that this assumption may be applied to series of compounds where one of the more easily dissociated members has been measured.

The e. m. f. data with fluorenone confirm the data previously obtained by equilibrium measurements and further emphasize the fact that the fluoryl group causes a molecule to have a higher electron affinity than would be produced by diphenylmethylene.

The values for tetraphenylethylene are the first quantitative data for this compound, the equilibrium measurements giving only a maximum value. The very low value for this compound is in striking contrast to the values previously obtained for free radicals and ketones.

The results for α-γ-bis-diphenylene-β-phenylallyl are perhaps a little surprising in view of the fact that this compound contains two diphenylene groups. One might have expected a very great tendency to add sodium by analogy with phenylfluoryl. It may be that the electron affinity is high for this compound, but that the shape of the molecule prevents a close approach of the sodium ion to the negative charge.

The author wishes to thank Professor Henry E. Bent for suggesting this problem and for offering many valuable suggestions and criticisms.

Summary

1. The potentiometric method has been shown to be applicable to the study of ketones and unsaturated compounds as well as free radicals.

2. The results obtained by the two methods agree within the experimental limits for fluorenone, tetraphenylethylene and dibiphenylene diphenylethane.

3. ΔH of dissociation of dixanthyl is calculated to be 24 kcal.

4. ΔF of addition of sodium to α-γ-bis-diphenylene-β-phenylallyl = 25 kcal.

CAMBRIDGE, MASS. RECEIVED JULY 30, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Effect of Polar Groups upon Esterification Velocities of Substituted Benzoic Acids

BY ROBERT J. HARTMAN AND ALVIN M. BORDERS[1]

In recent years attempts have been made to correlate the effects of substituents upon many types of side chain reactions under a single comprehensive theory. Williams[2] classifies reactions into three groups according to the effect on their rate by polar substituents: (A) those favored by accession of electrons to the point of reaction; (B) those favored by recession of electrons from the point of reaction; (C) those in which the data available are insufficient to classify in either group A or B.

Of the three esterification studies which Williams cites, he places two, those by Goldschmidt[3] and Kailan[4] in Group C. The third by Michael[5] is placed in group B, *i. e.*, the esterification reaction was accelerated by a substituent such as the nitro group.

Hammett[6] has expressed the effect of a substituent in the meta or para position on the benzene ring upon the rate of a side chain reaction by the equation $\log k = \log k_0 + \sigma\rho$, where σ is a constant depending upon the substituent and ρ is a constant depending upon the reaction, medium, and temperature, k is the velocity constant for the substituted reactant and k_0 the constant for the unsubstituted reactant.

For a series of thirty-nine reactions (including equilibrium as well as velocity constants) the equation was found to predict the constants for the substituted reactants with a probable error for $\log k$ of less than 0.1 in thirty-three of the thirty-nine reactions. The only esterification work to which the equation was applied was that of Goldschmidt[3] and the probable error in $\log k$ was 0.118. The order of the effect of the different groups as found by Goldschmidt is quite different than that followed in the majority of the reactions cited by Hammett. The values of σ used by Hammett were determined from the data

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[1] This paper is constructed from a dissertation presented by Alvin M. Borders to the Faculty of the Graduate School of Indiana University in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Williams, *J. Chem. Soc.*, 37 (1930).

[3] Goldschmidt, *Ber.*, **28**, 3220 (1895).

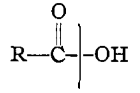
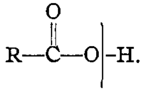
[4] Kailan, *Ann.*, **351**, 186 (1907).

[5] Michael and Oeschlin, *Ber.*, **42**, 317 (1909).

[6] Hammett, THIS JOURNAL, **59**, 97 (1937).

for the dissociation constants in water of substituted benzoic acids measured by Dippy.[7]

Other investigations of esterification of substituted benzoic acids have been carried out by Kellas,[8] who determined the percentage of ester formation of various benzoic acids at the end of fixed times using 3% dry hydrogen chloride in ethyl alcohol. Velocity constants were not determined. Sudborough and Turner[9] studied the esterification velocities of ortho substituted benzoic acids in dry methyl alcohol with small concentrations of hydrogen chloride as a catalyst.

In the literature there is a lack of accurate data for the velocity constants of acid catalyzed esterification of substituted benzoic acids, *e. g.*, in calculating the velocity constants, the retarding effect due to the water formed during the course of the reaction was disregarded. Hinshelwood and Legard[10] point out that in auto-catalyzed esterification the effect of a polar group may be decreased by opposing influence of the group upon the bond ruptures  $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}\vert{-}OH}$ and  $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O\vert{-}H}$. This compensation effect does not take place when added hydrions are the catalyst.

The object of this investigation was to determine the velocity constants of hydrion-catalyzed esterification of substituted benzoic acids with methyl alcohol and to correlate the results with data of other investigators on the effect of substituents on the velocity of other side chain reactions.

Experimental

Materials.—Synthetic, acetone-free methanol was dried by the method of Bjerrum and Lund[11] with magnesium methylate. The acids were purchased from the Eastman Kodak Co. They were dried carefully over phosphorus pentoxide. In cases where the melting points permitted they were first dried in an oven at 110°.

Procedure.—The anhydrous methanol–hydrogen chloride solution was prepared by passing carefully dried hydrogen chloride gas into the absolute methanol. The strength of the solution was determined by titration with aqueous baryta and the solution diluted to the desired strength. The concentration of the diluted solution was then checked and used immediately thereafter.

The concentration of hydrogen chloride was approximately 0.02 normal except in the concentration of the slowest reaction where 0.1 normal was used. To check the proportionality of speed of esterification to concentration of hydrogen chloride catalyst, velocities were measured with benzoic acid at these two concentrations of hydrogen chloride. Within the limits of experimental error, the velocity constants obtained were the same.

The organic acids were weighed into 125-ml. glass-stoppered Erlenmeyer flasks. The calculated amount of hydrogen chloride–methanol solution was then added to make the concentration of the organic acid approximately 0.1 normal. The total acid concentration was determined at the beginning and at intervals throughout the course of the reaction by titration with baryta of 10-ml. samples. The concentration of the organic acid was determined by subtraction of the hydrogen chloride concentration from the total acid concentration. For temperatures above 25° all concentrations were corrected for the expansion of the solvent. The thermostats were maintained at 25.00 ± 0.02° and 40.00, 49.90, and 60.00 ± 0.05°.

Calculations.—The velocity constants were calculated using the formula developed by Goldschmidt[12] which corrects for the retardation of esterification due to the water formed during the reaction

$$k = \frac{[(a + r) \ln a/a - x] - x}{rct}$$

where a is the original organic acid concentration, x, the amount of acid esterified at time t, and c the H^+ concentration. The units are g. moles/liter/sec. The constant r allows for the retardation of the hydrion-catalyzed esterification by water. It has been shown that r at a given temperature depends only upon the alcohol and not upon the acid. The values of r adopted for the calculation were

t	25	40	50	60
r	0.22	0.36	0.50	0.65

The values at 25 and 40° were those found by Williamson and Hinshelwood[13] and the values at 50 and 60 were extrapolated from their values, disregarding their 45° point.

In most cases the Goldschmidt formula[12] was found to represent the course of the reaction as shown by the following figures for a typical esterification

o-Toluic acid, temp. 40°, $a = 0.1005$, $c = 0.0200$

Time, min.	960	1440	2340	4320	6840
$a - x$	0.0826	0.0735	0.0608	0.0400	0.0256
$k \times 10^4$	2.05	2.06	2.02	2.04	1.96

Two or more measurements for each acid were made at each of the four temperatures. At the lower temperatures good reproducibility was obtained but the inherent experimental difficulties at the higher temperatures prevented exact dupli-

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[7] Dippy, *J. Chem. Soc.*, 644 (1936).

[8] Kellas, *Z. physik. Chem.*, **24**, 221 (1897).

[9] Sudborough and Turner, *J. Chem. Soc.*, **101**, 237 (1912).

[10] Hinshelwood and Legard, *ibid.*, 587, 1588 (1935).

[11] Bjerrum and Lund, *Ber.*, **64B**, 210 (1931).

[12] Goldschmidt, *ibid.*, **39**, 711 (1906)

[13] Williamson and Hinshelwood, *Trans. Faraday Soc.*, **30**, 1145 (1934).

cation. The average value of k at each temperature is reported for the determination in which k varied the least. The values of the energy of activation, E, were calculated in the usual manner.

Results and Discussion

TABLE I

VELOCITY CONSTANTS AND ENERGIES OF ACTIVATION FOR HYDRION-CATALYZED ESTERIFICATION OF AROMATIC ACIDS WITH METHYL ALCOHOL

Acid	$k \times 10^5$ 25°	40°	49.9°	60°	Energy of activation, E
o-Nitrobenzoic	0.546	2.43	...	17.2	19,000
o-Bromobenzoic	5.55	19.0	38.7	...	15,200
o-Toluic	6.41	20.2	40.9	81.4	14,400
m-Nitrobenzoic	7.28	23.4	48.1	93.6	14,600
o-Chlorobenzoic	7.83	25.1	50.2	102.0	14,600
p-Nitrobenzoic	8.67	27.4	57.7	115.0	14,700
p-Chlorobenzoic	11.4	36.6	76.7	154.0	14,600
m-Chlorobenzoic	12.4	38.3	80.4	157.0	14,600
p-Bromobenzoic	12.3	40.0	80.3	...	14,600
m-Bromobenzoic	12.5	40.2	82.5	157.0	14,400
Benzoic	19.2	65.2	...	293.0	15,500
p-Toluic	19.7	59.0	120.0	225.0	13,800
m-Toluic	21.7	65.5	137.0	265.0	14,200

Table II gives the values of log k_{25} obtained in this investigation for the esterification of the meta and para substituted acids and the corresponding values as calculated from Hammett's equation.[6] The value of σ adopted, 0.58, was obtained in a manner similar to that used by Hammett. Table III gives the same comparison using Goldschmidt's data.[3]

TABLE II

COMPARISON OF LOG k_{25} OBSERVED WITH LOG k CALCULATED WITH THE EQUATION: LOG $k = -4.717 + \sigma(-0.58)$

Acid	Log k, obsd.	Log k, calcd.	Error
m-Toluic	−3.663	−3.677	0.013
p-Toluic	−3.705	−3.618	.087
m-Bromobenzoic	−3.903	−3.943	.040
m-Chlorobenzoic	−3.907	−3.933	.026
p-Bromobenzoic	−3.910	−3.851	.059
p-Chlorobenzoic	−3.943	−3.848	.095
p-Nitrobenzoic	−4.062	−4.168	.106
m-Nitrobenzoic	−4.138	−4.129	.009
		Av.	.054

TABLE III

COMPARISON OF LOG k_{25} OBSERVED BY GOLDSCHMIDT[3] WITH LOG k CALCULATED WITH THE EQUATION: LOG $k = -1.410 + \sigma(0.085)$

Acid	Log k, obsd.	Log k, calcd.	Error
m-Bromobenzoic	−1.258	−1.443	0.185
m-Toluic	−1.328	−1.404	.076
p-Bromobenzoic	−1.347	−1.430	.083
m-Nitrobenzoic	−1.529	−1.470	.059
p-Nitrobenzoic	−1.584	−1.476	.108
p-Toluic	−1.618	−1.395	.223
		Av.	.122

The average error of log k for the work of this investigation, 0.054, compares favorably with the mean value of probable errors of 0.067 found by Hammett[6] for a series of thirty-nine reactions. It is seen from Table III that the corresponding average error for the data of Goldschmidt[3] is 0.122. Since the order of the effect of the groups in Goldschmidt's data varies considerably from the order predicted by Hammett's equation, the high average error is to be expected.

The most outstanding differences in results found for the esterification velocities in this paper, and those predicted by Hammett's equation, Table II, are the reversal of the order of the meta and para toluic acids and of the meta and para nitrobenzoic acids. As previously stated the order as predicted by Hammett and the basis for his values of σ were those found by Dippy[7] for the dissociation constants of the benzoic acids in water. Some of these differences in order disappear if the acidity constants measured in methyl and ethyl alcohols by Bright and Briscoe[14] are considered.

TABLE IV

VALUES OF LOG k FOR ESTERIFICATION AND OF LOG K_a IN VARIOUS SOLVENTS

Substituted benzoic acid	$-$Log k_{25} (Table II)	$-$Log K_a in water (Dippy[7])	$-$Log K_a in MeOH (Bright and Briscoe[14])	$-$Log K_a in EtOH (Bright and Briscoe[14])
m-NO_2	4.138	3.493	5.12	5.70
p-NO_2	4.062	3.425	5.20	5.54
p-Cl	3.943	3.976	6.10	6.84
m-Cl	3.907	3.830	6.02	6.70
p-Br	3.910	3.971	...	...
m-Br	3.903	3.812	...	...
H	3.716	4.203	6.50	7.29
m-CH_3	3.663	4.272	...	7.50
p-CH_3	3.705	4.373	...	7.36

The data listed in Table IV are shown graphically in Fig. 1. From Table IV and Fig. 1 it is seen that the order of the effect of the meta-tolyl and para-tolyl groups is the same upon esterification velocity and upon the acidity constants of the acids in ethyl alcohol. In methyl alcohol no acidity constants are recorded for the toluic acids. The order of the effect of the meta and para nitro groups upon the acidity constants in methyl alcohol is the same as that found for the effect of those groups upon the speed of acid-catalyzed esterification. This order does not hold in ethyl alcohol.

The study of Evans, Morgan, and Watson[15] of

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[14] Bright and Briscoe, *J. Phys. Chem.*, **37**, 787 (1933).

[15] Evans, Morgan, and Watson, *J. Chem. Soc.*, 1168 (1935).

acid-catalyzed prototropy of substituted acetophenones is of interest in connection with esterification since, according to Evans[16] the addition of an acid catalyst in esterification eliminates the resonance usually associated with the carboxyl group and therefore acid-catalyzed esterification is comparable to prototropy of ketones.

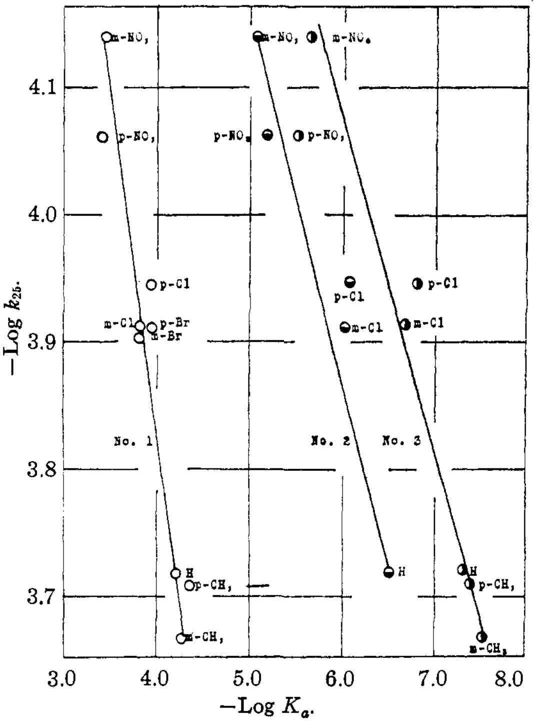

Fig. 1.—Relationship between log k for esterification and log K_a for various solvents (see Table IV): No. 1 ○, K_a for H_2O; No. 2 ◒, K_a for MeOH; No. 3 ◑, K_a for EtOH.

It was found that the velocity of bromination of the substituted acetophenones decreased in the following order: m-CH_3, H, p-Br, p-Cl, m-Br, m-Cl, p-NO_2, and m-NO_2.[15] This order agrees very closely with that found in the present investigation for the effect of the same groups upon the acid-catalyzed esterification of the substituted benzoic acids. In both series the p-NO_2 substituted compound reacts more rapidly than the corresponding m-NO_2 derivative. In both cases Br precedes Cl in the series when in the same ring position, but the relative order of the meta and para groups is reversed. The experimental agreement of the effect of polar substituents upon these two reactions seems to verify the prediction of their similarity in mechanism.

Anomalies in the order of the effect of halogen substituents upon the velocity of side chain reactions have been noted by Evans, Morgan, and Watson,[15] who state that the para halogen substituents often give peculiar velocity effects, but that the meta halogen derivatives usually behave as would be predicted. In connection with this it is to be noted that the para halogen acids deviate more from the linear relationship between log k for esterification and log K_a than do the meta halogen acids (Fig. 1).

Since the effect of a substituent in the ortho position upon the velocity of side chain reactions is of an entirely different mechanism than that of the meta and para groups, the velocity of esterification of the ortho substituted acids will not be discussed except to say that the order of the rates of their esterification observed in this work was the same as that found by Sudborough.[9]

In their work upon the bromination of the substituted acetophenones, Evans, Morgan, and Watson found what they considered to be significant variations in the non-exponential factor, P, of the Arrhenius equation: $k = PZe^{-E/RT}$. This conclusion was criticized by Nathan and Ingold[17] on the basis that the velocity range of the reactions studied was not sufficient for accurate separation of the factors E and P.

Since the relationship between velocities and dissociation constants would be expected to hold only if no factor other than E were changed by the introduction of a substituent, the disagreement between the order of the effect of groups upon dissociation constants and upon the velocity acid-catalyzed bromination of substituted acetophenones is in harmony with the fact that variations in the factor P were found.

Since there are similar variations in the linear relationship between the log k of acid-catalyzed esterification and log K_a, it is of interest to find whether or not there is a variation in the non-exponential factor in the Arrhenius equation upon passing from the esterification of one acid to another.

As shown in Table I the values of E found for most of the esterifications measured fall between 14,400 and 14,700 calories. The values do not fall in their proper order but the difference in the values obtained is not beyond that of a rather large experimental error in this work. It is apparent that for most of the acids studied the range of velocities was not sufficient to permit

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[16] Evans, *J. Chem. Soc.*, 785 (1936).

[17] Nathan and Ingold, *ibid.*, 222 (1936).

accurate analysis of the factors of the Arrhenius equation. All of the acids but one fall within a range in which the ratio of velocities of the fastest to the slowest is about 3 to 1. Including *o*-nitrobenzoic acid the range is 39 to 1.

The value of 15,500 calories found for benzoic acid is in fair agreement with that of 15,700 calories found by Hinshelwood and Legard;[10] but no reason can be given for the fact that although benzoic acid was esterified more rapidly than all but two of the substituted acids, *p*- and *m*-toluic, it has a higher energy of activation than all but the very slowest, *o*-nitrobenzoic. Accurate conclusions in this direction cannot be reached until these values of E have been verified or the experimental error reduced.

The high energy of activation of benzoic acid is indicated by the fact that at 60° benzoic acid was esterified more rapidly than *m*-toluic acid while at 25° *m*-toluic was esterified more rapidly than benzoic. This reversal of order is substantiated when one considers the data of Goldschmidt[3] and Kellas.[8] At 25° Goldschmidt found *m*-toluic acid to be esterified more rapidly than benzoic acid and Kellas observed that at 51° benzoic acid was esterified more rapidly than *m*-toluic acid. In fact he found that at 51° benzoic acid was esterified more rapidly than any of the substituted acids. This agrees with the data of this investigation for 60°.

An approximation of the change in the factors of the Arrhenius equation may be obtained by plotting the values of E for the esterification of the various acids against log k at 25°. These values are plotted in Fig. 2 including both the data recorded in this paper and the points for the esterification of benzoic and diphenylacetic acids with methyl alcohol and hydrogen chloride as found by Hinshelwood and Legard.[10] The diphenylacetic acid point from Hinshelwood's data and the point for *o*-nitrobenzoic acid from the data of this investigation give a sufficient range for drawing a straight line. The intermediate points as already pointed out are too close together for accurate deductions.

If the change in velocity of esterification of the acids produced by the substituents were entirely due to changes in E, the points on the graph would lie on a straight line having a slope of $2.303RT$. From the data, therefore, it may be concluded tentatively that the factor P varies, since the line has a slope different than that of the theoretical line shown by the dotted line in Fig. 2.

Apparently P increases simultaneously with E. Such an increase of both factors of the Arrhenius equation was found by Hinshelwood and Legard[10] in the esterification of different alcohols with acetic and benzoic acids and in the hydrion-catalyzed esterification of acetic and benzoic acids.

Let it be stressed again, however, that in view of the small range of the velocities studied and of the effect of large experimental error at high temperature upon the values of E, the conclusions drawn from consideration of the values of E given cannot be asserted as proven.

The variation of the factor P might account for the deviations from the linear relationship between log k for esterification and log K_a of the benzoic acids.

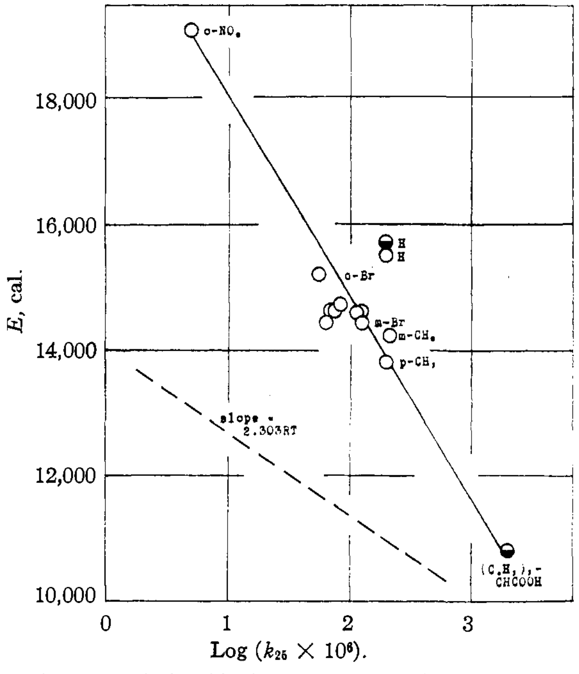
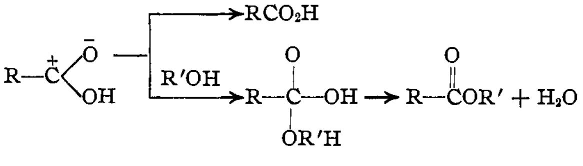


Fig. 2.—Relationship between change in speed of reaction and activation energy: ○, Table I; ◒, Hinshelwood and Legard.

Evans, Morgan, and Watson[15] suggest that the factor P of catalytic reactions may be due to the stepwise nature of the reaction and that while E



is determined in the first stage, the variation in *P* arises in the second stage. Thus they propose the preceding mechanism for catalyzed esterification.

Summary

1. The study of the effect of polar groups has shown that the velocity of hydrion-catalyzed esterification of benzoic acids is increased by displacement of electrons toward the carboxyl group.

2. Good agreement was found between the experimental values of log *k* for the esterification and the values predicted by Hammett's equation.

3. It appears that the non-exponential factor of the Arrhenius equation as well as the activation energy increases upon passing from the rapidly esterified acids to those more slowly esterified.

BLOOMINGTON, INDIANA RECEIVED AUGUST 4, 1937

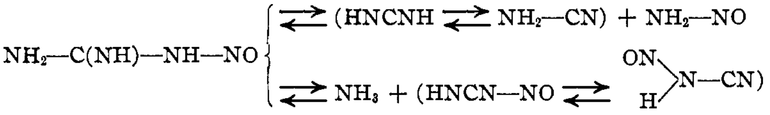
[CONTRIBUTION NO. 156 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Studies in the Urea Series. XV.[1] Transformations of Nitrosoguanidine. Alkylnitrosoguanidines. N-R,N'-R'-Dialkylguanidines

BY TENNEY L. DAVIS AND EDWARD N. ROSENQUIST

It has been shown that nitroguanidine in aqueous solution dearranges in two modes,[2] to produce on the one hand cyanamide and nitroamide, on the other ammonia and nitrocyanamide, and advantage has been taken of the dearrangement for the preparation of guanidine carbonate by the action of ammonium carbonate on nitroguanidine, and of N-alkyl,N'-nitroguanidines[3] by the action of aliphatic amines. Nitrosoguanidine evidently dearranges in aqueous solution to produce cyanamide and nitrosoamide,[2] for the solution on boiling gives off nitrogen and yields dicyandiamide, and in the presence of mineral acids nitrosates certain aromatic compounds. Fuller, Lieber and Smith in a recent paper[4] have reported that nitrosoguanidine yields nitrogen when treated with sodium in liquid ammonia, and have taken the fact to be evidence that dearrangement occurs. In the present work we have studied the dearrangement of nitrosoguanidine and of several N-alkyl,N'-nitrosoguanidines procured by the reduction of the corresponding alkylnitroguanidines, and have been led to the preparation of alkylated guanidines containing different alkyl groups on two different nitrogen atoms. Very few substances of this type have been reported. Nitrosoguanidine and the N-alkyl,N'-nitrosoguanidines appear to dearrange to produce the unknown and unstable nitrosoamide.[5]

Corresponding to the two modes in which nitroguanidine dearranges, nitrosoguanidine might be expected to dearrange as follows.



$$\mathrm{NH_2{-}C(NH){-}NH{-}NO}\left\{\begin{array}{l} \rightleftarrows (\mathrm{HNCNH} \rightleftarrows \mathrm{NH_2{-}CN}) + \mathrm{NH_2{-}NO} \\ \rightleftarrows \mathrm{NH_3} + (\mathrm{HNCN{-}NO} \rightleftarrows {\mathrm{ON} \atop \mathrm{H}}\!\!>\!\mathrm{N{-}CN}) \end{array}\right.$$

In the presence of ammonia the dearrangement is largely in the first of these modes. Refluxed with a large excess of ammonia water, nitrosoguanidine yields guanidine, melamine (the trimer of cyanamide), ammeline and ammelide (products formed either by the partial hydrolysis of melamine or by the mixed polymerization of cyanamide and cyanic acid), and a small quantity of urea. Repeated slow evaporation with ammonia water gives less guanidine and more ammeline, while refluxing with ammonium carbonate gives an excellent yield of guanidine carbonate comparable to that which has been obtained from nitroguanidine by similar treatment. The mass action effect of ammonia in these experiments might be expected to inhibit any dearrangement in the second of the above-indicated modes, but the production of a small amount of urea indicates that it probably occurs to some extent. Nitrosocyanamide

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[1] No. XIV of this series, THIS JOURNAL, **59**, 1993 (1937).

[2] Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, **61**, 437 (1926).

[3] Davis and Luce, THIS JOURNAL, **49**, 2303 (1927); Davis and Elderfield, *ibid.*, **55**, 731 (1933).

[4] Fuller, Lieber and Smith, *ibid.*, **59**, 1150 (1937).

[5] Schwarz and Giese, *Ber.*, **67**, 1108 (1934), attempted to prepare nitrosoamide by the action of nitrosyl chloride on potassium amide in liquid ammonia. They observed a flash of color during the reaction and were able to show the formation of ammonium nitrite, water and nitrogen. They evidently had nitrosoamide momentarily, but the substance in the presence of ammonia was unstable even at the low temperature at which they worked.