23. **Genshun Sunagawa** : Decomposition of Benzylamine Derivatives. IV.[1] Aromatic Electrophilic Substitution Reactions of Benzyl Cation. (1).

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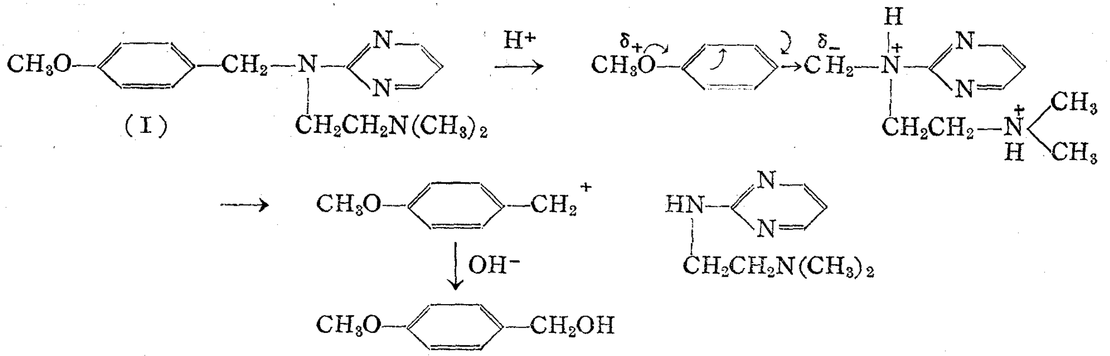
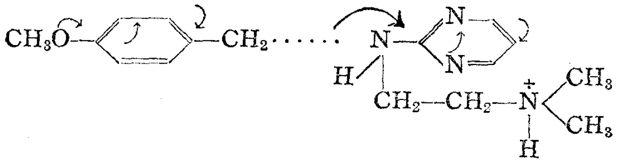
The writer has shown in the preceding paper[1] that thonzylamine and compounds possessing similar structure undergo facile decomposition on being heated with dilute hydrochloric acid, as long as they fulfill the following two conditions : (1) The presence of an aromatic residue in the amino group in benzylamine ; and (2) the presence of a substituent with marked +M effect in the *para*- or *ortho*-position of the benzene ring.

As for the mechanism of this decomposition, it seems more appropriate to assume that the reaction proceeds through the same route in spite of the different products formed from this reaction. As was pointed out in the previous paper, the decomposition does not occur in compounds satisfying the second condition if it does not fulfill the first condition. For example, *p*-methoxybenzylamine itself is stable to dilute mineral acids. Therefore, it is probably correct to assume that in the first stage of this reaction, the benzylamine substituted with an aromatic residue alone undergoes cleavage of the C-N bond. Of course, the aromatic residue substituted in the nitrogen plays the chief rôle in this cleavage but, on the other hand, the substituent with +M effect in the *ortho*- or *para*-position of the benzene ring in the benzyl group also helps in effecting this cleavage because, as is indicated by the second condition, the absence of such a substituent is known to make this reaction impossible. The first stage of this reaction, for example, in thonzylamine (I), is thought to proceed in the following order.



The sequence would be as follows : (1) The +M effect of the methoxyl group in the benzene ring would be transferred to $-CH_2-$ where the electron density becomes greater, with lessening of the electron affinity. On the other hand, attachment of H^+ to N of aminopyrimidine increases the electron affinity of the nitrogen. (2) In the transition state, resonance accompanying the electron releasing effect of the *p*-methoxybenzyl group and the resonance between the nitrogen and the aromatic ring effects the stabilization of the two portions by resonance energy, as shown below.



It goes without saying that, in this case, the second resonance will not occur if the nitrogen is an aliphatic amine. Therefore, by assuming that the duplication of the

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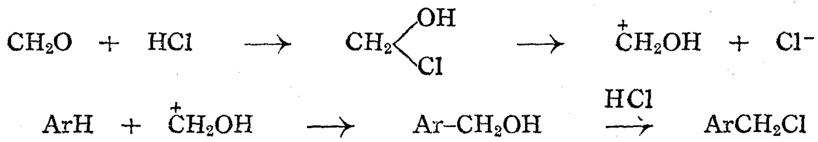
[1] Part III. Sunagawa, Ichii, Yoshida : This Bulletin, 3, 109 (1955).

foregoing (1) and (2) effects easy severance of the C–N bond, it makes it possible to understand the reason why the reaction proceeds only when the afore-mentioned two conditions are met.

Such being the case, the products formed in the first stage of this reaction would be an aromatic amine and a benzylcarbonium cation. The former has actually been isolated in the many examples shown1) but the latter has not been isolated in the majority of cases except in the case of *o*-dimethylaminobenzylaniline (II) from which *o*-dimethylaminobenzyl alcohol was isolated and this may be said to offer a strong basis for endorsing this assumption.

The reason why benzyl alcohol, assumed to be formed in the first stage of this decomposition, is not isolated in the majority of cases was assumed to be due to the fact that the compound easily undergoes further reaction in an acid medium.

A chloromethylation of aromatic hydrocarbons proceeds well and Dewar has explained this reaction as follows:



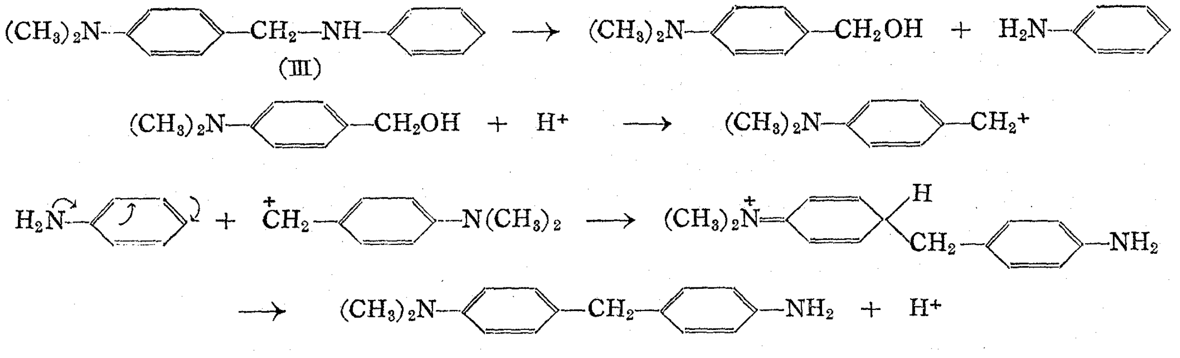
$$CH_2O + HCl \longrightarrow CH_2\begin{matrix}OH\\Cl\end{matrix} \longrightarrow \overset{+}{C}H_2OH + Cl^-$$

$$ArH + \overset{+}{C}H_2OH \longrightarrow Ar\text{-}CH_2OH \xrightarrow{HCl} ArCH_2Cl$$

However, when a substituent with a stronger +M effect is present, rather than the hydrocarbon, this reaction does not stop at this stage but proceeds to the diarylmethane derivatives or even further to high polymers, such as bakelite. When sulfuric acid is used in place of hydrochloric acid, diphenylmethane derivatives are obtained and Dewar has explained this reaction with mechanisms similar to the foregoing reaction. In other words, benzene and formaldehyde form benzyl alcohol in the presence of a strong acid, and this intermediate reacts further with unreacted benzene, in the presence of H^+, to form a diphenylmethane.

Okata2) studied the acid catalyzed reaction of dimethylaniline and formaldehyde and obtained *p,p'*-bis(dimethylaminodiphenyl)methane. He reached the same conclusion as that of Dewar with regard to this reaction mechanism.

In applying this theory to the experimental results obtained in the present series of works, it is seen that the reaction can easily be understood by assuming that, in the case of *p*-dimethylaminobenzylaniline (III), the compound would be decomposed into *p*-dimethylaminobenzyl alcohol and aniline in the first stage and these would react in the manner explained by Dewar.



However, no explanation can be forwarded for the mechanism whereby *p,p'*-bis-(dimethylaminodiphenyl)methane is formed as a by-product in the decomposition of (III) because, if the reaction is assumed to proceed as theorized by Dewar, it must necessarily proceed in the following sequence but such a compound has not been isolated.

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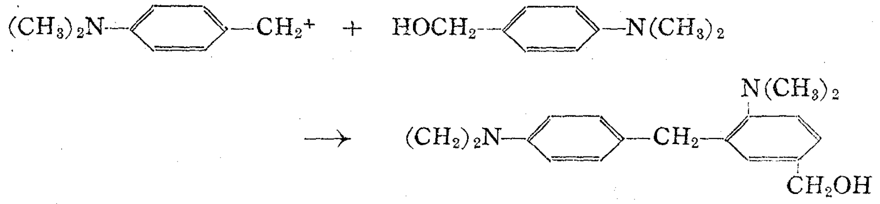
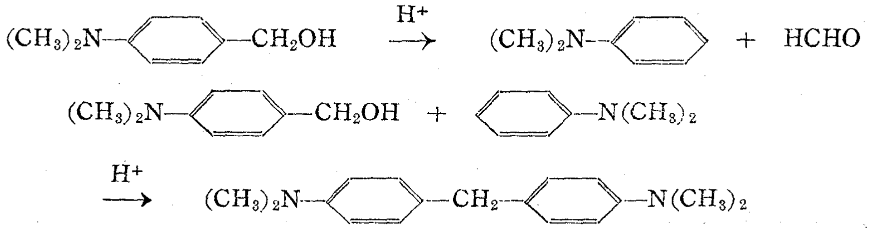
2) M. Okata: J. Am. Chem. Soc., **72**, 1459(1950).



It follows, therefore, that in order to give a rational explanation for the by-product formation as well as in comprehending the reaction mechanism of the decomposition of benzylamine derivatives, it may be possible to assume that the ring-substituted benzyl alcohol undergoes decomposition into benzene and formaldehyde and these decomposition products then react with ring-substituted benzyl alcohol, in accordance with Dewar's theory, to form the symmetric diphenylmethane compound.



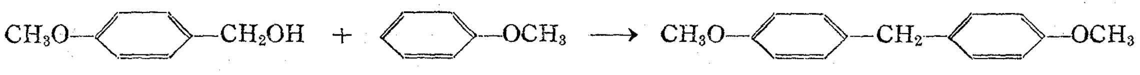
The fact that formaldehyde is invariably detected in the products of the foregoing decomposition reactions seems to indicate the authenticity of this hypothesis. However, the writer is of the opinion that this hypothesis is contrary to following facts :

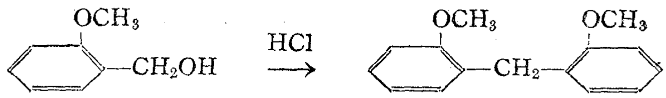
(1) If, for example, *p*-methoxybenzyl alcohol decomposes into anisole and formaldehyde, and this anisole reacts with undecomposed *p*-methoxybenzyl alcohol, this anisole formed as an intermediate should be recovered from the reaction solution, even in a small amount, but there has been no evidence of the formation of anisole on heating *p*-methoxybenzyl alcohol with hydrochloric acid.

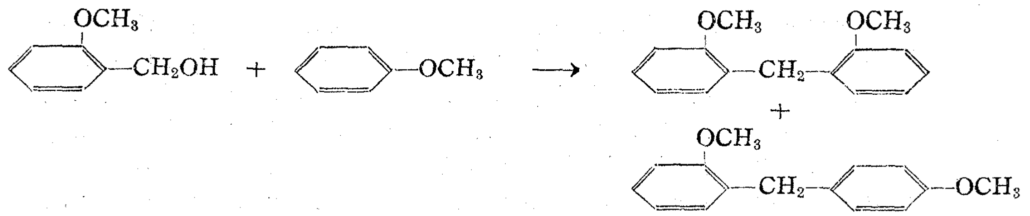
It is true, however, that *p,p'*-dimethoxydiphenylmethane and formaldehyde are formed and, in the case of *p*-dimethylaminobenzyl alcohol, the experimental evidence is the same and although there is no formation of dimethylaniline, formation of formaldehyde with *p,p'*-bis(dimethylaminodiphenyl)methane has been detected. In this connection, Okata[2] had carried out this reaction and reported that he did not observe the formation of formaldehyde, differing from the results of the present series of experiments.

(2) In this case, the fact might be interpreted as being due to the fast reaction velocity of anisole and *p*-methoxybenzyl alcohol but the addition of an excess of anisole and heating with *p*-methoxybenzyl alcohol failed to show any evidence of the complete disappearance of anisole during the same period of time as the above reaction.

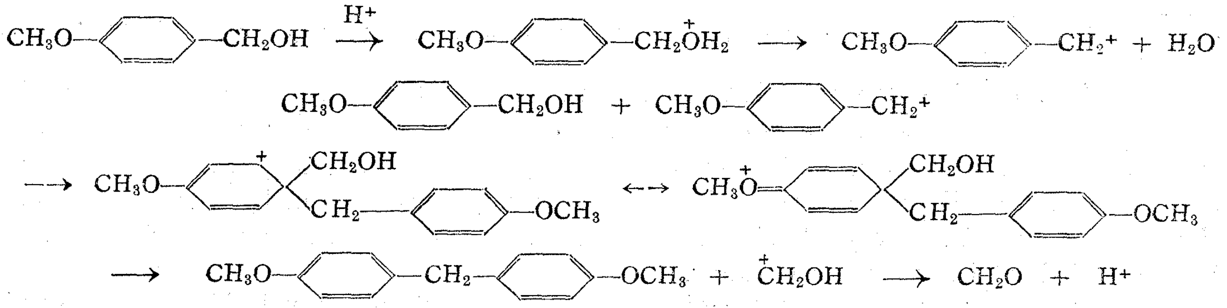
(3) Heating of *p*-methoxybenzyl alcohol and anisole with hydrochloric acid results in the formation of *p,p'*-dimethoxydiphenylmethane alone and no evidence has been obtained of the formation of *o,p'*-derivative. On the other hand, heating of *o*-methoxybenzyl alcohol with hydrochloric acid results in the formation of *o,o'*-dimethoxydiphenylmethane. However, heating of *o*-methoxybenzyl alcohol and anisole with hydrochloric acid yields a mixture of *o,o'*- and *o,p'*-dimethoxydiphenylmethane.



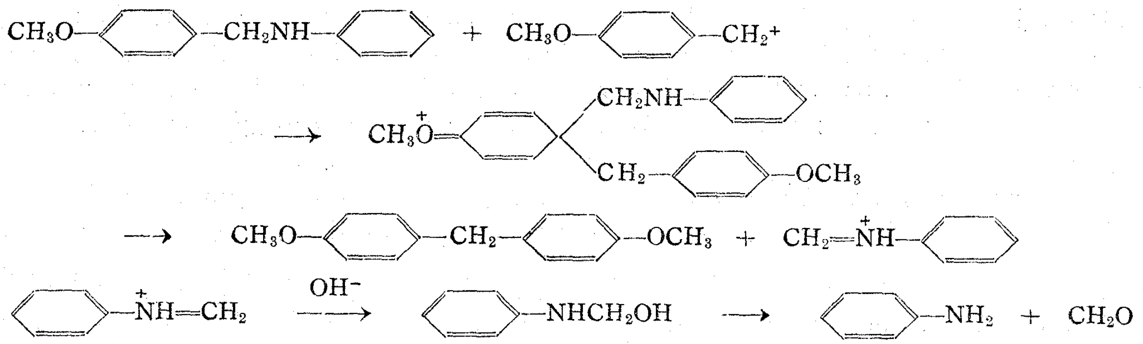




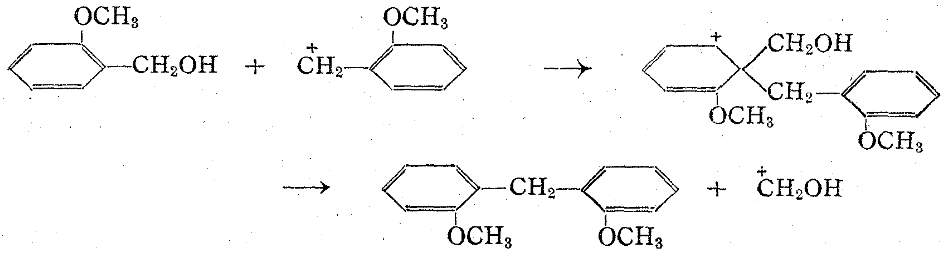
Considering these facts, the writer has assumed the occurence of a still unknown aromatic electrophilic substitution in nuclear substituted benzyl alcohols, as shown below :



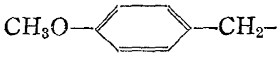
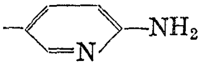
On the other hand, it may be supposed that the benzylcarbonium cation reacts directly with benzylamine, as shown below, but in this case also, the reaction takes the form of an aromatic electrophilic substitution.



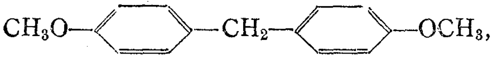
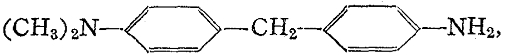
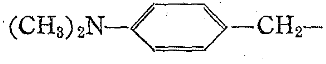
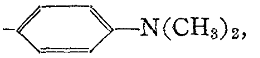
This trend of thought is similar to that taken in the case of *p*-methoxybenzyl alcohol in which the alcohol was assumed to be cleaved into anisole and formaldehyde and unites again. However, the fact that only *o,o′*-dimethoxydiphenylmethane is formed on heating *o*-methoxybenzyl alcohol with hydrochloric acid cannot be explained unless the present new assumption is taken into consideration, because, if *o*-methoxybenzyl alcohol is cleaved into anisole and formaldehyde and then this anisole undergoes condensation with *o*-methoxybenzylcarbonium cation, the formation of *o,p′*-dimethoxydiphenylmethane, as evidenced by experimental results, would naturally follow. As was described above, this substance is actually formed when *o*-methoxybenzyl alcohol and anisole are heated and not when *o*-methoxybenzyl alcohol alone is heated. When *o*-methoxybenzyl alcohol and anisole are heated, the two reactions seem to proceed at the same time.



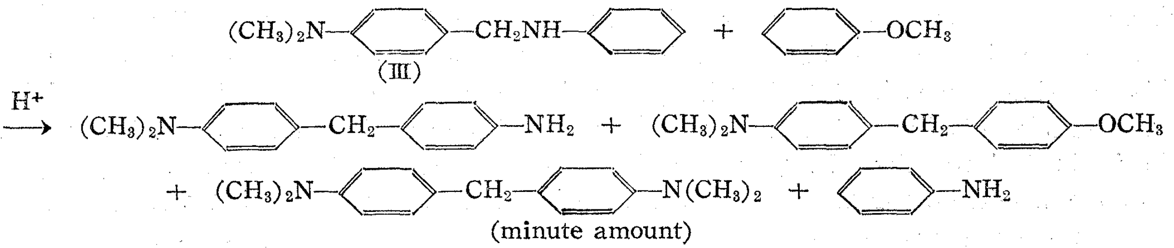
It follows, therefore, that the decomposition of the benzylamine derivatives can most rationally be explained by assuming that the new reaction mechanism indicated by the writer and that based on existing data proceed concurrently in a definite ratio.

To give individual examples, 2-(*p*-methoxybenzylamino)pyrimidine (IV), thonzylamine (I), 2-(*p*-methoxybenzylamino)pyrimidine (V), and 2-(*o*-methoxybenzylamino)-pyrimidine (VI) are decomposed into benzyl alcohol and aromatic amines (2-aminopyrimidine, 2-dimethylaminoethylaminopyrimidine, and 2-aminopyridine) in the first stage of this reaction. In this case, the *para-* or *ortho-*position of the amino group in these heterocyclic compounds is not active enough to form, for example,   by the foregoing substitution (or condensation) reaction. Therefore, they are left outside the reaction range and are isolated, *per se*, from the reaction mixture. The second stage of this reaction proceeds then according to the new mechanism formulated by the writer in the case of *p*-methoxybenzyl derivatives, and formaldehyde and *p,p'*-dimethoxydiphenylmethane, or polymers formed by further condensation of these products, are obtained. The reaction of *o*-methoxybenzyl derivatives can also be explained in the same manner.

Further, the reaction of 2-(*p*-dimethylaminobenzylamino)pyrimidine (VII) would probably be the same. The fact that *p*-dimethylaminobenzylamine was formed as a by-product in this case alone seems to be contrary to the foregoing examples but, since the dimethylamino group is thought to possess weaker +M effect in acid medium than the methoxyl, the decomposition velocity of (VII) should be slower than that of (IV) and the experimental results also endorse this assumption. Because of such sluggishness in reaction velocity, a separate reaction such as the hydrolysis of the pyrimidine ring proceeds to a fair extent and benzylamine is formed in enough amounts to allow detection.

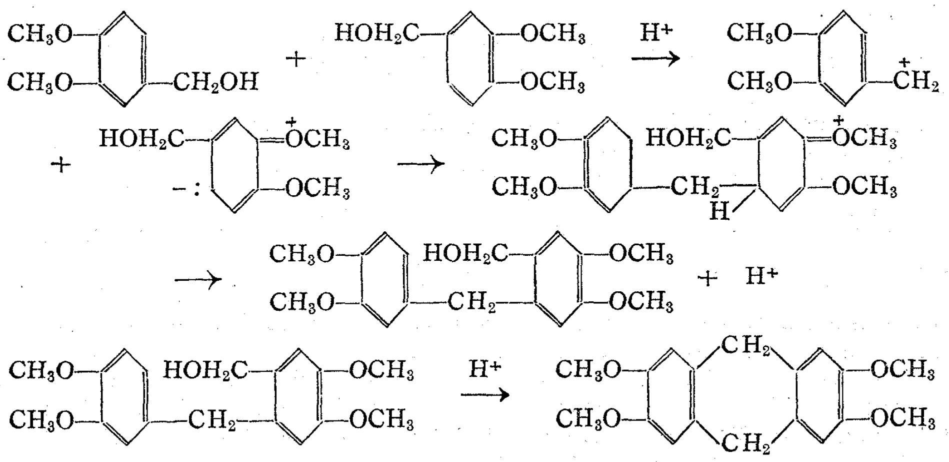
In the case of *p*-methoxybenzylaniline (VIII), *p*-hydroxybenzylaniline (IX), *p*-dimethylaminobenzylaniline (III), and 2,6-dimethyl-N-(*p*-dimethylaminobenzyl)aniline (X), a symmetric diphenylmethane,  is formed chiefly from (VIII) and aniline is removed outside of the reaction range. This can be explained more rationally by assuming that the decomposition reaction has proceeded in accordance with the new mechanism proposed by the writer, rather than by the old type. However, a minute amount of *p,p'*-diaminodiphenylmethane was detected by paper chromatography from the reaction products. As will be described later, this diphenylmethane should be formed from aniline and formaldehyde or from *p*-methoxybenzyl alcohol and aniline. The reaction is the same in the case of (IX) but in this case, it is easy to see that, due to the effect of the hydroxyl group, the diphenylmethane formed and formaldehyde further undergoes condensation to form compounds of the bakelite type. Contrary to these, non-symmetric diphenylmethane,  is obtained in the case of (III) and the formation of the symmetric type,   is very small. In short, this result shows that the old-type reaction mechanism occurs more preferentially in this case than the new-type reaction form. The foregoing reasonings cannot fully explain the reason why the adduct with aniline cannot be isolated even when the *para*-position in the *p*-methoxyl derivatives is active enough, in spite of the fact that the *p*-dimethylamino derivatives follow the existing, old-type reaction form. Some experiments were carried out in order to probe this point and these results will be shown in subsequent papers.

In the case of (III) and (X), the point in question is the doubt that whether the formation of *p*-dimethylamino-*p*′-aminodiphenylmethane from (III) is not the two-stage reaction shown previously of the cleavage of the C–N bond followed by the new formation of a C–C bond but a reaction belonging to some intramolecular rearrangement. As an outwardly similar reaction, the benzidine rearrangement may be cited. The fact that the present reaction is not an intramolecular rearrangement can clearly be shown by the following evidences: (1) Formation of aniline as a by-product and of *p*, *p*′-bis(dimethylaminodiphenyl)methane, even in a small amount; (2) heating of (III) and anisole with hydrochloric acid yields a compound in which anisole has been substituted; and (3) the same results as (2) are obtained on heating *p*-dimethylaminobenzyl alcohol with aniline and anisole, in the presence of hydrochloric acid. In this case, therefore, the reaction is in the nature of an intermolecular, causing rearrangement of diazoaminobenzene to *p*-aminoazobenzene.

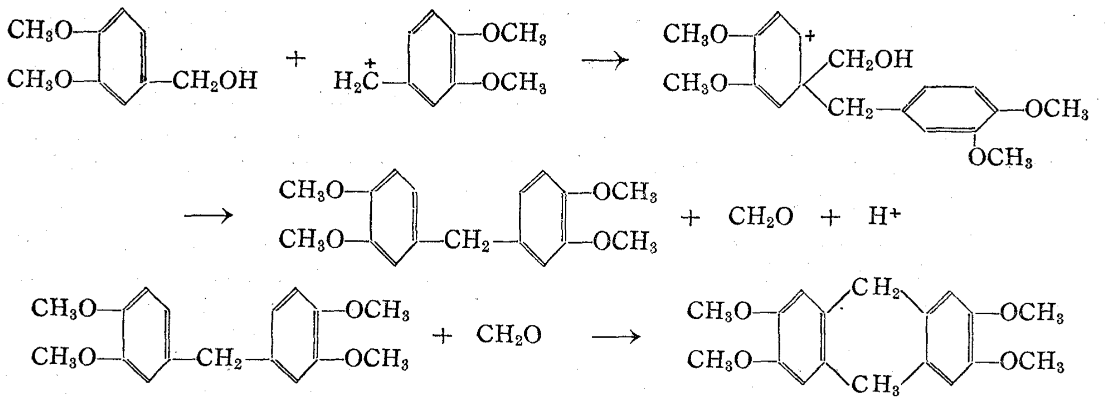


o-Dimethylaminobenzylaniline (II) decomposes into *o*-dimethylaminobenzyl alcohol and aniline and does not form diphenylmethane compounds. This can be assumed to be due to the steric interference of the dimethylamino group in the *ortho*-position of the methylene. *o*-Dimethylaminobenzyl alcohol does not undergo any change when heated with hydrochloric acid or with anisole. This is the point of difference from the case of *o*-methoxybenzyl alcohol and it may be assumed that the point might be closely related to the fact that the atomic volume of dimethylamino group is larger than that of the methoxyl.

In the case of 2-(3,4-dimethoxybenzylamino)pyrimidine (XI) and 2-piperonylaminopyridine (XII), they are cleaved respectively into 3,4-dimethoxy- and 3,4-methylenedioxybenzyl alcohol and heterocyclic amines. It is certain that two moles of this benzyl alcohol bonded to form a compound of the dihydroanthracene series but it is still too early to make a definite conclusion as to its reaction mechanism, whether this dimethoxyl compound had undergone the reaction in accordance with the existing theory, as follows:



or whether it has formed 3,4,3′,4′-tetramethoxydiphenylmethane by the new mechanism and then reacted with formaldehyde to form dihydroanthracene compounds, in the following manner:



In either case, the product is an identical compound. The fact that the formation of formaldehyde has been detected during the reaction seems to indicate that the reaction mechanism proposed by the writer was responsible to some extent in this reaction. If this reaction occurs in 2,3-dimethoxybenzylaniline and if this reaction were to follow the writer's mechanism, 1,2,7,8-tetramethoxydihydroanthracene should be formed, while if it follows the old-type reaction mechanism, 1,2,5,6-tetramethoxydihydroanthracene would be formed. Such an experiment has not be carried out as yet.

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Experimental

Reaction of *p*-Methoxybenzyl Alcohol (XIII) with Hydrochloric Acid—A mixture of 5 g. of (XIII) and 50 cc. of 10% HCl was stirred at 100° for about 3 hrs., cooled, and extracted with ether. The ether residue was submitted to low-pressure distillation and 0.8 g. of the unreacted starting material ($b.p_2$ 90~110°) and 1.5 g. of a fraction of $b.p_2$ 150~153° (later solidified on cooling) were obtained. The latter was recrystallized from EtOH to scaly crystals of m.p. 51~52°. Ultraviolet absorption: λ_{max} 231 mμ ($\log \varepsilon = 4.26$), 278 (3.53), 285 (3.46). Infrared absorption maxima: 12.35, 13.2, and 13.4 μ. No depression of the m.p. occurred on admixture with *p,p'*-dimethoxydiphenylmethane prepared by the method described in the literature.³⁾ *Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 78.65; H, 7.21.

The aqueous solution left after extraction with ether gave orange red coloration by resorcinol for the detection of formaldehyde and formed a yellow 2,4-dinitrophenylhydrazone of m.p. 165°, thereby proving the presence of CH_2O.

Reaction of *p*-Dimethylaminobenzyl Alcohol (XIV) with Hydrochloric Acid—A mixture of 3 g. of (XIV) and 40 cc. of 10% HCl was heated at 100° for 3 hrs., cooled, rendered strongly alkaline, and treated as above. One g. of the unreacted material ($b.p_3$ 115~118°) and 0.9 g. of a fraction of $b.p_3$ 182~185° (later solidified on cooling) were obtained. Recrystallization of the latter from EtOH yielded 0.6 g. of scaly crystals, m.p. 90°, undepressed on admixture with *p,p'*-bis(dimethylaminodiphenyl)methane, prepared in accordance with the method described in the literature.⁴⁾ Ultraviolet absorption: λ_{max} 260 mμ ($\log \varepsilon = 4.45$), 300 (3.57). The presence of CH_2O was detected in the reaction mixture.

Reaction of *o*-Methoxybenzyl Alcohol (XV) and Hydrochloric Acid—A mixture of 10 g. of (XV) (obtained by the Cannizzaro reaction of *o*-methoxybenzaldehyde) and 100 cc. of 10% HCl was reacted as in the foregoing cases and the acid reaction mixture was submitted to steam distillation. The distillate was extracted with ether and about 20 mg. of crystals were obtained. Recrystallized from EtOH to crystals of m.p. 60~61°, undepressed on admixture with *o,o'*-dimethoxydiphenylmethane.¹⁾ The presence of CH_2O was detected in the reaction mixture.

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3) Edm. ter Meer: Ber., **7**, 1200(1874).

4) G. Cohn: Chem. Ztg., **24**, 564(1900).

Synthesis of *o*-Dimethylaminobenzyl Alcohol (XVI)—To a mixture of 6 g. of $LiAlH_4$ and 150 cc. of dry ether being refluxed, a solution of 8.2 g. of *o*-dimethylaminobenzoic acid[5] dissolved in 300 cc. of ether was added dropwise during about 50 min., and the whole was refluxed with agitation for further 2 hrs. The mixture was then cooled with water and 100 cc. of water was added dropwise to decompose the excess of $LiAlH_4$. To this was added 250 cc. of 10% NaOH, ether layer was separated, and the ethereal residue was distilled under a reduced pressure. A fraction of b.p$_{21.5}$ 136∼137°, yield, 7.2 g. (96%). Picrate: m.p. 129∼130°. *Anal.* Calcd. for $C_9H_{13}ON \cdot C_6H_3O_7N_3$: C, 47.36; H, 4.24; N. 14.73. Found: C, 47.62; H 4.44; N, 14.68.

Reaction of *o*-Dimethylaminobenzyl Alcohol (XVI) and HCl—A mixture of 4 g. of (XVI) and 40 cc of 10% HCl was heated at 100° for 4 hrs., treated in the usual manner, and 3.8 g. of a fraction of b.p$_{23}$ 134∼140° was obtained. Picrate of m.p. 129∼130° was found by admixture to be identical with the picrate of (XVI). CH_2O was detected in the reaction mixture.

Reaction of *p*-Methoxybenzyl Alcohol (XIII) and Anisole with HCl—A mixture of 5 g. of (XIII), 3 g. of anisole, and 50 cc. of 10% HCl was heated at 100° for 3 hrs. under stirring. Worked up as usual, 0.2 g. of the unreacted anisole (b.p$_{18}$ 43∼44°) and 5.4 g. of a fraction of b.p$_{2.5}$ 150∼154° were obtained. The latter crystallized on cooling; m.p. 51°, undepressed on admixture with *p,p'*-dimethoxydiphenylmethane.

Reaction of *o*-Methoxybenzyl Alcohol (XV) and Anisole with HCl—A mixture of 20 g. of (XV), 16 g. of anisole, and 200 cc. of 10% HCl was heated for 7 hrs., treated as in the case of (XIII), and 5.1 g. of unreacted anisole (b.p$_{28}$ 61°) and 14 g. of a fraction of b.p$_2$ 158∼165° were obtained. Two g. of the latter was dissolved in 20 cc. of benzene and purified by liquid chromatography through alumina. The column was developed with 110 cc. of benzene and the effluent was divided into 17 fractions. A minute amound of crystals, m.p. 55∼60°, were obtained from fraction No. 3, and this melted at 58∼60° on admixture with *o,o'*-dimethoxydiphenylmethane, m.p. 62°. Oily substances were obtained from fraction Nos. 4∼6 which was further fractionally distilled to give a fraction of b.p$_5$ 164∼167°. *Anal.* Calcd. for $C_{15}H_{16}O_2$ (Dimethoxydiphenylmethane): C, 78.92; H, 7.07. Found: C, 77.90; H, 6.88.

Oxidation with $KMnO_4$: A mixture of 4 g. of the oily substance, b.p$_2$ 158∼165°, and 70 cc. of 20% H_2SO_4 was warmed on a boiling water bath and oxidized with 16 g. of $KMnO_4$. Treated in the usual manner, 1.8 g. of crystals, m.p. 60∼75°, were obtained as a neutral substance. Recrystallization from EtOH afforded 1.3 g. of white prisms, m.p. 100°, undepressed on admixture with the known *o,p*-dimethoxybenzophenone. *Anal.* Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.47; H, 5.92. 2,4-Dinitrophenylhydrazone: Red platelets (from EtOH+AcOEt), m.p. 196°. *Anal.* Calcd. for $C_{21}H_{18}O_6N_4$: N, 13.27. Found: N, 13.29.

As an acid substance 0.1 g. of white microprisms, m.p. 184°, were obtained, which showed no depression of m.p. on admixture with anisic acid.

Reaction of *p*-Dimethylaminobenzyl Alcohol (XIV), Aniline, and Anisole with HCl—A mixture of 5 g. of (XIV), 7 g. of aniline, 6 g. of anisole, and 200 cc. of 10% HCl was boiled for 4 hrs., and separated into basic and neutral portions by the usual method. The neutral portion yielded 1.5 g. of anisole, b.p$_{27}$ 59°, and the basic portion yielded 3 g. of aniline, b.p$_{18}$ 86∼87°, and 2.9 g. of a fraction of b.p$_2$ 186∼192°, which underwent crystallization on cooling to crystals of m.p. 60∼82°. One g. of this substance was dissolved in benzene and purified by chromatography through alumina. Fraction Nos. 2 and 3 afforded 0.2 g. of crystals, m.p. 46°, which showed no depression on admixture with *p*-methoxy-*p'*-dimethylaminodiphenylmethane, prepared from (XIV) and anisole. Fraction Nos. 5∼10 gave 0.4 g. of crystals, m.p. 92°, undepressed on admixture with *p*-amino-*p'*-dimethylaminodiphenylmethane, obtained from (XIV) and aniline. The crystals obtained from fraction No. 4 was submitted to paper partition chromatography which confirmed the presence of *p,p'*-bis(dimethylaminodiphenyl)-methane (Rf 0.86).

Reaction of *p*-Dimethylaminobenzylaniline (III) and Anisole with HCl—A mixture of 5 g. of (III), 5 g. of anisole, and 100 cc. of 10% HCl was boiled for 3 hrs., and separated into a basic and neutral portions by the usual method. The neutral portion yielded 2.1 g. of recovered anisole and fractionation of the basic portion afforded 0.6 g. of a fraction of b.p$_{21}$ 75°. Its picrate, m.p. 183°, showed no depression on admixture with aniline picrate. Fraction of b.p$_2$ 177∼183° (1.8 g.). One g. of this fraction was dissolved in benzene, submitted to liquid chromatography, and developed with 70 cc. of benzene. The effluent was fractionated into 10 portions. Fraction No. 3 afforded 0.2 g. of crystals, m.p. 46°, undepressed on admixture with *p*-methoxy-*p'*-dimethylaminodiphenylmethane. *Anal.* Calcd. for $C_{16}H_{19}ON$: N, 5.81. Found: N, 5.95.

Fraction Nos. 5∼8 yielded 0.5 g. of crystals, m.p. 90°, which showed no depression on admixture with *p*-amino-*p'*-dimethylaminodiphenylmethane. *Anal.* Calcd. for $C_{15}H_{18}N_2$: C, 79.60; H, 8.02; N, 12.38. Found: C, 79.9; H 8.3; N, 12.51.

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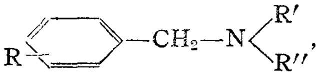
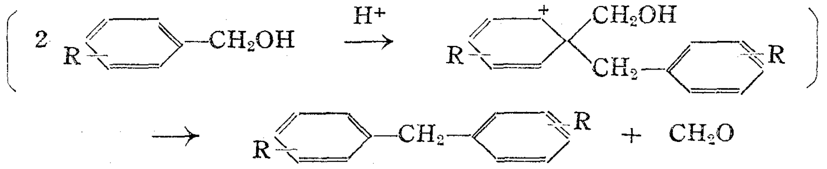
[5] Mills, Dazeley: J. Chem. Soc., **1939**, 460.

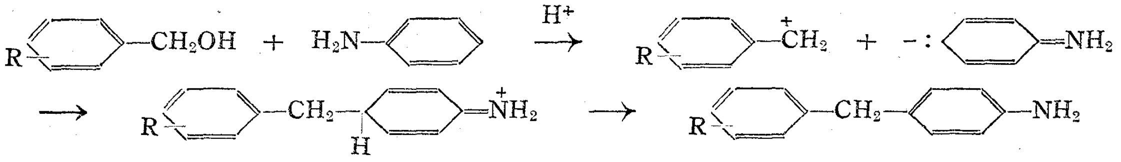
Fraction No. 4 was an oily substance whose paper chromatography (developer, BuOH : AcOH : $H_2O=4:1:3$) revealed the presence of *p,p′*-bis(dimethylaminodiphenyl)methane (Rf 0.86).

Summary

The compounds of the general formula  where R is a substituent with +M effect in the *ortho*- or *para*-position of $-CH_2-$, R′ is H or alkyl (or aminoalkyl) group, and R″ is an aromatic residue, when heated with dilute hydrochloric acid, are cleaved first into benzyl alcohol and an aromatic amine. When the reaction proceeds further, a diphenylmethane compounds are formed by the aromatic electrophilic substitution of the following order :



In some cases, the aromatic amine liberated in the first stage of the reaction takes part in the second stage of the reaction which proceeds in the following order, as had earlier been recognized.



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24. Genshun Sunagawa : Decomposition of Benzylamine Derivatives. V.[1] Aromatic Electrophilic Substitution of Benzyl Cation. (2).

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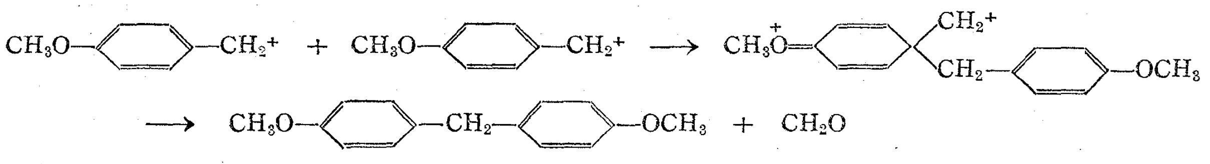
The reaction mechanisms on the decomposition of thonzylamine and its allied compounds by dilute hydrochloric acid were discussed in the preceding paper.[1] It was therein shown that thonzylamine is decomposed into *p,p′*-dimethoxydiphenylmethane, dimethylaminoethylaminopyrimidine, and formaldehyde in two steps; the first stage of the reaction consisting of decomposition into *p*-methoxybenzylcarbonium cation and an aromatic amine, and in the second stage, the *p*-methoxybenzylcarbonium cations formed undergo aromatic electrophilic substitution to form *p,p′*-dimethoxydiphenylmethane and formaldehyde.



On the other hand, in the case of *p*-dimethylaminobenzylaniline, non-symmetric *p*-dimethylamino-*p′*-aminodiphenylmethane, a compound which seems to have been formed

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[1] Part IV : This Bulletin, 3, 116(1955).