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Acid-Catalyzed Benzidine Rearrangement of Unsymmetrical Hydrazoaromatics

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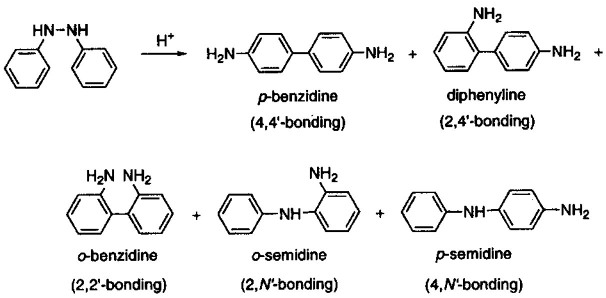
Acid-catalyzed benzidine rearrangements of new unsymmetrical diazanes **1-3**, prepared from the reduction of corresponding diazenes **4-6**, were carried out in ethanolic solutions. The results are as follows; rearrangement of (3-carbomethoxyphenyl)(3-methoxyphenyl)diazane **1** gave 4,4'-diamino-2-carbomethoxy-2'-methoxybiphenyl **12** (*p*-benzidine type) in 71% and 10-amino-3-methoxyphenanthridin-6(5*H*)-one **13**, 8-amino-3-methoxyphenanthridin-6(5*H*)-one **14** in 7.1% and 3.4%, respectively. Product **13** and **14** were formed by the condensation reaction of primarily formed *o*-benzidine and diphenyline type product, respectively. (5-Carbomethoxy-2-chlorophenyl)(4-methoxyphenyl)diazane **2** and (5-carbomethoxy-2-methylphenyl)(4-methoxyphenyl)diazane **3** underwent mainly disproportionations to give fission amines and corresponding diazenes in about 53% and 40% yields, respectively. The results obtained from the rearrangements of diazanes **1-3** indirectly indicated the importance of disproportionations to understand the benzidine rearrangements. The structures of benzidine rearrangement products were determined by usual NMR techniques such as DEPT, 2D H-H COSY, H-C COSY, 2D NOESY, and Gaussian function multiplication.

Introduction

Acid-catalyzed benzidine rearrangement has been studied extensively for more than 130 years since the rearrangement was discovered accidentally by Hofmann in the reduction of azobenzene.[1] Benzidine rearrangements refer to reactions in which diazanes are converted to two kinds of products in the presence of acid (eq. 1).[2]



(1)

One kind comprises diaminobiphenyl compounds such as benzidine (4,4'-bonding), diphenyline (2,4'-bonding), and *o*-benzidine (2,2'-bonding). In the other are aminodiphenylamine derivatives such as *o*-semidine (2,*N'*-bonding) and *p*-semidine (4,*N'*-bonding). Also formed are disproportionation products such as azobenzenes and arylamines, which are unavoidable in the usual benzidine rearrangments. At present it has been well established, by heavy atom kinetic isotope effects, that the rearrangement follow the patterns of the sigmatropic shifts.[3] Recently, a [9,9]-sigmatropic shift in the acid-catalyzed benzidine rearrangement of bis[4-(2-furyl) phenyl]diazane was discovered, supporting that the benzidine rearrangement follow the patterns for sigmatropic processes.[4] Described herein are benzidine rearrangements of new unsymmetrically substituted diazanes **1-3** containing carbomethoxy and methoxy groups separately at *meta* and *meta*/*para* positions of benzene rings. This work was undertaken in order to study the effects of unsymmetrical electron donating and attracting substituents on the benzidine rearrangement products for non-kinetic purposes.

Experimental

Materials and Apparatus

All the chemicals were purchased and used without further purification unless otherwise specified. 1D ^{1}H and ^{13}C, DEPT, and 2D NMR spectra were taken on Bruker AC 80, AM 300, ARX 300, DPX 300, and AMX 500 spectrophotometers using tetramethylsilane as an internal standard. Infrared spectrum was recorded on a Jasco IR-reporter 100 and IRA-1 models. Melting points were taken on an Electrothermal Melting Point Apparatus. Mass spectra were obtained on a HP-5970 MSD with HP-5890 series GC and Triple Quadrupole LC/MS (VG Quattro Triple Quadrupole Mass Spectrometer with HP-100 HPLC).

Synthesis of Diazanes

(3-Carbomethoxyphenyl)(3-methoxyphenyl)diazane 1. A general procedure for the preparation of diazanes from diazenes[5] was adopted to get pale yellow liquid **1** from diazene **4** (0.27 g, 1.0 mmol). After filtering off the remaining zinc powder, the filtrate was extracted with methylene chloride. Drying over the anhydrous $MgSO_4$ followed by filtration and evaporation under reduced pressure gave **1** (0.26 g, 96%). ^{1}H NMR (80 MHz, acetone-d$_6$) δ 3.69 (CH_3, s), 3.83 (CH_3, s), 5.57 (2H, s), 6.2-6.5 (3H, m), 6.9-7.6 (5H, m).

(5-Carbomethoxy-2-chlorophenyl)(4-methoxyphenyl)diazane 2. Similar procedure for the preparation of **1** was carried out except the use of diazene **5** (1.5 g, 5.0 mmol). Pale yellow solid obtained from 10% ammoniacal solution was washed with water twice followed by drying in the vacuum desiccator. Yield; 1.3 g (91%), mp 100 °C (dec.). ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.75 (3H, s), 3.64 (3H, s), 5.50 (1H, s), 6.2 (1H, s), 6.79 (4H, s), 7.36-7.9 (3H, m).

(5-Carbomethoxy-2-methylphenyl)(4-methoxyphenyl)diazane 3. Similar procedure for the preparation of **2** was carried out except the use of diazene **6** (0.28 g, 1.0 mmol). Yield; 0.27 g (96%), mp 110-111 °C (dec.). ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.24 (3H, s), 3.73 (3H, s), 3.81 (3H, s), 5.48 (1H, s), 5.54 (1H, s), 6.77 (4H, s), 7.21 (1H, d), 7.44 (1H, dd), 7.66 (1H, d).

Synthesis of Diazenes

(3-Carbomethoxyphenyl)(3-methoxyphenyl)diazene 4. According to the known procedure, methanolic solution (50 mL) of diazene **8** (3.84 g, 10.0 mmol) was treated with triethylamine.[6] Recrystallization from ethanol gave the product **4** (2.1 g, 78%). mp 69-70 °C.[7]

(5-Carbomethoxy-2-chlorophenyl)(4-methoxyphenyl)diazene 5. A mixture of diazene **11** (1.8 g, 6.0 mmol), methyl iodide (0.5 mL, 5.0 mmol) and potassium carbonate (1.0 g, 5.8 mmol) in acetone (100 mL) was refluxed for 12 h. The reaction mixture was filtered, concentrated, and recrystallized from acetonitrile to give diazene **5** (1.8 g, 96%) as red crystals. mp 122.6 °C.

GC/MS: 304 (M^+). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.89 (CH_3, s), 3.92 (CH_3, s), 7.0 (2H, d), 7.57 (1H, d), 7.97-7.99 (3H, m), 8.31 (1H, m).

(5-Carbomethoxy-2-methylphenyl)(4-methoxyphenyl)diazene 6. A mixture of (5-carbomethoxy-2-methylphenyl)(4-hydroxyphenyl)diazene (1.97 g, 7.0 mmol), methyl iodide (1.0 mL, 10.0 mmol), and potassium carbonate (1.8 g, 10.4 mmol) in acetone (100 mL) was refluxed for 12 h. After filtering off the remaining potassium carbonate, the filtrate was evaporated. Recrystallization from acetonitrile gave diazene **6** (2.06 g, 99%) as red crystals. mp 110-110.3 °C.

GC/MS: 284 (M^+). ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.73 (CH_3, s), 3.69 (CH_3, s), 3.92 (CH_3, s), 7.0 (2H, dd), 7.37 (1H, dd), 7.64-8.04 (3H, m), 8.24 (1H, d).

(4-Amino-3-methoxyphenyl)(3-carbomethoxyphenyl)diazene 7. By following the general procedure, coupling reaction of 3-carbomethoxyenzene diazonium ion and *o*-anisidine afforded orange product. Yield; 91%, mp 100-102 °C.

Diazene 8. Diazene **7** was diazotized by aqueous solution (5 mL) of sodium nitrite (1.04 g, 15.0 mmol), followed by addition of sodium tetrafluoborate (2.81 g, 26.0 mmol). Recrystallization from acetone and *n*-hexane gave the product **8** (2.8 g, 73%). mp 152 °C (dec.).[7]

3-Carbomethoxybenzenediazonium tetrafluoroborate. To a solution of 6 N HCl (44 mL) was added methyl 3-aminobenzoate (7.56 g, 50.0 mmol). The solution was cooled in an ice-bath, and was diazotized by adding aqueous solution (20 mL) of sodium nitrite (5.2 g, 75.0 mmol), followed by addition of sodium tetrafluoborate (16 g, 0.15 mol). After stirring for 30 min, the precipitate was filtered and washed with cold water, cold ethanol, and several times with ethyl ether. Recrystallization from acetone and n-hexane gave the colorless product (11.4 g, 91%). mp 134-135 °C (dec.).

(5-Carbomethoxy-2-chlorophenyl)(4-hydroxyphenyl)diazene 11. To a solution of 6 N HCl (12 mL) was added methyl 3-amino-4-chlorobenzoate (0.93 g, 5.0 mmol). This solution was cooled in an ice-bath, and was diazotized by adding sodium nitrite (0.35 g, 5.2 mmol), followed by dropwise addition of a cold solution of phenol in 21% NaOH solution (6 mL). After 20 min, the solution was acidfied by 4 N HCl. The reaction mixture was poured into the cold water and the crude product was filtered and washed with water. Recrystallization from ethanol gave the product **11** (1.1 g, 75%) as red crystals. mp 213-214 °C. GC/MS: 290 (M^+). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 3.90 (CH_3, s), 7.01 (2H, dd), 7.7-8.2 (5H, m), 10.6 (OH, s).

(5-Carbomethoxy-2-methylphenyl)(4-hydroxyphenyl)diazene. To a solution of 6 N HCl (6 mL) was added methyl 3-amino-4-methylbenzoate (1.62 g, 10.0 mmol). The solution was cooled in an ice-bath, and was diazotized by adding sodium nitrite (0.9 g, 12.0 mmol). To a cold solution of phenol in 21% aqueous NaOH solution (6 mL) was added diazotized solution slowly. After 20 min, the solution was acidfied by adding 4 N aqueous HCl and was poured into the cold water, filtered, and washed with water. Recrystallization from ethanol gave the product (2.0 g, 74%) as red crystals. mp 181.3-182.2 °C. GC/MS: 270 (M^+). ^{1}H NMR (80 MHz, DMSO-d$_6$) 2.70 (3H, s), 3.87 (3H, s), 6.96 (2H, d), 7.54 (1H,d), 7.80-8.90 (4H, m), 10.35 (1H, s).

Benzidine Rearrangements and Products

Benzidine Rearrangement of 1. To a solution of **1**

(2.7 g, 10.0 mmol) in degassed ethanol (50 mL) was added a solution of ethanol (10 mL) and conc. HCl (5 mL) for 1h at 0 °C under nitrogen atmosphere. After standing for 48 h at room temperature, the precipitate (rearrangement product) was filtered and the filtrate was concentrated repeatedly until no more precipitate separated out, finally affording a brown liquid. The brownish liquid was neutralized with 1 N $NaHCO_3$, extracted with ethyl acetate, and dried by anhydrous $MgSO_4$. Evaporation afforded brownish liquid (0.52 g) consisting of disproportionation products such as diazene **4** and amines (see Scheme 3). The combined precipitate (rearrangement product, 1.98 g), after neutralization with 1 N $NaHCO_3$ and drying under vacuum, was recrystallized from acetonitrile (80 mL) to get pale yellow solid which was recrystallized twice to obtain pure 10-amino-3-methoxyphenanthridin-6(5*H*)-one **13**. When the filtrate was concentrated a little bit and standing for a while, pale brownish 4,4'-diamino-2-carbomethoxy-2'-methoxybiphenyl **12** was obtained. The remaining filtrate was concentrated further and was subjected to MPLC (Yamazen with Merck Lichroprep RP-18 column) eluting with acetonitrile to get dark straw colored solid which was purified by column chromatography (hexane : ethyl acetate : DMF=4 : 4 : 2) to afford straw colored solid. Recrystallization from acetonitrile afforded 8-amino-3-methoxyphenanthridin-6(5*H*)-one **14**.

Product **12**, mp 187-189 °C. GC/MS: 272 (M^+), 241, 226, 221, 198, 164. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 3.51 (3H, s), 3.54 (3H, s), 4.99 (2H, s), 5.17 (2H, s), 6.14-6.17 (2H, m), 6.69 (1H, dd), 6.76 (1H, d), 6.86-6.89 (2H, m). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 51.06, 54.34, 97.02, 105.96, 113.81, 116.40, 118.09, 125.90, 129.83, 131.56, 132.03, 146.61, 148.68, 156.43, 168.92.

Product **13**, mp 252-254 °C. LC/MS: 240.8 (M^++H); ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 3.82 (3H, s), 5.49 (2H, s), 6.82 (1H, dd), 6.92 (1H, d), 7.21-7.30 (2H, m), 7.70 (1H, dd), 8.75 (1H, d), 11.42 (1H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 56.18, 99.52, 108.33, 109.69, 112.33, 120.47, 122.95, 123.05, 123.53, 125.74, 135.91, 147.98, 158.46, 161.30.

Product **14**, mp 265.5-266.7 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$): 3.76 (3H, s), 5.55 (2H, s), 6.79 (1H, dd), 6.85 (1H, d), 7.07 (1H, dd), 7.40 (1H, d), 8.04 (2H, d), 11.27 (1H, s). ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 55.12, 99.68, 108.60, 112.17, 117.02, 121.37, 121.42, 126.38, 126.64, 127.22, 137.53, 145.91, 158.53, 161.33.

Benzidine Rearrangement of 2. Similar procedure for the rearrangement of **1** was carried out except the amount of acid. *i.e.* 2.5 mL of conc HCl in 10 mL of ethanol was used to effect the rearrangement. After standing for 48 h, precipitate was filtered to get red solid and brownish liquid. Each of these was neutralized with 1 N $NaHCO_3$. Red solid was washed with distilled water, dried, and identified to be diazene **5** (0.3 g) by GC. The brownish liquid was extracted with ethyl acetate and dried over anhydrous $MgSO_4$ finally affording a mixture (0.99 g) of diazene **5** and fission amines.

Benzidine Rearrangement of 3. Similar procedure for the rearrangement of **1** was carried out except the amount of acid. *i.e.* 5.0 mL of 6 N HCl cooled to 0 °C was used to effect the rearrangement.. After standing for 48 h, the rearrangement solution was neutralized with 1 N $NaHCO_3$ followed by extraction with ethyl acetate. Ethyl acetate solution was dried over anhydrous $MgSO_4$, followed by evaporation to afford brownish liquid (0.86 g) consisting of diazene **6** and fission amines.

Quantitative Analysis of Products

Rearrangement of 1. Relative ratio of integration obtained from ^{1}H NMR spectra of rearrangement products gave the quantitative results as follows. 4,4'-Diamino-2-carbomethoxy-2'-methoxybiphenyl **12**, 71%; 10-amino-3-methoxyphenanthridin-6(5*H*)-one **13**, 7.1%; 8-amino-3-methoxyphenanthridin-6(5*H*)-one **14**, 3.4%.

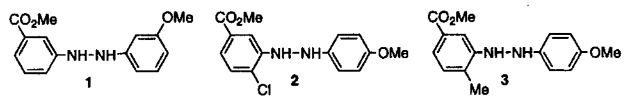
On the other hand, disproportionation products was analyzed by GC using *n*-decanol as an internal standard. Stock solution of *n*-decanol (20 mM) in methanol was prepared and used to make standard solutions of authentic samples such as diazene **4**, methyl 3-aminobenzoate, and *m*-anisidine (20 mM, 12 mM, 8 mM, 4 mM). Quantitative results are as follows. Diazene **4**, 0.43 mmol (4.3%); methyl 3-aminobenzoate, 0.45 mmol (4.5%); *m*-anisidine, 0.22 mmol (2.2%). Yield of disproportionation products was approximately 9%.

Disproportionation of 2. Similar procedure used for quantitative analysis of the disproportionation products from **1** was used to get following results. Diazene **5**, 1.40 mmol (34%); methyl 3-amino-4-chlorobenzoate, 0.8 mmol (19%); *p*-anisidine, 0.7 mmol (17%). Yield of disproportionation products was approximately 54%.

Disproportionation of 3. Similar procedure used for quantitative analysis of the disproportionation products from **1** was employed to get following results. Diazene **6**, 0.7 mmol (20%); methyl 3-amino-4-methylbenzoate, 0.7 mmol (20%); *p*-anisidine, 0.4 mmol (11%). Yield of disproportionation products was approximately 40%.

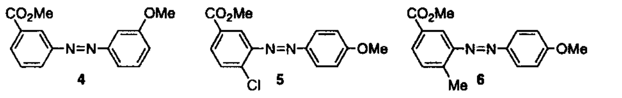
Results and Discussion

We undertook to study the acid-catalyzed benzidine rearrangements of unsymmetrically substituted diazanes having electron donor and acceptor at benzene rings, respectively. For the purpose, (3-carbomethoxyphenyl)(3-methoxyphenyl)diazane **1**, (5-carbomethoxy-2-chlorophenyl)(4-methoxyphenyl) diazane **2**, and (5-carbomethoxy-2-methylphenyl)(4-methoxyphenyl)diazane **3** have been chosen.



In particular carbomethoxy at *meta* position and methoxy groups at either *meta* or *para* position were introduced into the diazanes as an electron acceptor and donor respectively. There were several reasons for the choice of the diazane **1-3**. One of them was to study how the electronic perturbations affect the rearrangement products compared with symmetrically disubstituted diazanes which have been studied extensively in the benzidine rearrangements. The other was to utilize the benzidine rearrangement to synthesize organic molecule of novel structure which can hardly be feasible by conventional methods. Considering that benzidine rearrangement products have two amino groups, we could expect the secondary reactions of amino group with the carbomethoxy group at *meta* position of the diazanes.

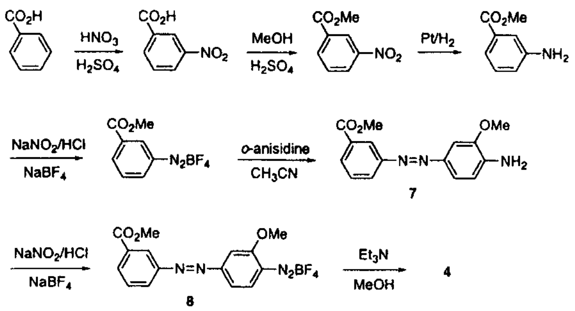
Preparation of Diazanes 1-3. The objective in each case was to prepare stable diazenes **4-6** which can give diazanes **1-3** just before use by reducing with Zn and saturated ammonium chloride solution.[5]



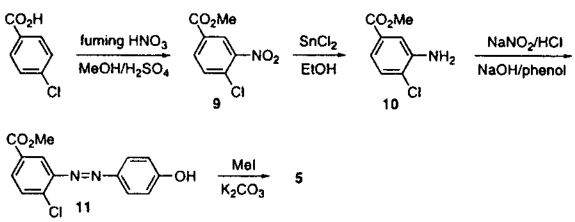
Diazene **4** was prepared according to the conventional methods except the hydrodediazoniation of diazene **8** to **4** as shown in Scheme 1.

Among the various reductants such as hypophosphorous acid,[8] hot ethanol,[8,9] triphenylphosphine,[10] and *N,N*-dimethylformamide[11,12] etc., triethylamine in methanol turned out to be very efficient.[6] Preparation of diazene **5** is shown in Scheme 2 in which reduction of nitroarene **9** to aniline derivative **10** was achieved with stannous chloride.

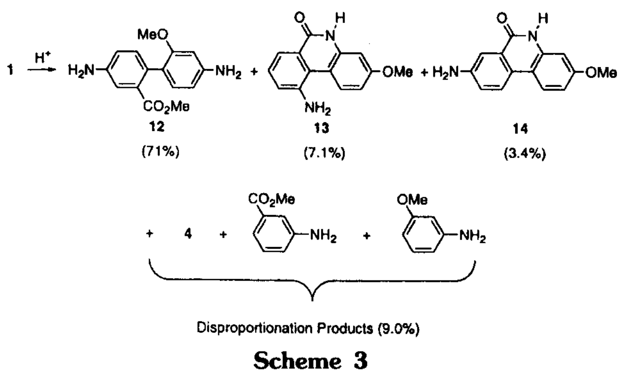
Catalytic hydrogenation by Pt or PtO_2 was not successful since dechlorination also took place in addition to the desired product **10**. Diazenee **6** was prepared by following the similar procedures employed for diazene **5** as shown in Scheme 2 except the reduction of nitroarene to aniline derivative. For the purpose Pd/C gave satisfactory results.



Scheme 1



Scheme 2

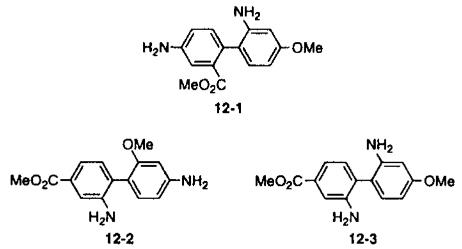


Scheme 3

Rearrangement Products and Structures Determination. Benzidine rearrangement of diazane **1** was conducted in ethanol by adding conc. HCl solution. After work-up, three compounds were isolated as shown in Scheme 3.

The products were 4,4'-diamino-2-carbomethoxy-2'-methoxybiphenyl **12** (71%), 10-amino-3-methoxyphenanthridin-6(5*H*)-one **13** (7.1%), and 8-amino-3-methoxyphenanthridin-6(5*H*)-one **14** (3.4%). Obviously products **13** and **14** were formed by condensation between carbomethoxy and amino groups present in primary products such as *o*-benzidine and diphenyline type, respectively. Also obtained were disproportionation products (9.0%).

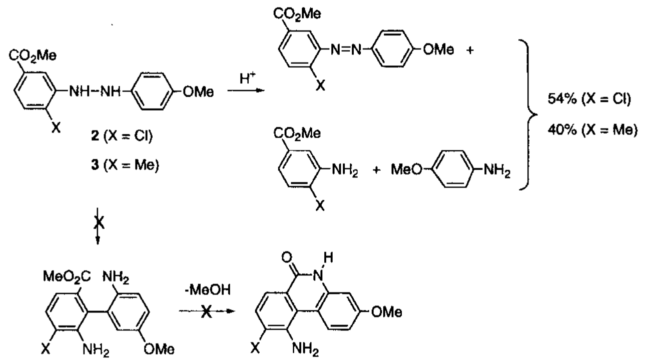
The structure of **12** was deduced as follows. Since ^1H NMR spectra of **12** showed only doublets and singlets in the aromatic regions together with two NH_2 groups, following three compounds were also conceived in addition to **12**.



The chemical shifts of two Me groups in carbomethoxy and methoxy were observed upfield by 0.3-0.4 ppm compared to those of anisole (δ 3.81), *m*-anisidine (δ 3.78), 3,3'-dimethoxybenzidine (δ 3.85), methyl benzoate (δ 3.91), and methyl 4-aminobenzoate (δ 3.80), indicating the two methyl substituents located at 2,2'-positions in the biphenyl rings. This phenomena might be interpreted by the magnetic anisotropy of ring current exerting on the 2,2'-substituents orienting towards the benzene rings since the two benzene rings in the biphenyl are twisted each other ranging from 40° (biphenyl) to 60° (diphenic acid). The two amino groups, on the other hand, were observed to be shifted downfield by about 1.5 ppm compared to those of ethyl 3-aminobenzoate (δ 3.80) and *m*-anisidine (δ 3.65), indicating these groups not to be located at 2,2'-positions. In addition to these data, 2D H-H COSY, H-C COSY, and DEPT spectrum gave the information consistent with the structure **12**.

Structure of **13** was deduced as follows. LC/MS gave the molecular weight 240.8 (M^++H). This indicated that one methanol was lost from the expected molecular weight (M^+; 272) of usual benzidine products. Also, IR spectra showed the carbonyl group (C=O) at 1650 cm^{-1} indicating a 6-membered lactam. Based on these informations, we could deduce the structure to be formed by the secondary condensation reactions between amino and carbomethoxy groups. ^1H NMR spectrum showed that the aromatic protons in two benzene rings consisted of two doublets and a triplet, and two doublets and a singlet, respectively. This information indicated the presence of three adjacent aromatic protons, two adjacent protons, and one isolated proton. In addition to ^1H NMR, not only 2D H-H COSY but also 2D NOESY spectrum were well consistent with the structure **13**.[13]

Identification of **14** was deduced as follows. At first sight, ^1H NMR spectrum was difficult to be interpreted clearly.



Scheme 4

However when we supposed that the two peaks at δ 8.024 and 8.051 were exactly overlapped by two doublets, the structure was consistent with **14**. Therefore, Gaussian function multiplication was carried out in order to get the well resolved the peaks. Since the peaks obtained by Gaussian function multiplication are much narrower than that obtained by Lorentzian function multiplication by 5 times, we can in general obtain the well resolved spectrum of much narrower peak by applying Gaussian function to the FID obtained from Lorentzian function.[14] Thus, it turned out that the two peaks at δ 8.024 and 8.051 were really overlapped by two doublets. 2D COSY and 2D NOESY spectra also confirmed this. *i.e.* magnifying two cross peaks showed the different chemical shifts.[15]

Conclusion

Acid-catalyzed benzidine rearrangements of new unsymmetrical diazanes **1-3** were carried out in ethanolic solutions. Rearrangement of diazane **1** gave *p*-benzidine type **12** in 71% and two kinds of 6(5*H*)-phenanthridinone derivatives **13, 14** in 7.1% and 3.4%, respectively. Formations of **13** and **14** gave us an information that the benzidine rearrangement might be utilized to prepare organic molecules of novel structures which can be hard to synthesize by conventional methods. In these regards diazanes **2** and **3** were chosen for the rearrangements hopefully to get the increased yields of 6(5*H*)-phenanthridinone type derivatives similar to **13** and **14**. Rearrangements, however, proceeded quite unexpectedly mostly to give disproportionation products such as fission amines and corresponding diazenes in 54% and 40% yields, respectively (Scheme 4).

Considering that the disproportionation is a part of benzidine rearrangement, the results obtained from the rearrangements of diazanes **1-3** indirectly seem to indicate the importance of disproportionations to understand the benzidine rearrangements. Further investigations would be necessary in order to clarify the effects of substituents on the rearrangment products.

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13. 2D NOESY spectrum showed two cross peaks resulting from NH_2-H_1 and NH_2-H_9 indicating the NH_2 group to be radially close to both H_1 and H_9. Considering that H_1 and H_9 are present in different benzene rings respectively, NH_2 group should be positioned at C-10. On the other hand, aromatic protons H_1, H_2, and H_4 in the same benzene ring gave cross peaks made between H_1-H_2, CONH-H_4 providing an information that H_4 should be close to CONH having *o*-substituent, well consistent with the structure **13**.
14. Elsewhere in NMR textbooks.
15. 2D NOESY spectra were well corroborated with the structure **14**, giving cross peaks made between H_1-H_2, H_9-H_{10}, NH_2-H_7, NH_2-H_9, and CONH-H_4.