1,2-Deoxygenation of *vic*-Dihydroxyindenoimidazoles: Optimization of a Novel Deoxygenation Reagent

Hans-Jörg Hemmerling[a], Angelika Merschenz-Quack[b,*], and Hartmut Wunderlich[b]

[a] Institut für Pharmazeutische Chemie
[b] Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstr.1, D-40225 Düsseldorf
[*] *Present address:* FH Jülich, Dep. Jülich, Ginsterweg 1, D-52428 Jülich

Reprint requests to Dr. H.-J. Hemmerling. E-mail: H-J.Hemmerling@uni-duesseldorf.de

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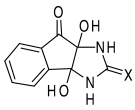
Dedicated to Prof. Dr. Hans-Dieter Höltje on the occasion of his 65th birthday

Treatment of *vic*-dihydroxyindeno[1,2-*d*]imidazoles with *N,N,N',N'*-tetraalkyl sulfurous diamides yields indeno[1,2-*d*]imidazoles by deoxygenation. Isochromeno[3,4-*d*]imidazoles are formed as byproducts. An X-ray crystal structure analysis confirmed the structure of deoxygenated products. The ratio of products depending on the reaction conditions was analyzed. A mechanism of the reaction is discussed.

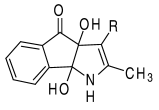
Key words: Indeno[1,2-*d*]imidazoles, Isochromeno[3,4-*d*]imidazoles, *N,N,N',N'*-Tetraalkylsulfurous Diamides, 1,2-Bis-deoxygenation, Crystal Structure

Introduction

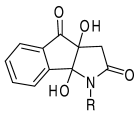
Ninhydrin (**1**), the hydrate of indan-1,2,3-trione, is well known as an analytical reagent for the detection of α-amino acids and its forensic application in fingerprint development. In synthetic applications of **1** with suitable 1,3-dinucleophiles, the carbonyl functionalities are involved in a (2+3)-cyclization to form indene-annulated heterocycles [1]. Thus the addition of urea or thiourea to **1** gives imidazole derivatives **2a** [2a]. The reaction of β-aminocrotonic acid derivatives and **1** yields indenopyrroles **2b** [2b]. The addition of acetamides to **1** gives rise to the formation of indenopyrrole derivatives **2c** [2c].



2a: X: O, S

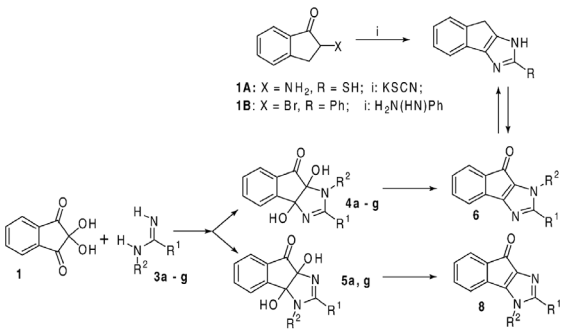


2b: R: $COOCH_3$, $COCH_3$, CN



2c: R: Alkyl

We recently reported on the addition of N-substituted amidines **3a – g** to **1** which afforded mixtures of regioisomeric indenoimidazoles **4** and **5** (Scheme 1) [3]. Because indenoimidazoles show some biological and pharmaceutical effects, syntheses have been developed using the reaction of 2-amino-



Scheme 1.

indan-1-one with thiocyanates (Scheme 1: **1A**) or 2-bromoindan-1-one with amidines (Scheme 1: **1B**) [4]. But these synthetic routes suffer from unefficiency and no general applicability. We therefore realized that the direct transformation of **4** and **5** to the fully unsaturated indenoimidazoles **6** and **8** would represent a particularly useful tool. As one way to reach this goal we considered the 1,2-bis-deoxygenation of **4** and **5**. Though 1,2-bis-deoxygenations of *vic*-diols to generate an olefinic bond are well known in the literature [5], compounds such as **2** or **4**, **5**, respectively, have not been subject to this type of reaction till now. We there-

fore decided to study the reaction of **4**, **5** with electrophilic reagents used in the syntheses of olefins from *vic*-diols.

In the present work we report on the results of our studies of developing a novel 1,2-deoxygenation reagent and its use for the olefination of the *vic*-diols **4** and **5**.

Results

We recently published the synthesis of mixtures of regioisomeric indenoimidazoles **4** and **5** by addition of N-substituted amidines **3a**–**g** to **1** [3]. The major products were identified as compounds **4a**–**g**. Due to equilibria in solutions, attempts to isolate the pure regioisomers **5** were not successful. Therefore the following experiments refer to purified mixtures of **4** and **5** even if not explicitly mentioned.

Preliminary experiments to deoxygenate **4g** were made using procedures which have proven to be efficient in olefin synthesis by deoxygenation of *vic*-diols. The Corey-Winter elimination proved unsuited because the cyclic precursors, needed in this reaction, could not be obtained when **4g** was allowed to react with thioxocarbonyldiimidazole [6]. In another approach attempts to get the cyclic precursor of the Eastwood fragmentation by reacting **4g** with dimethylformamide dimethyl acetal gave small amounts of **7g** as the only product [7].

Reaction of *vic*-Dihydroxyindenoimidazoles with Sulfurous Acid Derivatives

The olefin forming radical 1,2-elimination of 2,1,3-thiadioxolane-2,2-dioxides has been published recently [8, 9]. The substrates of this reaction usually are synthesized by reacting *vic*-diols and thionyl chloride to yield 2,1,3-thiadioxolane-2-oxides, which after oxidation gave the heterocyclic precursors of the olefination. The approach to synthesize 2,1,3-thiadioxolan-2-oxides *via* the reaction of **4g** and thionyl chloride / pyridine (**10**) resulted in the formation of largely intractable polymers from which two compounds could be isolated. Besides isochromene **7g** deoxygenation product **6g** was found in small amounts.

The structure of **6g** was confirmed by X-ray diffraction analysis of the $HClO_4$ adduct (Fig. 1) [10] which was validated by spectral and analytical data. The mass spectrum of **6g** with a molecular ion of 238 amu and the elemental analysis confirm the loss of two OH

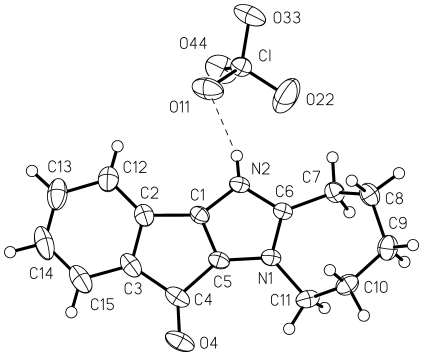
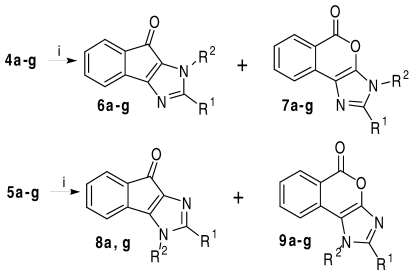


Fig. 1. Molecular structure of **6g** × **$HClO_4$** in the solid state with displacement parameters of 25% probability [10].



i: $O=S(R^3)_2$: **10:** R^3 = Cl, **a:** R^3 = 1-imidazolyl, **b:** $R^3 = N(CH_3)_2$, **c:** $R^3 = N(C_2H_5)_2$, **d:** $R^3 = N(iso\text{-}C_3H_7)_2$

Scheme 2. R^1, R^2 refer to Scheme 1.

groups in full agreement with the result of X-ray analysis. In the ^{1}H NMR spectra the expected aromatic and aliphatic protons could be detected but no exchangeable proton was found; likewise the ^{13}C NMR spectra include no signals corresponding to hydroxy substituted aliphatic bridgehead carbons of the educts. The carbonyl resonance appears at $\delta = 180$ ppm indicating the incorporation in an unsaturated cyclus.

Mass spectrum and elemental analysis of isochromenoimidazole **7g** confirm the loss of water. ^{1}H and ^{13}C NMR spectra are consistent with the proposed structure. In the ^{1}H NMR spectrum the anisotropy of the carbonyl group causes a significant downfield shift of aromatic *ortho*-proton 4-H to $\delta = 8.3$ ppm. The ^{13}C NMR spectrum shows a carbonyl resonance at $\delta = 160.9$ ppm indicating a lactone carbonyl [11]. No resonances of hydroxy substituted aliphatic bridgehead carbons were detected.

Because **6g** represented just the type of product we were searching for we were prompted to study this reaction in detail.

When **4** suspended in trichloromethane was allowed to react with thionyl chloride, only small amounts of

Table 1. Yields of deoxygenation products **6** (**+8**) and transformation products **7** (**+9**)[a].

Reagent	**10** ($SOCl_2$/pyridine)		**10a**		**10b**		**10b** (acetic acid)	
Starting compounds[b]	Yield [%] **6**	**7**	Yield [%] **6**	**7**	Yield [%] **6**	**7**	Yield [%] **6**	**7**
4a (+**5a**)	21[c]	56	45[c]	11	–	–	46[c]	< 1
4b (+**5b**)	7	49	10	24	11	9	80	16
4c	13	64	35	44	21	2	–	–
4d (+**5d**)	20	69	52	28	64	0	65	0
4f (+**5f**)	4	37	–	–	25	< 1	–	–
4g (+**5g**)	23[c]	65	23[c]	12	25[c]	< 1	52[c]	7

[a] The ratio of products were analyzed by means of ^{1}H NMR spectroscopic analysis and by HPLC of the crude reaction products; [b] the experiments were performed with purified mixtures of regioisomers as indicated; [c] yields refer to mixtures of **6** and **8**.

7 were found besides recovered educts. When this reaction was executed in the presence of pyridine, the compounds dissolved and the colour of the solution quickly changed from light yellow to deep orange. After several hours at ambient temperature, work-up resulted in the isolation of deoxygenation product **6** in poor yields besides a 3 – 8 fold excess of transformation product **7**. Column chromatographic separation on silica yielded mixtures of **6** and **7** which were analyzed by integration of the downfield aromatic multiplets in the ^{1}H NMR spectra and by HPLC and UV detection. Neither a cyclic nor acylic sulfurous acid ester could be isolated. Changing the reaction conditions by modifying solvent and temperature gave only very limited improvements (Table 1).

In order to enhance the yields of the deoxygenation products **6** and to avoid the formation of the transformation products **7**, the sulfurous acid diamides $SO(NR_2)_2$ **10a – d** (**a**: R = 1-imidazolyl, **b**: R = CH_3, **c**: R = C_2H_5, **d**: R = *iso*-C_3H_7) were synthesized and allowed to react with **4** and **5**.

Treatment of mixtures of **4/5** with **10a** in DMF resulted in a rapid coloring of the solution with formation of **6/8** in higher yields besides still considerable amounts of **7/9** and with decreased overall yields (Table 1). Using **10b**, no significant change of the rate of formation of deoxgenation products **6/8** was observed monitoring by tlc. The mixture of products contained only small amounts of **7/9** but the overall yields decreased. This may be caused by decomposition of educts, due to the prolonged reaction times necessary. Only small yields of **6b** and **7b/9b** could be detected when **4b/5b** was treated with **10b**, whereas **4d/5d** gave pure deoxygenation product **6d** in 64% yield under the same conditions. No reaction was observed when **4d/5d** was used with the same reagent in dichloromethane. The addition of 20% acetic acid to the solution of **4/5** in dimethyl formamide caused a significant improvement in the formation of deoxygenation products. The yields of **6a/8a** raised to 46%, for **6b** from 11% to 80 % and for **6g/8g** from 25% to 52%. In all cases only small amounts of **7/9** could be detected.

No deoxygenated compound could be obtained from the reaction of the highly sensitive diol **4e** with **10b**, but **10c** gave the deoxygenation product **6e** with a yield of 35%. No reaction at all could be observed in the reaction of **10d** with **4/5**.

From DMF destillates of the reaction mixtures a crystalline solid deposited, which produced a mass spectrometric molecular ion of 125 amu or 153 amu, respectively, depending on whether **10b** or **10c** had been used for deoxygenation. However, analytically pure samples of the corresponding sulfonic acids R_2NSO_3H (R = CH_3; R = C_2H_5) could not be obtained.

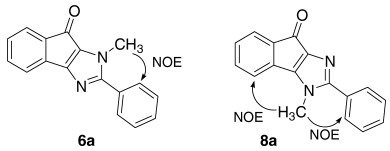
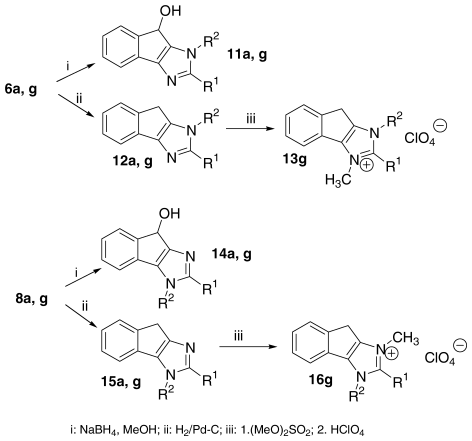


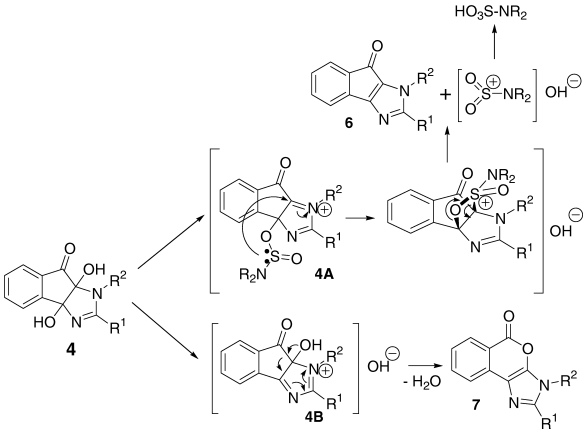
Fig. 2. Intramolecular NOE-enhancement of regioisomers **6a** and **8a**.

The deoxygenation of the mixtures of **4a/5a** and **4g/5g** respectively gave mixtures of the regioisomers **6a/8a** and **6g/8g**. Distinction of the regioisomers **6a** and **8a** was established by ^{1}H NMR spectroscopy. After assignment of protons had been accomplished by H,H correlation, the structures of **6a** and **8a** were confirmed by measuring homonuclear NOE difference spectra (Fig. 2). Upon irradiation of the methyl-H resonance of **8a** a marked enhancement of the 4-H multiplet and of the *ortho*-protons of the phenyl substituent in 2-position was observed. Irradiation of the methyl-H resonance of **6a** only caused enhancement of the latter protons but not of the 4-H multiplet.

Additionally, reduction experiments were done with compounds **6a,g** and **8a,g** for further characterisation of the regioisomers. The reduction with sodium borohydride afforded the hydroxy compounds **11a,g** and**14a,g**, respectively. Catalytic hydrogenation yielded **12a,g** or **15a,g** which were subsequently quaternized by methylation with dimethyl sulfate. The treatment of the sulfates with 70% perchloric acid gave



Scheme 3. Reduction experiments of regioisomers **6a**, **8a** and **6g**, **8g**.



Scheme 4. Proposed mechanism of deoxygenation products formation **6**, **8** and transformation products formation **7**, **9**.

the quaternary perchlorates **13g** and **16g**, respectively (Scheme 3).

Discussion

The formation of regioisomeric indenoimidazoles **6** and **8** from the diols **4** and **5** requires the 1,2-elimination of hydroxy groups which then results in an olefinic bond. Examples of this type of deoxygenation have been published but to the best of our knowledge never by reaction of *vic*-diols with sulfurous diamides. In the formation of **6** we assume that a cyclization to β-sultins could be accomplished by alcoholysis of *N,N,N',N'*-tetraalkylsulfurous diamides and the intramolecular nucleophilic addition of sulfur to the intermediate iminium compound **4A** (Scheme 4) generated by dissociation of the second *gem*-hydroxyamine functionality [12]. The fragmentation of the tricyclic intermediate results in the formation of **6**. The addition of acetic acid to the reaction may increase the formation of **4A** and probably enhances the reactivity by intermediate formation of a mixed amidosulfurous acid anhydride [13].

The process and our results may have some similarities to the olefin forming 1,2-elimination of β-hydroxy sulfinamides reported by Corey and Durst. They argued for a 1,2-cycloelimination pathway, which required hydroxy- and sulfinic acid amide functionalities standing *cis* to one another and the intermediate formation of β-sultins which gave olefins by decomposition [14]. The easy fragmentation of β-sultins at ambient temperature was already reported elsewhere [15].

The formation of the isochromeno-imidazoles which is favored in the reaction of thionyl chloride can be explained by dissociation of the *gem*-hydroxy group and formation of iminium compound **4B** with α-hydroxy ketone functionalities. Intermediate **4B** undergoes a rearrangement to form isochromeno-imidazoles **7**. Similar transformations of α-hydroxy-indanones have been published [16].

In conclusion, we found a facile and efficient method for the synthesis of indeno[1,2-*d*]imidazoles and indeno[2,1-*d*]imidazoles *via* 1,2-bis-deoxygenation of the respective *vic*-diols **4** and **5**. The applicability of this previously unreported reaction to further *vic*-diols with hemi-N,O-ketal functionalities will be studied.

Experimental Section

General Information: Melting points: Büchi melting point apparatus by Dr. Tottoli; not corrected. IR spectra: Perkin Elmer 177 and FT-IR 1600, using KBr discs. ^{1}H NMR spectra and ^{13}C NMR spectra: Varian FT 80 (80 MHz/20 MHz), Bruker AC 200F (200 MHz/50 MHz) and Varian VXR 300 (300 MHz/75 MHz) in the designated solvents with TMS as internal standard, using the δ (ppm) scale; signals labeled by * exchanged by addition of D_2O. EI mass-spectra: Finnigan 4200 quadrupole mass spectrometer, equipped with a MASPEC datasystem; 70 eV ionizing potential. Microanalyses: Perkin Elmer Elemental Analyzer 2400. HPLC-analyses: Hewlett-Packard 1084B, equipped with a Waters PAD-Detector 990. Catalytic hydrogenation: Low-pressure apparatus "Roche-Kühner". Solvents were purified by standard methods and dried over molecular sieves or sodium. Thionyl chloride was purified by the procedure of Martin and Fieser [17]. Bis-(1-imidazolyl)sulfoxide **10a** [18a], *N,N,N',N'*-tetramethylsulfurous diamide **10b**, *N,N,N',N'*-tetraethylsulfurous diamide **10c** [18b] and *N,N,N',N'*-

tetraisopropylsulfurous diamide **10d** [18c] were prepared according to the literature.

General Procedures

*A) Reaction with thionyl chloride/pyridine (**10**)*

vic-Dihydroxyindenoimidazoles **4/5** (0.01 mol) and dry pyridine (0.1 mol), dissolved in 100 ml of $CHCl_3$, were placed in a round-bottom flask. Nitrogen was passed through the solution. To the stirred and cooled solution thionyl chloride (0.05 mol in 20 ml of $CHCl_3$) was added, so that the temperature did not exceed 30 °C. After stirring for several hours at 20 °C, water (30 ml) was added under cooling and vigorous stirring. The organic layer was separated and the solvent removed *in vacuo*. The residue was purified by column chromatography on silica ($CHCl_3$).

B) Deoxygenation with bis(1-imidazolyl)sulfoxide **10a**

The diols **4/5** (0.01 mol) were dissolved in 30 ml of an appropriate solvent (DMF or tetramethylurea) and a solution of **10a** in 80 ml of THF was added by suction. Nitrogen was passed through the solution and stirring was continued for several hours. Then the solvent was removed *in vacuo*, 150 ml of water were added to the residue and the solution was extracted with $CHCl_3$. After removing the solvent from organic extracts, the residue was purified by column chromatography on silica.

C) Deoxygenation with N,N,N',N'-tetraalkylsulfurous diamides **10b**, **10c**

The diols **4/5** (0.01 mol) were dissolved in 30 ml of DMF or tetramethylurea and **10b** or **10c** (0.05 mol) in 20 ml of the same solvent was added. After stirring at 20 °C for 48 h 300 ml of water were added and the solution was extracted with $CHCl_3$. The reaction products were separated by column chromatography on silica ($CHCl_3$).

D) Deoxygenation in DMF-acetic acid

According to general procedure C, but 5 ml of acetic acid were added just before addition of **10b** or **10c**.

*1-Methyl-2-phenyl-1H-indeno[1,2-d]imidazol-8-one (**6a**)*

M. p. 126 – 7 °C (MeOH). – IR (KBr): $\tilde{\nu} = 1704$ (C=O), 1613, 1492, 1467, 1405, 1161 cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.83$ (s, 3H, CH_3), 7.10 – 7.13 (m, 1H, 6-H), 7.24 – 7.27 (m, 2H, 4-H, 5-H), 7.34 – 7.37 (m, 1H, 7-H), 7.48 – 7.52 (m, 3H, 3'-H, 4'-H, 5'-H), 7.8 – 8.1 (m, 2H, 2'-H, 6'-H). – $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta =$ 33.6 (CH_3), 118.4, 123.5, 128.4, 128.7, 128.8, 128.9, 130.0, 132.0, 133.3, 136.8, 138.5, 156.7, 163.8, 180.2 (C=O). – MS (EI, 70 eV): *m/z* (%) = 260 (17) [M^+], 177 (30), 159 (100). – $C_{17}H_{12}N_2O$ (260.30): calcd. C 78.44, H 4.65, N 10.76; found C 78.34, H 4.80, N 10.43.

*3-Methyl-2-phenyl-3H-indeno[2,1-d]imidazol-8-one (**8a**)*

Following general procedure A, a mixture of **4a**/**5a** (2.94 g, 0.01 mol) was treated with **10**. After 12 h at 20 °C $CHCl_3$ (100 ml) was added and the solution was extracted with 5×20 ml portions of aeqeous 5% HCl solution. The organic layers were washed with water, dried over sodium sulfate and the solvent removed *in vacuo*. The residue was purified by flash chromatography on silica, elution with $CHCl_3$/MeOH (98 : 2; v/v), to yield 380 mg (14.6%) of **6a**. The HCl-extracts were unified, washed with $CHCl_3$, and basified by adding aqueous 10% sodium carbonate. Extraction of the aqueous solution with trichloromethane gave organic extracts which were evaporated. The residue was purified by flash chromatography on silica, elution with $CHCl_3$/MeOH (98 : 2; v/v) to yield 165 mg (6.5%) of **8a**. M. p. 195 °C (MeOH). – IR (KBr): $\tilde{\nu} = 1710$ (C=O), 1612, 1529, 1519 cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.80$ (s, 3H, CH_3), 6.93 – 6.96 (m, 1H, 4-H), 7.05 – 7.10 (m, 1H, 6-H), 7.16 – 7.21 (m, 1H, 5-H), 7.28 – 7.31 (m, 1H, 7-H), 7.42 – 7.45 (m, 3H, 3'-H, 4'-H, 5'-H), 7.60 – 7.64 (m, 2H, 2'-H, 6'-H). – ^{13}C $\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta =$ 34.0 (CH_3), 116.9, 123.7, 128.6, 128.8, 129.1, 129.4, 129.6, 132.8, 133.0, 137.9, 141.2, 154.4 154.5, 183.8 (C=O). – MS (EI, 70 eV): *m/z* (%) = 260 (1) [M^+], 149 (2), 135 (29), 134 (32), 105 (100). – $C_{17}H_{12}N_2O$ (260.30): calcd. C 78.44, H 4.65, N 10.76; found C 78.16, H 4.55, N 10.78.

*1-Cyclohexyl-2-phenyl-1H-indeno[1,2-d]imidazol-8-one (**6b**)*

M. p. 169 – 70 °C (MeOH/H_2O). – IR (KBr): $\tilde{\nu} = 1697$ (C=O), 1616, 1603 cm^{-1}. – ^1H NMR (80 MHz, $CDCl_3$): $\delta =$ 1.3 – 2.4 (m, 10H, cyclohexyl-H), 4.1 (m, 1H, NC*H*$(CH_2)_2$), 6.95 – 7.7 (m, 9H, aromat. H). – ^{13}C NMR (20 MHz, $CDCl_3$): $\delta = 24.6$, 25.5, 32.4 (5 CH_2), 57.0 (NCH), 118.1, 123.5, 128.4, 128.9, 129.0, 130.0, 130.4, 135.2, 137.0, 138.3, 156.3, 165.3, 179.3 (C=O). – MS (EI, 70 eV): *m/z* (%) = 328 (18) [M^+], 246 (100), 218 (8), 190 (9), 143 (6), 130 (10), 115 (43), 114 (33), 89 (11), 88 (20), 77 (10), 41 (61). – $C_{22}H_{12}N_2O$ (328.41): calcd. C 80.46, H 6.14, N 8.53; found C 80.45, H 6.13, N 8.48.

*1-Benzyl-2-phenyl-1H-indeno[1,2-d]imidazol-8-one (**6c**)*

M. p. 135 – 6 °C (MeOH). - IR (KBr): $\tilde{\nu} = 1690$ (C=O), 1608, 1485, 1446, 1402, 1275, 1245 cm^{-1}. – ^1H NMR (80 MHz, [D_6]-DMSO): $\delta = 5.31$ (s, 2H, CH_2), 7.0 – 7.7 (m, 14H; aromat. H). – $^{13}C\{1H\}$ NMR (20 MHz, [D_6]-DMSO): $\delta = 21.6$ (CH_2), 118.4, 123.6, 127.0, 127.7, 128.3, 128.5, 129.0, 129.2, 130.2, 133.3, 135.8, 136.9, 138.4, 157.1, 164.4, 179.9 (C=O). – MS (EI, 70 eV): *m/z* (%) = 336 (10) [M^+], 245 (3), 114 (14), 91 (100), 98 (4), 88 (4), 65 (13). –

$C_{23}H_{16}N_2O$ (336.39): calcd. C 82.12, H 4.79, N 8.33; found C 82.02, H 5.01, N 8.39.

*1,2-Diphenyl-1H-indeno[1,2-d]imidazol-8-one (**6d**)*

M. p. 211 – 2 °C (MeOH). – IR (KBr): $\tilde{\nu} = 1704$, 1700 sh (C=O), 1614, 1595 cm^{-1}. – ^1H NMR (80 MHz, $CDCl_3$): $\delta = 7.0 - 7.55$ (m, 14H, aromat. H). – ^{13}C $\{^1H\}$ NMR (20 MHz, $CDCl_3$): $\delta = 118.8$, 123.9, 125.7, 126.6, 128.7, 128.8, 129.0, 129.2, 129.7, 130.2, 131.4, 133.7, 135.5, 136.1, 138.1, 155.7, 164.3, 179.5 (C=O). – MS (EI, 70 eV): *m/z* (%) = 322 (54) [M^+], 321 (20), 294 (6), 219 (11), 190 (49), 164 (12), 114 (26), 88 (36), 77 (100), 76 (11), 51 (56). – $C_{22}H_{14}N_2O \times HClO_4$ (422.82): calcd. C 62.49, H 3.58, N 6.63; found C 62.64, H 3.61, N 6.52.

*2,3,4a,9a-Tetrahydro-4a,9a-dihydroxy-1H-indeno[1,2-d]-pyrrolo[1',2'-a]imidazol-9-one (**4e**); 2,3,4a,9b-tetrahydro-4a,9b-dihydroxy-1H-indeno[2,1-d]pyrrolo[1',2'-a]imid-azol-5-one (**5e**)*

Equimolar amounts of **1** and 2-iminopyrrolidine hydrochloride (**3g**) were suspended in methanol and stirred several days at ambient temperature. The solid was separated and washed with $CHCl_3$. A mixture of regioisomeric hydrochlorides was obtained in 95% yield. M. p. 164 – 6 °C – IR (KBr): $\tilde{\nu} = 3375$ (OH), 3190, 3020, 1740 (C=O), 1618, 1605, 1588, 1575, 1420, 1360, 1207, 1148 cm^{-1}. – ^1H NMR (80 MHz, [D_6]-DMSO): $\delta = 2.0 - 2.6$ (m, 2H, CH_2(CH_2)$_2$), 2.6 – 3.0 (m, 2H, CCH_2 CH_2), 3.2 – 3.9 (m, 2H, NCH_2), 7.2 – 8.0 (m, 4H, aromat. H), 11 – 13* (broad, 3H). – ^{13}C $\{^1H\}$ NMR (20 MHz, [D_6]-DMSO): $\delta = 20.2$, 22.6, 22.9, 23.8, 24.3 (all CH_2), 89.2, 90.7, 96.9, 98.0 (all COH), 124.3, 124,6, 125.6, 131.4, 131.6, 133.1, 133.4, 137.7, 146.8, 148.7, 170.4, 170.9, 171.3, 192.1, 193.7 (2 C=O). – $C_{13}H_{12}N_2O_3 \times HCl$ (280.71): calcd. C 55.62, H 4.67, N 9.98; found C 55.52, H 4.62, N 9.83.

*2,3-Dihydro-1H-indeno[1,2-d]pyrrolo[1',2'-a]imidazol-9-one (**6e**)*

To a suspension of the hydrochlorides of **4e, 5e** (1.40 g, 0.005 mol) in DMF (20 ml), acetic acid (5 ml) and **10c** (3.84 g, 0.02 mol) were added. The mixture was stirred for 12 h at ambient temperature and then evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (100 ml) and washed with water (3 × 50 ml). The organic layers were unified, dried and concentrated. The residue was subjected to column chromatography (silica, $CHCl_3$-MeOH, 99 : 1, v/v). M. p. 197 – 8 °C (EtOAc) – IR (KBr): $\tilde{\nu} = 1697$ (C=O), 1608, 1503, 1404, 1384 cm^{-1}. – ^1H NMR (200.13 MHz, $CDCl_3$): $\delta = 2.6 - 2.85$ (m, 2H, 2-H), 2.88 – 3.0 (m (t), 2H, 3-H), 4.0 – 4.15 (m (t), 2H, 1-H), 7.0 – 7.5 (m, 4H, aromat. H). – $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): $\delta = 23.4$, 25.7, 44.7, 117.9, 123.5, 127.3, 128.3, 133.0, 137.5, 137.7, 164.5, 170.3, 178.9. MS (EI, 70 eV): *m/z* (%) = 210 (100) [M^+], 209 (29), 182 (14), 181 (10), 154 (11), 149 (8), 130 (13), 127 (11), 115 (11), 114 (14), 57 (11). – $C_{13}H_{10}N_2O$ (210.23): calcd. C 74.27, H 4.79, N 13.32; found C 74.11, H 4.90, N 13.10.

*6,7,8,9-Tetrahydro-indeno[1',2':4,5]imidazo[1,2-a]pyridin-11-one (**6f**)*

M. p. 124 – 5 °C (MeOH). – IR (KBr): $\tilde{\nu} = 2967$, 1698 (C=O), 1674, 1611, 1499, 1481, 1409, 1392, 1296, 1142 cm^{-1}. – ^1H NMR (200.13 MHz, $CDCl_3$): $\delta = 1.9 - 2.1$ (m; 4H; 7-H, 8-H), 2.85 – 3.05 (m, 2H; 6-H), 4.0 – 4.15 (m, 2H, 9-H), 7.0 – 7.4 (m, 4H; aromat. H). – $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): $\delta = 20.0$, 22.2, 25.2, 44.5, 118.0, 123.4, 128.3, 129.4, 133.0, 137.0, 138.5, 155.3, 164.6, 179.4. – MS (EI, 70 eV): *m/z* (%) = 224 (100) [M^+], 196 (32), 195 (29), 169 (8), 168 (8), 130 (29), 129 (17), 115 (17), 114 (33), 102 (18), 101 (10), 88 (23). – $C_{14}H_{12}N_2O$ (224.26): calcd. C 74.98, H 5.39, N 12.49; found C 74.78, H 5.28, N 12.32.

*7,8,9,10-Tetrahydro-6H-indeno[1',2':4,5]imidazo[1,2-a] azepin-12-one (**6g**)*

From **4g**/**5g** by procedure A, work-up as described for **6a**/**8a**. – M. p. 149 – 50 °C (MeOH). – IR (KBr): $\tilde{\nu} = 2930$, 1718 sh, 1699 (C=O), 1610, 1477, 1411, 1337, 1306 cm^{-1}. – ^1H NMR (200.13 MHz, $CDCl_3$): $\delta = 1.8$ (m, broad, 6H, 7-H, 8-H, 9-H), 2.9 (m (broad), 2H, 6-H), 4.25 (m (broad), 2H, 10-H), 6.8 – 7.4 (m, 4H, aromat. H). – $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): $\delta = 25.1$, 28.3, 29.9, 30.7, 46,7, 117.8, 123.4, 128.0, 133.0, 137.1, 138.4, 161.2, 162.9, 180.0. – MS (EI, 70 eV): *m/z* (%) = 238 (100) (M^+), 210 (18), 209 (39), 197 (27), 184 (5), 183 (10), 812 (7), 181 (6), 168 (6), 130 (16), 115 (14), 114 (19), 102 (11), 88 (14). – $C_{15}H_{14}N_2O$ (238.29): calcd. C 75.61, H 5.92, N 11.76; found C 75.66, H 5.93, N 11.68.

*7,8,9,10-Tetraahydro-6H-indeno[2',1':4,5]imidazo[1,2-a]-azepin-12-one (**8g**)*

From **4g**/**5g** by procedure A, work-up as described for **6a**/**8a**. – M. p. 165 – 6 °C (MeOH). – IR (KBr): $\tilde{\nu} = 2928$, 1704 (C=O), 1608, 1533, 1508, 1448 cm^{-1}. – ^1H NMR (80 MHz, $CDCl_3$): $\delta = 1.85$ (m (broad), 6H, 7-H, 8-H, 9-H), 2.85 (m (broad), 2H, 6-H), 4.0 (m (broad), 2H, 10-H), 6,7 – 7.5 (m, 4, aromat. H). – $^{13}C\{^1H\}$ NMR (20 MHz, $CDCl_3$): $\delta = 25.5$, 28.7, 29.8, 30,7, 47.7, 116.4, 123.6, 128.5, 132.4, 133.4, 138.1, 139.6, 153.4, 158.2, 183.4. – MS: *m/z* (%) = 238 (100) [M^+], 237 (51), 210 (24), 209 (39), 197 (8), 195 (10), 183 (10), 182 (29), 181 (29), 154 (12), 130 (41), 129 (23), 128 (13), 127 (17), 115 (23), 114 (25), 103 (20), 102 (39), 101 (11), 89 (12), 88 (18). – $C_{15}H_{14}N_2O$ (238.29):

calcd. C 75.61, H 5.92, N 11.76; found C 75.44, H 5.97, N 11.56.

*3-Methyl-2-phenyl-3H-isochromeno[4,3-d]imidazol-5-one (**7a**)*

M. p. 185 – 6 °C (MeOH). – IR (KBr): $\tilde{\nu}$ = 1746 (C=O), 1710, 1626, 1557, 1531, 1514, 1469, 1251, 1003 cm^{-1}. – ^1H NMR (200,13 MHz, $CDCl_3$): δ = 3.79 (s, 3H, CH_3), 7.3 – 7.9 (m, 7, aromat. H), 8.06 (d, J = 7.6 Hz, 1H, 8-H), 8.29 (d, J = 7.9 Hz, 1H, 6-H). – $^{13}C\{^1H\}$ NMR (50.32 MHz, [D_6]-DMSO): δ = 30.8, 116.2, 117.6, 120.2, 126.0, 128.5, 128.8, 129.3, 129.5, 131.4, 134.7, 135.6, 142.5, 143.8, 160.8. – MS (EI, 70 eV): *m/z* (%) = 276 (67) [M^+], 233 (30), 138 (14), 130 (10), 118 (100), 102 (17), 91 (11), 77 (65), 51 (27). – $C_{17}H_{12}N_2O_2$ (276.31): calcd. C 73.90, H 4.38, N 10.14; found C 73.78, H 4.45, N 10.09.

*1-Methyl-2-phenyl-1H-isochromeno[3,4-d]imidazol-5-one (**9a**)*

M. p. 233 – 4 °C (MeOH). – IR (KBr): $\tilde{\nu}$ = 1712 (C=O), 1614, 1518, 1470, 1450, 1421, 1366, 1258 cm^{-1}. – ^1H NMR (80 MHz, $CDCl_3$): δ = 4.11 (s, 3H, CH_3), 7.4 – 7.9 (m, 8H, aromat. H), 8.42 (d, J = 7.8 Hz, 1H, 6-H). MS (EI, 70 eV): *m/z* (%) = 276 (22) [M^+], 145 (19), 130 (8), 117 (100), 102 (12). – $C_{17}H_{12}N_2O_2$ (276.30): calcd. C 73.90, H 4.38, N 10.14; found C 73.95, H 4.44, N 9.91.

*3-Cyclohexyl-2-phenyl-3H-isochromeno[4,3-d]imidazol-5-one (**7b**)*

M. p. 206 °C. (EtOH). – IR (KBr): $\tilde{\nu}$ = 2934, 1737 (C=O), 1627, 1501, 1250, 1000, 990 cm^{-1}. – ^1H NMR (200.13 MHz, $CDCl_3$): δ = 1.1 – 2.5 (m, 10H, 5 cyclohexyl-CH_2), 4.19 (tt, $J_{ax,ax}$ = 12.2 Hz, $J_{ax,eq}$ = 3.7 Hz, 1H, CH-cyclohexyl), 7.41 (m, $J_{7-H,6-H} = J_{7-H,8-H}$ = 7.6 Hz, $J_{7-H,9-H}$ = 1.0 Hz, 7-H), 7.45 – 7.65 (m, 5H, H-phenyl), 7.78 (m, $J_{8-H,7-H} = J_{8-H,9-H}$ = 7.8 Hz, 1H, 8-H), 8.08 (d, J = 7.7 Hz, 1H, 9-H), 8.31 (d, J = 7.7 Hz, 1H, 6-H). – MS (EI, 70 eV): *m/z* (%) = 344 (17) [M^+], 262 (100), 234 (5), 207 (9), 159 (6), 130 (22), 104 (26), 103 (38), 102 (14), 55 (20). – $C_{22}H_{20}N_2O_2$ (344.40): calcd. C 76.72, H 5.85, N 8.14; found C 76.78, H 6.02 N 8.04.

*3-Benzyl-2-phenyl-3H-isochromeno[4,3-d]imidazol-5-one (**7c**)*

M. p. 164 °C (EtOH). - IR (KBr): $\tilde{\nu}$ = 1736 (C=O), 1628, 1506, 998 cm^{-1}. – ^1H NMR (200.13 MHz, $CDCl_3$): δ = 5.33 (s, 2H, CH_2), 7.0 – 7.65 (m, 11H; aromat. H), 7.78 (m (t), $J_{8-H,7-H} = J_{8-H,9-H}$ = 7.8 Hz, 1H, 8-H), 8.09 (d, J = 7.8 Hz; 1H, 9-H), 8.29 (d, J = 7.9 Hz, 1H, 6-H). – $^{13}C\{^1H\}$ NMR (50.23 MHz, $CDCl_3$): δ = 47.3, 116.3, 117.8, 120.2, 126.1, 126.5, 128.1, 128.8, 129.0, 129.3, 129.5, 131.4, 134.6 135.4, 135.6, 142.3, 144.1, 160.5. – MS (EI, 70 eV): *m/z* (%) = 352 (40) [M^+], 261 (18), 130 (64), 102 (71), 91 (100). – $C_{23}H_{16}N_2O_2$ (352.38): calcd. C 78.39, H 4.58, N 7.95; found C 78.37, H 4.54 N 7.84.

*2,3-Diphenyl-3H-isochromeno[4,3-d]imidazol-5-one (**7d**)*

M. p. 234 °C (EtOH). – IR (KBr): $\tilde{\nu}$ = 1738 sh; 1728 (C=O), 1624, 1595, 1500, 992 cm^{-1}. – ^1H NMR (80 MHz, $CDCl_3$): δ = 7.15 – 7.6 (m, 11H, aromat. H), 7.81 (m, $J_{8-H,7-H} = J_{8-H,9-H}$ = 8.0 Hz, $J_{8-H,6-H}$ = 1.1 Hz, 1H, 8-H), 8.15 (d, J = 8.3 Hz, 1H, 9-H), 8.30 (dd, J = 8.1, 1.1 Hz, 1H, 6-H). – MS (EI, 70 eV): *m/z* (%) = 338 (38) [M^+], 207 (4), 180 (100), 130 (7), 102 (12), 77 (97). – $C_{22}H_{14}N_2O_2$ (338.37): calcd. C 78.09, H 4.17, N 8.28; found C 78.10, H 4.08, N 8.26.

*8,9,10,11-Tetrahydroisochromeno[4',3':4,5]imidazo[1,2-a]-pyridin-5-one (**7f**)*

Perchlorate: M. p. 254 – 5 °C (EtOH). - IR (KBr): $\tilde{\nu}$ = 2948, 1857, 1628, 1556, 1530 cm^{-1}. – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.85 – 2.2 (m, 4H, 9-H,10-H), 2.9 – 3.05 (m, 2H, 11-H), 3.95 – 4.2 (m, 2H, 8-H), 7.1 – 8.35 (m, 4H, aromat. H). – $C_{14}H_{12}N_2O_2 \times HClO_4$ (340,71): cald. C 49.35, H 3.84, N 8.22; found C 49.45, H 3.78, N 8.22.

*9,10,11,12-Tetrahydro-8H-isochromeno[4',3':4,5]imidazo-[1,2-a]azepin-5-one (**7g**)*

M. p. 184 – 5 °C (EtOH). – IR (KBr): $\tilde{\nu}$ = 1758 sh, 1748 (C=O), 1625 cm^{-1}. – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.9 (m (broad), 6H, 9-H, 10-H, 11-H), 3.0 (m (broad), 2H, 12-H), 4.1 (m (broad), 2H; 8-H), 7.3 – 7.45 (m, 1H, aromat. H), 7.65 – 7.8 (m, 1H, aromat. H), 7.92 (m (d), 1H, aromat. H), 8.26 (m (d), 1H, aromat. H). – $^{13}C\{^1H\}$ NMR (20 MHz, $CDCl_3$): δ = 25.9, 28.6, 30.2, 30,9, 43.6, 114.0, 117.3, 119.9, 125.5, 131.4, 135.0, 135.5, 140.9, 147.4, 160.9. – $C_{15}H_{14}N_2O_2$ (254.29): calcd. C 70.85, H 5.55, N 11.01; found C 70.53, H 5.53, N 10.96.

*9,10,11,12-Tetrahydro-8H-isochromeno[3',4':4,5]imidazo-[1,2-a]azepin-5-one (**9g**)*

M. p. 221 – 2 °C ($CHCl_3$/Et_2O). – IR (KBr): $\tilde{\nu}$ = 2950, 1722 (C=O), 1710, 1615, 1494, 1470, 1383, 1352, 1261 cm^{-1}. – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.95 (m, broad, 6H; 9-H, 10-H, 11-H), 2.95 (m, broad, 2H, 12-H), 4.45 (m, broad, 2H, 8-H), 7.28 (m, 1H, aromat. H), 7.64 (m, 2H, aromat. H), 8.29 (m (t), 1, aromat. H). – $^{13}C\{^1H\}$ NMR (20 MHz, [D_6]-DMSO): δ = 25.1, 28.0, 29.3, 30.4, 47.3, 107.7, 117.6, 118.6, 125.3, 130.6, 132.4, 134.9, 149.7, 151.3, 161.8. – $C_{15}H_{14}N_2O_2$ (254.29): calcd. C 70.85, H 5.55, N 11.01; found C 71.03, H 5.70, N 11.01.

*1,8-Dihydro-8-hydroxy-1-methyl-2-phenylindeno[1,2-d]-imidazole (***11a***)*

6a (300 mg, 1.2 mmol), dissolved in 20 ml of methanol, was treated with sodium borohydride (1.00 g, 26.4 mmol). After 2 h, water (100 ml) was added and the aqueous solution was extracted with CH_2Cl_2. The extract was separated by column chromatography on silica. Yield: 162 mg (67%). M. p. 219 – 20 °C (EtOH). – IR (KBr): $\tilde{\nu} = 3125, 3060, 1617, 1604, 1495, 1470, 1288, 1278$ cm^{-1}. – ^{1}H NMR (80 MHz, [D$_6$]-DMSO): $\delta = 3.84$ (s, 3H, CH_3), 5.37, 5.47 (B-part of AB-type subspectrum, 1H, 8-H), 5.83, 5.93 (A-part of AB-type subspectrum, 1H*, OH), 7.0 – 7.8 (m, 9H, aromat. H). – MS (EI, 70 eV): *m/z* (%) = 262 (52) [M$^+$], 245 (12), 159 (65), 130 (49), 118 (100). – $C_{17}H_{14}N_2O$ (262.31): calcd. C 77.84, H 5.38, N 10.68; found C 77.94, H 5.58, N 10.68.

*6,7,8,9,10,12-Hexahydro-12-hydroxyindeno[1',2':4,5]imidazo[1,2-a]azepine (***11g***)*

6g (1.00 g, 4.2 mmol) was treated with lithium aluminium hydride (500 mg, 13.2 mmol) in dry THF (50 ml). After 2 h, water was added under cooling and the solution was extracted with Et_2O. The solvent was removed *in vacuo* to yield a white solid which was crystallized. Yield: 560 mg (55%). M. p. 235 – 6 °C (toluene). – IR (KBr): $\tilde{\nu} = 3100, 2940, 1610, 1498, 1470, 1440, 1394, 1295$ cm^{-1}. – ^{1}H NMR (80 MHz, [D$_6$]-DMSO): $\delta = 1.4 - 1.9$ (m (broad), 6H, 7-H, 8-H, 9-H) 2.75 – 2.95 (m (broad), 2H, 6-H), 4.0 – 4.2 (m (broad), 2H, 10-H), 5.21, 5.30 (B-part of AB-type subspectrum, after addition of D_2O: s, 12-H), 5.68*, 5.77* (A-part of AB-type subspectrum; 1H, OH), 6.9 – 7.45 (m, 4H, aromat. H). – ^{13}C{^{1}H} NMR (20 MHz, [D$_6$]-DMSO): $\delta = 25.6, 28.3, 29.2, 30.1, 45.9, 66.2, 116.1, 123.8, 124.6, 127.9, 136.7, 140.6, 148.8, 154.4$. – MS (EI, 70 eV): *m/z* (%) = 240 (100) [M$^+$], 239 (35), 238 (40), 223 (23), 211 (12), 197 (14), 183 (12), 167 (11), 158 (24), 156 (11), 130 (13), 116 (15), 115 (15), 103 (11), 102 (14), 101 (11), 96 (25), 90 (11), 89 (48). – $C_{15}H_{16}N_2O$ (240.30): calcd. C 74.97, H 6.71, N 11.66; found C 75.10, H 6.73, N 11.46.

*3,8-Dihydro-8-hydroxy-3-methyl-2-phenylindeno[1,2-d]-imidazole (***14a***)*

8a (300 mg, 1.2 mmol) was hydrogenated as described for the syntheses of **11a**. Yield: 195 mg (62%). – M. p. 192 °C (EtOH/Et_2O). – IR (KBr): $\tilde{\nu} = 3505, 3320, 1638, 1595, 1575, 1483, 1440, 1178$ cm^{-1}. – ^{1}H NMR (80 MHz, [D$_6$]-DMSO): $\delta = 1.4 - 1.9$ (broad, 6H, 7-H, 8-H, 9-H), 2.75 – 2.95 (m (broad), 2H, 6-H), 5.21, 5.30 (B-part of AB-type subspectrum, after addition of D_2O: s, 1H, 12-H), 5.68*, 5.77* (A-part of AB-type subspectrum, 1H, OH), 6.9 – 7.45 (m, 4H, aromat. H). – ^{13}C {^{1}H} NMR (20 MHz, [D$_6$]-DMSO): $\delta = 25.6, 28.3, 29.2, 30.1, 45.9, 66.2, 116.1, 123.8, 124.6, 127.9, 136.7, 140.6, 148.8, 154.4$. – MS (EI, 70 eV): *m/z* (%) = 240 (100) [M$^+$], 239 (35), 238 (40), 223 (23), 211 (12), 197 (14), 183 (12), 167 (11), 158 (24), 156 (11), 130 (13), 116 (15), 115 (15), 103 (11), 102 (14), 101 (11), 96 (25), 90 (11), 89 (48). – $C_{17}H_{14}N_2O$ (262.31): calcd. C 77.84, H 5.38, N 10.68; found C 77.91, H 5.38, N 10.66.

*6,7,8,9,10,12-Hexahydro-12-hydroxyindeno[2',1':4,5]imidazo[1,2-a]azepine (***14g***)*

8g (300 mg, 1.2 mmol) was hydrogenated as described for the syntheses of **11g**. Yield: 188 mg (46%). M. p. 203 – 4 °C (toluene). – IR (KBr): $\tilde{\nu} = 3170, 2925, 1610, 1510, 1503$ sh, 1462, 1435, 1405, 1052 cm^{-1}. – ^{1}H NMR (80 MHz, [D$_6$]-DMSO): $\delta = 1.76$ (broad, 6H, 7-H, 8-H, 9-H), 2.85 (m, broad, 2H, 6-H), 4.25 (m, broad, 2H, 10-H), 4.93, 5.02 (B-part of AB-type subspectrum, after addition of D_2O: s, 1H, 12-H), 5.44*, 5.68* (A-part of AB-type subspectrum, 1H, OH), 6.9 – 7.45 (m, 4H, aromat. H). – ^{13}C {1H} NMR (20 MHz, [D$_6$]-DMSO): $\delta = 25.5, 28.5, 29.3, 30.1, 46.1, 67.2, 115.8, 124.2, 124.9, 127.8, 132.5, 134.7, 148.7, 154.5$. – MS (EI, 70 eV): *m/z* (%) = 240 (74) [M$^+$], 239 (20), 238 (14), 211 (28), 184 (14), 183 (32), 159 (13), 158 (38), 157 (14), 145 (17), 130 (13), 129 (10), 117 (10), 116 (16), 115 (15), 103 (14), 102 (18), 96 (100), 90 (10), 89 (29). – $C_{15}H_{16}N_2O \times HClO_4$ (340.76): calcd. C 52.87, H 5.03, N 8.22; found C 52.86, H 5.01, N 8.11.

*6,7,8,910,12-Hexahydroindeno[1',2':5,4]imidazo[1,2-a]-azepine (***12g***)*

A solution of **6g** (1.00 g, 4.2 mmol) in 50 ml of ethanol and 1 ml of conc. hydrochloric acid was hydrogenated over Pd/carbon. The hydrogen uptake ceased after 185 ml. After filtration of the catalyst, the solvent was removed *in vacuo* to yield a white solid which was suspended in dilute hydrochloric acid and extracted with dichloromethane. Evaporation of organic extracts gave a colourless solid, which was crystallized. An analytically pure sample was obtained by generation of the perchlorate. Yield: 677 mg, (72%). M. p. 154 °C ($CHCl_3$/Et_2O). – IR (KBr): $\tilde{\nu} = 2930, 1610, 1512, 1447, 1413, 1388$ cm^{-1}. – ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 1.85$ (broad, 6H, 7-H, 8-H, 9-H), 2.95 (m (broad), 2H, 6-H), 3.42 (s, 2H, 12-H), 3.90 (m (broad), 2H, 10-H), 7.0 – 7.6 (m, 4H, aromat. H). – ^{13}C{^{1}H} NMR (20 MHz, $CDCl_3$): $\delta = 26.0, 28.1, 28.9, 30.2, 31.0, 47.4, 117.3, 123.2, 125.1, 127.0, 138.1, 142.9, 144.2, 154.3$. – $C_{15}H_{16}N_2O \times HClO_4$, M. p. 210 °C, calcd. (324.76): C 55.48, H 5.28, N 8.63; found C 55.32, H 5.08, N 8.46.

*3,8-Dihydro-3-methyl-2-phenylindeno[1,2-d]imidazole (***15a***)*

10% Pd/carbon (0.30 g) was added to a solution of **8a** (200 mg, 0.77 mmol) in 100 ml of methanol. The solu-

tion was hydrogenated at atmospheric pressure. The reaction finished after a hydrogen uptake of 18 ml. After removal of the catalyst, the solvent was evaporated *in vacuo* and the residue was crytallized. An analytical sample was obtained by generation of the perchlorate. Yield: 138 mg (73%). M. p. 194 °C (CH_2Cl_2/Et_2O). – IR (KBr): $\tilde{\nu}$ = 3326, 3208, 3107, 3071, 2940, 1609, 1583, 1564, 1483 cm^{-1}. – ^1H NMR (80 MHz, CD_3CN): δ = 3.98 (s, 2H, 8-H), 4.08 (s, 3H, CH_3), 7.35 – 7.9 (m, 9H, aromat. H). Perchlorate: M. p. 238 – 9 °C (EtOH/Et_2O). – $C_{17}H_{14}N_2 \times HClO_4$ (346.77): calcd. C 58.88, H 4.36, N 8.08; found C 58.54, H 4.42, N 8.01.

*6,7,8,9,10,12-Hexahydroindeno[2',1':4,5]imidazo[1,2-a]-azepine (***15g***)*

A solution of **8g** (0.80 g, 3.4 mmol) in 80 ml of ethanol was hydrogenated on 10% Pd/carbon (0.50 g). Hydrogen uptake ceased after 155 ml. Filtration of the catalyst and removal of the solvent yielded an oily residue which was dissolved in CH_2Cl_2. The extraction with 3% hydrochloric acid, followed by basification of the aeqeuous extracts with aqueous ammonia gave an oil, which was separated. The purification by flash chromatography on alumina (activation III, elution with $CHCl_3$) gave **15g**. Yield: 548 mg (72%). M. p. 157 – 8 °C (cyclohexane). – IR (KBr): $\tilde{\nu}$ = 2910, 1607, 1513, 1450, 1445, 1434, 1402, 1358 cm^{-1}. – ^1H NMR (80 MHz, $CDCl_3$): δ = 1.87 (broad, 6H, 7-H, 8-H, 9-H), 2.98 (m (broad), 2H, 6-H), 3.47 (s, 2H, 12-H), 4.25 (m (broad), 2H, 10-H), 7.0 – 7.5 (m, 4H, aromat. H). – $^{13}C\{^1H\}$NMR (20 MHz, $CDCl_3$): δ = 25.9, 29.0, 30.2, 30.4, 31.1, 47.1, 115.4, 123.4, 125.8, 126.4, 134.3, 135.8, 145.1, 146.8, 154.8. – MS (EI, 70 eV): *m/z* (%) = 224 (100) [M^+], 195 (10), 183 (10), 168 (18), 156 (6), 142 (15). – $C_{15}H_{16}N_2O$ (224.31): calcd. C 80.32, H 7.19, N 12.49; found C 80.41, H 7.49, N 12.36.

*6,7,8,9,10,12-Hexahydro-11-methylindeno[1',2':4,5]imidazo[1,2-a]azepinium Perchlorate (***13g***)*

12g (400 mg, 1.8 mmol) was dissolved in dry toluene. After addition of dimethylsulfate (2 ml, 11.9 mmol) a white solid was formed which was isolated after 48 h (m. p. 105 – 6 °C) and dissolved in acetic acid. Addition of 70% perchloric acid gave a precipitate which was isolated by suction. Yield: 255 mg (42%). M. p. 215 °C (EtOH). – IR (KBr): $\tilde{\nu}$ = 2940, 1748, 1510, 1436, 1402, 1090 cm^{-1}. – ^1H NMR (80 MHz, [D_6]-DMSO): δ = 1.86 (broad, 6H, 7-H, 8-H, 9-H), 3.20 (m (broad), 2H, 6-H), 3.93 (s, 2H, 12-H), 4.08 (s, 3H, CH_3), 4.30 (broad, 2H, 10-H), 7.3 – 7.9 (m, 4H, aromat. H). – $^{13}C\{^1H\}$ NMR (20 MHz, [D_6]-DMSO): δ = 23.3, 23.8, 26.4, 28.8, 29.0, 33.7, 49.1, 118.4, 126.1, 127.3, 130.9, 134.7, 137.7, 143.0, 151.5. – $C_{16}H_{19}N_2^+$ ClO_4^- (338.79): calcd. C 56.72, H 5.65, N 8.27; found C 56.54, H 5.71, N 8.15.

*6,7,8,910,12-Hexahydro-5-methylindeno[2',1':4,5]imidazo-[1,2-a]azepinium Perchlorate (***16g***)*

Preparation from **15g** (200 mg, 0.9 mmol) as described for **13g**. Yield: 138 mg (46%). M. p. 239 – 40 °C (EtOH/Et_2O). – IR (KBr): $\tilde{\nu}$ = 2934, 1521, 1436, 1400 cm^{-1}. – ^1H NMR (80 MHz, [D_6]-DMSO): δ = 0.88 (broad, 6H, 7-H, 8-H, 9-H), 3.20 (m (broad), 2H, 10-H), 3.89 (s, 5, 12-H, CH_3), 4.60 (broad, 2H, 6-H), 7.3 – 7.95 (m, 4H, aromat. H). – $^{13}C\{^1H\}$ NMR (20 MHz, [D_6]-DMSO): δ = 23.2, 24.0, 26.5, 28.7, 29.0, 33.7, 48.7, 118.6, 126.2, 126.3, 127.2, 130.6, 134.7, 137.4, 143.0, 151.7. – $C_{16}H_{19}N_2$ $^+ClO_4^-$ (338.79): calcd. C 56.72, H 5.65, N 8.27; found C 56.73, H 5.49, N 8.25.

Crystal Structure Analysis of 6g×$HClO_4$ by X-Ray Diffraction

The solid-state structure of the $HClO_4$-adduct of **6g** was established by X-ray crystal structure analysis. The molecular structure is displayed in Fig. 1. Except atoms C8, C9, and C10 the cation is planar within 0.127(2) Å. The ions are linked together by a hydrogen bond N2-HN…O11 with distances N…O 2.869(4), N-H 0.80(3), H…O 2.10(3) Å and an angle N-H…O of 162(3)°.

Crystal data: $C_{15}H_{15}ClN_2O_5$, molecular mass: 338.7, monoclinic space group $P2_1/n$, a = 13.472(4), b = 6.356(2), c = 18.581(6) Å, β = 106.42(2)°, V = 1526.2(8) $Å^3$ (by refinement of 25 reflections, 27 < 2θ < 32°, λ(Mo-K_α) = 0.71073 Å), Z = 4, D_c = 1.474 mg mm^{-3}, D_m = 1.466 mg mm^{-3}, F(000) = 704; μ(Mo-K_α) = 0.28 mm^{-1}, approximate dimensions of crystal (yellow color) 0.7 × 0.3 × 0.2 mm.

Data collection: X-ray intensities were measured with monochromatized Mo-K_α-radiation on a Siemens/STOE diffractometer AED2, variable ω/θ-scan, scan range 1.17° (plus separation) in ω, scan speed 0.6 – 3.5° min^{-1}. 3098 intensities measured (3 < 2θ < 50°), indices *hkl* ranged from 0,0,−22 to 15, 7, 21. The final set of data contained 2428 symmetry-independent reflections (R_{int} = 0.016) of which 1808 were classified observed ($F_0 > 4\sigma_F$).

Structure solution and refinement: Direct methods [19] revealed all non-H atoms. Full matrix least-squares refinement [20] on F^2 using anisotropic displacement parameters (212 parameters) converged at $wR2$ = 0.136 for all data and $R1$ = 0.043 for the observed data. H atoms were included in a riding mode except the one at N2 which was refined freely. The residual electron density ranged from −0.25 to 0.57 e$Å^{-3}$, with the maximum in the vicinity of the Cl atom. However, a split model for the ClO_4^--ion did not improve the results. Preliminary results have been reported [10]. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre

CCDC-103288. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (U.K.) (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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