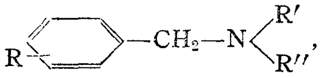
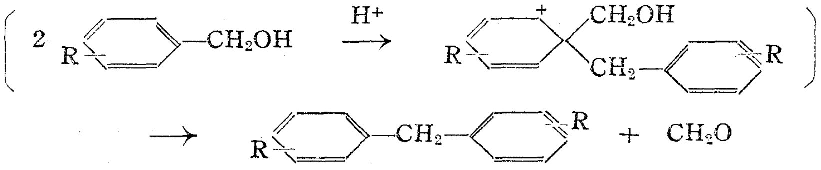
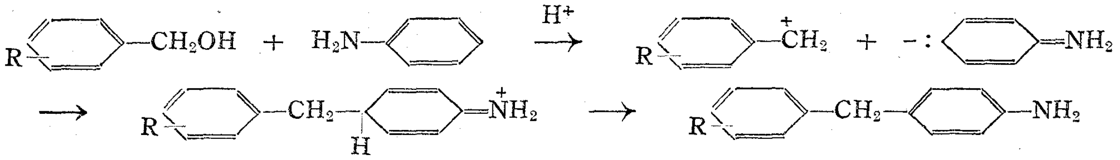
Fraction No. 4 was an oily substance whose paper chromatography (developer, BuOH : AcOH : $H_2O=4:1:3$) revealed the presence of *p,p'*-bis(dimethylaminodiphenyl)methane (Rf 0.86).

Summary

The compounds of the general formula  $R\text{-}C_6H_4\text{-}CH_2\text{-}N\langle^{R'}_{R''}$, 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.



(Received January 23, 1955)

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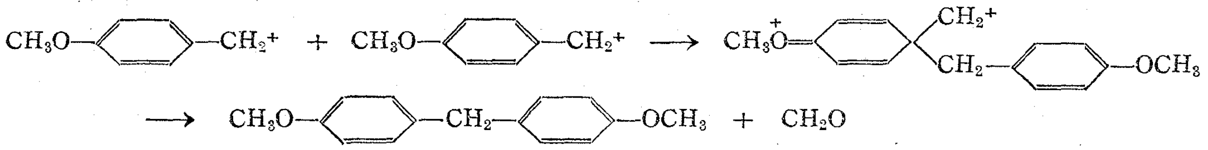
24. **Genshun Sunagawa**: Decomposition of Benzylamine Derivatives. V.[1] Aromatic Electrophilic Substitution of Benzyl Cation. (2).

(*Takamine Research Laboratory, Sankyo Co., Ltd.**)

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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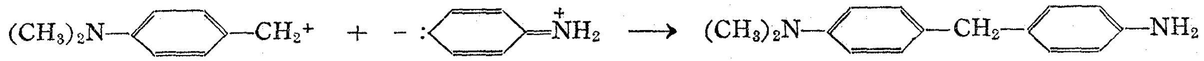
* Nagarahamadori, Ohyodo-ku, Osaka (砂川玄俊).

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

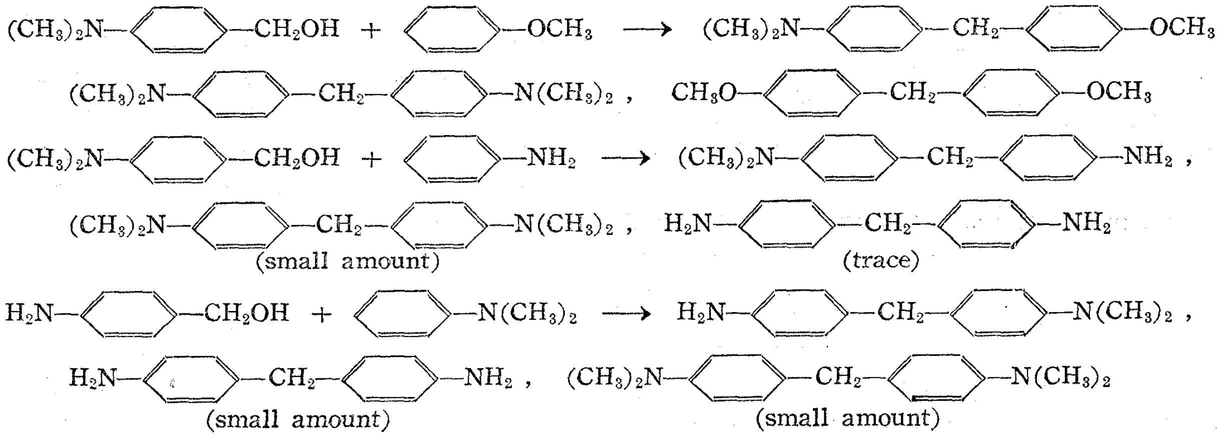
by the attachment of the *p*-dimethylaminobenzylcarbonium cation formed in the first stage of the reaction to the *para*-position of the amino group in aniline, is obtained as the chief product, suggesting that the two decomposition products have undergone bonding by the hitherto well-known reaction mechanism.

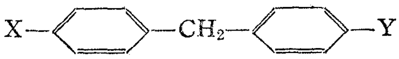


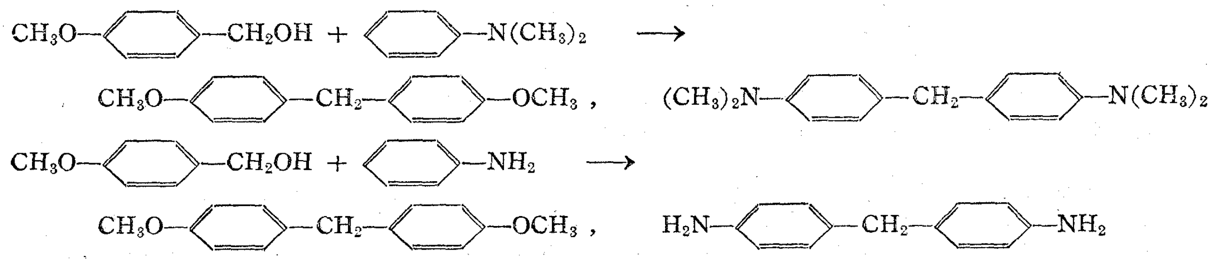
From such observations, it was thought possible to assume that one of these two forms of reactions might chiefly occur but it seemed that a more systemized and uniform theory could be established that a few supplementary experiments were carried out.

As has already been shown, heating of *p*-methoxy- or *p*-dimethylaminobenzyl alcohol with dilute hydrochloric acid respectively yields *p,p'*-dimethoxydiphenylmethane and *p,p'*-bis(dimethylaminodiphenyl)methane. Heating of anisole or dimethylaniline with formaldehyde in dilute hydrochloric acid results in the formation of the corresponding diphenylmethanes.

Taking X and Y as the substituents, the products to be formed on reacting *p*-X-benzyl alcohol and Y-C_6H_5 would be one of the following three : (1) *p,p'*-diX-diphenylmethane and formaldehyde, in accordance with the reaction mechanism proposed by the writer ; (2) *p*-X-*p'*-Y-diphenylmethane by the hitherto known reaction mechanism ; and (3) *p,p'*-diY-diphenylmethane if formaldehyde formed by (1) reacts further with Y-C_6H_5. Experimental results have actually shown that when X is dimethylamino or amino group, the reaction products are approximately as stated above, and may be summarized as follows :

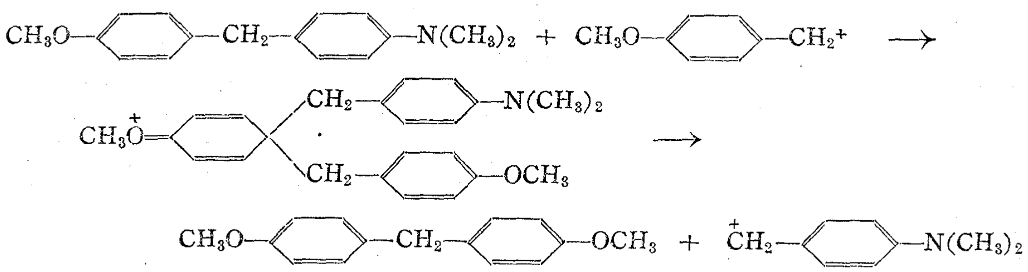


However, when X is a methoxyl, the experimental results were as shown below and the non-symmetric diphenylmethane corresponding to  could not be isolated.

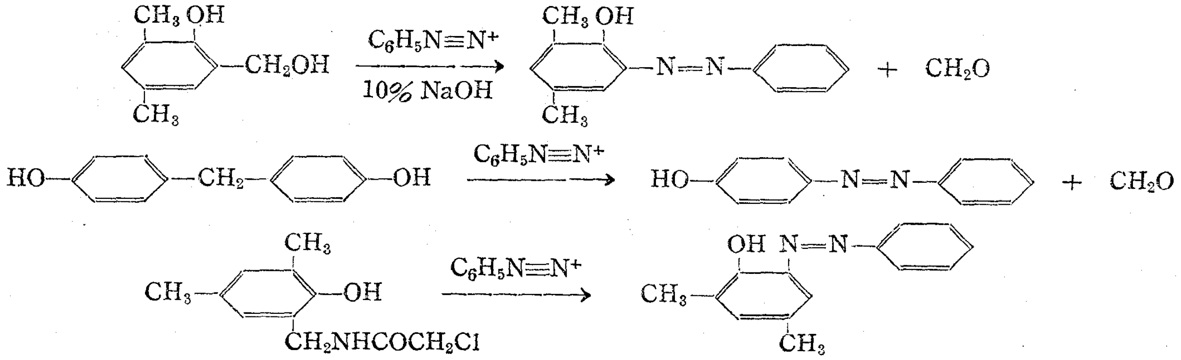


These results endorse the experimental facts outlined at the beginning and, in order to explain this phenomenon, it must be assumed that *p*-methoxybenzyl alcohol has a strong tendency to form *p,p'*-dimethoxydiphenylmethane by the substitution reaction proposed by the writer that this reaction occurs preferentially over the bonding with compounds with +M effect, such as aniline or dimethylaniline, but that in *p*-amino- or *p*-dimethylaminobenzyl alcohol, the reaction velocity for the bimolecular substitution is so much smaller than that of the above that bonding with the benzene derivative possessing a substituent with +M effect occurs first by the hitherto known reaction mechanism. Another experimental evidence which endorses this assumption is the fact that the heating of dimethylaminobenzyl alcohol with aniline and anisole, in dilute hydrochloric acid, still chiefly yields non-symmetric diphenylmethane, and only an extremely small amount of the symmetric type which can be thought to be formed by the bimolecular substitution reaction of dimethylaminobenzyl alcohol.

On the other hand, even when the tendency for bimolecular substitution of *p*-methoxybenzyl alcohol is strong, it is unthinkable that it would not react with dimethylaniline or aniline when it is present. A basis for this doubt is the fact that the yield of *p,p'*-dimethoxydiphenylmethane is so much better when *p*-methoxybenzyl alcohol is heated in dilute hydrochloric acid in the presence of anisole, than when heated alone.** These evidences have prompted the writer to assume that diphenylmethane might also undergo a substitution reaction with benzylcarbonium cation, in the following manner :



A reaction of this type, where the carbonium cation drives out the substituent in the benzene ring and itself goes into the position vacated, has not been described in any existing literature but substitution reactions of similar type have already been reported. Ziegler and others revealed that benzenediazonium cation and *o*- or *p*-hydroxybenzyl alcohol,[2] *p, p'*-dihydroxydiphenylmethane,[3] and *o*-hydroxy-N-acetobenzylamide[4] underwent aromatic electrophilic substitution and formed azobenzene derivative in each case.



Yukawa[5] proved that *p*-dimethylaminoaniline behaved in the following manner when in the presence of photosensitized silver halide.

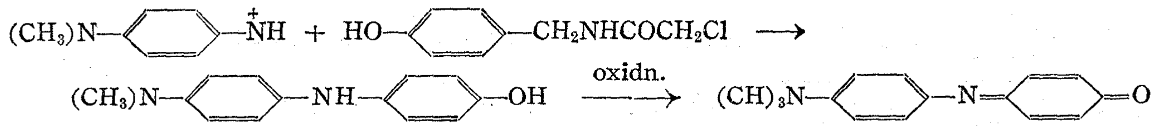
** In this degree of acidity, it seems impossible that the *para*-position of anisole is more active than that of dimethylaniline or aniline, because the yields of the two kinds of non-symmetric diphenylmethanes formed from dimethylaminobenzyl alcohol in the presence of aniline and anisole do not differ greatly.

[2] E. Ziegler, G. Zigeuner : Monatsh., **79**, 42(1948) ; **79**, 89(1948).

[3] *Idem.*, **79**, 363(1948).

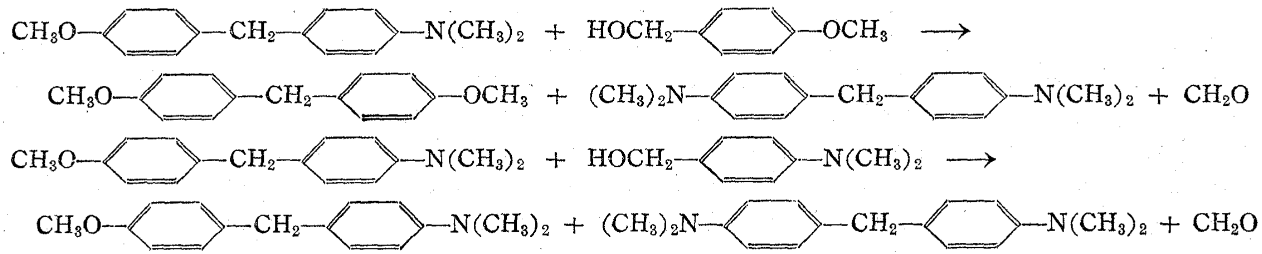
[4] G. Zigeuner, E. Ziegler, E. Aspan, E. Wiesenberger : *Ibid.*, **81**, 480(1950).

[5] Y. Yukawa : Paper read before the Chemical Society of Japan, 1953.

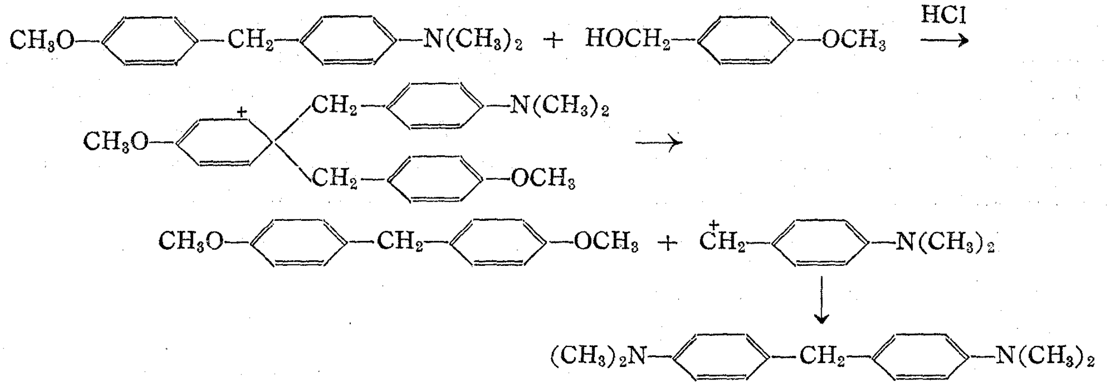


All these reactions indicate that they are substitution reactions of a molecule possessing :N:$^+$ group and such a fact seems to show that there is a possibility in the writer's suggested reaction theory.

In order to prove this theory, the following series of experiments were carried out. One of the non-symmetric diphenylmethane, *p*-methoxy-*p′*-dimethylaminodiphenylmethane, was boiled with dilute hydrochloric acid and the fact that no change occurred in this case was confirmed. Further, this compound was then boiled with dilute hydrochloric acid after the addition of (a) *p*-methoxybenzyl alcohol or (b) dimethylaminobenzyl alcohol and the following results were obtained :

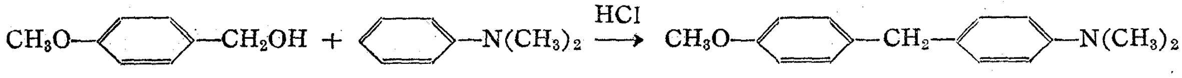


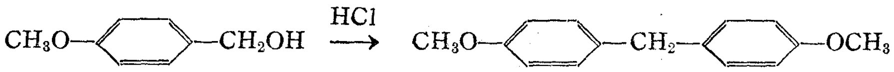
The fact that *p*, *p′*-bis(dimethylaminodiphenyl)methane was obtained in (a) clearly shows that *p*-methoxybenzyl alcohol and diphenylmethane had reacted in the following manner :

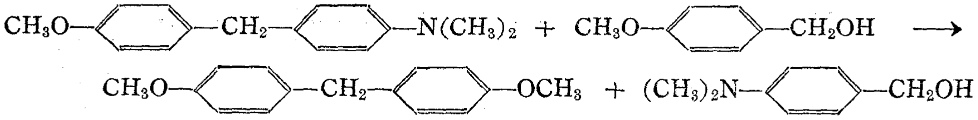


It has become quite clear, therefore, that the compounds of the diphenylmethane series also undergo substitution with *p*-methoxybenzylcarbonium cation, as anticipated by the writer. On the other hand, non-basic compounds could not be isolated from the (b) reaction which indicates that *p*, *p′*-dimethoxydiphenylmethane is not formed in this reaction. In other words, *p*-methoxybenzylcarbonium cation was not formed in this case and it indicates that dimethylaminobenzylcarbonium cation does not have the ability to react with diphenylmethane or if it had, the activity is extremely weak. It has thereby been revealed that even the same benzylcarbonium cations show a great difference in the ability to undergo substitution reaction according to the kind of a substituent present in the *para*-position. It is believed that the apparently inconsistent experimental results obtained with *p*-methoxybenzyl alcohol and aniline and dimethylaniline, as shown above, could be explained on the basis. First, *p*-methoxybenzyl alcohol reacts with dimethylaniline or aniline in the following two (a) and (b) directions.

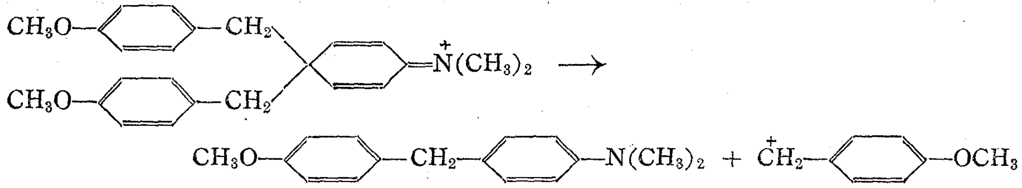
(a)



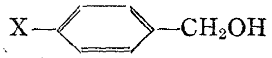
(b) 

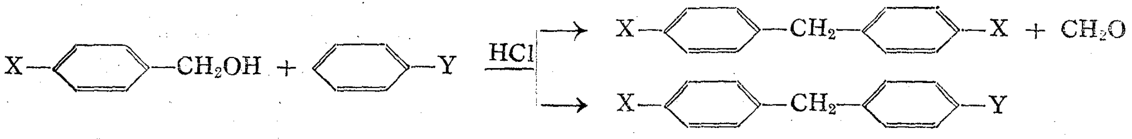
(c) 

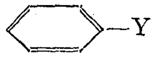
There is no problem about the reaction (b). The non-symmetric type compound formed by the reaction (a) undergoes the reaction shown by (c) in the presence of an excess of *p*-methoxybenzyl alcohol. In such a case, the formation of an intermediate of

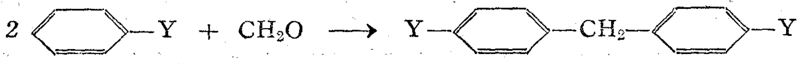


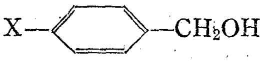
can also be assumed but since this reaction means the regeneration of the starting material, it has no connection with the reaction mechanism whereby the non-symmetric type compounds are formed by reaction (a). If *p*-dimethylaminobenzyl alcohol formed in (c) undergoes mutual substitution reactions, *p,p'*-bis(dimethylaminodiphenyl)methane would be formed. If these three reactions, (a), (b), and (c), occur consecutively, then the phenomenon which the writer had at first found difficult to explain, can be explained very conveniently. On the contrary, dimethylaminobenzyl alcohol does not react with diphenylmethane, i.e. they do not undergo the reaction corresponding to (c), and this will help to explain the fact that non-symmetric diphenylmethane can be obtained in a fairly good yield as long as such compounds are used as the starting materials. In short, the writer believes that these facts have made it possible to prove, for the first time, that the diphenylmethane derivatives undergo aromatic electrophilic substitution reactions with some kinds of benzylcarbonium cation. Since *p*-methoxybenzylcarbonium cation can undergo the reaction of this type, consideration of such a reaction mechanism would enable generalization of the conclusion obtained regarding the reactions between nuclear substituted benzyl alcohol and benzene substituted in the ring.

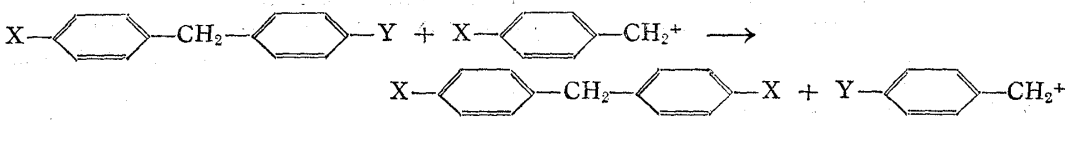
In general, heating  and  (where X and Y indicate a substituent with +M effect) in dilute hydrochloric acid results in two kinds of reactions shown by (a) :

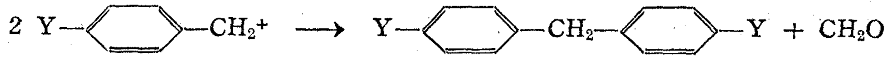
(a) 

Formaldehyde formed in (a) then reacts with unreacted  and reaction of the type (b) also proceeds, though generally in a minute amount.

(b) 

Next, if  further undergoes substitution reaction with the diphenylmethane compounds thereby formed, like *p*-methoxybenzylcarbonium cation, then the reaction (c) should occur and the two kinds of symmetric diphenylmethane compounds are chiefly formed, and the non-symmetric type cannot be isolated as the final product.

(c) 



On the contrary, in the case of *p*-dimethylaminobenzylcarbonium cation, which is not able to undergo reaction of (c) type, non-symmetric type compounds are obtained in a good yield.

The author expresses his gratitude to Prof. Eiji Ochiai of the University of Tokyo for reviewing this manuscript, to Prof. Shojiro Uyeo for his kind guidance, and to Prof. Yasuhide Yukawa for valuable advices regarding the electronic theory. The writer is indebted to Mr. T. Yuasa, Dr. Genichiro Fukuchi, and Mr. S. Matsui, all of this company, for their encouragement, to Messrs. Ichii, Yoshida, and Nakazawa for their cooperation in these experiments, and to Messrs. Soma and Ono for the microanalytical data.

Experimental

1) **Reaction of *p*-Dimethylaminobenzyl Alcohol (I), Aniline, and HCl**—a) A mixture of 5 g. of (I), 7 g. of aniline, and 100 cc. of 10% HCl was refluxed for 4 hrs. and treated by the usual method from which 2.2 g. of aniline (b.p$_{11}$ 66°) and 4.2 g. of a fraction of b.p$_{1}$ 184~190° were obtained. One g. of the latter fraction was purified by chromatography through alumina and 0.5 g. of white plate crystals, m.p. 75°, was obtained which showed no depression of m.p. on admixture with *p*-dimethylaminobenzylaniline. *Anal.* Calcd. for $C_{15}H_{18}N_2$: N, 12.38. Found : N, 12.13.

Further elution of the alumina column yielded 0.2 g. of prismatic crystals, m.p. 90°, alone or in admixture with *p*-amino-*p′*-dimethylaminodiphenylmethane. *Anal.* Calcd. for $C_{15}H_{18}N_2$: C, 79.10; H, 8.01; N, 12.38. Found : C, 79.63; H, 8.05; N, 12.09.

b) A mixture of 5 g. of (I), 7 g. of aniline, and 200 cc. of 10% HCl was treated as in a) and 2 g. of aniline (b.p$_{11}$ 66°) and 3.1 g. of a fraction of b.p$_{1.5}$ 193~195° were obtained. The latter (0.8 g.) was purified by chromatography as a benzene solution and the effluent was fractionated into 10 portions of about 5 cc. each. Fraction Nos. 4~8 yielded 0.5 g. of crystals, m.p. 90°, which showed no depression on admixture with *p*-amino-*p′*-dimethylaminodiphenylmethane. Fraction Nos. 2~3 yielded 0.1 g. of crystals, m.p. 60~80°, which was submitted to paper chromatography, developing with a mixture of BuOH:AcOH:H_2O (4 : 1 : 3). Two spots appeared respectively at Rf 0.77 and 0.86. The former gave positive reactions to the Dragendorff and the diazo reagents and the Rf agreed with that of *p*-amino-*p′*-dimethylaminodiphenylmethane. The latter gave positive reaction only to the Dragendorff reagent and the Rf value agreed with that of *p,p′*-bis(dimethylaminodiphenyl)methane.

2) **Reaction of *p*-Dimethylaminobenzyl Alcohol (I), Anisole, and HCl**—a) In aqueous solution : A mixture of 5 g. of (I), 5 g. of anisole, and 70 cc. of 10% HCl was heated for 4 hrs. with agitation and treated in the usual manner. The neutral portion afforded 0.4 g. of anisole (b.p$_{18}$ 48°) and 0.9 g. of a fraction of b.p$_{3}$ 160~165°, which later solidified. Recrystallization of the latter from EtOH gave 0.5 g. of crystals, m.p. 52°, which showed no depression on admixture with *p,p′*-dimethoxydiphenylmethane. The basic portion yielded 0.2 g. of *p*-dimethylaminobenzyl alcohol (b.p$_{2}$ 125°) and 1.8 g. of a fraction of b.p$_{2.5}$ 188~192°, which was recrystallized from EtOH to 0.4 g. of white plates, m.p. 90°, undepressed on admixture with the known *p,p′*-bis(dimethylaminodiphenyl)methane. The crystals recovered from the mother liquor were submitted to liquid chromatography and the initial fractions afforded 0.9 g. of crystals, m.p. 46°(from MeOH). This substance is easily soluble in ether, benzene, and EtOH, sparingly soluble in water, and soluble in HCl. *Anal.* Calcd. for $C_{16}H_{19}ON$: (*p*-Methoxy-*p′*-dimethylaminodiphenylmethane) : C, 79.63; H, 7.94; N, 5.81. Found : C, 79.29; H, 8.24; N, 5.95.

Demethylation of *p*-Methoxy-*p′*-dimethylaminodiphenylmethane : A mixture of 0.6 g. of *p*-methoxy-*p′*-dimethylaminodiphenylmethane and 7 cc. of 46% HBr was heated for 7 hrs. in an oil bath of 170°. On cooling, water was added to the mixture, neutralized with K_2CO_3, and the crystals that separated out were collected by filtration. After washing with water, 0.5 g. of the crude crystals thereby obtained were recrystallized from ligroine (b.p. 97~99°) to white plates, m.p. 108°, which showed no depression on admixture with *p*-hydroxy-*p′*-dimethylaminodiphenylmethane prepared by another route.[6] *Anal.* Calcd. for $C_{15}H_{17}ON$: C, 79.26; H, 7.54; N, 6.16. Found : C, 78.80; H, 7.76; N, 6.35.

b) In ethanolic solution : A mixture of 5 g. of (I), 5 g. of anisole, and 10% HCl in 56 v% EtOH was reacted as in (a). The neutral portion afforded 0.1 g. of *p,p′*-dimethoxydiphenylmethane, m.p. 50°. The basic portion yielded 0.9 g. of unreacted (I), b.p$_{2}$ 110~127°, and 2.3 g. of a fraction of b.p$_{2}$ 187~192°. The latter was treated as in (a) and yielded 0.3 g. of *p,p′*-bis(dimethylaminodiphenyl)-methane, m.p. 90°, and 1.4 g. of *p*-methoxy-*p′*-dimethylaminodiphenylmethane, m.p. 46°.

3) **Reaction of *p*-Aminobenzyl Alcohol (II), Dimethylaniline, and HCl**—A mixture of 1.5 g. of (II), 2.3 g. of dimethylaniline, and 70 cc. of 10% HCl was heated for 4 hrs. Treatment of the reaction

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[6] Smith, Welch : J. Chem. Soc., **1934**, 1136.

mixture in the usual manner afforded 1.1 g. of dimethylaniline (b.p$_{16}$ 76～77°) and 1.5 g. of a fraction of b.p$_3$ 182～183°, which later solidified. Recrystallization of the latter from EtOH gave 0.9 g. of crystals, m.p. 92°, undepressed on admixture with *p*-amino-*p′*-dimethylaminodiphenylmethane. *Anal.* Calcd. for $C_{15}H_{18}N_2$: C, 79.60; H, 8.01; N, 12.38. Found : C, 79.45; H, 8.25; N, 12.41.

The mother liquor obtained after separation of the above crystals afforded 0.9 g. of crystals, m.p. 45～60°, which were submitted to paper chromatography and the presence of *p*,*p′*-bis(dimethylaminodiphenyl)methane (Rf 0.86～0.88), *p*-amino-*p′*-dimethylaminodiphenylmethane (Rf 0.78～0.8), and *p*,*p′*-diaminodiphenylmethane (Rf 0.67) was detected.

4) **Reaction of *p*-Methoxybenzyl Alcohol (III), Dimethylaniline, and HCl**—a) In aqueous solution : A mixture of 5 g. of (III), 8.8 g. of dimethylaniline, and 75 cc. of 10% HCl was heated for 3 hrs. Treatment of the reaction mixture by the usual method afforded 0.3 g. of unreacted (III), b.p$_2$ 83～110°, and 1.6 g. of a fraction of b.p$_2$ 150～158°, which later solidified, from the neutral portion. The solid was recrystallized from EtOH to 1 g. of scaly crystals, m.p. 52°, undepressed on admixture with *p*,*p′*-dimethoxydiphenylmethane. The basic portion yielded 5.2 g. of dimethylaniline, b.p$_{18}$ 80°, and 1.6 g. of a fraction of b.p$_2$ 183～186°, which later solidified. Recrystallization of the latter from EtOH gave 1 g. of white platelets, m.p. 90°, undepressed by admixture with *p*,*p′*-bis(dimethylaminodiphenyl)methane.

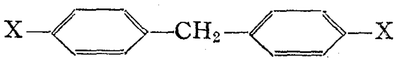
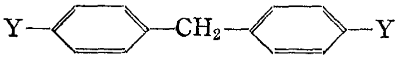
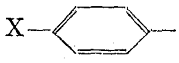
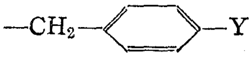
b) In ethanolic solution : A mixture of 10 g. of (III), 12 g. of dimethylaniline, and 200 cc. of 10% HCl prepared with 56 v% EtOH was heated for 5 hrs. and treated in the same manner as for (a). The neutral portion afforded 1.2 g. of *p*,*p′*-dimethoxydiphenylmethane, m.p. 52°. The basic portion yielded 0.4 g. of a fraction of b.p$_3$ 188～193°, which was purified through liquid chromatography and yielded 0.1 g. of *p*,*p′*-bis(dimethylaminodiphenyl)methane, m.p. 86～89°. Its paper chromatogram also revealed the presence of *p*,*p′*-bis(dimethylaminodiphenyl)methane (Rf 0.86) but not of *p*-methoxy-*p′*-dimethylaminodiphenylmethane (Rf 0.93).

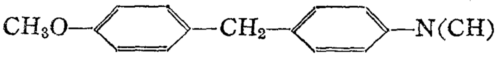
5) **Reaction of *p*-Methoxybenzyl Alcohol (III), Aniline, and HCl**—A mixture of 10.4 g. of (III), 14 g. of aniline, and 225 cc. of 10% HCl prepared with 56 v% EtOH was heated for 5 hrs. and treated by the usual method. The neutral portion afforded 3.1 g. of a fraction of b.p$_5$ 177～220° whose purification gave 1.3 g. of *p*,*p′*-dimethoxydiphenylmethane, m.p. 51～52°. The basic portion afforded 8.3 g. of aniline (b.p$_{13}$ 74°) and 1.3 g. of a fraction of b.p$_5$ 195～205°. Application of benzaldehyde to the latter fraction yielded *p*,*p′*-bis(benzylideneaminodiphenyl)methane as white scaly crystals, m.p. 125～126°.

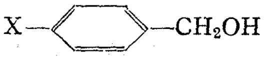
6) **Reaction of *p*-Methoxy-*p′*-dimethylaminodiphenylmethane (IV), *p*-Methoxybenzyl Alcohol (III), and HCl**—A mixture of 1.5 g. of (IV), 4.3 g. of (III), and 64 cc. of 10% HCl prepared with 56 v% EtOH was heated for 5 hrs. and treated in the usual manner. The neutral portion afforded 1.3 g. of a fraction of b.p$_2$ 150～160° which was purified to *p*,*p′*-dimethoxydiphenylmethane, m.p. 52°. The basic portion yielded 0.6 g. of crude crystals, m.p. 35～75°, which were recrystallized from EtOH to 0.2 g. of crystals melting at 87～89°, alone and in admixture with *p*,*p′*-bis(dimethylaminodiphenyl)methane.

7) **Reaction of *p*-Methoxy-*p′*-dimethylaminodiphenylmethane (IV), *p*-Dimethylaminobenzyl Alcohol (I), and HCl**—A mixture of 1.5 g. of (IV), 4.7 g. of (I), and 78 cc. of 10% HCl was heated for 5 hrs. The reaction mixture remained clear and no separation of a neutral substance was detected. Treatment of the reaction mixture in the usual manner afforded nothing from the neutral portion and 2.7 g. of a fraction of b.p$_3$ 182～188° from the basic portion. Recrystallization of the latter from EtOH gave 0.9 g. of *p*,*p′*-bis(dimethylaminodiphenyl)methane, m.p. 88°. The crystals obtained from this mother liquor were purified through liquid chromatography and afforded 0.8 g. of the unreacted (IV).

Summary

1) The reaction between *p*-X-C_6H_4-CH_2OH (X=substituent with +M effect) and *p*-Y-C_6H_5 (Y=substituent with +M effect) in acid was examined and it was found that the products formed in the case of X=CH_3O were mainly  and , while in the case of X=$(CH_3)_2N$ and H_2N,   is chiefly formed.

2) *p*-Methoxybenzyl alcohol undergoes aromatic electrophilic substitution with  and hydrochloric acid.

3) The reaction mechanism whereby diphenylmethane is formed by the aromatic electrophilic substitution of  has been clarified.

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25. Hisakichi Matsumura, Sadao Iguchi, Shigeru Miyamoto, and Magobei Yamamoto: Colloid Chemical Researches on Suspensions in Pharmacy. I. On Thixotropy in Vegetable Oil-Aluminum Stearate System.

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In the field of pharmacy, the problem of drug form is of great importance. Studies on this problem have made tremendous advances in the past few years with the successive discovery of antibiotics and enlargement of their applications. As one of the problems of drug form, thixotropy, which has often been observed in the now widely used penicillin injection in oil, especially when a mixture of vegetable oil and aluminum stearate system is used as the base, was taken up and fundamental colloid chemical studies were carried out in order to examine its nature.

Studies on thixotropy have been carried out in many laboratories and the characteristics of aluminum and other metallic soaps in various solvents have also been studied extensively,[1~10] in which the phenomenon of thixotropy has often been observed.[4,5,11~13] On the other hand, rheological measurements of the systems showing thixotropy have also been made[14~21] and, with other means of studying gels, such as the dielectric constant,[22,23] scattering[24] and absorption of light,[25] and propagation of sound waves,[26] much knowledge has been gained. However, no such studies have been made on the

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