22. **Genshun Sunagawa, Takeshi Ichii, and Norio Yoshida** : Decomposition of Benzylamine Derivatives. III.1)

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Some time ago, the authors reported that thonzylamine easily underwent decomposition by diluted hydrochloric, sulfuric, and nitric acids, as well as by 10% phosphoric acid.2) It seemed of interest to find requisite conditions for chemical structures to cause such decomposition reactions and the decomposition of compounds possessing structures similar to that of thonzylamine by dilute hydrochloric acid was examined. It was thereby found that 2-benzylaminopyrimidine (I), 2-(*p*-chlorobenzylamino)pyrimidine (II), 2-(*p*-nitrobenzylamino)pyrimidine (III), 2-[(2-dimethylaminoethyl)benzylamino]pyrimidine (IV), 2-[(2-dimethylaminoethyl)(*p*-chlorobenzyl)amino]pyrimidine (V), *p*-methoxybenzylamine (VI), and N-(*p*-methoxybenzyl)-N′-dimethylethylenediamine (VII) did not undergo such decomposition but 2-(*p*-methoxybenzylamino)pyrimidine (VIII), 2-(*p*-methoxybenzylamino)pyridine (IX), and *p*-methoxybenzylaniline (X) were easily decomposed.

The foregoing results indicated that, in order for the compounds to undergo decomposition on heating with mineral acids, as in the case of thonzylamine, it is necessary that, (1) there be a methoxyl group in the *para*-position of the benzyl group, and (2) the so-called aromatic ring, such as the phenyl, pyridyl, or pyrimidyl, be directly attached to the nitrogen in benzylamine.

When such conditions are not fulfilled, even if a part of the conditions is met, the compounds are generally stable towards acids. Considering such experimental results, the following conclusions were reached. The fact that the decomposition does not occur when there is a hydrogen, chlorine, or nitro group in the *para*-position of the benzyl group, as given in the first condition, indicates that the strong +M effect* of the methoxyl group contributes to the decomposition. This was clearly indicated by the fact that compounds possessing a substituent with a strong −M effect, such as the nitro group, or a weak +M effect and −I effect, such as chlorine, and those not having any substituent in the *para*-position, did not undergo such decomposition reactions.

Subsequently, compounds possessing hydroxyl or dimethylamino group, which also show strong +M effect, in the *para*-position of the benzyl group and also fulfilling the second condition, i.e. aromatic ring bonded to the nitrogen in the benzylamine, were prepared and their decomposition by mineral acids was examined. It was thereby observed that *p*-hydroxybenzylaniline (XI), *p*-dimethylaminobenzylaniline (XII), 2,6-dimethyl-N-(*p*-dimethylaminobenzyl)aniline (XIII), and 2-(*p*-dimethylaminobenzylamino)-pyrimidine (XIV) underwent facile decomposition when heated with mineral acids furnishing evidence that the +M substituent in these compounds contributed in accelerating the decomposition reactions, as had been anticipated.

If the +M substituent in the *para*-position of the benzyl group takes part in accelerating the decomposition, it should theoretically be possible to effect similar decomposition by mineral acids in compounds possessing such +M effect in the *ortho*-position of the benzyl group. Therefore, 2-(*o*-methoxybenzylamino)pyridine (XV) and *o*-dimethylaminobenzylaniline (XVI) were prepared and submitted to reaction with

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1) Part II. Sunagawa, Kushima, Ichii : J. Pharm. Soc. Japan, **72**, 1570 (1952).

2) Sunagawa, Kushima : *Ibid.*, **72**, 119 (1952).

* The signs + and − in this article follw those adopted by Ingold in his book, "The Structure and Mechanism in Organic Chemistry." The signs will be reversed if they followed the designation adopted by Dewar in his book, "The Electronic Theory of Organic Chemistry."

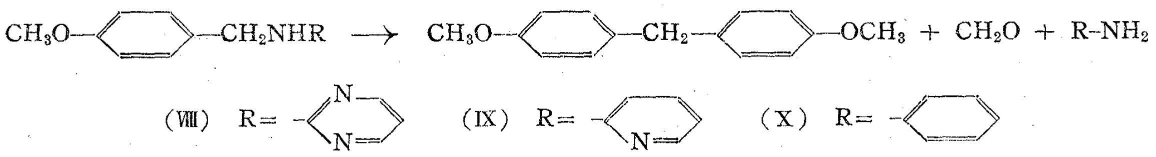
mineral acids. As was anticipated, both (XV) and (XVI) were found to undergo decomposition by 10% hydrochloric acid.

Next, two kinds of compounds possessing substituent with +M effect in the *para*- and *meta*-positions of the benzyl group, 2-(3,4-dimethoxybenzylamino)pyrimidine (XVII) and 2-piperonylaminopyridine (XVIII) were prepared and each was heated with dilute hydrochloric acid by which they were also found to undergo similar decomposition.

The foregoing experiments have shown that the two conditions for the chemical structures necessary to effect decomposition of the benzylamine derivatives by mineral acids were the absolute and sufficient requisites.

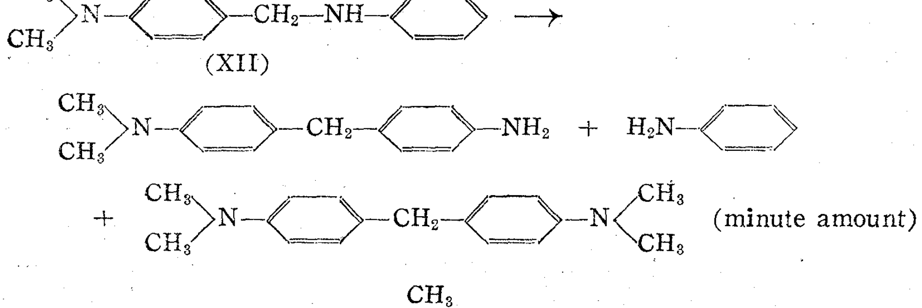
Examination of the Products from the Decomposition of the Allied Compounds of Thonzylamine by Mineral Acid :

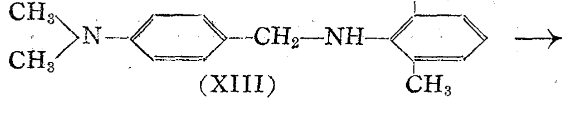
The experimental procedures adopted for the detection of the products formed by mineral acid decomposition of the allied compounds of thonzylamine were approximately similar. The solution obtained on acid decomposition was submitted to steam distillation to find the volatile component, and the distillation residue was extracted, first in original acidity by organic solvents and then basified and extracted, giving the neutral portion and a basic portion. Each portion was then submitted to recrystallization, fractionation, column or paper chromatography, as deemed necessary, and isolated into each component which was duly confirmed. It has already been shown[1)] that the following products are obtained from (VIII), (IX), and (X). The presence of a trace of p,p'-diaminodiphenylmethane was detected from the product of (X) by paper chromatography.

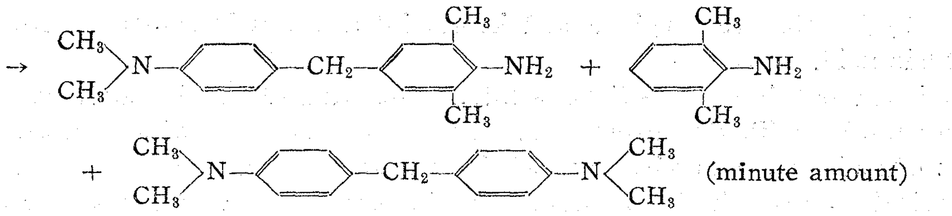


Besides the foregoing, the neutral portion contained a fair amount of high molecular compounds, not submitting to distillation. These are assumed to have been formed by a secondary condensation of p,p'-dimethoxydiphenylmethane and formaldehyde. Tendency to form such a polymer product was especially marked in the case of (XI) where acid hydrolysis occurred and, in spite of the precipitation of non-basic substances, p,p'-dihydroxydiphenylmethane and formaldehyde could not be detected, and only aniline was obtained as the decomposition product.

The presence of a symmetric compounds in the decomposition products from (XII) and (XIII) was only detected by paper chromatography and the majority was a non-symmetric diphenylmethane derivatives. This seemed to be a rather unexpected but interesting fact, considering the foregoing examples.

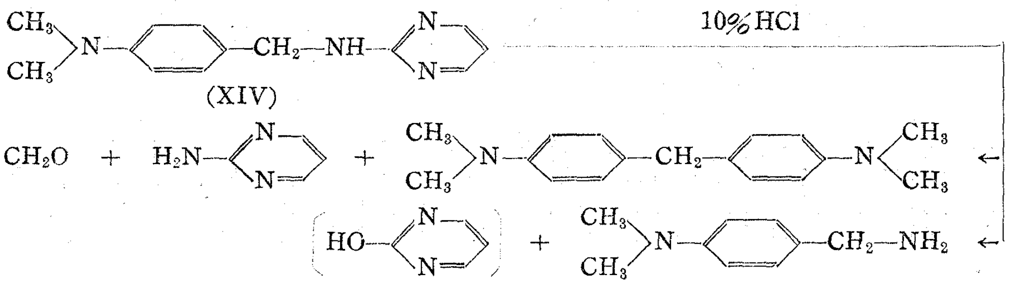





(minute amount)

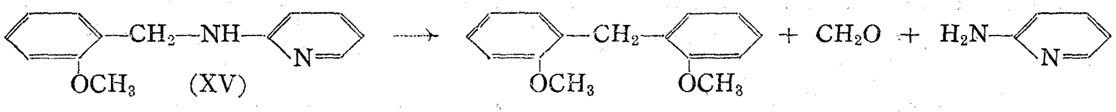
(XIV) seemed to behave differently from (XII) or (VIII), and *p*–dimethylaminobenzylamine and ammonia were isolated from the decomposition product, besides *p,p'*–bis(dimethylaminodiphenyl)methane, 2–aminopyrimidine, and formaldehyde.

The fact that *p*–dimethylaminobenzylamine had been obtained in this reaction seems to be rather specific, compared to thonzylamine and (VIII), but the reaction velocity of (XIV) was slower than that of the latter two and consequently, there was a larger recovery of the unreacted substances. From such a fact and the fact known generally that aminopyrimidines undergo hydrolysis by an acid to form ammonia and hydroxypyrimidine, the latter further undergoing cleavage of the pyrimidine ring by an acid to form ammonia and others, it may be assumed that these decomposition products were not formed by one and the same reaction and that the decomposition of (XIV) proceeds in the following two directions, more markedly than that of thonzylamine or (VIII) :

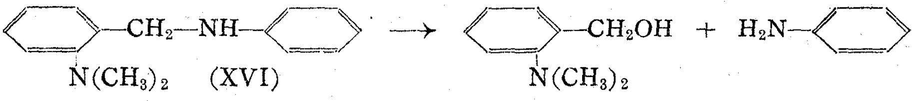

(XIV)

10% HCl

The decomposition product of (XV) yielded, as the neutral substance, prismatic crystals of m.p. 62~63°, and formaldehyde and 2–aminopyridine. The analytical values and ultraviolet absorption spectrum of the crystals of m.p. 62~63° indicated that it might be the isomer of *p,p'*–dimethoxydiphenylmethane, m.p. 52°, probably the *o,p'*– or *o,o'*–isomer, from its higher melting point. The infrared absorption spectrum of this substance revealed that it is the *o,o'*–isomer and identified as such by the direct comparison with *o,o'*–dimethoxydiphenylmethane, an unknown compound obtained by the reduction of *o,o'*–dimethoxybenzophenone with metallic sodium and ethanol. It follows, therefore, that the decomposition reaction of (XV) can be represented as follows :


(XV)

(XVI), possessing a structure similar to (XV), unexpectedly failed to form diphenylmethane compound and was found to decompose into *o*–dimethylaminobenzyl alcohol and aniline.


(XVI)

The products obtained on heating (XVII) with 10% hydrochloric acid were a neutral substance of m.p. 226~227°, 2–aminopyrimidine, and formaldehyde. The properties of this neutral substance was found to agree well with 2,3,6,7–tetramethoxydihydroanthracene obtained by Robinson[3] on reacting veratrole, formaldehyde, and 70% sulfuric

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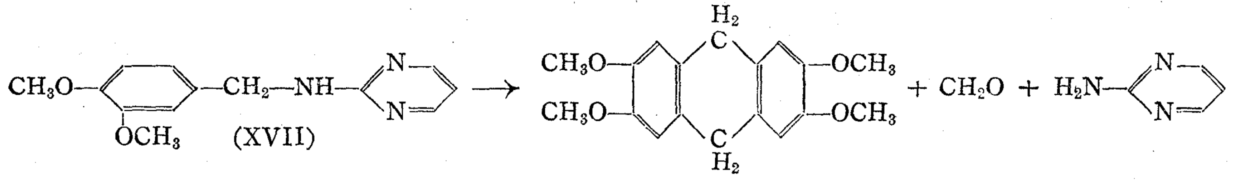
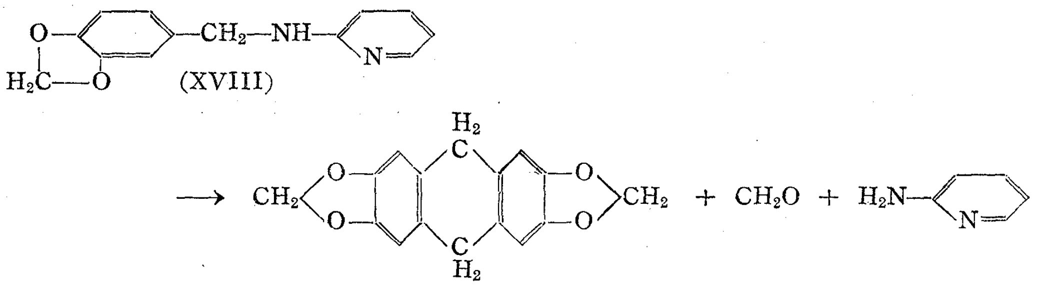
[3] R. Robinson : J. Chem. Soc., **1915**, 267.

acid, or by heating veratryl alcohol in glacial acetic acid solution with a small amount of sulfuric acid.

Robinson obtained 6,6′-dinitro-3,4,3′,4′-tetramethoxydiphenylmethane by heating this tetramethoxydihydroanthracene. Therefore, the neutral substance obtained in the present experiment was also treated in the same manner and a substance assumed to be identical was obtained. It seems certain, therefore, that the substance of m.p. 226~227° obtained here is 2,3,6,7-tetramethoxydihydroanthracene and this decomposition may be represented as follows:



It was also found that (XVIII) underwent similar decomposition.



The writers take this opportunity to extend their deep gratitude to Prof. Shojiro Uyeo of the University of Osaka for kind guidance throughout the course of this work, to Mr. T. Yuasa, Director of Osaka Plant and Director of this Company, to Dr. G. Fukuchi, Director of this Laboratory, and to Mr. Matsui, the Vice-Director, for their kind encouragement, and to Messrs. N. Soma and K. Ono for the analytical data.

Experimental

Syntheses of Benzylamine Derivatives: *p*-Hydroxybenzylaniline (XI)—Catalytic reduction was carried out on 7.5 g. of *p*-hydroxybenzylideneaniline dissolved in 400 cc. MeOH, with PtO_2 as a catalyst, at ordinary temperature and pressure. Evaporation of MeOH left 8 g. of syrup, which failed to crystallize but formed a hydrochloride by EtOH and HCl as crystals of m.p. 152~153° (from EtOH). *Anal.* Calcd. for $C_{13}H_{13}ON \cdot HCl$: C, 66.24; H, 5.99; N, 5.94. Found: C, 66.68; H, 6.2; N, 5.92.

The m.ps. reported of (XI) are 208° by Emmerich,[4] and 156° by Bischoff and Frohlich[5], Bamberger and Muller[6] giving it as an oily substance.

***p*-Dimethylaminobenzylaniline (XII)**—The same catalytic reduction as above of 12 g. of *p*-dimethylaminobenzylideneaniline, m.p. 100°, yielded 10 g. of white crystals, m.p. 75~76° (from EtOH). *Anal.* Calcd. for $C_{15}H_{18}N_2$: C, 79.60; H, 8.02; N, 12.38. Found. C, 79.45; H, 8.21; N, 12.35.

Zechmeister[7] obtained *p*-dimethylaminobenzylaniline, m.p. 62°, by the reduction of *p*-dimethylaminobenzylideneaniline with Mg and MeOH.

2,6-Dimethyl-N-(*p*-dimethylaminobenzyl)aniline (XIII)—i) N-(*p*-Dimethylaminobenzylidene)-*m*-2-xylidine: A solution of 20 g. of *m*-2-xylidine and 30.7 g. of *p*-dimethylaminobenzaldehyde dissolved in 80 cc. BuOH was refluxed in an oil bath for about 8 hrs., BuOH was distilled off, and the residue was distilled under a reduced pressure. The fraction of b.p$_3$ 195~205° was recrystallized from EtOH to pale yellow crystals, m.p. 75~76°. Yield, 26 g. *Anal.* Calcd. for $C_{19}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 81.20; H, 7.96; N, 10.97.

ii) 2,6-Dimethyl-N(*p*-dimethylaminobenzyl)aniline: A solution of 20 g. of the *m*-xylidine compound obtained above dissolved in MeOH was submitted to catalytic reduction. A pale yellow oil of b.p$_{2.5}$ 182~188°; yield, 14.8 g., gave positive nitrosamine and the Liebermann reactions, proving it to

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4) Emmerich: Ann., **241**, 355 (1887).
5) Bischoff, Frohlich: Ber., **39**, 3966 (1906).
6) Bamberger, Muller: Ann., **313**, 110 (1900).
7) Zechmeister, Rom: *Ibid.*, **468**, 117 (1929).

be a secondary amine. Benzoyl compound: White needles, m.p. 134°. *Anal.* Calcd. for C, 80.41; H, 7.31; N, 7.82. Found: C, 80.38; H, 7.42; N, 7.60.

2-(*p*-Dimethylaminobenzylamino)pyrimidine (XIV)—A mixture of 20 g. of *p*-dimethylaminobenzylamine, 15 g. of 2-chloropyrimidine, and 30 g. anhyd. K_2CO_3 was heated to 140° by which a vigorous reaction set in. After heating for about 20 min., the mixture was allowed to cool, and water was added to the residue. The crystals that separated out were recrystallized from EtOH to crystals of m.p. 118°, giving positive nitrosamine and Libermann's reactions. *Anal.* Calcd. for $C_{13}H_{16}N_4$: C, 68.39; H, 7.06; N, 24.55. Found: C, 68.43; H, 6.84; N, 24.06.

2-(*o*-Methoxybenzylamino)pyridine (XV)—A mixture of 44.9 g. of *o*-methoxybenzaldehyde, 30.9 g. of 2-aminopyridine, and 32 g. of HCO_2H was refluxed in an oil bath (140~145°) for 12 hrs., cooled, and extracted with dil. HCl. The acid extract was washed with ether and the aqueous layer was alkalized. The crude crystals thereby obtained were recrystallized from EtOH to 59 g. of crystals melting at 74°. Yield, 83.9%. *Anal.* Calcd. for $C_{13}H_{14}ON_2$: C, 72.86; H, 6.58; N, 13.07. Found: C, 72.51; H, 6.72; N, 12.81.

***o*-Dimethylaminobenzylaniline (XVI)**—Catalytic reduction was carried out on 18.1 g. of *o*-dimethylaminobenzylideneaniline, b.p$_8$ 170~175°, obtained by the reaction of 17.3 g. of *o*-dimethylaminobenzaldehyde[8] and 12.1 g. of aniline in ethanolic solution, and the crude crystals thereby obtained were recrystallized from petr. ether to 9.6 g. of white needles, m.p. 56~57°. *Anal.* Calcd. for $C_{15}H_{18}N_2$: C, 79.60; H, 8.02; N, 12.38. Found: C, 80.01; H, 8.29; N, 12.25.

2-(3,4-Dimethoxybenzylamino)pyrimidine (XVII)—A mixture of 16.6 g. of 3,4-dimethoxybenzaldehyde, 10.5 g. of 2-aminopyrimidine, and 6.7 g. of HCO_2H was heated at 140~150° for about 12 hrs. After the mixture cooled, it was treated as in the case of (XV) and the crude crystals were recrystallized from EtOH to 18.8 g. of prisms, m.p. 123~124°. *Anal.* Calcd. for $C_{13}H_{15}O_2N_3$: C, 63.67; H, 6.16; N, 17.13. Found: C, 63.72; H, 6.43; N, 17.12.

2-Piperonylaminopyridine (XVIII)—A mixture of 16.6 g. of 30 g. of heliotropine, 18.8 g. of 2-aminopyridine, and 18.4 g. of HCO_2H was refluxed at around 150° for about 10 hrs., cooled, and treated as in the case of (XV). Recrystallization from EtOH yielded 26 g. of prisms, m.p. 95~96°. *Anal.* Calcd. for $C_{13}H_{12}O_2N_2$: C, 68.40; H, 5.30; N, 12.28. Found: C, 68.46; H, 5.19; N, 12.15.

Decomposition of Benzylamine Derivatives with Hydrochloric Acid: Decomposition of (XI) with HCl—A solution of 3 g. of (XI) dissolved in 30 cc. dil. HCl was warmed in a boiling water bath for 2 hrs. by which the reaction mixture became gradually cloudy. The acid reaction mixture was submitted to steam distillation. Addition of 2,4-dinitrophenylhydrazine·HCl solution to the distillate failed to show any presence of CH_2O.

Basic portion: The acid solution was basified, submitted to steam distillation, and the distillate was evaporated to dryness after acidification with HCl. The residue was recrystallized from EtOH to crystals of m.p. 190~191°, giving a positive diazo reaction. Benzoyl compound: m.p. 161°, which showed no depression on admixture with benzanilide. *Anal.* Calcd. for $C_{13}H_{11}ON$: N, 7.1. Found: N, 7.21.

Neutral portion: The alkaline distillation residue was practically insoluble in benzene and other organic solvents, did not distill out by low-pressure distillation, and seemed to be composed of polymers alone.

Decomposition of (XII) by HCl—A solution of 0.4 g. of (XII) dissolved in 40 cc. dil. HCl was warmed in a boiling water bath. The reaction mixture colored slightly yellow but did not become cloudy. CH_2O was not detected in the distillate from the steam distillation of the acid reaction mixture.

Basic portion: The distillate from alkaline steam distillation was acidified with HCl, evaporated under a reduced pressure, basified, and extracted with ether. The ether residue was distilled and about 0.5 g. of a distillate, giving a positive diazo reaction, was obtained. Its benzoyl compound, m.p. 161~162°, showed no depression of m.p. on admixture with benzanilide. The alkaline steam distillation residue was extracted with ether, from which about 0.9 g. of a fraction of b.p$_{1.5}$ 158~161° (unreacted material, b.p. 75~76°) and about 1.4 g. of a fraction of b.p$_2$ 179~183°, were obtained. Recrystallization of the latter from EtOH yielded 1 g. of crystals of m.p. 89~90°, giving a positive diazo reaction. This substance showed marked depression of m.p. on admixture with *p*,*p'*-bis(dimethylaminodiphenyl)-methane, m.p. 90°. *Anal.* Calcd. for $C_{15}H_{18}N_2$ (*p*-Amino-*p'*-dimethylaminodiphenylmethane): C, 79.60; H, 8.02; N, 12.38. Found: C, 79.40; H, 8.35; N, 12.44. Benzoyl compound: m.p. 143°. *Anal.* Calcd. for $C_{22}H_{22}ON_2$: C, 79.99; H, 6.71; N, 8.48. Found: C, 79.58; H, 6.79; N, 8.66.

It is certain that this compound of m.p. 89~90° is *p*-amino-*p'*-dimethylaminodiphenylmethane.

The crystallization mother liquor obtained after separation of the foregoing crystals was submitted to paper chromatography and developed with a mixture of BuOH:AcOH:H_2O (4:1:2), from which spots appeared at Rf 0.77 and at 0.86~0.87. The former was positive to the Dragendorff reagent and to diazo reaction, and agreed with the Rf for *p*-amino-*p'*-dimethylaminodiphenylmethane. The latter spot was positive to the Dragendorff reagent and gave negative diazo reaction, agreeing with the

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8) Wesley Cocker, J. O. Harris, J. V. Looch: J. Chem. Soc., **1938**, 751.

Rf for *p,p'*-bis(dimethylaminodiphenyl)methane.

Decomposition of (XIII) with HCl—A solution of 7 g. of (XIII) dissolved in 70 cc. of 10% HCl was boiled for 10 hrs. Steam distillation of alkalized mixture yielded 0.1 g. of an oily substance which formed an acetylated compound of m.p. 196°, and this showed no depression of m.p. on admixture with N-aceto-*m*-2-xylidide. The distillation residue yielded 5.5 g. of a fraction of b.p$_{2.5}$ 197~201°, a pale yellow oil which showed negative nitrosamine and Liebermenn's reactions, but positive diazo reaction, indicating the presence of an aromatic primary amine. Paper chromatography of this substance, developed with a mixture of BuOH:AcOH:H_2O (5:4:1), gave a spot at Rf 0.93. Benzoyl compund: White needles, m.p. 173°, which showed marked depression on admixture with the benzoylated compound of the starting material but no depression on admixture with 4-dimethylamino-3',5'-dimethyl-4'-benzylaminodiphenylmethane. *Anal.* Calcd. for $C_{24}H_{26}ON_2$: C, 80.41; H, 7.31; N, 7.82. Found: C, 80.13; H, 7.32; N, 7.55.

Synthesis of 4-Dimethylamino-3',5'-dimethyl-4'-aminodiphenylmethane: A solution of 3 g. of *p*-dimethylaminobenzyl alcohol and 2.4 g. of 2,6-dimethylaniline dissolved in 54 cc. of 10% HCl was heated for 5 hrs. and worked up as usual. Positive to formaldehyde reaction. Some unreacted 2,6-dimethylaniline was recovered and 3.7 g. of a fraction of b.p$_{2.5}$ 201~206°, giving positive diazo reaction, was obtained. Benzoyl compound: White needles, m.p. 173°.

Decomposition of (XIV) with HCl—A solution of 7 g. of (XIV) dissolved in 70 cc. dil. HCl was heated above a direct flame for 7 hrs., by which no apparent change took place. The distillate from acid steam distillation gave positive resorcinol reaction and formed a 2,4-dinitrophenylhydrazone, indicating the presence of CH_2O.

Basic portion: The residue left after acid steam distillation was basified, submitted to steam distillation, and the distillate was evaporated under a reduced pressure after acidification with HCl. This was adjusted to pH 6.8 with alkali, extracted with ether, and ether residue was recrystallized from EtOH to 0.25 g. of crystals of m.p. 125°, undepressed by admixture with 2-aminopyrimidine. The aqueous layer left after the extraction was rendered alkaline, extracted with ether, and 0.38 g. of an oil, b.p$_3$ 103°, was obtained. Benzoyl compound: Needles, m.p. 135°, which showed no depression on admixture with N-(*p*-dimethylaminobenzyl)benzamide. *Anal.* Calcd. for $C_{16}H_{18}ON_2$: C, 75.56; H, 7.13; N, 11.02. Found: C, 75.48; H, 7.18; N, 11.35.

Residual solution after alkaline steam distillation was extracted with ether and 5.1 g. of crude crystals were obtained. This was recrystallized from EtOH to 4 g. of crystals, 1 g. of which was dissolved in 5 cc. of benzene and purified by liquid chromatography through alumina. The column was developed with 50 cc. of benzene and the effluent was divided into 9 fractions. Fractions No. 1~3 yielded 0.19 g. of crystals of m.p. 90°, which showed no depression on admixture with *p,p'*-bis(dimethylaminodiphenyl)methane. Fractions No. 4~6 yielded 0.19 g. of crystals of m.p. 118°, undepressed on admixture with the starting material.

Reaction of 2-Aminopyrimidine with HCl—A mixture of 10 g. of 2-aminopyrimidine and 100 cc. of 10% HCl was heated for 10 hrs., by which the reaction mixture gradually became dark and finally colored reddish brown. Rendering of the reaction mixture strongly alkaline resulted in evolution of a large amount of NH_3, indicating that the decomposition had taken place. The mixture was extracted with benzene, from which 7.4 g. of the starting material, m.p. 117~123°, was recovered. The aqueous layer was adjusted to pH 4.5, evaporated to dryness under a reduced pressure, and the residue was extracted with AcOEt, from which 0.3 g. of crystals melting at 159~160°, undepressed on admixture with 2-hydroxypyrimidine, was obtained.

Decomposition of (XV) with HCl—A solution of 6 g. of (XV) dissolved in 60 cc. of 10% HCl was warmed on a boiling water bath for 1 hr., submitted to steam distillation in acid reaction, and the crystals obtained were recrystallized from EtOH to 20 mg. of white prisms, m.p. 62~63°. Ultraviolet absorption: λ_{max} 272 mμ (log ε=3.65) and 278 (3.63). Infrared absorption max.: 13.2 and 13.4 μ. This substance showed no depression of m.p. on admixture with newly synthesized *o,o'*-dimethoxydiphenylmethane. *Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07; CH_3O, 26.75. Found: C, 78.34; H, 7.22; CH_3O, 26.99. Formaldehyde was detected in the distillate.

Basic portion: After removing the neutral portion, the basic portion was extracted by the usual method and submitted to distillation, from which 0.3 g. of a fraction of b.p$_4$ 80~90° or m.p. 55~56°, undepressed on admixture with 2-aminopyridine, was obtained.

Synthesis of *o,o'*-Dimethoxydiphenylmethane: To a solution of 8 g. of *o,o'*-dimethoxybenzophenone, m.p. 101~102°, dissolved in 100 cc. abs. EtOH, 13 g. of Na was added in small portions during about 1 hr., under stirring. The mixture was then boiled for 1.5 hrs., cooled, diluted with 200 cc. of water, and allowed to stand over night. The crystals that separated out were collected by filtration and recrystallized from EtOH to white prisms, m.p. 62~63°. *Anal.* Calcd. for $C_{15}H_{16}O_2$: C, 78.98; H, 7.07. Found: C, 78.58; H, 7.40.

Decomposition of (XVI) with HCl—A solution of 5 g. of (XVI) dissolved in 50 cc. of 10% HCl was warmed on a boiling water bath for 4 hrs. CH_2O was detected in the reaction mixture, which was rendered alkaline, and extracted with ether. Fractional distillation of the ether residue gave three fractions.

(i) b.p$_{21}$ 96∼110° : 1 g. Benzoyl compound, m.p. 161∼162°, undepressed on admixture with benzanilide.

(ii) b.p$_{21}$ 110∼144° : 2.8 g. Crude crystals obtained on the application of phenyl isocyanate were recrystallized from EtOH to crystals melting at 103∼104°, undepressed on admixture with *o*-dimethylaminobenzyl phenylcarbamate. *Anal.* Calcd. for $C_{16}H_{18}O_2N_2$: C, 71.1; H, 6.66; N, 10.39. Found : C, 70.75; H, 6.66; N, 10.59.

Picrate of this fraction : 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, 47.16; H, 4.38; N, 14.73.

(iii) b.p$_3$ 172∼173° : 0.6 g. Purification by liquid chromatography yielded crystals of m.p. 56°, undepressed on admixture with the starting material.

Decomposition of (XVII) with HCl—A solution of 5 g. of (XVII) dissolved in 50 cc. of 10% HCl was heated for 3.5 hrs., by which the reaction mixture gradually became cloudy and separated a precipitate. The crude crystals thereby obtained were recrystallized from EtOH to needles, m.p. 226∼227°. *Anal.* Calcd. for $C_{18}H_{20}O_4$ (2,3,6,7-Tetramethoxy-9,10-dihydroanthracene) : C, 71.98; H, 6.71. Found : C, 71.65; H, 6.84.

A mixture of 0.8 g. of these crystals suspended in 6 cc. of glacial AcOH was added with 2.4 cc. of 70% HNO_3 and warmed slightly, by which the crystals dissolved and reaction proceeded. On cooling, the mixture was diluted with water, and the yellow precipitate thereby formed was recrystallized from AcOEt to 0.15 g. of slightly yellowish needles, m.p. 179∼180°. *Anal.* Calcd. for $C_{17}H_{18}O_8N_2$ (6,6′-Dinitro-3,4,3′,4′-tetramethoxydiphenylmethane) : C, 53.69; H, 4.8. Found : C, 54.14; H, 4.68.

Basic portion : The acid filtrate was rendered alkaline, from which 0.3 g. of the unreacted starting material was recovered. The mother liquor was made strongly alkaline, extracted with benzene, and 0.7 g. of crystals, m.p. 125∼126° (from benzene), were obtained which showed no depression of m.p. on admixture with 2-aminopyrimidine.

CH_2O was detected in the distillate from the steam distillation of the acid reaction mixture.

Decomposition of (XVIII) with HCl—A solution of 4 g. of (XVIII) dissolved in 40 cc. of 10% HCl was heated for 1.5 hrs., the crude crystals collected by filtration were recrystallized from dimethylformamide, and 0.7 g. of needles, m.p. over 355°, were obtained. *Anal.* Calcd. for $C_{16}H_{12}O_4$ (2,3,6,7-bis(methylenedioxy)-9,10-dihydroanthracene) : C, 71.56; H, 4.51. Found : C, 71.89; H, 4.93.

Nitration of 1 g. of these crystals in glacial AcOH, as in the case of (XVII), and recrystallization from glacial AcOH yielded pale yellow prisms, m.p. 214∼215°. *Anal.* Calcd. for $C_{15}H_{10}O_8N$ (6,6′-Dinitro-3,4,3′,4′-bis(methylenedioxy)diphenylmethane) : C, 52.03; H, 2.91. Found : C, 52.13; H, 3.12.

Basic portion : The acid filtrate was rendered strongly alkaline, extracted with benzene, and 1.4 g. of the product obtained was recrystallized from EtOH to crystals of m.p. 57°, which showed no depression on admixture with 2-aminopyridine. The starting material was hardly recovered. CH_2O was detected in the reaction mixture.

Summary

Benzylamine derivatives possessing a substituent of marked +M effect (e.g. methoxyl, hydroxyl, dimethylamino, methylenedioxy) in the *para-* or *ortho*-position of the benzyl group and an aromatic residue (e.g. phenyl, pyridyl, pyrimidyl) attached to the amino nitrogen were shown to undergo facile decomposition by mineral acids to form benzyl alcohol, diphenylmethane, or dihydroanthracene derivatives and aromatic amines.

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