion and the other alkylbenzenes occurred in the complex layer. Consequently, almost all 5-ethyl-*m*-xylene found in the complex layer was protonated, giving benzenium ion. It is of interest that no 5-ethyl-*m*-xylene was found in the upper hydrocarbon layer. On the other hand, di- and triethylbenzene were not

TABLE 1. REACTION OF ETHYLBENZENE WITH *m*-XYLENE COMPLEX LAYER (Reaction time: 1 h)

Reaction temp (°C)	Layer	Reaction products (mol%)					
		$C_6H_4Me_2$-(1,3-)	C_6H_5Et	C_6H_6	$C_6H_4Et_2$	Me_2(1,3-)-C_6H_3Et(5-)	$C_6H_3Et_3$-(1,3,5-)
2	Hydrocarbon	45.1	54.9	—	—	—	—
	complex	54.1	45.9	—	—	—	—
30	Hydrocarbon	42.2	36.4	15.1	6.3	—	—
	complex	33.2	26.5	15.0	2.6	22.4	0.3

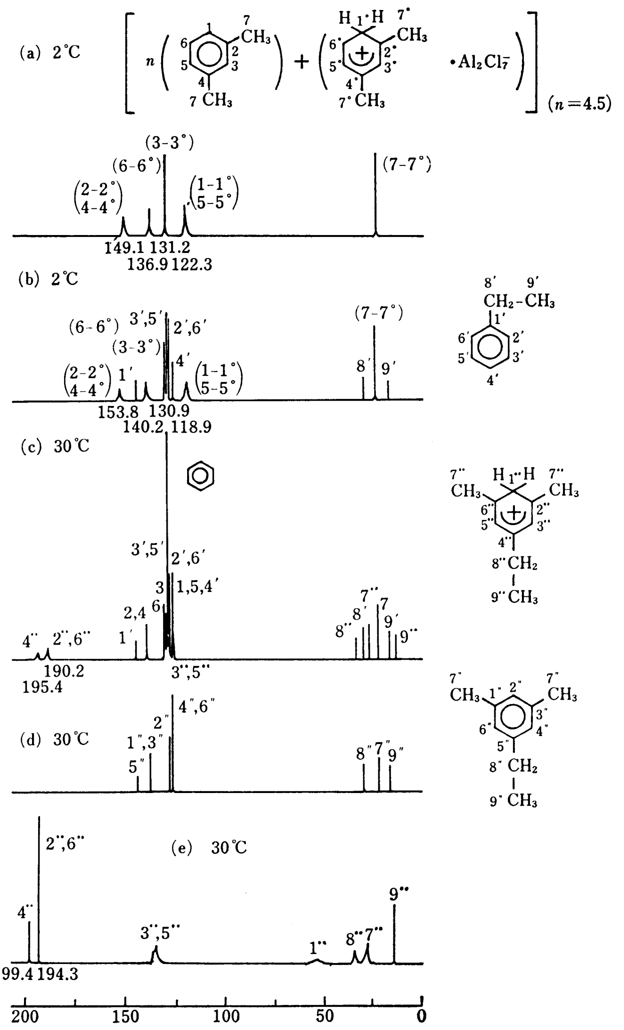


Fig. 1. ^{1}H decoupled ^{13}C NMR spectra of *m*-xylene complex layer (a), the complex layer treated with ethylbenzene for 1 h at 2 °C (b) and at 30 °C (c), 5-ethyl-*m*-xylene (d), and 5-ethyl-*m*-xylene(1 mol)-Al_2Cl_6(1 mol)-HCl complex (e).

detected in the NMR spectra owing to the small contents. Probably, the former was unprotonated and the latter gave a benzenium ion[5] such as 5-ethyl-*m*-xylene. However, the content of triethylbenzene might be too small to have serious influence on the spectrum.

Reaction with Toluene Complex. The reaction products are given in Table 2. In both the reactions at 2 and 30 °C for 1 h (equilibrium conditions), transalkylated products were obtained as in the reaction with *m*-xylene at 30 °C.

In the reaction at 2 °C, trisubstituted products were obtained in a negligible amount, disubstituted products being found predominantly in the toluene complex layer. This indicates the formation of disubstituted benzenium ions. Proton exchange occurred probably between the disubstituted benzenium ions and their parent disubstituted benzenes.

However, in the reaction at 30 °C, substantial amounts of trisubstituted products were obtained in the complex layer. Almost all the benzenium ions might arise from trisubstituted benzenes as in the reaction with the *m*-xylene complex at 30 °C. All the results were confirmed by NMR spectroscopy.

TABLE 2. REACTION OF ETHYLBENZENE WITH TOLUENE COMPLEX LAYER (Reaction time: 1 h)

Reaction temp (°C)	Layer	Reaction products (mol%)						
		C_6H_5Me	C_6H_5Et	C_6H_6	MeC_6-H_4Et	C_6H_4-Et_2	MeC_6H_3-Et_2(3,5-)	$C_6H_3Et_3$-(1,3,5-)
2	Hydrocarbon	38.8	35.3	16.0	7.8	2.1	—	—
	complex	37.1	27.8	15.1	15.0	3.0	2.0	trace
30	Hydrocarbon	35.6	22.2	27.4	12.2	2.6	—	—
	complex	31.3	15.3	26.8	10.0	2.3	11.5	2.8

Reaction with Mesitylene Complex. No transalkylation took place in both the reactions at 2 and 30 °C. Ethylbenzene was partly dissolved into the mesitylene complex layer and mesitylene was also partly transferred into the upper layer. The NMR spectrum of the complex layer shows a set of fused signals resulting from mesitylene and its ion. Proton exchange between mesitylene and mesitylenium ion then took place, but ethylbenzene remained unchanged in the complex layer. The reaction of ethylbenzene with the mesitylene complex layer was initiated at about 50 °C (for 1 h), giving a small amount of transalkylated products.

All the present reactions provide the following order in the relative stability of the methylbenzenium ions: toluenium ion<*m*-xylenium ion<mesitylenium ion. This is in line with the basicity of the parent methylbenzenes: toluene<*m*-xylene<mesitylene.[6] Thus the reactivity of the methylbenzenium ions for transalkylation shows the opposite trend.

Experimental

All alkylbenzenes used in the reaction were dried over metallic sodium and distilled prior to use. VPC analyses were performed on a Shimadzu GC-3AF chromatograph using a 3 m×3 mm column packed with Apiezon grease L (10 wt%). All the reaction mixtures were treated with water before VPC analyses. NMR spectra were obtained on a JEOL JNM-PS-100/EC-100 spectrometer equipped with a Fourier transform unit at 25.15 MHz under complete proton decoupling. The spectra were observed at 6250 Hz (data point 8191), the pulse width 12 μs (about $\pi/4$ pulse), and repetition time 6 s. The sample was placed in a 10 mmϕ tube with an internal lock standard (acetone-d_6 and TMS) in a coaxially centered capillary tube (3 mmϕ). All chemical shifts are referred to TMS standard.

References

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