

change in absorbance. No CO<sub>2</sub> evolution was observed, and attempts to isolate a crystalline product were unsuccessful.

**Reaction of 4,4'-Dihydroxychalcone with HNO<sub>2</sub>.**—To a solution of 4,4'-dihydroxychalcone<sup>15</sup> (2 g., 0.0083 mole) in dioxane (60 ml.) was added a solution of NaNO<sub>2</sub> (1.2 g., 0.0174 mole) in 60 ml. of water. The mixture was acidified with 5 N HCl to pH 2 and shaken for 3 hours at room temperature, and the crystalline precipitate that separated was filtered, washed with water and ethanol, and dried; m.p. 287–290°. Additional material (m.p. 285–290°) crystallized from the filtrate when it was allowed to stand at room temperature for 8 hours. The orange-red product (total yield 1.25 g.) was recrystallized twice from ethyl acetate-benzene; m.p. 290°. Calcd. for C<sub>15</sub>H<sub>11</sub>NO<sub>5</sub> (285.3): C, 63.2; H, 3.9; N, 4.9. Found: C, 63.0; H, 4.1; N, 4.7.

On acetylation of 0.1 g. of the product with 4 ml. of acetic anhydride in the presence of 0.25 g. of sodium acetate, a crystalline product (0.1 g., m.p. 160°) was obtained. Calcd. for C<sub>19</sub>H<sub>15</sub>NO<sub>7</sub> (369.3): C, 61.7; H, 4.1; N, 3.8. Found: C, 62.0; H, 4.1; N, 3.7.

On methylation of 0.2 g. of the product with 0.4 ml. of dimethyl sulfate in the presence of methanolic KOH, the dimethoxy derivative was obtained. After recrystallization from methanol, it melted at 167° dec. Calcd. for C<sub>17</sub>H<sub>13</sub>NO<sub>5</sub> (313.3): N, 4.5. Found: N, 4.5. A mixed m.p. determination with an authentic sample of 4,4'-dimethoxy-3-oximinoflavanone<sup>11</sup> (m.p. 168–170° dec.) gave a melting point of 140–143°, showing that the two compounds are not identical.

Alkaline degradation of the product (1 g.) with 50% KOH

(15) T. A. Geissman and R. O. Clinton, *THIS JOURNAL*, **68**, 697 (1946).

(25 ml.) at 170–180° for 3 hours, followed by neutralization with CO<sub>2</sub>, and extraction with ether, gave, upon evaporation of the ethereal solution, *p*-hydroxyacetophenone (m.p. 105°, no depression of mixed m.p. with an authentic sample). The neutralized aqueous solution was acidified and extracted with ether; evaporation of the ethereal extract gave 3-nitro-4-hydroxybenzoic acid (m.p. 183°, reported<sup>16</sup> 183°). Calculated for C<sub>7</sub>H<sub>5</sub>NO<sub>5</sub> (183.1): C, 45.9; H, 2.7; N, 7.6. Found: C, 46.1; H, 2.7; N, 7.4. The structure of the product obtained by treatment of 4,4'-dihydroxychalcone with HNO<sub>2</sub> is therefore 3'-nitro-4,4'-dihydroxychalcone. The dimethoxy derivative of this compound has been reported to melt at 160° dec.<sup>17</sup>

**Reaction of 2,4'-Dihydroxychalcone with HNO<sub>2</sub>.**—This chalcone<sup>14</sup> was treated with HNO<sub>2</sub> in the same manner as the 4,4'-isomer to yield 1.8 g. of a product which, after recrystallization from ethanol, melted at 230°. Calcd. for C<sub>15</sub>H<sub>11</sub>NO<sub>5</sub> (285.3): C, 63.2; H, 3.9; N, 4.9. Found: C, 62.9; H, 4.1; N, 4.8. On acetylation, the diacetate (m.p. 93–94°) was obtained. Calcd. for C<sub>19</sub>H<sub>15</sub>NO<sub>7</sub> (369.3): N, 3.7. Found: N, 3.8. On degradation with alkali as above, followed by acidification and steam distillation, *o*-hydroxyacetophenone was identified by its ultraviolet absorption spectrum (as compared with that of an authentic sample); after extraction of the residue with ether, 3-nitro-4-hydroxybenzoic acid (m.p. 183°) was isolated, indicating that the product of the reaction with HNO<sub>2</sub> is 3'-nitro-2,4'-dihydroxychalcone.

(16) P. Griess, *Ber.*, **20**, 408 (1887).

(17) P. Pfeiffer and B. Segall, *Ann. Chem.*, **460**, 130 (1928).

NEW HAVEN, CONN.

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

## Disproportionation of Alkylbenzenes. IV. Ethylbenzene and Diethylbenzene

By D. A. McCaulay and A. P. Lien

RECEIVED MAY 27, 1957

In the presence of hydrogen fluoride plus excess boron trifluoride, ethylbenzene disproportionates rapidly and soon reaches a primary equilibrium having the composition: benzene, 45%; ethylbenzene, 10%; *m*-diethylbenzene, 45%. Little triethylbenzene is formed because the *m*-diethylbenzene takes on a proton and is tied up as a positively charged complex. However, at higher temperatures or after longer times diethylbenzene gradually reacts and a new equilibrium is slowly approached containing four components: benzene, ethylbenzene, 1,3-diethylbenzene and 1,3,5-triethylbenzene. The equilibrium composition is found to be a function of the number of ethyl groups per benzene ring in the starting hydrocarbon mixture.

Ethylbenzene, in the presence of hydrogen fluoride plus excess boron trifluoride, disproportionates rapidly and almost completely at room temperature into benzene and *m*-diethylbenzene.<sup>1</sup> The completeness of reaction and the production of the *meta* isomer were attributed to the preferential formation of a complex of *m*-diethylbenzene with HF-BF<sub>3</sub>. Although diethylbenzene as well as ethylbenzene should accept alkyl groups, no triethylbenzene was formed. This result was surmised to be a rate rather than an equilibrium effect. As part of a continued study of the reaction, therefore, ethylbenzene and diethylbenzene were disproportionated with longer reaction times and at higher temperatures. Under these more vigorous reaction conditions the product distribution was found to be different and to be a function of the ratio of ethyl groups to benzene rings present.

### Experimental

Ethylbenzene, diethylbenzenes and triethylbenzenes from Eastman Kodak Co. were used without further purification.

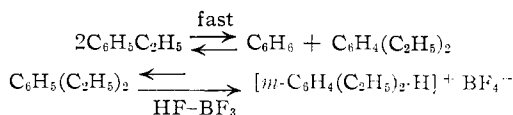
(1) D. A. McCaulay and A. P. Lien, *THIS JOURNAL*, **75**, 2407 (1953); (III) **76**, 2354 (1954); (V) **79**, 5808 (1957).

Commercial grades of hydrogen fluoride, 99.6% pure, and boron trifluoride, about 99% pure, were obtained from the Harshaw Chemical Co.

The experiments were carried out in a 1000-ml. Hastelloy autoclave fitted with a 1725-r.p.m. stirrer. Hydrocarbon, hydrogen fluoride and boron trifluoride were charged to the autoclave and the mixture was stirred at a controlled temperature. After reaction, the entire contents were withdrawn into crushed ice. The hydrocarbon product was separated into successive carbon-number fractions by distillation through a column of thirty theoretical plates. Individual fractions were identified by their physical properties and by spectrometric analysis.

### Discussion

The results obtained on treating ethylbenzene with hydrogen fluoride plus a large excess of BF<sub>3</sub> are given in Table I. At low temperatures and short reaction times the products are benzene and *m*-diethylbenzene. At higher temperatures and at longer times, triethylbenzene appears and approaches 25 mole % of the mixture. The explanation for this behavior is that the first step reaches equilibrium rapidly; because a large excess of BF<sub>3</sub> is used, most of the primary product, *m*-diethylbenzene, is tied up as a positively charged aronium ion.



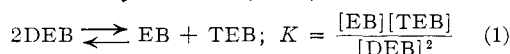
This cation will not accept a migrating positively charged ethyl group. The concentration of uncomplexed diethylbenzene relative to ethylbenzene is so low that the rate of formation of triethylbenzene is slow. But if reaction time is lengthened, or if all reactions are accelerated by an increase in temperature, more and more diethylbenzene reacts and equilibrium amounts of triethylbenzene are gradually approached. The 1,3,5-trialkylbenzenes are extremely basic<sup>2</sup> and,

TABLE I  
DISPROPORTIONATION OF ETHYLBENZENE AND  
200 VOL. % HF

Temp., °C.	11	37	80	25
Reaction time, min.	30	5	60	5640
Moles BF <sub>3</sub> per mole ethylbenzene	1.1	1.2	1.2	1.0
Product distribution, mole %				
Benzene	45	45	47	58
Ethylbenzene	10	10	9	3
1,3-Diethylbenzene	45	45	40	14
1,3,5-Triethylbenzene	0	Trace	4	25

once formed, are almost completely tied up as an aronium ion. Further reaction to tetraalkylbenzenes is much slower, therefore, than is the reaction by which trialkylbenzenes are formed.

In Table II are given the results of treating either diethylbenzene or an equimolar mixture of ethylbenzene and triethylbenzene under conditions which bring about disproportionation equilibrium. The apparent equilibrium constant for the conversion of diethylbenzene (DEB) into ethylbenzene (EB) and triethylbenzene (TEB)



does not change much with BF<sub>3</sub> concentration. Contrary to what was observed with ethylben-

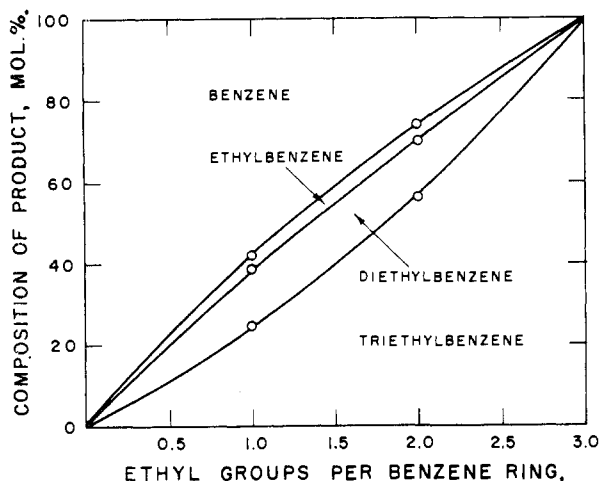


Fig. 1.—Equilibrium product distribution.

(2) D. A. McCaulay and A. P. Lien, *THIS JOURNAL*, **73**, 2013 (1951).

zene,<sup>1</sup> the equilibrium is not appreciably shifted by selective complex formation with a proton. Both diethylbenzene and triethylbenzene form complexes (DEB, H<sup>+</sup> and TEB, H<sup>+</sup>) in the presence of excess BF<sub>3</sub>, but because they are on opposite sides of the equation, the effects seem to cancel.

TABLE II  
DISPROPORTIONATION OF DIETHYLBENZENE AND  
150 VOL. % HF

Feed composition, mole %			
Ethylbenzene	...	...	50
Diethylbenzene	100	100	...
Triethylbenzene	...	...	50
Temp., °C.	80	25	25
Reaction time, min.	30	2880	4320
Moles BF <sub>3</sub> per mole arene	1.3	0.26	0.28
Product distribution, mole %			
Benzene	25	5	2
Ethylbenzene	4	24	32
Diethylbenzene	13 <sup>b</sup>	35 <sup>c</sup>	30 <sup>c</sup>
Triethylbenzene	55 <sup>d</sup>	35 <sup>e</sup>	36 <sup>e</sup>
Tetraethylbenzene	3	Trace	Trace
App. equil. constant <sup>a</sup>	1.3	0.7	1.3

<sup>a</sup> For the disproportionation of diethylbenzene into ethylbenzene and triethylbenzene. <sup>b</sup> 100% 1,3-diethylbenzene. <sup>c</sup> Mixed diethylbenzenes. <sup>d</sup> 100% 1,3,5-triethylbenzene. <sup>e</sup> Mixed triethylbenzenes.

#### Calculation of Equilibrium Product Distributions

Knowledge of the equilibrium constants for disproportionation of diethylbenzene and of ethylbenzene<sup>1</sup> provide information needed for calculating the product distribution expected on treating any mixtures of benzene, ethylbenzene, diethylbenzene and triethylbenzene with HF and excess BF<sub>3</sub>. The equilibrium constants for two disproportionation reactions are

$$\frac{[\text{B}][\text{DEB}]}{[\text{EB}]^2} = 0.25$$

$$\frac{[\text{EB}][\text{TEB}]}{[\text{DEB}]^2} = 1$$

Multiplication of the first by the second gives

$$\frac{[\text{B}]}{[\text{EB}]} = \frac{1}{4} \frac{[\text{DEB}]}{[\text{TEB}]}$$

But the expression for the relative basicity of a tri- and a dialkylbenzene is<sup>2</sup>

$$\frac{[\text{DEB}]}{[\text{TEB}]} = 150 \text{ or } \frac{[\text{DEB}]}{[\text{TEB}]} = 150 \frac{[\text{DEB.H}^+]}{[\text{TEB.H}^+]}$$

Substitution of this value for [DEB]/[TEB] gives the relation for [B]/[EB]

$$\frac{[\text{B}]}{[\text{EB}]} = \frac{1}{4} \times 150 \frac{[\text{DEB.H}^+]}{[\text{TEB.H}^+]} = 37.5 \frac{[\text{DEB.H}^+]}{[\text{TEB.H}^+]}$$

In the strong acid medium, HF plus excess BF<sub>3</sub>, the very weak bases, benzene and ethylbenzene, are not appreciably complexed, whereas the strong bases diethylbenzene and triethylbenzene are practically completely complexed. Therefore, the above equation, which is a relation between concentrations, is the same as the following equation, which is a relation between the total number of moles of each component.

$$\frac{B}{EB} = 37.5 \frac{DEB}{TEB}$$

Other relationships between the components of a mixture and the number of ethyl groups and benzene rings it contains are

$$EB + 2DEB + 3TEB = \text{moles ethyl groups}$$

$$B + EB + DEB + TEB = \text{moles benzene rings} = 100$$

These equations define a family of curves expressing the composition of an equilibrated mixture as a function of the ratio of ethyl groups to benzene

rings. One such family, chosen because it passes through the experimental points, is plotted in Fig. 1. The vertical distances between the curves at any ratio of ethyl groups to benzene rings are equal to the amounts of each of the four components in the equilibrium product distribution. From this graph, therefore, the equilibrium product composition obtained from any mixture of benzene, ethylbenzene, diethylbenzene and triethylbenzene can be estimated.

WHITING, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH BRANCH, AERONAUTICAL RESEARCH LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

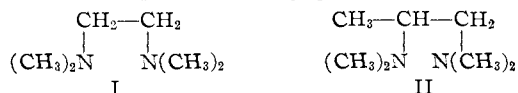
## Amines. IV. The Base Strengths of Tetramethylated 1,2-Ethanediamines<sup>1</sup>

BY LEONARD SPIALTER AND ROSS W. MOSHIER

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The base strengths of *N,N,N',N'*-tetramethyl-1,2-ethanediamine and *N,N,N',N'*-tetramethyl-1,2-propanediamine have been experimentally determined. It is shown that apparently anomalous values for the latter are explicable in terms of the inductive effect of the added methyl substituent together with the decrease of effective internal dielectric constant arising from a volume increase in the Kirkwood-Westheimer type of molecular cavity.

In the course of determining the base strengths of *N,N,N',N'*-tetramethyl-1,2-ethanediamine (I) and *N,N,N',N'*-tetramethyl-1,2-propanediamine (II), both diprotic amines, unusual relations were found between the values for the first and second dissociation steps of the conjugate acids of the two



compounds. The data of Rometsch, Marxer and Miescher<sup>2</sup> led them to formulate four dissociation rules for polyamines. Of these, an important one states that the dissociation interval (the difference between the  $pK$  values for consecutive dissociation steps) depends on the length of the chain between the two basic centers involved. Little effect is indicated for any other molecular structure features. It was therefore interesting to observe disagreement with such an assumption for the case of the diamine II compared to diamine I and the work of Rometsch, *et al.*<sup>2</sup>

The base strength data on the two diamines are presented in Table I. The convention adopted here for expressing base strengths, and apparently the preferred one,<sup>3,4</sup> is the use of  $pK_{ai}$ , the negative common logarithm of the acidity constant,  $K_{ai}$ , for the *i*th dissociation step of the conjugate acid of the amine base. Thus  $pK_{a1}$  and  $pK_{a2}$ , as applied here, have the same meaning as  $pK_{AH_2}$  and  $pK_{AH}$ , respectively, used by Carlson, *et al.*,<sup>5</sup> in the description of a diprotic base.

(1) For previous paper in this series see L. Spialter and J. A. Papalardo, *J. Org. Chem.*, **22**, 840 (1957).

(2) R. Rometsch, A. Marxer and K. Miescher, *Helv. Chim. Acta*, **34**, 1611 (1951).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XIII, p. 722-750.

(4) D. Davidson, *J. Chem. Ed.*, **32**, 550 (1955).

(5) G. A. Carlson, J. P. McReynolds and F. H. Verhoeck, *THIS JOURNAL*, **67**, 1334 (1945).

TABLE I  
ACIDITY CONSTANTS OF THE CONJUGATE ACIDS OF  
RCH—CH<sub>2</sub> AT 30°

R	RCH—CH <sub>2</sub> AT 30°		$\Delta pK_a$
	$(\text{CH}_3)_2\text{N}$ $pK_{a1}$	$\text{N}(\text{CH}_3)_2$ $pK_{a2}$	
—H (I)	5.85 <sup>a</sup>	8.97 <sup>a</sup>	3.12
—CH <sub>3</sub> (II)	5.40	9.49	4.09

<sup>a</sup> Rometsch, *et al.*,<sup>2</sup> report 5.7 and 9.1, respectively, for  $pK_{a1}$  and  $pK_{a2}$ .

The data of Table I show an apparent violation of the Rometsch, *et al.*, rule when a hydrogen atom is replaced by a methyl group. Moreover, the result of such a structure change is to increase the  $\Delta pK_a$  (in contrast to the decrease of this difference when a methylene is interposed in the molecular backbone<sup>2</sup>) and to do this by operating in two directions: lowering  $pK_{a1}$ , and raising  $pK_{a2}$ . These peculiar anomalies between two such closely related molecules clearly suggest that the C-methyl substituent in II must be exerting two different specific influences, with one being more important for the first dissociation step and the other for the second.

The greater value for  $pK_{a2}$  in the case of II compared to that of I reflects a substantially increased basicity in the former diamine for coordinating with the first acidic proton. This is undoubtedly attributable to the inductive ( $-I$ ) effect of the additional methyl group whose contribution with respect to decreasing the acidity of acids and increasing the basicity of amines has been previously discussed.<sup>3,6</sup>

Additional experimental verification for the enhancement of base strength in a related tertiary amine as a consequence of the introduction of a  $\beta$ -methyl group is to be found in the work of Gero.<sup>7</sup> This investigator found *N,N,N',N'*-tetraethyl-1,2-

(6) (a) J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939); (b) H. C. Brown and co-workers, *THIS JOURNAL*, **66**, 435, 846 (1944).

(7) A. Gero, *ibid.*, **76**, 5158 (1954).