tion of methyl aromatics.[14] Although the degree of deviation from first-order kinetics, *i*-propyl > ethyl > methyl, correlates inversely with basicity, the basicity differences alone are probably not large enough to account for the rate deviations. It seems more likely that the rate deviations are due to alkyl hydrogen transfer and cracking reactions.[15]

If the above values for τ are introduced into the equations for three of the four remaining trajectories, the curved lines shown on Fig. 3 are obtained. The points represent the experimental data. The agreement indicates that the relation of τ to time is fairly consistent from one reaction mixture to another. That is, although the reactions are not pseudo first order, their deviation from a pseudo-first-order rate are somewhat reproducible.

If the above treatment is applied to the equations from the rate constant set in which $k_{po} = k_{op} = 0$, Fig. 4 is obtained. The 100% *p*-trajectory was not included in either figure because its deviation from the experimental data obscured the figures without adding any useful information. If any conclusion may be drawn from the deviation of the 100% *o*-trajectory in Fig. 4, the most reasonable conclusion would be that the ratio of β to α is more accurate from the rate constants set for Fig. 3 than the rate constant set for Fig. 4. Thus, the absolute rate data tends to support the thesis that the isomerization of ethyltoluenes is not exclusively an intramolecular 1,2-shift.

(14) W. von E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(15) We wish to thank Dr. D. A. McCaulay for this explanation.

[CONTRIBUTION FROM THE POLYMER RESEARCH LABORATORY, THE DOW CHEMICAL CO., MIDLAND, MICH.]

Kinetics of Three-compound Equilibrations. IV. The Isomerization of Alkylaromatics

BY ROBERT H. ALLEN

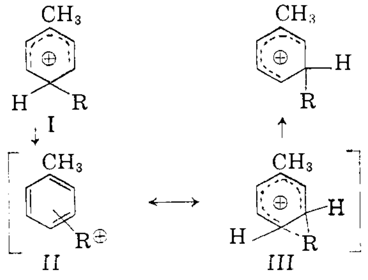
RECEIVED DECEMBER 2, 1959

The isomerization of xylene in toluene solution by the action of $AlCl_3 \cdot HCl$ has been shown to proceed by an intramolecular 1,2-shift. The present work provides evidence that under the above conditions, the isomerization of *t*-butyltoluenes proceeds by alkylation of the toluene, and the isomerization of ethyltoluenes and isopropyltoluenes proceed by both mechanisms.

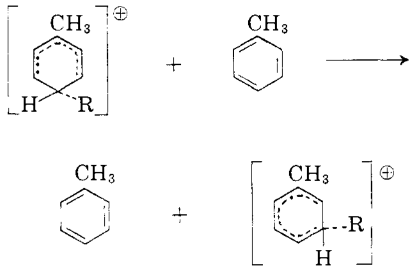
Introduction

Data presented in this paper indicate that the Friedel–Crafts positional isomerization of alkyltoluenes in toluene proceeds by either an intramolecular 1,2-shift mechanism, an alkylation–dealkylation mechanism, or both. The alkyl shift mechanism has been offered for the isomerization of xylenes.[1] The alkyl transfer mechanism is here offered for the isomerization of *t*-butyltoluenes, and a combination of both mechanisms for ethyltoluenes ane isopropyltoluenes.

The intramolecular 1,2-shift mechanism may be pictured as



The alkyl group of the aromatic σ-complex bridges two adjacent aromatic carbons and then swings over to its final position. Loss of proton yields the product. The intermolecular mechanism may be pictured as is shown in the next diagram. Nucleophilic attack by a second aromatic on the electronically deficient alkyl group of the σ-complex displaces the first aromatic ring. Loss of proton from the second aromatic ring yields the product. This mechanism is quite similar to that proposed for the disproportionation of alkylaromatics.[2]



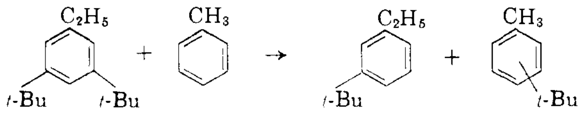
Isomerization of *t*-Butyltoluene.—The postulate that *t*-butylaromatics isomerize by alkylation-dealkylation is supported by the ease with which *t*-butyl groups split off of molecules under acidic conditions; for example, from *t*-butylbenzene[2c] and methyl pentamethylethyl ketone.[3] More direct evidence for the present argument has been reported by Schlatter.[4] The hydrogen fluoride-catalyzed reaction of 3,5-di-*t*-butylethylbenzene with toluene produced *m*-*t*-butylethylbenzene that was better than 90% pure. Thus *t*-butyl groups

(1) (a) G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 100 (1952); (b) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **74**, 6246 (1952); (c) H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955).

(2) (a) K. L. Nelson and H. C. Brown in "The Chemistry of Petroleum Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1955, p. 528; (b) A. P. Lien and D. A. McCaulay, THIS JOURNAL, **75**, 2407 (1953); (c) D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953); (d) R. E. Kinney and L. A. Hamilton, *ibid.*, **76**, 786 (1954).

(3) H. D. Zook, W. E. Smith and J. L. Greene, *ibid.*, **79**, 4436 (1957).

(4) M. J. Schlatter, U. S. Patent 2,768,985 (Oct. 30, 1956).



can be transferred from 3,5-di-*t*-butylethylbenzene to toluene under conditions that are too mild to extensively isomerize *m*-*t*-butylethylbenzene.

We have found it possible to transfer *t*-butyl groups from *p*-*t*-butyltoluene to *o*-xylene under conditions that are too mild to isomerize the *p*-*t*-butyltoluene. A reaction mixture containing a stirred solution at 0° of 4.5 moles of *o*-xylene, 0.5 mole of *p*-*t*-butyltoluene, 0.05 mole of aluminum chloride, 0.06 mole of nitromethane and anhydrous hydrogen chloride was sampled periodically and analyzed by differential infrared analysis[5] with the results given in Table I. Thus the transalkylation was orders of magnitude more rapid than the isomerization.

TABLE I

ALKYLATION OF *o*-XYLENE WITH *p*-*t*-BUTYLTOLUENE

Time, minutes	3	20	45	180
Composition, wt. %				
Toluene	0.73	3.4	5.8	8.5
3,4-Dimethyl-*t*-butylbenzene	2.3	6.9	11.5	18.6
m-*t*-Butyltoluene			0.12	0.32

The intermolecular isomerization of pure undiluted *p*-*t*-butyltoluene should not be possible, since *p*-*t*-butyltoluene cannot alkylate itself.[6] Treatment of pure *p*-*t*-butyltoluene with anhydrous HCl and one mole % aluminum chloride at 0° gave the results given in Table II.

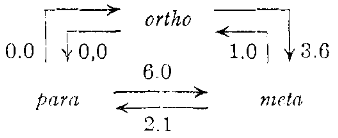
TABLE II

EFFECT OF $AlCl_3(HCl)$ ON *p*-*t*-BUTYLTOLUENE

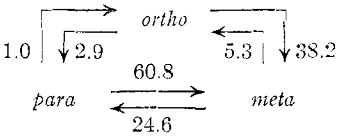
Time, minutes	1	5	15	45	90
t-Butyl chloride, wt. %	0.25	0.25	0.5	0.5	1.1
m-*t*-Butyltoluene, wt. %		Trace	0.3	0.3	1.5

Therefore *p*-*t*-butyltoluene alkylates chloride ion more readily than it undergoes isomerization intramolecularly. The toluene formed then permits intermolecular isomerization. Since the isomerization of *p*-*t*-butyltoluene in the presence of toluene under comparable conditions is essentially complete in 15 minutes, the isomerization most likely proceeds by alkylation of the toluene.

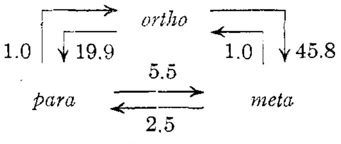
Kinetics of Alkylaromatic Isomerization.—The isomerization of alkyltoluenes in toluene with aluminum chloride activated with hydrogen chloride has been studied as three-compound isomerizations involving six rate constants.[7] The relative rate constants for the equilibration of the xylene,[8] ethyltoluenes[9] and cymenes[7] are



XYLENES



ETHYLTOLUENES



CYMENES

If an alkyltoluene isomerization were to proceed exclusively by alkylation–dealkylation, the nucleophilic displacement mechanism would require that $k_{op}/k_{om} > 0.5$, since the *p*-position of toluene, due to its higher electron density, would be more nucleophilic than the two *m*-positions. In the isomerization of xylene, $k_{op}/k_{om} = 0$, so that probably none of the isomerization is intermolecular. In the isomerization of ethyltoluene, $k_{op}/k_{om} = 0.08$, so that probably a maximum of 16% of the isomerization is intermolecular. In the isomerization of cymenes $k_{op}/k_{om} = 0.43$, so that probably a maximum of 86% of the reaction proceeds intermolecularly. The contribution of the two mechanisms to each alkyl toluene isomerization is summarized in Table III.

TABLE III

MECHANISM OF ALKYLTOLUENE ISOMERIZATION

Alkyltoluene	Intra, %	Inter, %
Xylene	100	0
Ethyltoluene	>84	<16
i-Propyltoluene	>14	<86
t-Butyltoluene	0	100

Since the change in contribution of mechanisms is much too small to account for the increase in relative rates of isomerization in the above series,[1c] the relative rates of intramolecular isomerization must increase in the order Me < Et < *i*-Pr. This order is consistent with the relative migratory rates reported for alkyl groups in the pinacol rearrangement.[10]

The direct transfer of alkyl groups between the *o*- and *p*-positions of toluene can also be explained by the intramolecular delocalized π-complex mechanism of Dewar,[11] but the alkylation–dealkylation mechanism seems preferable for two reasons. First, the evidence that *t*-butyltoluene isomerizes by the alkylation–dealkylation mechanism is fairly compelling. Second, in the study of the three-compound equilibration of xylene, when xylene was isomerized without using toluene as a diluent, the xylene disproportionated at a rate

---

[5] L. W. Herscher, H. D. Ruhl and N. Wright, *J. Opt. Soc. Am.*, **48**, 36 (1958).

[6] M. J. Schlatter and R. D. Clark, THIS JOURNAL, **75**, 361 (1953); M. J. Schlatter, *ibid.*, **76**, 4952 (1954).

[7] R. H. Allen, T. Alfrey, Jr., and L. D. Yats, *ibid.*, **81**, 42 (1959).

[8] R. H. Allen and L. D. Yats, *ibid.*, **81**, 5289 (1959).

[9] R. H. Allen, L. D. Yats and D. S. Erley, *ibid.*, **82**, 4853 (1960).

[10] M. Stiles and R. P. Mayer, *ibid.*, **81**, 1497 (1959).

[11] M. J. S. Dewar, in "Theoretical Organic Chemistry," Butterworths Publication, London, 1959, p. 179.

comparable to the isomerization rate.[8] Thus, even the alkyltoluene with least tendency to isomerize intermolecularly disproportionates under conditions only slightly more drastic than those required for isomerization.

Discussion

It is reasonable to assume that in the alkylaromatic σ-complex I, the electron deficiency is distributed between the alkyl group and the aromatic ring. For a given aromatic ring the electron deficiency on the alkyl group should increase in the order Me<Et<*i*-Pr<*t*-Bu since this is the order of carbonium ion stability. Furthermore, the greater the electron deficiency on the alkyl group, the more nearly will the α-carbon approach a trigonal configuration, and the weaker the alkyl to aromatic bond should be. All three factors would tend to facilitate a nucleophilic displacement of the aromatic ring by a second aromatic ring. Thus the fact that the relative rates of isomerization[1c] and disproportionation[12] of alkyl aromatics increase in the above order can be rationalized.

Since the above order of alkyl group electron deficiency is the reverse of the order of relative aptitude for intramolecular *vs.* intermolecular isomerization (Table III), the ability of an alkyl group to stabilize a positive charge does not facilitate the alkyl shift as much as it does the alkyl transfer. Therefore it appears likely that some structure such as III which does not involve a positive charge on the alkyl group contributes to the stability of the intermediate in the intramolecular 1,2-shift. This structure is similar to those postulated for Wagner–Meerwein type rearrangements and may be described as an internal electrophilic aliphatic displacement. The contribution of such a structure is consistent with the reported order of relative rates for electrophilic aliphatic substitution[13] (Me < Et < *i*-Pr), and the stereochemistry of electrophilic aliphatic substitution[14] (retention of configuration). The contribution of such a structure appears to conflict with the reported ability of aluminum alkyls to dimerize, Me> Et> *i*-Pr.[15] But since the dimer structure requires aluminum to accommodate four alkyl groups rather than three, the above order may well be a B-strain effect.[16]

Thus the intermolecular mechanism for alkylaromatic positional isomerization bears a resemblance to the mechanism for SN1 solvolyses, and the intramolecular mechanism bears some resemblance to the mechanism for SE2 displacements.

Experimental

The experimental procedures were similar to those used previously.[7-9] The toluene and *o*-xylene and anhydrous hydrogen chloride were commercial grade materials. The *p*-*t*-butyltoluene was obtained by fractionation of commercial material and contained no impurities that could be detected by infrared analysis. The aluminum chloride was Baker and Adams powdered anhydrous reagent grade.

Acknowledgment.—The author is indebted to D. S. Erley of the Dow Spectroscopy Department for the infrared data.

---

[12] G. Baddeley, *Quart. Revs.*, **8**, 355 (1954).

[13] R. E. Dessy and T. J. Flautt, Abstracts of the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 83-O.

[14] F. R. Jensen, L. H. Gale, L. D. Whipple and D. Wedergaertner, *ibid.*, p. 80-O; H. B. Charman, *ibid.*, p. 81-O.

[15] K. S. Pitzer and H. S. Gutowsky, THIS JOURNAL, **68**, 2204 (1946).

[16] H. C. Brown, *Science*, **103**, 385 (1946); H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF NEW SOUTH WALES, SYDNEY, AUSTRALIA]

The Effects of *m*-Substituents on the pK_a Values of Anilines, and on the Stretching Frequencies of the N–H Bonds

BY A. BRYSON

RECEIVED OCTOBER 14, 1959

The pK_a values and N–H stretching frequencies of 19 anilines substituted in the 3- and 3,5-positions have been determined and a statistical analysis carried out to determine whether the ΔpK_a–σ_m relationships are significantly different for substituents with –M and +M character. The test is inconclusive, but it is shown that the regression coefficient ρ for all substituents is greater than previously supposed, and that the regression line does not pass through the origin. The relation between pK_a values and N–H frequencies is linear for *m*-substituents.

In the two following papers, the effects of substituents on the pK_a values of 1- and 2-naphthylamines, pyridines, quinolines and isoquinolines will be examined, and in the case of the naphthylamines some unexpected relations between pK_a values and N–H frequencies will be presented. For the purposes of comparison between the relative effects of substituents, especially in the "*meta*" positions in these compounds, upon which with other evidence a new theory of substituent action will be proposed, it was necessary to have an accurate picture of the effects of *m*-substituents on the pK_a values of anilines, and this paper will survey the available evidence and will present new and supplementary data on 22 anilines substituted in the 3- and 3,5-positions.

Results and Discussion

Table I gives the experimental results; pK_a values previously recorded are shown in column 3, and recently published values for the N–H frequencies of substituted anilines are shown in parentheses.

Discussion

pK_a Relationships.—The relation between the ΔpK_a ($= \log K/K_0$) values of *m*- and *p*-substituted anilines and the substituent constants σ originally formulated by Hammett was reinvestigated