

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Disproportionation of Alkylbenzenes. II. Mechanism of Alkyl-group Transfer

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The mechanism of alkyl-group transfer has been studied by the disproportionation of six alkylbenzenes in the presence of hydrogen fluoride and boron trifluoride. In experiments at room temperature with alkylbenzenes containing *n*-propyl, *n*-butyl and *s*-butyl groups, the alkyl group maintained its configuration while transferring from one ring to another. A bimolecular mechanism is followed wherein the migrating alkyl group, before its bond with the first ring is broken, forms a partial bond to the second arene. In support of this theory, ethylbenzene was about 90% disproportionated at room temperature, whereas neopentylbenzene was unconverted. Presumably the *t*-butyl segment of the neopentyl group sterically interferes with the back-side approach of the attacking arene and thereby prevents reaction. At higher temperatures, experiments with *t*-butylbenzene and hexaethylbenzene showed that the mechanism changes. The arene cation dissociates unimolecularly into an arene and an alkylcarbonium ion. The carbonium ion then reacts by isomerization, alkylation, polymerization and hydride-ion abstraction to yield a complex product.

Alkylation of arenes with alkyl halides in the presence of a Friedel-Crafts catalyst has been shown¹ to proceed by way of either a unimolecular (S_N1) or a bimolecular (S_N2) nucleophilic displacement mechanism,² the path depending upon the temperature and the nature of the catalyst and alkylating agent. However, the mechanism of the related reaction, alkylbenzene disproportionation, has not been established with the same certainty.

Heise³ and Baddeley and Kenner⁴ reported that disproportionation of *n*-propylbenzene into benzene and dipropylbenzene, with aluminum chloride, involves no modification of the propyl group. This evidence favors an S_N2 mechanism. Nightingale and Smith,⁵ on the other hand, found that, when 1,3-dimethyl-4-butylbenzenes were heated with aluminum chloride to form the 1,3-dimethyl-5-butylbenzenes, the migrating butyl groups isomerized. This finding supports an S_N1 mechanism in which the migrating alkyl group forms a carbonium ion intermediate.

Recent studies in our laboratories of alkylbenzene disproportionation with $HF-BF_3$ provide some insight into the nature of the reaction and may help to resolve the hitherto contradictory hypotheses concerning mechanism.

Experimental

Ethylbenzene, isopropylbenzene, *s*-butylbenzene and hexaethylbenzene (Eastman Kodak Co. White Label grade), after spectrometric analysis, were used without further purification. Eastman *n*-propylbenzene was fractionated through a Podbielniak Hypercal distillation column, and a 159–160° fraction was selected. Neopentylbenzene was prepared by the reaction of *t*-butyl bromide with benzylmagnesium chloride⁶; the product was fractionally distilled and the fraction boiling at 188° (n_D^{20} 1.4871) was chosen. The hydrogen fluoride and boron trifluoride were commercial grades of 99.6 and about 99% purity, respectively, and were obtained from the Harshaw Chemical Company.

The six alkylbenzenes were disproportionated by treatment with hydrogen fluoride and boron trifluoride in the manner previously described.⁷ In each case the hydrocar-

bon was stirred with the catalyst under controlled conditions and, after a predetermined time, the entire mixture was withdrawn into crushed ice. The hydrocarbon product was fractionated through a column of thirty theoretical plates. The successive carbon-number fractions were identified by their physical properties and by spectrometric analysis.

Results and Discussion

The experiments reported in Table I, carried out at or below room temperature, show that the alkyl groups maintained their configuration while transferring from one ring to another. Thus, in experiment 1, *n*-propylbenzene produced di-*n*-propylbenzene; in experiment 3 a mixture of *n*-butylbenzene and *s*-butylbenzene gave only normal and secondary polybutylbenzenes. Identification of the polyalkylbenzene products was confirmed by reverse-disproportionation experiments 2 and 4, in which each of the polyalkylbenzene fractions reacted with benzene. The only monoalkylbenzene products were *n*-propyl-, *n*-butyl- and *s*-butylbenzene. No rearrangement of alkyl groups occurred in either the forward or the reverse direction.

TABLE I

TRANSFER OF NORMAL AND SECONDARY ALKYL GROUPS				
Experiment number	1	2	3	4
Alkylbenzene	<i>n</i> -Propyl ^a	Di- <i>n</i> -propyl ^b	<i>s</i> -Butyl ^d	Poly-butyl ^e
Moles	2.16	0.19	1.47	0.33
Benzene, moles/mole alkylbenzene	0	9.05	0	6.75
BF_3 , moles/mole alkylbenzene	0.32	0.08	0.38	0.06
HF , moles/mole alkylbenzene	3	6	6	6
Temperature, °C.	5	23	26	23
Reaction time, min.	10	60	5	60
Product distribution, mole %				
Benzene	19.9	88.1	36.7	75.8
Mono- <i>n</i> -alkylbenzene	59.3	2.1 ^c	10.9	3.9 ^f
Mono- <i>s</i> -alkylbenzene	0.0	0.0	21.8	15.2 ^f
Di- <i>n</i> -alkylbenzene	19.4	9.8		4.7
Di- <i>s</i> -alkylbenzene	0.0	0.0	30.6	
Tri- <i>n</i> -alkylbenzene	1.4	0.0		
Tri- <i>s</i> -alkylbenzene	0.0	0.0		0.4
	100.0	100.0	100.0	100.0

^a B.p. 159–160°, n_D^{20} 1.4932. ^b Product of experiment 1, b.p. 220–222°, n_D^{20} 1.4905. ^c B.p. 160°, n_D^{20} 1.4922. Infrared analysis showed no isopropylbenzene. ^d Infrared analysis showed composition to be 80% *s*-butylbenzene, 20% *n*-butylbenzene. No *t*-butyl- or isobutylbenzene present. ^e Product of experiment 3. ^f Infrared analysis showed no *t*-butyl- or isobutylbenzene present.

(1) H. C. Brown, L. P. Eddy, W. J. Wallace, J. Grayson and K. L. Nelson. Presented before the Division of Petroleum Chemistry, Catalysis Symposium, Sept. 14–19, 1952, (Preprint).

(2) The terms S_N1 and S_N2 are defined by E. D. Hughes, *J. Chem. Soc.*, 968 (1946).

(3) R. Heise, *Ber.*, **24**, 768 (1891).

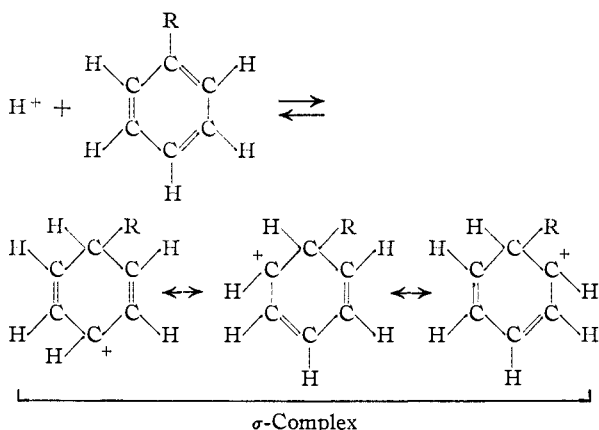
(4) G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303 (1935).

(5) D. Nightingale and L. J. Smith, *THIS JOURNAL*, **61**, 101 (1939).

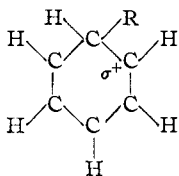
(6) A. Bygden, *Ber.*, **45**, 3479 (1912).

(7) D. A. McCaulay and A. P. Lien, *THIS JOURNAL*, **74**, 6246 (1952).

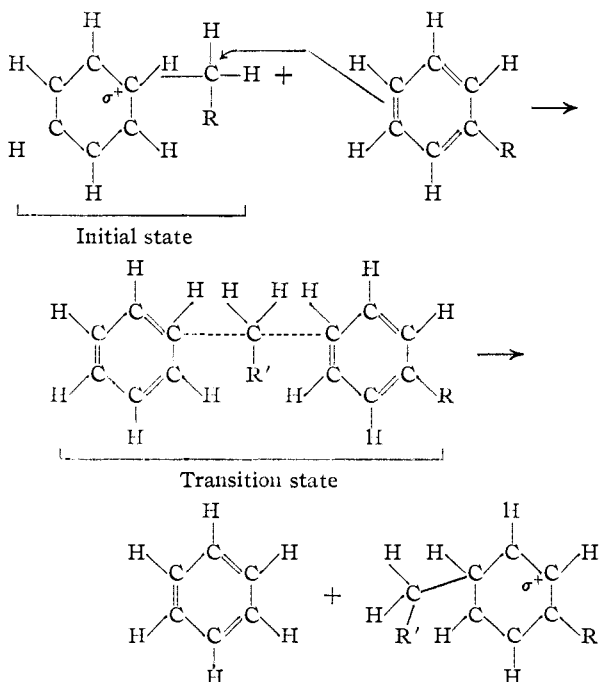
These results indicate that the migrating alkyl group, before its bond with the first ring was broken, formed a partial bond to the second aromatic ring. Otherwise the free alkyl carbonium ion would have isomerized to the more stable secondary or tertiary configuration. The following mechanism is therefore proposed: The first step is the rapid and reversible addition of a proton, furnished by the acid catalyst, to the alkylbenzene at the ring carbon atom holding one of the alkyl groups. The aromatic cation formed is a σ -complex⁸



The σ -complex, for convenience, is denoted by the shortened form



The second step is an S_N2 displacement of an arene from the cation by another arene



(8) H. C. Brown and J. D. Brady, *THIS JOURNAL*, **74**, 3570 (1952).

Methyl substitution at the α -carbon atom of the migrating alkyl group increases the stability of the transition state because of resonance by hyperconjugation. This lowering of the transition-state energy accounts for the fact that ethylbenzene disproportionates more readily than toluene, and *t*-butylbenzene more readily than ethylbenzene.^{9,10}

This bimolecular theory of disproportionation was tested by the experiments of Table II wherein neopentylbenzene and ethylbenzene were treated under almost identical conditions with HF-BF_3 . The neopentylbenzene was unconverted, whereas ethylbenzene was about 90% disproportionated into benzene and diethylbenzene. This difference in behavior is in accord with the bimolecular mechanism. The *t*-butyl segment of the neopentyl group sterically interferes with the back-side approach of the attacking benzene ring to the α -carbon atom of the neopentyl group.

TABLE II
TRANSFER OF ETHYL AND NEOPENTYL GROUPS
8 moles HF /mole hydrocarbon, 5°, 10-min. reaction time

Experiment number	5	6
Arene, benzene	Ethyl-	Neopentyl-
BF_3 , moles/mole arene	0.80	1.15
Product distribution, mole %		
Benzene	41	0
Monoalkylbenzene	10	100
Dialkylbenzene	49	0

Although simple disproportionation appears to be a bimolecular reaction, there are conditions under which alkyl-group elimination from the aromatic cation can occur by an S_N1 mechanism. The reaction is then much less specific than simple disproportionation, as is illustrated by the experiments reported in Table III. At 25°, hexaethylbenzene is inert to HF-BF_3 ; this result is expected because no aromatic hydrocarbons containing

TABLE III
 S_N2 vs. S_N1 DISPROPORTIONATION

Experiment number	7	8	9	10
Arene, benzene	Hexaethyl-	Hexaethyl-	<i>t</i> -Butyl-	<i>t</i> -Butyl-
BF_3 , moles/mole arene	0.48	1.3	0.46	0.58
HF , moles/mole arene	10	10	5	5
Temperature, °C.	25	166	45	0
Reaction time, min.	10	30	10	10
Product distribution, mole %	^a	^b	^c	^c
Benzene	0	0	60	52
Monoalkylbenzene	0	22	5	19
Dialkylbenzene	0	11	13 ^c	9 ^d
Trialkylbenzene	0	11	11 ^c	20 ^e
Tetraalkylbenzene	0	15	11 ^c	...
Pentaalkylbenzene	0	}41
Hexaalkylbenzene	100	

^a About 5 wt. % of the starting material was recovered as ethane and isobutane, and 15 wt. % as tar. ^b About 15 wt. % of starting material was recovered as isobutane. ^c Identity of these three fractions not established; ultraviolet absorption studies indicate they may be β -methylstyrenes. ^d 1,3-Di-*t*-butylbenzene. ^e 1,3,5-Tri-*t*-butylbenzene.

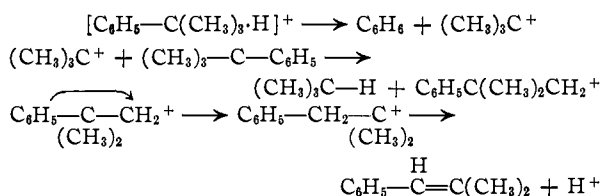
(9) A. P. Lien and D. A. McCaulay, *ibid.*, **75**, 2407 (1953).

(10) This order is the reverse of that met in ordinary S_N2 reactions. In these cases, however, the replacing and replaced groups are negative ions; the transition state therefore bears a negative charge. Resonance by hyperconjugation, then, increases the charge separation. It does not distribute the charge as is true in the present case in which the transition state bears a positive charge.

replaceable hydrogen are present to take part in the bimolecular displacement reaction. However, at 166°, hexaethylbenzene reacts to give ethane, isobutane, ethylbenzene, polyethylbenzenes and tar. Under severe conditions, ethylcarbonium ions appear to split off from the aromatic cation. Some of these highly reactive ions abstract a hydride ion from an alkyl side-chain and are converted to ethane. Some dissociate to a proton and ethene; others, after reaction with ethene, form isobutane. The hydrogen-poor alkylaromatics condense to tar.

The change in mechanism with increase in temperature is also illustrated by experiments 9 and 10. At 0°, *t*-butylbenzene disproportionates smoothly into benzene, 1,3-di-*t*-butylbenzene and 1,3,5-tri-*t*-butylbenzene.¹¹ However, at 45°, *t*-butylbenzene forms a complicated mixture including isobutane, benzene and β -alkylstyrenes boiling mostly in the range 220 to 280°. Hydrogen-transfer reactions occur, possibly according to the scheme

(11) This material, a white crystalline solid, m.p. 73°, b.p. 248°, is apparently a new compound not previously reported in the literature. Evidence for its identification will be presented in a subsequent paper.



The mechanism of alkyl-group transfer in disproportionation reactions therefore depends upon the severity of reaction conditions. Under moderate conditions, simple alkyl disproportionation is a bimolecular reaction between an aromatic cation and a neutral aromatic molecule. Under severe conditions, the aromatic cation dissociates unimolecularly into a neutral aromatic molecule and an alkyl carbonium ion. The carbonium ion then reacts further by isomerization, alkylation, polymerization and hydride-ion abstraction. Disproportionation by the unimolecular mechanism is accompanied by a considerable amount of side reaction and may lead to a complex product.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK & CO., INC.]

Reduction of Lactones to Hydroxyaldehydes with Lithium Aluminum Hydride

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The addition of a solution of one-fourth of a mole of lithium aluminum hydride to a solution of one mole of α -methyl- δ -caprolactone has provided a good yield of α -methyl- δ -hydroxycaproaldehyde. The latter compound was dehydrated to 3,4-dihydro-2,5-dimethyl-2,5H-pyran. This new partial reduction reaction has been successfully applied to γ -valerolactone and (-)- α -hydroxy- β , β -dimethyl- γ -butyrolactone (pantoyllactone).

Hexoses have been prepared in a practical manner by the partial reduction of polyhydroxy- γ -lactones with sodium amalgam.¹ This partial reduction fails when applied to non-hydroxylated lactones.² Lithium aluminum hydride³ in excess reduces saturated γ - and δ -lactones to 1,4- and 1,5-diols, respectively. The same reagent is reported⁴ to reduce α -angelica lactone to γ -acetopropanol and β -angelica lactone to the diol. In 1949, Friedman⁵ described an interesting partial reduction of amides and nitriles to aldehydes. Similarly Claus and Morgenthau⁶ disclosed the partial reduction of orthoesters to the corresponding acetals using lithium aluminum hydride and Wolfrom and Wood⁷ used sodium borohydride to replace sodium amalgam in the classical partial reduction of sugar lactones.

An attractive synthesis of γ - and δ -hydroxyaldehydes would be provided by a partial reduction of the corresponding lactones. The latter are, in

many cases, readily prepared. For this partial reduction to be successful the intermediate must be less easily reduced than the starting lactone. It is clear that an aldehyde would not fulfill this condition. However, should an intermediate in this reduction, such as II (R = LiAlH₄), arising from I by addition of lithium aluminum hydride to the lactone carbonyl,⁸ prove more resistant to reduction than the starting lactone, or if an intermediate should precipitate then the desired effect could be achieved. *The addition of lithium aluminum hydride to the lactone* (one-fourth mole of reducing agent per mole of lactone) *does indeed effect the desired partial reduction in good yield.* Since all of the available hydrogen is used, it would appear that II (R = LiAlH₄) is first formed, is soluble, and reacts successively with three more molecules of lactone until V (whatever its fine structure) is formed and precipitates. The hydroxyaldehydes are isolated by extraction of the acidified reaction mixture and purified by distillation. In this manner α -methyl- δ -caprolactone (I) was reduced to α -methyl- δ -hydroxycaproaldehyde (II, R = H) or IIa; γ -valerolactone gave γ -hydroxyvaleraldehyde (III, R = H) or IIIa; (-)- α -hydroxy- β , β -dimethyl- γ -butyrolactone (pantoyllactone) gave α , γ -dihydroxy- β , β -dimethylbutyraldehyde (one-half mole of lithium aluminum hydride per mole of lactone was used in this case). All of the hydroxy-

(1) Cf. E. Fischer, *Ber.*, **22**, 2204 (1889); N. Sperber, H. Zaugg and W. Sandstrom, *THIS JOURNAL*, **69**, 915 (1947).

(2) F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1931, pp. 146, 420-444.

(3) W. G. Brown in R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.

(4) F. A. Hochstein, *THIS JOURNAL*, **71**, 305 (1949).

(5) L. Friedman, Abstracts of Papers, 116th Meeting A.C.S., Sept., 1949, p. 5M.

(6) C. J. Claus and J. L. Morgenthau, Jr., *THIS JOURNAL*, **73**, 5005 (1951).

(7) M. L. Wolfrom and Harry B. Wood, *ibid.*, **73**, 2933 (1951).