position of whale oil than previous investigations. In Table XIII we have attempted to summarize the main points of our data in the form of an estimate of the percentage composition of the fatty acids of the sample of whale oil studied (from the west coast of the United States).

Summary

The composition of whale oil has been studied by fractionally distilling the methyl esters of the solid, liquid and mixed fatty acids of the oil and also the methyl esters of the fatty acids of the hydrogenated oil. Whale oil, like other marine animal oils, contains a complicated mixture of fatty acids of carbon content varying from 14 to 22, probably with a small amount of C_{24} acids. The highly unsaturated acids are chiefly those containing 20 and 22 carbon atoms. The percentage composition of the fatty acids has been approximately estimated.

IVORYDALE, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE MECHANISM OF THE HOFMANN REARRANGEMENT OF METHYL ANILINE HYDROCHLORIDE[1]

BY J. W. HOWARD WITH C. G. DERICK[2]

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Introduction

The Hofmann rearrangement consists in the change of methyl aniline hydrochloride to *p*-toluidine hydrochloride under the influence of heat. Hofmann[3] suggested as a possible mechanism that methyl chloride was dissociated and then added again, the reaction going through the formation of dimethyl aniline. Then the methyl chloride acted on the dimethylaniline giving dimethyltoluidines, -xylidines, -cumidines, etc. Some of these products were isolated. In the case of trimethylphenylammonium iodide he states that the methyl groups "wander" from the aminic nitrogen to the carbon ring, giving rise to a series of quaternary, tertiary, secondary and primary amines.

Work of a more recent date makes it possible to predict as to the correctness of Hofmann's views. Chattaway[4] found that disubstitution of acyl groups upon the amino nitrogen was necessary to produce substances

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[1] From a thesis presented by J. W. Howard in partial fulfilment of the requirements for the degree of Doctor of Philosophy, at the University of Illinois, June, 1915.

[2] The experimental work of this paper was performed by J. W. Howard in collaboration with C. G. Derick. The original thesis manuscript was revised and condensed for publication by J. W. Howard.

[3] Hofmann, *Ber.*, **4**, 742 (1871).

[4] Chattaway, *J. Chem. Soc.*, **75**, 1046 (1899); **77**, 134, 789, 797 (1900); **85**, 386, 589, 1187 (1904).

unstable toward rearrangement. Derick[5] discovered that such substitution produced electrolytes whose ionization constants were at least ten thousand times as strong as the rearranged product. Hence a similar difference in the ionization constants of *N* alkyl anilines would be expected before rearrangement would take place.

A consideration of the observed constants[6] for the possible N methylated anilines and toluidines produced as a result of the rearrangement makes it obvious that no great difference in ionization constants exists between the *N* alkyl anilines and the isomeric toluidines which might result from their rearrangements until the quaternary stage is reached. Thus neither methyl- nor dimethylaniline can rearrange into toluidine since there is neither acid nor negative radical present to aid in the formation of a quaternary compound. The ionization constant data are also in accord with Hofmann's explanation of the mechanism of the reaction.

TABLE I

CONSTANTS OF METHYLANILINES AND TOLUIDINES

Subs.	K_b	Temp. °C.	Subs.	K_b	Temp. °C.
Methylaniline	2.55×10^{-10}	18	*o*-Toluidine	3.0×10^{-10}	18
Dimethylaniline	2.42×10^{-10}	18	*m*-Toluidine	3.9×10^{-10}	15
			Dimethyl-*o*-toluidine	3.08×10^{-9}	15
Trimethylphenylammonium hydroxide	1.0	18	Dimethyl-*m*-toluidine	2.4×10^{-9}	25
p-Toluidine	1.6×10^{-9}	18	Dimethyl-*p*-toluidine	6.36×10^{-9}	15

In order to test the correctness of the above predictions as well as to study the effect of temperature, time and pressure on the rearrangement the following work has been carried out.

Experimental Part

Construction of Carius Electric Furnace

As an accurate heat control was desired in the rearrangement study, the ordinary Carius gas furnace and a furnace in which vapor baths of different liquids were the heat media were replaced by an electrically-controlled Carius furnace. This furnace gave a constant heat to within 10° or for the last half of the furnace to within 1°.

Preparation of Materials

Methylaniline.—The methylaniline used was an imported sample and was purified by steam distillation and subsequent fractional distillation. The constant-boiling portion distilled at 189–190° (uncorr.), and gave no traces of primary or tertiary amines with benzene sulfonyl chloride.

Dimethylaniline.—This was also an imported product and was purified in the same manner as was the methylaniline. The constant-boiling portion distilled at 187–189° (uncorr.).

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[5] Derick, THIS JOURNAL, 35, 1269 (1913).

[6] These are apparent ionization constants not true ionization constants, but in the light of this work the conclusions would not be changed.

p-Toluidine.—The p-toluidine was purified by recrystallization from ligroin. The last traces of ligroin present were removed by drying in a vacuum desiccator over sulfuric acid and then over calcium chloride.

Methylaniline Hydrochloride.—Twenty-five g. of the purified methylaniline was dissolved in 400 cc. of *dry* ether. A stream of dry hydrogen chloride was passed into this ether solution. The hydrochloride precipitated as a beautiful white solid, which was thoroughly washed with ether and dried on a porous plate over the radiator. The preparation of the hydrochloride was attempted with a more concentrated ether solution, but colored liquid products were also obtained.

Trimethylphenylammonium Iodide.—This compound was prepared by heating molecular proportions of methyl iodide and dimethylaniline in a pressure flask over the steam-bath for two hours. It was purified by crystallization from 95% alcohol, and dried on a porous plate and then in a vacuum desiccator over calcium chloride; yield, 74%.

Trimethylphenylammonium Chloride.—The trimethylphenylammonium iodide was dissolved in water, and moist silver oxide added in excess above that necessary to give a complete precipitation of the iodine as silver iodide. The silver iodide was removed by filtration and the remaining solution saturated with hydrogen chloride and evaporated to dryness. The product was crystallized from alcohol, dried by centrifuging for five minutes and placing in a vacuum desiccator over calcium chloride.

Benzenesulfonyl Chloride.—This compound was prepared by mixing 100 g. of phosphorus trichloride and 100 g. of sodium benzenesulfonate (previously dried at 120°). The products of the reaction were poured into large portions of water and shaken vigorously to destroy the phosphorus oxychloride formed in the reaction. The benzenesulfonyl chloride was extracted with ether and fractionally distilled. It was necessary to distil three times to get a perfectly clear product. At 20 mm. the boiling point (uncorr.) was 134°; at 22 mm., 136°; at 25 mm., 140°; yield, 50 g.

Quantitative Separation and Determination of the Three Classes of Aromatic Amines

In order to find the best conditions for the quantitative formation of the sulfonyl derivatives in a quantitative separation and determination of aromatic amines, an investigation of the effect of different media was first made on methylaniline (a secondary amine). The knowledge thus gained was used with p-toluidine (a primary amine), and later in the separation of and determination of methylaniline, p-toluidine and dimethylaniline.

The ordinary textbook method for the formation of sulfone derivatives by the treatment of the methylaniline with an excess of benzenesulfonyl chloride and potassium hydroxide solution (1–4) gives results much higher than those calculated. The direct combination in boiling ether solution appears to approach an equilibrium when only 50% combination is effected, while the direct combination in the absence of solvent and condensing agent is not complete after six hours' heating on the steam-bath. The method finally adopted follows.

A mixture of mono- and dimethylanilines and p-toluidine was shaken vigorously for ten minutes with 50 cc. of a 1:10 sodium carbonate solution and 20% excess benzenesulfonyl chloride. A solution of potassium hydroxide (1:1) was added in small portions to the carbonate solution until a solid, flocculent mass was formed which went into solution upon slight dilution. The formation of this solid may be taken as the end-point of this addition. The reaction mass was extracted quantitatively with ether (Extract I). The alkaline solution was acidified and quantitatively extracted with ether (Extract II).

Extract I contained the sulfonyl derivative of methylaniline, the disulfonyl derivative of *p*-toluidine[7] and unchanged dimethylaniline. The ether was evaporated and the residue refluxed with sodium alcoholate (made by dissolving 4 g. of metallic sodium in 50 cc. of 96% alcohol) for 30 minutes. The mass was diluted with water and the alcohol evaporated. The suspension was quantitatively extracted with ether (Extract III), removing the sulfonyl derivative of methylaniline and free dimethylaniline. The aqueous solution remaining was acidified and extracted with ether (Extract IV), removing the remainder of the sulfonyl derivative of *p*-toluidine.

Extracts II and IV were united, dried, evaporated and the sulfonyl derivative of *p*-toluidine was dried and weighed. Extract III was evaporated and 25 cc. of concd. hydrochloric acid was added to the residue. This formed the hydrochloride of dimethylaniline, and the sulfonyl derivative of methylaniline was removed from it by ether extraction. The hydrochloride was then neutralized with concd. sodium hydroxide solution and the free dimethylaniline extracted with ether. The final products in each case were dried in a current of dry air and then in a vacuum desiccator.

TABLE II

RESULTS

Quantity used G.	Wt. of derivative G.	Calc. wt. G.	Error %
	p-Toluidine		
0.586	1.375	1.353	1.6
.642	1.511	1.482	1.8
.693	1.644	1.601	2.6
	Methylaniline		
0.643	1.549	1.485	4.2
0.881	2.137	2.035	4.8
1.127	2.716	2.604	4.1
	Dimethylaniline		
0.823	...	0.823	...
.621	0.481	.621	−22.0
.876	.689	.876	−21.0

The low percentage for the tertiary amines is due to the formation of a blue dye. Subsequent work has shown, however, that if the sulfonyl chloride is allowed to act for only 20 minutes upon the initial quantity, the dye formation is greatly decreased. In the separation of the products of bomb experiments this error does not appear to exceed 6%.

Rearrangement Studies

Quantities of approximately the same weight of the aromatic amines or their salts were sealed in bomb tubes of known volumes, and heated under the conditions indicated in Table III.

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[7] Hinsberg, *Ber.*, **38**, 906 (1905).

When the tubes were opened the product was first extracted with ether and then with water. The extracts were evaporated to dryness and weighed. From the residue of the water extract two accurately weighed check portions (generally 7 to 9 g. each) were withdrawn and treated with sufficient 10% sodium carbonate solution to liberate completely the amines, which were extracted with ether, the extracts dried over anhydrous sodium sulfate, the ether evaporated, and the amines left accurately weighed. To a sample portion of the amines was then applied the quantitative separation into classes by benzenesulfonyl chloride as developed above. In the case of these unknown amines the separation was started, however, by adding to the mixture of amines 25 cc. of 10% sodium carbonate solution, and three times their weight of benzenesulfonyl chloride.

In every case where a substance was removed by ether extraction, at least three extractions were made and the combined extracts dried over anhydrous sodium sulfate, which after separation from the ether solution was also washed thrice with ether and the washings were added to the original solution so that none of the desired product was lost. It is thus obvious that in the course of a single analysis about 40 ether extractions were made.

In Table III are recorded typical examples of the weights of samples of free amines used from each experiment and the corresponding weights of primary derivatives, secondary derivatives and free tertiary amines obtained from each sample. Methylaniline hydrochloride was the original charge used in these experiments and the ether extract of the bomb contents in all of these cases was "nil" or only a trace.

TABLE III

REARRANGEMENT STUDIES

Expt.	Time of heating hours	Temp. of heating °C.	Bomb volume Cc.	Free amines G.	Primary derivs. G.	Secondary derivs. G.	Free Tertiary amines G.
1	8	200–210	120	5.789	2.956	8.102	1.465[a]
2	48	220–230	130	9.140	4.775	12.001	2.183[a]
3	96	220–230	120	6.049	2.781	9.261	1.019[a]
4	2	240–250	120	8.324	4.264	11.580	1.419[a]
5	3	300	140	5.765	6.915	1.053	2.324
6	4	300	140	6.170	7.776	1.751	2.365
7	6	300	140	5.380	5.178	1.247	2.656
8	12	220–230	150	4.750	2.684	5.990	0.745[a]
9	12	220–230	75	4.232	2.242	6.014	0.974[a]

[a] Blue dye in tertiary.

Expt. 10.—Free methylaniline was heated for 3 hours at 330–340°; 96.8% remained unchanged. There was slight decomposition in the tube.

Expt. 11.—Dimethylaniline was heated for 12 hours at 350–360°; 87.54% was recovered unchanged. Partial decomposition took place but no primary amines were formed.

Expt. 12.—Trimethylphenyl ammonium chloride was heated for 12 hours at 220–230°. The ether extract of the bomb contents was identified as dimethylaniline.

The presence of the blue dye in the tertiary amines is convincing proof of the synthesis of dimethylaniline hydrochloride in the bomb from the methylaniline hydrochloride as assumed by Hofmann. This is true since the following tertiary amines, when treated with benzenesulfonyl chloride under the conditions of the analysis, failed to give a blue dye: diethylaniline, dipropylaniline, dimethyl-*o*-toluidine and dimethyl-*p*-toluidine. No *meta* compounds were experimented with, since no observations have indicated their synthesis by the Hofmann rearrangement.

Method of Testing Accuracy of Analyses

In order to check the analytical work in the simplest manner possible before attempting any interpretation of results (of Expts. 1 to 10) the following system was adopted. The weight of the free amine charge for each analysis was made the standard, as these checked each other within 0.5%. The following system of ratios was calculated for each check analysis. For the primary amines the ratio $\frac{\text{wt. of primary derivative}}{\text{wt. of free amine charge}}$; for secondary amines, $\frac{\text{wt. of secondary derivative}}{\text{wt. of free amine charge}}$; and for the tertiary amines $\frac{\text{wt. of free tertiary amine}}{\text{wt. of free amine charge}}$.

This showed that the analytical work does not possess a total error greater than 6% between check results for any single run. In many cases the error is only 3%.

Interpretation of Analytical Data

In the introduction it was stated that Hofmann's explanation agreed with the data for the ionization constant in predicting that methylaniline hydrochloride must change to a quaternary compound before a shift of a methyl group into the ring is possible. This view necessitates the change of methylaniline hydrochloride into dimethylaniline hydrochloride and aniline with the subsequent change of this product into phenyltrimethyl ammonium chloride with the further formation of free aniline. For each molecule of the quaternary compound formed, two molecules of aniline must be produced in order to furnish sufficient methyl groups. If the rearrangement occurs in the quaternary stage the first product of the rearrangement should be dimethylamino-methylbenzene hydrochloride. When all of the secondary amine has been changed to this product by the above reactions and rearrangement, two-thirds of the bomb contents should be aniline. But of course, more than one methyl group enters the ring and varies the amount of aniline formed.

Similarly, the methylated amino-methylbenzene dissociates so that the primary amino methylated benzenes will contaminate the aniline when rearrangements occur.

From the experiment consisting of a 20-hour run at 300° it is evident that decomposition will prevent final completion of rearrangement at this temperature, for in this experiment decompositions were the predominating reactions.

On the other hand, for rearrangements at lower temperatures for short time intervals it is evident that the primary amine fractions will consist mainly of aniline, if not entirely. Similarly, the secondary amines will consist mainly, if not entirely, of methylaniline. These facts are shown in the analytical data by a steady increase in the percentage of primary amines to a maximum corresponding to two molecules of aniline mentioned with subsequent decrease of secondary amines. In the case of the secondary amines there should be a steady decrease in the percentage found as the rearrangement proceeds, with a possible but not very probable increase when the primary amine has reached its maximum, since when free aniline is methylated by methyl chloride under the conditions of the experiment, it probably goes rapidly to the quaternary stage, which in turn rapidly rearranges, since at the moment of its formation its chance of rearrangement is best.

Since the primary and secondary amines were weighed as the sulfonyl derivatives of unknown amines, while the tertiary amines are weighed in the free state, it is impossible to calculate the percentage of primary and secondary amines formed in the rearrangement until their nature has been determined, unless they consist of aniline and methylaniline, respectively. This offers a preliminary method, however, of attacking the problem of the interpretation of the analytical data given above. If this interpretation is correct, the sum of the ratios of primary, secondary and tertiary amines to the total free amines in each experiment should equal unity within the limits of experimental error as discussed. Accordingly, the following calculation has been prepared on this basis, by multiplying weight ratios of the primary amines by the fraction $\frac{\text{mol. wt. of aniline}}{\text{mol. wt. of sulfonyl derivative}} = \frac{93}{233} = 0.399$, and the weight ratios of the secondary amines by $\frac{\text{mol. wt. of methyl aniline}}{\text{mol. wt. of sulfonyl derivative}} = \frac{107}{247} = 0.433$. It is to be noted that addition of a methyl group causes a change of from 15/197 for addition of methyl to methylaniline and 15/149 for the addition of methyl to *p*-methyl-dimethyl-*o*-toluidine, 14% and 10%, respectively, each being greater than the experimental error of 6%.

The blue dye was formed in these determinations but did not appear to influence the results within the range of the experimental error since in the determinations where no blue dye was formed the total error of analysis is practically the same.

It is obvious in this method of calculation that the fractional ratios of the free amines to the initial charges have been used rather than the percentage form of expression. So the sum of the fractions for each class of amines should equal unity within the limits of error, if the above assumption as to the nature of the primary and secondary amines is warranted. This was found to be the case for every experiment.

In order to confirm further the identification of the individual amines formed in each experiment, the sulfonyl derivatives of the primary and secondary amines were subjected to a very extended fractional crystallization by the gradual dilution with water of their alcohol solutions.

The primary derivatives were found to melt at 104° to 109° which is within the range of the melting point observed by previous investigators for aniline.

The secondary derivatives were found to melt at 76–78°, small amounts of tarry material lowering the melting point from 79°, that observed for methylaniline.

As previously stated, the presence of the blue dye confirmed the tertiary amine as dimethylaniline, in all cases where this was noted (see Table III).

The Influence of the Time on the Reaction

A summary of all the experiments carried on below 250° except the 96-hour run at 220–30° gives the same result within experimental error, for the primary, secondary and tertiary amines. The fact is, therefore, firmly established that when the gaseous volumes in the bombs are practically the same, a variation in time of heating from 2 to 48 hours has a negligible effect on the course of the reaction. These same data further show that a variation in temperature between 200° and 250° for 2 to 48 hours also has a negligible effect. These results are possible only if such a state of equilibrium exists within the bombs that when cooled the contents of each bomb pass through the same changes, and at a certain temperature the system is frozen by solid hydrochloride formation whose dissociation is negligible. No rearrangement, that is, no entrance of the methyl group into the ring could possibly have occurred in these experiments since this reaction is non-reversible and would alter the percentages of primary, secondary and tertiary amines, which is contrary to the experimental facts given for Expts. 1, 2, 4, 8 and 9.

Another interesting proof that such equilibria are established without the non-reversible rearrangement occurring in Expts. 1, 2, 4, 8 and 9 is seen in the fact that the percentage of primary amine must equal the percentage of tertiary amine. The experimental data show that this is the case even though the blue dye interferes somewhat with the determination of the tertiary amine.

Expt. 3, in which methylaniline hydrochloride was heated for 96 hours at 220–300°, however, shows clearly that the time of heating does slowly influence the course of the reaction and that rearrangement of the methyl group into the ring has taken place to a small extent due to the slight velocity of this reaction at this temperature. In this experiment the primary amines have decreased 12%, while the secondary amines show an increase of 13%. The tertiary amines have decreased 22%. The most striking feature of Expt. 3 is that it alone shows an increase in the percentage of secondary amines, and a decrease in both primary and tertiary amines. All other experiments show a steady decrease in secondary amines.

In the series of experiments numbered 5, 6 and 7 at 300° the time of heating is a decided factor. The most striking fact about this series of experiments is that the primary amines are practically constant and maximum for the three- and four-hour runs, but for the next two hours' heating a decrease of 22% is observed, while the percentage of secondary amines appears to increase to a maximum in the three- to the four-hour run, an increase of 36%, but falls from 11 to 10% during heating for two more hours. The percentages of tertiary amines for these experiments show a total increase of 24% for an increase of three hours in heating.

In Expts. 5, 6 and 7 it is clear that the methyl groups have entered the ring by the non-reversible rearrangement and, when the contents of the bomb tubes have cooled, cannot pass through the same state, as was the case in Expts. 1, 2, 4, 8 and 9, due to the non-reversibility of this rearrangement. This fact would reflect itself in different percentages of primary, secondary and tertiary amines in Expts. 5, 6 and 7 as compared with Expts. 1, 2, 4, 8 and 9. The experimental data given show that this occurs. Further the non-reversibility of this rearrangement would demand that the percentages of the primary, secondary and tertiary amines in Expts. 5, 6 and 7 should vary with the time of heating, and such is the fact shown by the experimental data.

Influence of Volume or Pressure on the Reaction

Since the equilibria of the reaction are established below 250°, and since there is no shift of the methyl group into the ring by non-reversible reaction at this temperature, the influence of volume or pressure cannot be studied in Expts. 8 and 9, for upon cooling, the equilibria go through the same changes as in Expts. 1, 2 and 4, and the system is fixed at the same temperature, that is, where the dissociation of the solid hydrochlorides of the primary, secondary and tertiary amines is negligible.

Furthermore, if the solid phase is in equilibrium with the gaseous phase, there would be only one degree of freedom, and since in this case the pressure (volume) is fixed, the temperature would be the only factor.

That such an equilibrium does exist here is borne out by the results of

Expts. 8 and 9, where equal charges of solid methylaniline hydrochloride were heated in bombs of approximately 150 cc. and 75 cc. gaseous volumes. The results of these experiments show the percentages of primary, secondary and tertiary amines, respectively, to be the same within experimental error.

Influence of Temperature on the Reaction

Increases from 250° to 300° demonstrate clearly that temperature is the main variable in the Hofmann rearrangement. This is obvious from the fact that the primary amines have changed from a constant value of 20% to the variable values 49, 51 and 39%, respectively, for 3, 4 and 6 hours' heating at 300°; for the secondary amines the constant value 60% to the varying values 7, 11 and 10%, and for the tertiary amines there is an increase from 22% to 38, 39 and 50%, respectively, for the same experiments. This is to be expected since the rearrangement is a non-reversible reaction.

Formation of Phenyltrimethylammonium Chloride in the Reaction

The hypothesis advanced in this paper as to the mechanism of the Hofmann rearrangement demands that in order to rearrange methylaniline hydrochloride, phenyltrimethylammonium chloride must first be formed since this is the compound which is postulated as rearranging. The analytical data in combination with the weight of the water extracts of the bomb contents afford a method of determining the percentage of the phenyltrimethylammonium chloride formed in each experiment. They also offer a means of justifying the interpretation deduced, namely, that the primary amine is aniline, the secondary amine is methylaniline and the tertiary amine is dimethylaniline.

The water extract of the bomb contents is made up of phenyltrimethylammonium chloride and the hydrochlorides of the primary, secondary and tertiary amines. This is true whether or not other substances have been formed during the rearrangement, since the initial ether extract would remove all other classes of organic compounds, which might be formed here, excepting the salts of the organic amines, as only the latter are insoluble in ether under the conditions of the experiments. Since the weights of the sulfonyl derivatives of the primary and secondary amines, and the free tertiary amines are given in each experiment, and since previous calculations give strong evidence that the primary amine is aniline, the secondary amine methylaniline and the tertiary amine dimethylaniline, at least for Expts. 1, 2, 3, 4, 8 and 9, their weights as hydrochlorides may be calculated as follows.

(a) For primary amines:

$$\frac{\text{Mol. wt. of aniline hydrochloride}}{\text{Mol. wt. of aniline sulfonyl derivative}} = \frac{129}{233} = 0.55$$

(b) For secondary amines:

$$\frac{\text{Mol. wt. of methylaniline hydrochloride}}{\text{Mol. wt. of methylaniline sulfonyl derivative}} = \frac{143}{247} = 0.58$$

(c) For tertiary amines:

$$\frac{\text{Mol. wt. of dimethylaniline hydrochloride}}{\text{Mol. wt. of dimethylaniline}} = \frac{151}{121} = 1.30$$

or

$$\frac{\text{Mol. wt. N Dimethylamino-trimethylbenzene HCl}}{\text{Mol. wt. N Dimethylamino-trimethylbenzene}} = \frac{199}{163} = 1.22$$

By means of these fractions and the data of the experiments the weights of the hydrochlorides of the primary, secondary and tertiary amines are calculated thus: (a) primary amines: wt. of sulfonyl derivatives × 0.55 = wt. of hydrochloride; (b) secondary amines: wt. of sulfonyl derivatives × 0.58 = wt. of hydrochloride; (c) tertiary amines: wt. of tertiary amines × 1.30 = wt. of hydrochloride, or wt. of tertiary amines × 1.22 = wt. of hydrochloride.

From this set of calculations it is evident that in Expts. 1, 2, 3 and 9, if any phenyltrimethylammonium chloride is formed it is not greater than the error of the analytical results, namely, 6%, and is certainly negligible in the interpretations which will follow. In Expts. 4 and 8 the sum of the weights of the hydrochlorides of the primary, secondary and tertiary amines equals only 90% of the total water extract and it would appear that at least 4% of phenyltrimethylammonium chloride was present in the bomb. This, however, is very questionable for Expt. 8, especially in the light of certain irregularities before noted in the percentage of secondary amines. It is possible that the higher temperature used in Expt. 4 may have produced a small amount of phenyltrimethylammonium chloride.

In conclusion, it appears from the present data that the amount of quaternary compound formed for all experiments at or below 250° is within the experimental error, or for the accuracy of the present work it may be stated that no phenyltrimethylammonium chloride is formed in these experiments.

In Expts. 5, 6 and 7, the hypothesis advanced demands that the quaternary compound shall be formed in the bomb since the tertiary amine is not dimethylaniline. It does not follow, however, that the phenyltrimethylammonium chloride will be found at the end of the experiment since it may rearrange at the moment of formation in these experiments. But if rearrangement has actually taken place it is equally possible that upon cooling the bomb a temperature may be passed through at which the quaternary compound may form but not rearrange. The last-mentioned method of calculation shows that upon either interpretation as to the nature of the tertiary amines, quaternary compounds must be present in amounts varying from 13 to 30%.

Summary

1. In the Hofmann rearrangement, methyl chloride dissociates from the methylaniline hydrochloride and adds to a second molecule until trimethylphenylammonium chloride is formed, and this is the compound that rearranges.
2. No rearrangement takes place at 220–250° unless the heating is continued for 96 hours.
3. The rearrangement takes place at 300° and is somewhat affected by time; however, temperature is the main variable.
4. Neither methylaniline nor dimethylaniline rearranges.
5. A quantitative separation and determination of the three classes of amines have been developed incident to studying the rearrangement.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

THE CATALYTIC CONDENSATION OF ACETYLENE WITH PHENOLS

BY HERMAN H. WENZKE AND J. A. NIEUWLAND

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The condensation of acetylene with phenols was effected in 95% alcoholic solution and in the presence of concd. sulfuric acid and mercury salts. The proportion of alcohol used to dilute the phenolic compound varied, but a sufficient amount was used so that there would be no precipitation when sulfuric acid was added to the solution. The acid content of the reaction mixture was approximately 15 to 20%, but in cases where the absorption proceeded slowly the acid concentration was increased to 40%. As mercuric sulfate is only very slightly soluble in the reaction mixture, its concentration is of slight importance. Care was taken, however, to have it in slight excess. The acetylene was under a pressure of from 0.1 to 0.16 atmosphere, and a closed absorption system was used. The quantity of gas that had reacted was determined by the increase in weight of the reacting mixture. In these experiments the object was rather to investigate the products formed than to determine the intermediate compounds.

Phenol, under the conditions mentioned, absorbed acetylene very readily, but the product formed did not have the properties of the ethylidene diphenylol prepared from acetaldehyde and phenol.[1] The entire product formed was soluble in sodium hydroxide and various organic solvents but attempts to obtain crystals from these solutions met with failure. Very little information was obtained as to the constitution of the acetylene-phenol condensation products. The results with *ortho, meta*

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[1] Claus and Trainer, *Ber.,* 19, 3009 (1886).