Synthesis of Diimidazo[1,2-*a*:2′,1′-*c*]pyrazines and Diimidazo[1,2-*a*:2′,1′-*c*][1,4]diazepines

P. Melloni (1) and D. Fusar-Bassini

Department of Chemistry, Carlo Erba Research Institute Milan, Italy

and

E. Dradi and C. Confalonieri

Department of Physical-Organic Chemistry, Carlo Erba Research Institute, Milan, Italy

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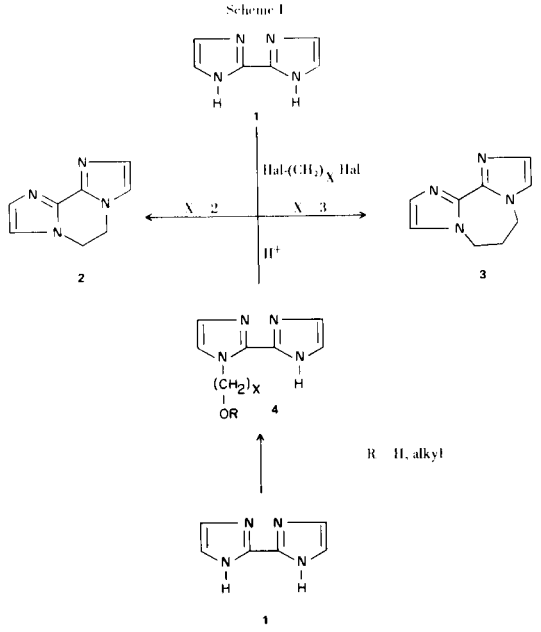
Two new heterocyclic compounds, diimidazo[1,2-*a*:2′,1′-*c*]pyrazine and 5*H*-diimidazo[1,2-*a*:2′,1′-*c*][1,4]diazepine have been synthesized by various routes from 2,2′-biimidazole (**1**) (2) together with some hydro, hydroxy and alkyl derivatives.

We here report the synthesis of some new heterocyclic compounds obtained by treating 2,2′-biimidazole (**1**) with aliphatic halides. With 1,2-dihaloethane compound **1** undergoes ring closure forming 5,6-dihydrodiimidazo[1,2-*a*:2′,1′-*c*]pyrazine **2** and 5*H*-6,7-dihydrodiimidazo[1,2-*a*:2′,1′-*c*][1,4]diazepine (**3**) with 1,3-dihalopropane. The same two compounds can be obtained by an alternative method also shown in Scheme I.

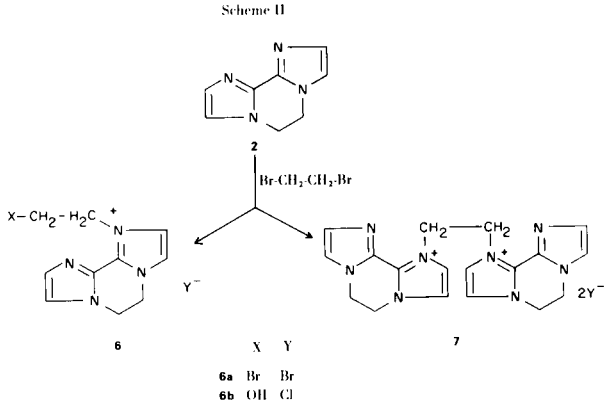
The nmr spectrum of **2** (in DMSO-d_6) shows a singlet at 4.34 δ due to the two equivalent methylene groups and two doublets at 7.18 and 6.96 δ due to the imidazole ring protons. Degeneracy of the hydrogen atoms of $-CH_2-CH_2-$ fragment is still retained at the lowest temperature allowed by the solvent, but the broadening of the band clearly indicates that the rate of inversion is decreased. The nmr spectrum of **3** is also consistent with the trimethylene bridge whose high-order spins system AA′XX′X″X‴ (3) is still due to fast ring mobility.

Scheme I



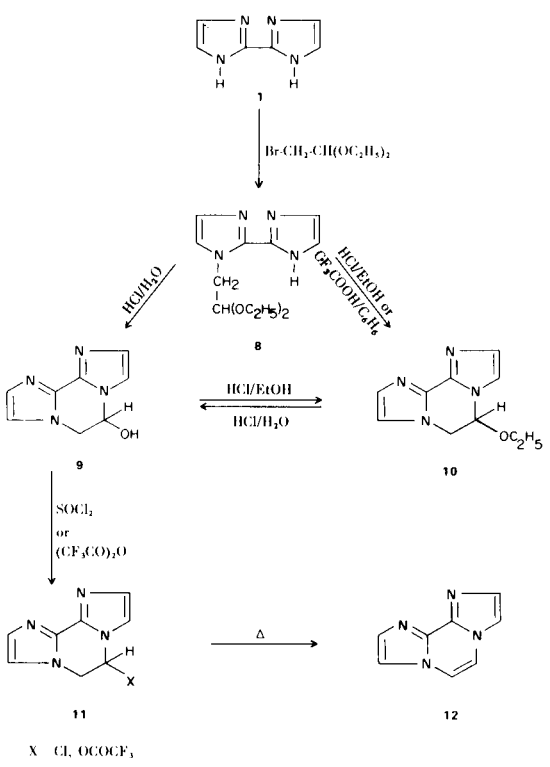
The method with α,ω-dihaloalkane is more direct as it involves only one passage from **1** to the end products; however, it has the drawback of producing several side-products as a result of the α,ω-dihaloalkane further attacking compounds **2** and **3** once they are formed. This has been demonstrated by reacting compound **2** with 1,2-dibromoethane. Under different reaction conditions (see Experimental) the two compounds **6a** and **7** shown in Scheme II were isolated. These two compounds correspond to the main side-products of the reaction of 2,2′-biimidazole with 1,2-dibromoethane.

Scheme II

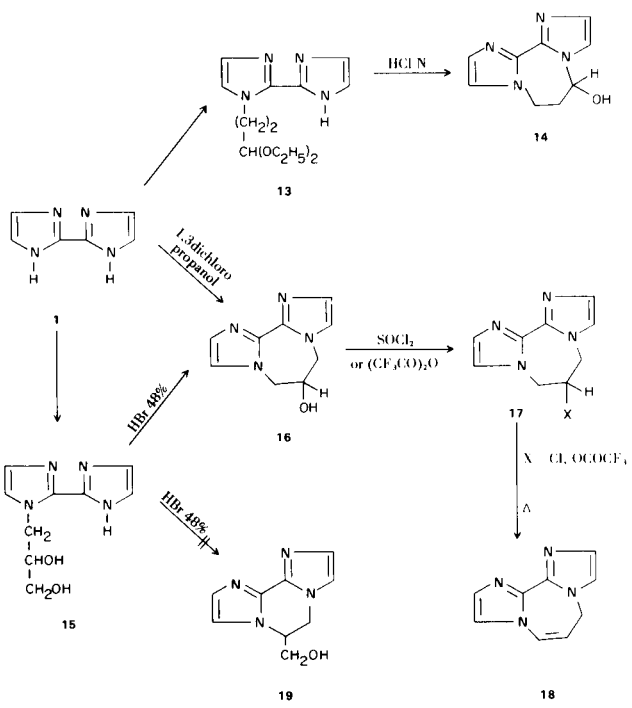


The structure of these compounds has been confirmed by microanalysis, ir and nmr data: these are consistent with an A_2X_2 system for the bromoethylene fragment of

Scheme III



Scheme IV



6a and with a symmetrical structure for **7** (see Experimental). A quaternary salt **6b** was also obtained where 2,2′-biimidazole was reacted with 2-chloroethanol; when heated at 270° under vacuum this salt is converted into compound **2**. In the upper reactions of Scheme I there is a marked decrease in side-products if the dibromohalides are replaced with the corresponding bromo-chloro derivatives. The main goal, however, was to synthesize compounds **12** and **18** which correspond to **2** and **3** with one more unsaturation. Scheme III and IV show the reactions employed to prepare these compounds; details are given in the Experimental.

All the intermediate products shown in the diagrams were isolated except for compound **11** (X = Cl) which was directly converted into derivative **12**. Compound **11** was also prepared with X = $OCOCH_3$ but it proved unsuitable to obtain **12** by the heat reaction indicated. The double bound $\Delta^{5,6}$ in compound **12** is highly resistant to catalytic hydrogenation, whereas the double bond in compound **18** is easily hydrogenated.

The uv spectrum for compound **12** shows a maximum at 224 nm and a hipsochromic effect of the 290 nm band of **2**, both signs of considerable disturbance of the system of the imidazolic rings, probably due to the benzenoid character of the pyrazine ring.

The compound **13** and **14** of Scheme IV, superior homologs of **7** and **8** are hard to purify: the method through **16** and **17** was therefore preferred to obtain compound **18**.

Compound **16** obtained from **15** was identified by comparison with the product obtained by reaction of 2,2′-biimidazole (**1**) with 1,3-dichloropropanol (reaction **1** → **16**) and also by substituting the hydroxyl group of **16** with hydrogen by reduction of the intermediate chloro derivative in strongly alkaline medium. The product obtained was identical with **3** which was already identified. No attempt was made to separate the enantiomers of compound **9**, **10** and **11**.

EXPERIMENTAL

Uv absorption spectra were measured in methanol on a Bausch and Lomb spectrophotometer. Ir spectra were determined on a Perkin-Elmer 125 spectrophotometer. Nmr spectra were recorded on Varian HA-100 with TMS as the internal standard.

5,6-Dihydrodiimidazo[1,2-*a*:2′,1′-*c*]pyrazine (**2**).

a) By Heating of **6b**.

Compound **6b** (1.2 g., 0.005 mole) was heated under vacuum at 270° for 45 minutes; the residue was crystallized from very little water, giving 0.5 g. of **2**, m.p. 216-218°.

b) To a boiling and stirred solution of 53.6 g. (0.4 mole) of 2,2′-biimidazole in 400 ml. of 95% ethanol, was added over 3 hours 7.16 ml. (0.1 mole) of 2-chloroethanol and 100.8 ml. (0.6 mole) of 20% sodium hydroxide. The solution was refluxed for 6 hours, neutralized with concentrated hydrochloric acid, cooled at 10° and filtered. The solid was washed with 150 ml. of boiling ethanol, which was then added to the reaction mother liquors. These were taken to dryness under vacuum, and the throughly dry residue was taken up with 300 ml. of absolute ethanol, to eliminate the sodium chloride. The ethanol was again evaporated to dryness and the residue crystallized from a little water, giving 9 g. (70.5%) of **4**

(R = H), m.p. 134-136°. The 9 g. of substance was refluxed for three days in 48% hydrobromic acid and then the mixture evaporated to dryness under vacuum. The residue was ground under ether and then the ether decanted to eliminate as much as possible the hydrobromic acid. The solid was dissolved in 20 ml. of water, decolorized and filtered. To the hot solution concentrated sodium hydroxide was added to neutrality. The solution was cooled, compound **2** filtered, and crystallized from a little water, giving 6.7 g. of **2** (83%), m.p. 214-216°.

c) The method, reaction conditions and yield for compound **2** through compound **4** (R = CH_3, C_2H_5) were the same as indicated in b), starting from β-bromoethyl methyl (ethyl) ether instead of 2-chloroethanol.

d) Starting from compound **4** (R = H) the cyclization could be accomplished with thionyl chloride in various solvents (dioxane, DMF, etc.); the reaction was much faster but gave slightly lower yields.

e) Thirty-five percent sodium hydroxide (16.5 ml. 0.2 mole) was slowly added to a well-stirred suspension of 13.4 g. (0.1 mole) of 2,2′-biimidazole in 100 ml. of DMF and then 14.4 ml. (0.175 mole) of 1-bromo-2-chloroethane was added. The temperature was maintained below 30° with ice, and stirring continued for 12 hours at room temperature. The solid was filtered and washed with a little absolute ethanol, the washes added to the reaction DMF, and the whole evaporated to dryness under vacuum with external temperature at 110°. The residue was finely powdered and extracted 4 times with 40 ml. of boiling acetonitrile, decanting each time. The acetonitrile was evaporated to dryness and the residue crystallized from 15-20 ml. of water; m.p. 214-216°, yield 6 g. (37.5%). 2,2′-Biimidazole (6.7 g.) was recovered from the solid residues of filtration and extraction, with means the yield of 2,2′-biimidazole rises to 75%, uv λ max: 283 nm (ε 15,100), 290 nm (ε 15,500), 304 nm (shoulder); ir ν max (chloroform): 1280, 1105 cm^{-1} (ring stretching); nmr (DMSO-d_6) δ 4.34 (s, 4H, CH_2CH_2), 6.96 (d, 2H, J = 1.0 Hz, H-2 and H-9), 7.18 (d, 2H, J = 1.0 Hz, H-3 and H-8).

Anal. Calcd. for $C_8H_8N_4$: C, 60.0; H, 5.0; N, 35.0. Found: C, 59.8; H, 5.0; N, 35.3.

5*H*-6,7-Dihydrodiimidazo[1,2-*a*:2′,1′-*c*][1,4]diazepine (**3**).

This compound was obtained as described for compound **2**. The cyclization was more difficult; in fact we succeeded in isolating 1-γ-chloropropyl-2,2′-biimidazole, but it proved impossible to isolate 1-β-chloroethyl-2,2′-biimidazole, which evidently is much more unstable: uv λ max (methanol): 278 nm (ε 12,100), 288 302 nm (shoulder); ir ν max (potassium bromide): 1310, 1130 cm^{-1} (ring stretching); nmr δ (DMSO-d_6) 2.25 (m, 2H, CH_2-CH_2-CH_2), 4.20 (m, 4H, NCH_2), 6.98 (d, 2H, J = 1.0 Hz, H-2 and H-10) 7.20 (d, 2H, J = 1.0 Hz); the signal at 2.25 collapses into a singlet after irradiation at 4.20 δ.

Anal. Calcd. for $C_9H_{10}N_4$: C, 62.1; H, 5.7; N, 32.2. Found: C, 62.1; H, 5.7; N, 32.0.

1-β-Bromoethyl-5,6-dihydrodiimidazo[1,2-*a*:2′,1′-*c*]pyrazinium Bromide (**6a**).

A suspension of 1.6 g. (0.01 mole) of compound **2** in 20 ml. of dibromoethane was refluxed for 12 hours, cooled and filtered; the solid was crystallized from absolute ethanol, giving 1.95 g. (56.5%) of a product which melted poorly between 320-330°; ir ν max (potassium bromide): 1615 cm^{-1} (=N$<^{+}$); nmr (perdeuteriomethanol): 3.98 (t, 2H, J = 6.0 Hz, CH_2Br), 4.72 (s, 4H, NCH_2), 5.60 (t, 2H, J = 6.0 Hz, $\overset{+}{N}CH_2$), 7.41 (d, 1H, J = 1.0 Hz, H-9), 7.58 (d, 1H, J = 1.0 Hz, H-8), 7.69 (d, 1H, J = 2.0 Hz, H-3), 7.75 (d, 1H, J = 2.0 Hz, H-2).

Anal. Calcd. for $C_{10}H_{12}Br_2N_4$: C, 34.5; H, 3.5; Br, 46.2; N, 16.1. Found: C, 34.8; H, 3.5; Br, 45.9; N, 16.1.

1-β-Hydroxyethyl-5,6-dihydrodiimidazo[1,2-*a*:2′,1′-*c*]pyrazinium Chloride (**6b**).

This compound was obtained as a side-product in the preparation of 1-β-hydroxyethyl-2,2′-biimidazole. A mixture of 13.4 g. (0.1 mole) of 2,2′-biimidazole, 8.2 g. (0.1 mole) of anhydrous sodium acetate and 21.4 ml. (0.3 mole) of 2-chloroethanol in 300 ml. of DMF was refluxed for 12 hours, cooled, filtered and the solid washed with a few ml. of absolute ethanol. The filtrate was evaporated to dryness, the residue mixed to an inert support and extracted for 20 hours in a Soxhlet apparatus with ethyl acetate; it was then exhausted with ethanol (6 hours). The ethanol extracts were taken to dryness and the residue crystallized first from 2-propanol and then from absolute ethanol. This gave 2 g. of **6b** m.p. 235-240°; ir ν max (potassium bormide): 1615 cm^{-1} (=N$<^{+}$), 1065 cm^{-1} (C-OH).

Anal. Calcd. for $C_{10}H_{13}ClN_4O$: C, 49.9; H. 5.4; Cl, 14.8; O, 6.7. Found: C, 50.2; H, 5.4; Cl, 14.9; O, 6.9.

1,2-[Bis(5,6-dihydrodiimidazo[1,2-*a*:2′,1′-*c*]pyrazinyl-1)]ethane Hydrobromide (**7**).

Compound **2** (0.32 g. 0.02 mole) dissolved in 50 ml. of DMF was placed in a sealed glass with 0.19 g. (0.001 mole) of 1,2-dibromethane, and held at 180° for 12 hours. The mixture was then cooled, filtered, and the solid crystallized from methanol, giving 0.2 g. (39%) of **7**, m.p. 330°; ir ν max (potassium bromide): 1620 cm^{-1} (=N$<^{+}$); nmr δ (deuterium oxide): 5.24 (s, 4H, $\overset{+}{N}CH_2CH_2\overset{+}{N}$), 4.57 (s, 8H, NCH_2CH_2N), 7.27 (d, 2H, J = 1.0 Hz, H-9), 7.54 (d, 2H, J = 1.0 Hz, H-8), 7.57 (d, 2H, J = 2.0 Hz, H-3), 7.59 (d, 2H, J = 2.0 Hz, H-2).

Anal. Calcd. for $C_{18}H_{20}Br_2N_8$: C, 42.6; H, 3.9; Br, 31.5; N, 22.0. Found: C, 42.5; H, 3.9; Br, 31.0; N, 21.8.

1-β-Diethoxyethyl-2,2′-biimidazole (**8**).

To 7.2 g. (0.3 mole) of sodium hydride was added 280 ml. of DMF and then slowly and under stirring 53.6 g. (0.4 mole) of 2,2′-biimidazole. Stirring was continued for 2 hours, then 19.7 g. (0.1 mole) of β-bromacetaldehyde diethylacetal was added. The solution was slowly heated to boiling, refluxed for 48 hours, filtered, and evaporated to dryness under vacuum. The residue was then taken up with 100-150 ml. of water, the solution brought to *p*H 5.5 with acetic acid and then extracted with 200 ml. of methylene chloride. The organic layers were dried, decolorized and then evaporated under vacuum. The residue was dissolved in a minimum amount of ether, the insoluble material filtered, and the ether extracted to exhaustion with 2*N* hydrochloric acid. The hydrochloric extracts were neutralized with concentrated sodium hydroxide, giving crystals which were filtered, yielding 7.65 g. of **8**. The neutralized mother liquor was extracted with methylene chloride, giving another 4.3 g. of the product, bringing the total to 11.95 g. (60% of the 2,2′-biimidazole had reacted). The product was crystallized from cyclohexane, m.p. 106-107°.

Non-reacted 2,2′-biimidazole (43 g.) was recovered during the above processes; ir ν max (chloroform): 3440 cm^{-1} (N-H); 1110, 1070 cm^{-1} (C-O-CH_2CH_3).

Anal. Calcd. for $C_{12}H_{18}N_4O_2$: C, 57.6; H, 7.2; N, 22.4. Found: C, 57.6; H, 7.3; N, 22.3.

5,6-Dihydro-5-hydroxydiimidazo[1,2-*a*:2′,1′-*c*]pyrazine (**9**).

A solution of 5.0 g. (0.02 mole) of compound **8** in 20 ml. of 23% hydrochloric acid was refluxed for 10 minutes, then dried,

giving the dihydrochloride of crude compound **9**. The free base was obtained by dissolving the hydrochloride in 50 ml. of water, and neutralizing with concentrated ammonium hydroxide. On cooling, 2.5 g. (71.5%) of compound **9** separated m.p. 190-191° after crystallization from water; uv λ max (methanol): 282 nm (ε = 13,860), 290 nm (ε = 13,640), 302 nm (shoulder); ir ν max (potassium bromide): ≅ 3000 cm^{-1} (O-H), 1100 cm^{-1} (C-OH); nmr δ (DMSO): 4.40 (d, 2H, J = 3.0 Hz, CH_2), 5.99 (t, 1H, J = 3.0 Hz, CHOH), 7.00 (s, 2H, H-8 and H-9), 7.30 (d, 1H, J = 1.0 Hz, H-2), 7.33 (d, 1H, J = 1.0 Hz, H-3).

Anal. Calcd. for $C_8H_8N_4O$: C, 54.5; H, 4.5; N, 31.8. Found: C, 54.2; H, 4.5; N, 31.6.

5,6-Dihydro-5-ethoxydiimidazo[1,2-*a*:2′,1′-*c*]pyrazine (**10**).

Compound **8** was refluxed for 2 hours in absolute ethanol, bubbling through hydrogen chloride gas, or else in benzene, with an excess of trifluoroacetic acid (10:1). The solvents were then evaporated to dryness, and the residue dissolved in water. The solution was made basic with sodium bicarbonate and then extracted with chloroform: the organic layer was then washed with water dried and evaporated to dryness. The residue was crystallized from ethyl acetate. Both methods gave a yield of about 80%, m.p. 137-139°. Compound **10** was also obtained by refluxing **9** in ethanol with hydrogen chloride bubbling in ; uv λ max (methanol): 283 nm (ε = 14,400), 291 nm (ε = 14,720), 302 nm (shoulder); ir ν max (chloroform): 1110 cm^{-1} (C-O-CH_2-CH_3).

Anal. Calcd. for $C_{10}H_{12}N_4O$: C, 58.8; H, 5.9; N, 27.4. Found: C, 58.9; H, 6.0; N, 27.5.

Trifluoracetate of 5,6-Dihydro-5-trifluoroacetoxy[1,2-*a*:2′,1′-*c*]-pyrazine (**11**). (X = $OCOCF_3$).

A suspension of 0.88 g. (0.005 mole) of finely powdered **9** in 20 ml. of trifluoroacetic anhydride was refluxed under vigorous stirring for 4 hours. The solvent was evaporated, giving compound **11** in a quantitative yield, m.p. 138-141°; ir ν max (potassium bromide): 1770 cm^{-1} (C=O), 1200-1120 cm^{-1} (-CF_3).

Anal. Calcd. for $C_{12}H_8F_6N_4O_4$: F, 29.4; N, 14.5. Found: F, 29.1; N, 14.4.

Diimidazo[1,2-*a*:2′,1′-*c*]pyrazine (**12**).

a) Compound **11** (1.93 g. 0.005 mole) (X = $OCOCF_3$) was heated under vacuum at 180-200° for 15 minutes. The compound which forms tends to sublime on the cold walls of the flask in these conditions. After cooling the residue was crystallized from water. This gave 0.62 g. (78.5%) of compound **12** m.p. 206-208°.

b) To a suspension of 10 g. (0.04 mole) of crude dihydrochloride of finely powdered **9** in 130 ml. of DMF were added at room temperature 8.7 ml. (0.06 mole) of thionyl chloride. The mixture was heated to 50°, left at this temperature for 12 hours, then cooled to 10°, filtered and the solid washed with a little ether. The solid was then placed in a rotary evaporator under vacuum with the external bath at 90°-100° for 1.5 hours. It was then dissolved in 40 ml. of water, decolourized, and the filtrate brought to *p*H 8 with concentrated ammonium hydroxide; the precipitate was filtered at 0°, and washed with a little cold water. This gave 4.2 g. (66.5%) of crude product, which was crystallized from a little water, m.p. 206-208°; uv λ max (methanol): 224, 231, 239, 248, 285 and 299 nm: ir ν max (potassium bromide): 1570, 1505 cm^{-1} (C=C, C=N), 1330, 1110 cm^{-1} (ring stretching); nmr δ (perdeuteriomethanol), 7.43 (d, 2H, J = 2.0 Hz, H-2 and H-9), 7.72 (d, 2H, J = 2.0 Hz, H-8 and H-3), 7.87 (s, 2H, H-5 and H-6).

Anal. Calcd. for $C_8H_6N_4$: C, 60.8; H, 3.8; H, 35.4. Found: C, 60.9; H, 3.9; N, 35.3.

1-γ-Diethoxypropyl-2,2′-biimidazole (**13**).

The reaction conditions to obtain this compound were the same as for compound **8**. The elaboration was necessarily different because when extraction was carried out as for **8** with hydrochloric acid - even at a low temperature and using 1*N* hydrochloric acid cyclization took place immediately. So the DMF was evaporated to dryness under vacuum, taken up with water, and extracted with methylene chloride; this was dried and decolourized, then evaporated to dryness, and the residue separated on a silica gel column with benzene-acetone-dimethylamine (140:70:2), giving a yield of 55% of the biimidazole reacted, m.p. 70-72° after crystallization from ligroin (60-80°); ir ν max (chloroform): 3440 cm^{-1} (N-H); 1110, 1055 cm^{-1} (C-O-CH_2CH_3).

Anal. Calcd. for $C_{13}H_{20}N_4O_2$: C, 59.0; H, 7.6; N, 21.2. Found: C, 59.0; H, 7.6; N, 21.1.

6,7-Dihydro-5*H*-5-hydroxydiimidazo[1,2-*a*:2′,1′-*c*][1,4]diazepine (**14**).

Cyclization **13** → **14** with aqueous hydrochloric acid is much faster than the corresponding reaction **8** → **9**. After only a few minutes' contact with 1*N* hydrochloric acid at 0°, no trace remains of the starting product. However, the reaction gives rise to side products, so that to obtain the pure product, separation on silica gel column with chloroform-methanol-ammonium hydroxide (150:10:0.5) proved necessary m.p. 158-160°; uv λ max (methanol): 272 nm (ε = 13.730); ir ν max (potassium bromide): ≅ 3000 cm^{-1} O-H); 1115 cm^{-1} (C-OH).

Anal. Calcd. for $C_9H_{10}N_4O$: C, 56.8; H, 5.3; N, 29.5. Found: C, 56.9; H, 5.2; N, 29.6.

1-β-γ-Dihydroxypropyl-2,2′-biimidazole (**15**).

This compound was prepared by the same method used for compound **8** giving a yield of 53% of the 2,2′-biimidazole reacted, m.p. 124-126°; ir ν max (potassium bromide): ≅ 3300 (N-H, O-H); 1100, 1030 (C-OH).

Anal. Calcd. for $C_9H_{12}N_4O_2$: C, 51.9; H, 5.8; N, 26.9. Found: C, 51.9; H, 5.9; N, 26.7.

6,7-Dihydro-5*H*-6-hydroxydiimidazo[1,2-*a*:2′,1′-*c*][1,4]diazepine (**16**).

a) A solution of 20.8 g. (0.1 mole) of **15** in 300 ml. of 48% hydrobromic acid was refluxed for 72 hours; the hydrobromic acid was evaporated under vacuum and the residue dissolved in 120 ml. of water. The solution was decolourized with charcoal and 120 ml. of chloroform were added. The solution was cooled with ice, and cautiously, under vigorous stirring, a saturated solution of sodium carbonate was added until the solution was alkaline. The organic phase was separated and the waters exhausted by extracting twice with 60 ml. of chloroform. After the chloroform was evaporated, the temperature of the external bath was raised to 110° for 30 minutes that caused the cyclization to **16**. The solid was then dissolved in 40 ml. of water, the solution decoloured, heated to 60° and then 35% sodium hydroxide added to bring the *p*H to 8. On cooling, 9.1 g. (48%) of compound **16** separated, m.p. 239-242°.

b) Compound **16** could be obtained directly by reacting 2,2′-biimidazole with 1,3-dichloro-2-propanol in exactly the same manner as for the preparation of compound **2** according to method e). After DMF was evaporated (see method), the residue was taken up with absolute ethanol the product finely crushed and the suspension filtered hot. The filtrate was evaporated to dryness, and the residue crystallized from water, giving 5.5 g. (29%) of **16**,

m.p. 239-241°; uv λ max (methanol) 272 nm (ε = 13.000); ir ν max (potassium bromide): 3300 cm^{-1} (O-H); 1130, 1110 cm^{-1} (C-OH).

Anal. Calcd. for $C_9H_{10}N_4O$: C, 56.8; H, 5.3; N 29.5. Found: C, 56.8; H, 5.2; N, 29.6.

6,7-Dihydro-5*H*-6-Chlorodiimidazo[1,2-*a*:2′,1′-*c*][1,4]diazepine (**17**). 5*H*-Diimidazo[1,2-*a*:2′,1′-*c*][1,4]diazepine (**18**).

The preparation methods were the same as for **11** (X = Cl) and **12**, except that here the chloride intermediate was isolated, and crystallized from dioxane, m.p. 150-152°. Compound **18** had a melting point of 156-158°, and crystallized from 2-butanol.

Anal. (**17**) Calcd. for $C_9H_9ClN_4$: C, 51.9; H, 4.3; N, 26.9; Cl, 17.0. Found: C, 52,0; H, 4.3; N, 26.5; Cl. 16.7.

Compound **18**; uv λ max (methanol): 229 nm (ε = 13,160); 290 nm (ε = 8.550); ir λ max (potassium bromide): 1660 cm^{-1} (C=C); 1285, 1175 cm^{-1} (ring stretching); nmr (**18**) (deuteriochloroform): 4.57 (d of d, 2H, $J_{5,6}$ = 6.5, $J_{5,7}$ = 0.75, H-5), 5.72 (d of t, 1H, $J_{2,6}$ = 8.5, $J_{6,5}$ = 6.5, H-6), 6.96 (d of t, 1H, $J_{7,6}$ = 8.5, $J_{2,5}$ = 0.75, H-7), 6.86 (d 1H, $J_{2,3}$ = 1.2, H-2), 7.03 (d, 1H, $J_{9,10}$ = 1.2, H-9), 7.13 (d, 1H, $J_{3,2}$ = 1.2, H-3), 7.17 (d, 1H, $J_{10,9}$ = 1.2, H-10).

Anal. (**18**) Calcd. for $C_9H_8N_4$: C, 62.8; H, 4.7; N, 32.5. Found: C, 62.9; H, 4.7; N, 32.6.

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(1) To whom correspondence should be addressed.

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(3) The details to be published of the conformational analysis were the subject of a communication to the VII Organic Chemistry Conference, Sept. 1973, Trieste, Italy.

Authors: E. Dradi, A. Forgione, P. Melloni and G. Tosolini.