# **112.** *Reactions of Hydrazoic Acid. Part II. A Quantitative Study of the Action with Substituted Benzoic Acids.*

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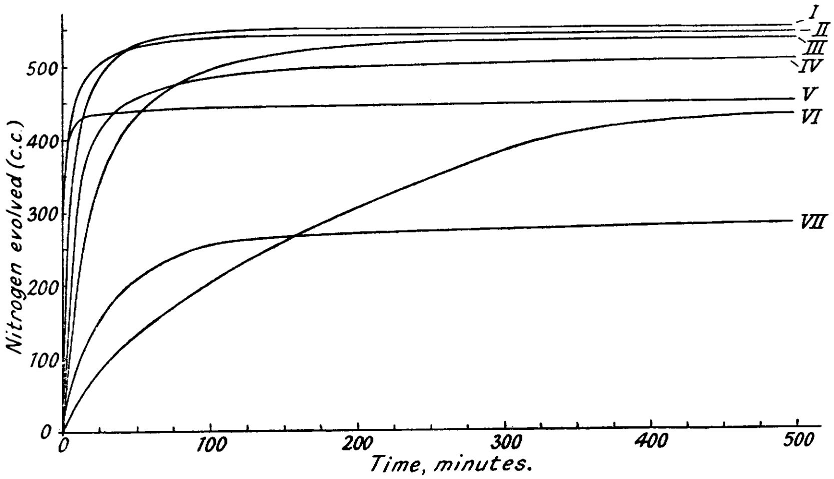
A quantitative study has been made of the decomposition of hydrazoic acid alone and of its action upon a series of substituted benzoic acids (mostly *m*-substituted) in trichloroethylene solution in the presence of concentrated sulphuric acid at 40°. The rate of reaction of the substituted benzoic acids as determined by the time of half the evolution of nitrogen is, in general, in the reverse order of their strength as acids measured by the dissociation constants, with the exception of *o*-nitrobenzoic acid where an "ortho-effect" is observed. The total yield of nitrogen evolved and the yield of amine produced, however, do not bear any similar close relation: explanations for this are suggested. The mechanism of the Schmidt reaction is discussed.

Schmidt (*Ber.*, 1924, **57**, 704; D.R.-P., 1928, 500,435; *et al.*) found that hydrazoic acid reacts with benzoic acid in chloroform or benzene solution in the presence of concentrated sulphuric acid 40° to give an 85% yield of aniline, whereas ketones such as acetophenone (Schmidt, *loc. cit.*; Briggs and De Ath, J., 1937, 456) react under similar conditions, but usually at lower temperatures, to give good yields of the corresponding amide, acetophenone forming acetanilide. Oesterlin (*Angew. Chem.*, 1932, **45**, 536; cf. also Part I, J., 1942, 61) has extended this work to substituted benzoic acids and other acids and found that the substituents markedly affect the yield of amine produced.

We now report a quantitative study of the influence exerted by substituents on the replacement of the carboxyl group by the amino-group in the Schmidt reaction, intended to elucidate the mechanism of the reaction.



I. *Benzoic acid.*
II. o-*Nitrobenzoic acid.*
III. m-*Chlorobenzoic acid.*
IV. m-*Hydroxybenzoic acid.*
V. m-*Toluic acid.*
VI. m-*Nitrobenzoic acid.*
VII. *Hydrazoic acid.*

Schmidt (Knoll and Co. and Schmidt, E.P. 250,897, 23.9.25; Schmidt and Zutavern, B.P. 331,947, 19.4.29; Knoll A.-G. Chem. Fabr. and Schmidt, B.P. 430,774, 23.7.34) has recorded that other catalysts besides concentrated sulphuric acid, *e.g.*, phosphorus penta- or oxy-chloride, or ferric, aluminium, or stannic chloride, may act as catalysts in the reaction. We have found, however, that with phosphorus oxychloride as a catalyst in homogeneous solution in both chloroform and trichloroethylene, benzoic acid is converted into aniline by hydrazoic acid at 40° to the extent of only 5 and 6% respectively. The effect of substituents could also be obtained by using substituted acetophenones, and in a similar experiment with acetophenone, hydrazoic acid, and phosphorus oxychloride in chloroform solution, after 3—4 hours at 25° and a further hour at 40°, only 40% of acetanilide was obtained, 56% of the acetophenone being recovered unchanged. As both these results are unsatisfactory for a quantitative study, we have used concentrated sulphuric acid as the catalyst in heterogeneous solution but under standard conditions as set out in the experimental section. This method does not give completely satisfactory results owing to the initial rise in temperature on mixing the reagents.

Schmidt (*loc. cit.*) found that benzene and xylene react with hydrazoic acid in the presence of concentrated sulphuric acid at 60—70° to form aniline and xylidine respectively. To evaluate this phase of the reaction at 40°, typical compounds exerting strong *op*-directing influence (anisole and dimethylaniline) and strong *m*-directing influence (nitrobenzene) were submitted to the Schmidt reaction at 40°. In all cases, however, no trace of amine could be detected, nearly the whole of the starting materials being recovered unchanged. It would appear, therefore, that nuclear substitution does not occur to any appreciable extent at 40°.

We have now examined the Schmidt reaction on benzoic acid and fourteen substituted acids, choosing the *m*-substituted acids for the main investigation, since a *m*-substituent exerts an influence almost exclusively by induction and only slightly and indirectly by a mesomeric effect. *o*- or *p*-Groups, however, have both types of effect, sometimes acting in opposite directions so that the activity on the nucleus is the algebraic sum of the two effects (Ingold, *Chem. Rev.*, **1934**, **15**, 231).

In our experiments we allowed 0·250 mol. of aromatic acid to react with 0·025 mol. of hydrazoic acid in trichloroethylene solution (100 c.c.) in the presence of concentrated sulphuric acid (0·15 mol.) at 40° under standard experimental conditions until all evolution of nitrogen had ceased. The gases evolved were passed through a soda–lime tower to absorb carbon dioxide, the remaining nitrogen being measured in a graduated burette over 50% potassium hydroxide solution. At the conclusion of the experiment the amount of amine formed and the unchanged acid were determined by direct isolation.

The experiments were repeated with *m*-toluic (extremely rapid), benzoic, and *m*-nitrobenzoic acids and were reproducible to within 5, 1, and <1%, respectively. A blank experiment with hydrazoic acid alone was also carried out. The results of these experiments are in the table, $t_{\frac{1}{2}}$ being the time of half-reaction, and typical curves of the rate of nitrogen evolution are in the figure.

| Acid. | Yield of amine, %. | Acid recovered, %. | Vol. of $N_2$ at N.T.P. c.c. | Vol. of $N_2$ at N.T.P. %. | $t_{\frac{1}{2}}$, mins. |
|---|---|---|---|---|---|
| *m*-Chlorobenzoic | 75 | — | 535 | 95·5 | 12 |
| *m*-Bromobenzoic | 72 | — | 515 | 92 | 10 |
| *m*-Iodobenzoic | 62 | 32 | 452 | 80 | 15 |
| *m*-Hydroxybenzoic (a) | 80 | 15 | 507 | 91 | 5 |
| *m*-Methoxybenzoic | 77 | 16 | 500 | 89 | 4 |
| *m*-Ethoxybenzoic | 73 | 23 | 494 | 88 | 4 |
| *m*-Nitrobenzoic | 63 | 32 | 432 | 77 | 100 |
| *m*-Cyanobenzoic (b) | 59 | 38 | 404 | 72 | 18 |
| *iso*Phthalic (b) | 57 | 40 | 447 | 80 | 17 |
| *m*-Toluic | 42 | 51 | 448 | 80 | 2 |
| Benzoic | 69 | 25 | 552 | 98 | 3 |
| *o*-Methoxybenzoic | 80 | 17 | 558 | 99 | 5 |
| *p*-Methoxybenzoic | 78 | 17 | 512 | 91 | 1½ |
| *o*-Nitrobenzoic | 68 | 26 | 541 | 96 | 2 |
| *p*-Nitrobenzoic (c) | 41 | 54 | 385 | 69 | 120 |
| Hydrazoic | — | — | 280 | 50 | 22 |

(a) The yield of amine was estimated from the recovered acid owing to the ready oxidation of the aminophenol.

(b) In these cases, the amine sulphate was not soluble in the sulphuric acid layer and separated as a sludge in the trichloroethylene layer.

(c) This acid was not completely soluble in the 100 c.c. of solvent and the conditions were therefore not standard.

*m*-Aminobenzoic acid has been omitted from the series since it would be immediately absorbed by the sulphuric acid and would therefore react under conditions not comparable with those for the other acids.

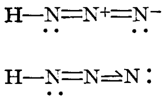
*Mechanism of the Schmidt Reaction.*—Before discussing the above results it is necessary to consider the mechanism of this reaction. Schmidt suggested that the essential part is the interaction of hydrazoic acid with concentrated sulphuric acid, with formation of the imino-radical : $HN_3 \longrightarrow N_2 + [HN<]$. When this radical reacts with benzene or water (indirectly), aniline or hydroxylamine is produced : $C_6H_6 + [HN<] \longrightarrow C_6H_5{\cdot}NH_2$; $H{\cdot}OH + [HN<] \longrightarrow NH_2{\cdot}OH$. Polymerisation of the radical, followed by disproportionation, gives hydrazine, another of the known products of the reaction : $4[HN<] \longrightarrow 2[HN{:}NH] \longrightarrow N_2 + H_2N{\cdot}NH_2$.

In the reaction with ketones and aldehydes addition of the imino-radical is assumed to form the oxime, which then undergoes the Beckmann rearrangement : $R{\cdot}CO{\cdot}R' + [HN<] \longrightarrow R{\cdot}C({:}NOH){\cdot}R' \longrightarrow R{\cdot}NH{\cdot}COR'$, the nitrile being formed if $R' = H$. A similar process is considered to occur in the case of the carboxylic acids, the amine being formed from the carbamic acid produced as an intermediate : $R{\cdot}CO{\cdot}OH + [HN<] \longrightarrow R{\cdot}C({:}NOH){\cdot}OH \longrightarrow R{\cdot}NH{\cdot}CO_2H \longrightarrow R{\cdot}NH_2 + CO_2$.

Oliveri-Mandalà (*Atti R. Accad. Lincei*, 1910, **19**, 228; *Gazzetta*, 1911, **41**, i, 59; ii, 430; 1913, **43**, i, 538, *et seq.*) criticised this mechanism (*ibid.*, 1925, **55**, 271) and suggested that the initial step is probably the addition of hydrazoic acid to the carbonyl group to form the corresponding azide, which would then undergo decomposition to give the products obtained by Schmidt : $R{\cdot}CO{\cdot}R' + HN_3 \longrightarrow R{\cdot}CR'(OH){\cdot}N_3 \longrightarrow R{\cdot}NH{\cdot}COR'$ or $R{\cdot}CO{\cdot}NHR'$.

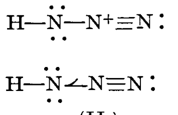
There is strong evidence that Schmidt's mechanism is incorrect. If the imino-radical is concerned, the rate of the reaction should be controlled according to the rate of decomposition of hydrazoic acid. Schmidt found, however, that decomposition does not occur below 30°, and even at 60—70° it is not complete for 5 hours, whereas a number of ketones, *e.g.*, *cyclo*hexanone and benzylacetone, react vigorously at 0°. That the oxime is also not an intermediate as postulated by Schmidt is proved by the fact that the oxime of α-hydrindone is unchanged by heating with concentrated sulphuric acid at 100° (Kipping, J., 1894, **65**, 480), whereas in the Schmidt reaction α-hydrindone is smoothly converted into hydrocarbostyril at 40° (Briggs and De Ath, *loc. cit.*).

Recently, Hurd (Gilman, " Organic Chemistry : An Advanced Treatise," Vol. I, p. 699) has advanced a mechanism for the Schmidt reaction with which we agree, as it does not involve the imino-radical or the formation of an oxime as intermediate. It is based on the linear formulation of hydrazoic acid as a resonance hybrid (cf. Hendricks and Pauling, *J. Amer. Chem. Soc.*, 1925, **47**, 2904; Sidgwick, *Trans. Faraday Soc.*, 1934, **30**, 801; Lindemann and Thiele, *Ber.*, 1928, **61**, 1529; Sidgwick, Sutton, and Thomas, J., 1933, 406), (I) being the



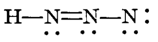
$\text{H—}\underset{\cdot\cdot}{\text{N}}\text{=N}^+\text{=}\underset{\cdot\cdot}{\text{N}}^-\text{:}$ or $\text{H—}\underset{\cdot\cdot}{\text{N}}\text{=N}\rightleftharpoons\text{N:}$

(I.)



$\text{H—}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}\text{—N}^+\equiv\text{N:}$ or $\text{H—}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}\rightarrow\text{N}\equiv\text{N:}$

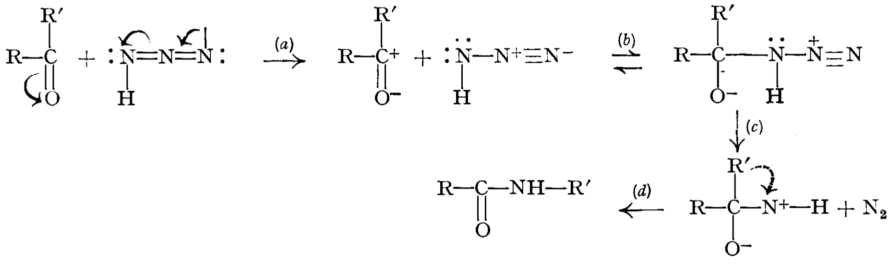
(II.)



$\text{H—}\underset{\cdot\cdot}{\text{N}}\text{=}\underset{\cdot\cdot}{\text{N}}\text{—}\underset{\cdot\cdot}{\text{N}}\text{:}$

(III.)

stable and (II) and (III) the reactive forms. For our purposes we have considered the formula (II) as being that involved in the Schmidt reaction, which can then be formulated as follows:

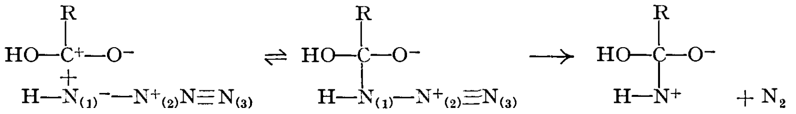


The first phase (*a*) is the activation of both the ketone or acid and hydrazoic acid under the influence of the strongly polar sulphuric acid, followed by addition (*b*) of the active hydrazoic acid molecule to the positive carbon of the carbonyl group. The addition complex loses nitrogen (*c*), and the remaining portion undergoes a further transformation (*d*) analogous to that postulated for the pinacol–pinacolone and allied transformations.

When R in the Schmidt reaction is an alkyl group, an amide is produced, but when R is OH (*i.e.*, in a carboxylic acid), a carbamic acid is formed which loses carbon dioxide spontaneously and yields the corresponding amine.

*Discussion of Results.*—A. *Rates of reaction.* If the time at which the reaction is half complete, as determined by the evolution of half the total volume of nitrogen, is considered to be a measure of the speed of the reaction, then by arranging the acids in descending order of speed, we have (*m*-series only) $CH_3 > H > O{\cdot}C_2H_5 > O{\cdot}CH_3 > OH > Br > Cl > I > CO_2H > CN > NO_2$, whereas acid strengths as measured by dissociation constants are nearly in the reverse order,* *viz.*, $NO_2 > CO_2H > CN > Br > Cl > I > OH > O{\cdot}CH_3 > O{\cdot}C_2H_5 > H > CH_3$. The Schmidt reaction is therefore of the same type as that of the decomposition of bromo-amides (Hauser and Renfrow, *J. Amer. Chem. Soc.*, 1937, **59**, 121) and the potassium salts of dihydroxamic acids (Renfrow and Hauser, *ibid.*, p. 2308; Bright and Hauser, *ibid.*, 1939, **61**, 618). In each case the speed of the reaction depends upon the character of the substituent, being slow or rapid according as this is electrophilic (*e.g.*, $NO_2$) or nucleophilic (*e.g.*, $CH_3$).

The phase representing the liberation of nitrogen involves the reaction:



In order to bring about the liberation of nitrogen in the second step, the charge on the nitrogen atom (2) must be neutralised by the transfer of an electron from the rest of the molecule to this atom. If R is nucleophilic, this step will occur rapidly and the rate of evolution of gas will be high; on the other hand, if R is electrophilic, the rate of nitrogen liberation will consequently be slow. In the case of the dissociation constants of the acids the converse argument will apply. An increased electron content of the carboxylic group caused by a nucleophilic substituent will repress the dissociation of the hydrogen as an ion, whereas withdrawal of electrons by an electrophilic group will enable ionisation to occur more readily. The inverted order of the acids with regard to their rates of reaction and dissociation constants is thereby explained.

In our experiments the inversion of the bromo- and chloro-acids, and of cyanobenzoic and *iso*phthalic acid, with almost identical curves, may be due to experimental error, but the former type of inversion also occurred in the experiments of both Hauser and Renfrew (*loc. cit.*) and Bright and Hauser (*loc. cit.*).

In the series, *o*-, *m*-, and *p*-methoxybenzoic acids, there should be no chelation of the *o*-isomer. This is confirmed, the difference in the order of rates of reaction $p > m > o$ from that of the dissociation constants $p < o < m$ being possibly due to experimental error, since the values of the *o*- and *m*-acids are very close in both cases.

In the nitro-acid series a definite " ortho-effect " is observed. The *o*-acid, from its acid strength (the

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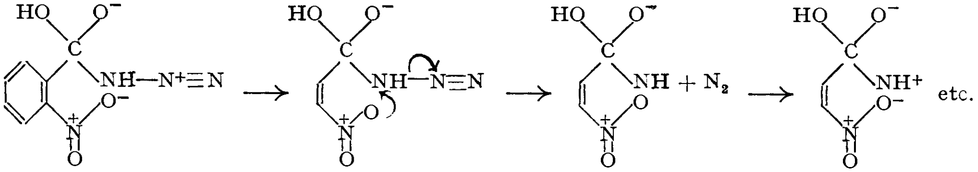
* We are indebted to Mr. D. A. Tait, M.Sc., for measuring the dissociation constant of *m*-ethoxybenzoic acid, who obtained the value $6{\cdot}76 \times 10^{-5}$ by potentiometric titrations using the cell, Normal calomel electrode | Satd. KCl solution | 0·0025M-Acid solution + quinhydrone | Pt.

strongest in the series), should, according to the above considerations, react extremely slowly, whereas it reacts very rapidly—in our opinion, according to the following scheme :



It will be seen that electrons are supplied to the positively charged nitrogen atom directly from the nitro-group and not through the chain of carbon atoms. This process does not necessitate a high electron density drawn through the carbon atom from the nucleus, and is thus independent of the normal electrophilic character of the nitro-group in so far as it deactivates the nucleus and hence the side chain. Indeed, this very withdrawal of electrons from the nucleus makes them more directly available to the nitrogen atom by a process of chelation, the co-ordinate link providing the electrons where they are expressly needed.

This result also shows a similarity to those obtained by Hauser and Renfrow (*loc. cit.*) on the decomposition of bromobenzamides. The *o*-nitro-compound, according to the strength of the corresponding acid, should react more slowly than the *m*- and the *p*-compound, but it was found to react more rapidly, although the magnitude of the divergence was not nearly as large as that observed in this investigation. Moreover, whereas the decomposition of other substituted bromo-amides gave good constants corresponding to a reaction of the first order, yet for all three nitro-compounds application of the equation for a first-order reaction gave a " constant " varying over a range of 18—65%. A completely analogous mechanism may be envisaged also for the apparently anomalous decomposition of *o*-nitrobromobenzamide.

B. *Total yield of nitrogen and amine.* When the acids are arranged in order of the amount of nitrogen evolved and amine produced, different orders are obtained from those derived from the rates of reaction, although individual groups retain the same relative order, *viz.*, *m*-series, $Cl > Br > I$, $OH > OCH_3 > OC_2H_5$, $CO_2H > NO_2 > CN$ ($NO_2 > CN > CO_2H$ in the yield of amine), $H > CH_3$; methoxy-series, $o > p > m$; nitro-series, $o > m > p$. Consideration of the mechanism, however, provides a possible explanation.

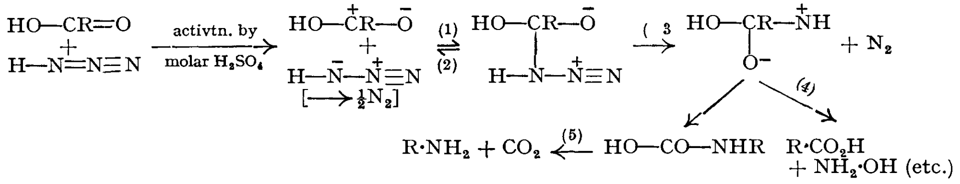
It must first be noticed that in the reaction with benzoic acid almost exactly 1 mol. of nitrogen is evolved, whereas hydrazoic acid alone under the same experimental conditions yields exactly ½ mol. Substituents on the benene nucleus, depending on their nucleophilic or electrophilic character, will affect the phases (*b*), (*c*), and (*d*) of the reaction in different ways.

In phase (*b*) an electrophilic group R′ affects the equilibrium in a forward direction by increasing the positive charge on the carbon atom and hence its readiness to undergo addition. Less free hydrazoic acid will thus decompose by itself and more through the Schmidt reaction, leading to relatively greater evolution of nitrogen and amount of amine formed. Where R′ is nucleophilic the reverse will hold. With *m*-nitrobenzoic acid the gas evolution is even much slower than that of hydrazoic acid itself, and it is obvious that the latter acid must be largely combined with the nitro-acid and not free to decompose by itself.

On the other hand, in phase (*c*) where R′ is electrophilic the reaction rate as already discussed is retarded, thus allowing any free hydrazoic acid a better chance to decompose by itself, and so leading to relatively lower evolution of nitrogen and amounts of amine formed.

If this were the complete explanation, a quantitative correlation should exist between the yields of nitrogen and amine, but this is not found. Since in some cases, such as benzoic acid itself, almost the theoretical amount of nitrogen is evolved but 25% of the acid is recovered, an alternative mechanism to phase (*d*) must occur, leading to regeneration of acid without affecting the nitrogen yield, and we suggest the following reaction with simultaneous formation of hydroxylamine or aminosulphuric acid, although there is so far no supporting experimental evidence : $R\cdot C\overset{-}{O}(OH)\cdot\overset{+}{N}H + H_2O$ (from $H_2SO_4$) $\longrightarrow R\cdot CO_2H + NH_2\cdot OH$ or $NH_2\cdot O\cdot SO_3H$. Where the substituent R is electrophilic, the aromatic nucleus is relatively more positively charged and there should be less tendency for it to migrate to the positively charged nitrogen and greater tendency for it to decompose by the alternative reaction. With the notable exception of toluic and benzoic acids, this is, in general, confirmed experimentally. A similar phenomenon is exemplified in Hauser and Renfrow's experiments; here, also, decomposition of substituted bromo-amides yields as main product the amine, as in the Schmidt reaction, as well as the corresponding acid. In their experiments the greater the electrophilic character of the substituent the greater was the yield of the corresponding acid up to 46% in the case of *m*-nitrobromobenzamide.

In conclusion, we may represent the mechanism of the Schmidt reaction with acids as follows :



Reaction (1) favoured by electrophilic nature of R. Reaction (4) influenced by electrophilic nature of R.
„ (3) hindered „ „ „ „ „ (5) is spontaneous.

The rate of the phase controlling the evolution of nitrogen can be correlated with other data such as the dissociation constant, but opposing effects of unknown magnitude prevent any such correlation in respect to the yield of amine and total nitrogen.

## EXPERIMENTAL.

The apparatus used throughout consisted of a three-necked flask immersed in a small thermostat maintained at 40° ± 0·5°, one neck being fitted with a dropping funnel, the central neck with a mercury-sealed stirrer of the Witt type driven directly at constant speed, and the other neck connected first through a small reflux condenser and then through a soda-lime tower to gas burettes. The gas burettes containing 50% potassium hydroxide solution were interconnected and of two sizes, a larger one being used to measure the first rapid evolution of gas and the second to measure subsequent slower evolution. Water of constant temperature was run through both the reflux condenser and the jacket of the gas burettes.

The aromatic acid (0·025 mol.) was dissolved in the solution of hydrazoic acid (0·025 mol.) in freshly purified trichloroethylene, and the solution made up to 100 c.c. with this solvent. This solution was placed in the three-necked flask and allowed to reach 40°, 8 c.c. of concentrated sulphuric acid (previously warmed to 40°) then being run in through the tap-funnel. Stirring was now commenced, and the evolution of nitrogen measured in either of the two gas burettes according to the rate of reaction. The reaction was continued until the rate of evolution did not exceed 1 c.c. in 15 minutes, the volume of nitrogen evolved being corrected to N.T.P.

At the conclusion of the reaction, the trichloroethylene layer was removed by suction, and any unchanged acid recovered as such in the ordinary way. The sulphuric acid layer was diluted with 250 c.c. of water (including washings), and any amine sulphate produced filtered off and weighed as such. The filtrate was freed from traces of trichloroethylene by gravity filtration and made alkaline with ammonia. If the amine was solid, it was filtered off and weighed as such together with further amounts formed after concentration, but if it was liquid, it was recovered by extraction with ether and removal of the ether after drying, first by distillation and finally by passing a current of dry air over the residue until the weight of amine was constant. All liquid amines were identified by the preparation of a solid derivative, usually benzoyl or acetyl. In no case was there any divergence in the identity of the amine from that expected from the substituted acid.

We are indebted to the Chemical Society for a grant.

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[*Received, April 20th,* 1942.]