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Synthesis of Polychlorinated Unsaturated Cyclic Dicarboxylic Acid Imides

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Abstract—A procedure has been developed for the synthesis of 3,4,5,6-tetrachlorocyclohexa-3,5-diene-1,2- and 7,8,9,10-tetrachlorobicyclo[4.4.0]deca-7,9-diene-3,4-dicarboximides from the corresponding 3,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3- and 1,8,9,10,11,11-hexachlorotricyclo[6.2.1.0^{2,7}]undec-9-ene-4,5-dicarboxylic anhydrides and pyridine in dimethylformamide. Steric structure of the products has been studied.

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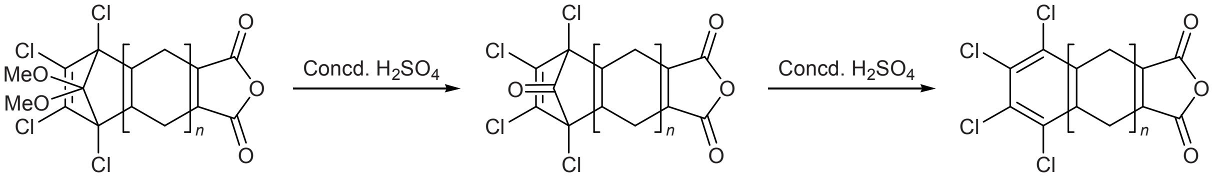
Chlorine-containing unsaturated cyclic carboxylic acid anhydrides **IIIa** and **IIIb** are promising monomers for the preparation of cage-like hinged polyimides that are characterized by enhanced fire and heat resistance [1, 2] and are available via Diels–Alder polycondensation of compounds **IIIa** and **IIIb** with various bismaleimides [3]. The synthesis of unsaturated cyclic anhydrides **IIIa** and **IIIb** was reported previously [4–7]. They were prepared by hydrolysis of the corresponding Diels–Alder adducts, 3,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-5-ene-2,3- [4] and 1,8,9,10-tetrachloro-11,11-dimethoxytricyclo[6.2.1.0^{2,7}]undec-9-ene-4,5-dicarboxylic anhydrides **Ia** and **Ib** with fixed steric structure, followed by thermolysis of intermediately isolated keto anhydrides **IIa** and **IIb** (Scheme 1).

According to the X-ray diffraction data, anhydride **Ia** has *endo* configuration. Among four possible stereoisomers, *endo*,*endo*, *endo*,*exo*, *exo*,*endo*, and *exo*,*exo*, compound **Ib** was found to exist as a single *endo*,*exo* isomer with a *boat* conformation of the cyclohexane ring [6, 7].

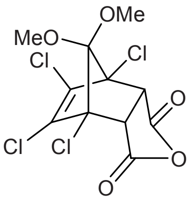
In continuation of our studies in this field, the present article describes a new procedure for the synthesis of anhydrides **IIIa** and **IIIb** and the corresponding dicarboximides **VIb**, **VIc**, **VIIb**, and **VIIc** from Diels–Alder adducts, 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3- and 1,8,9,10,11,11-hexa-

Scheme 1.

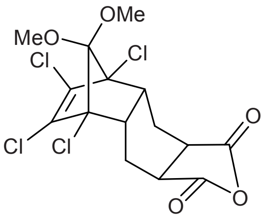


Ia, **Ib** **IIa**, **IIb** **IIIa**, **IIIb**

n = 0 (**a**), 1 (**b**).

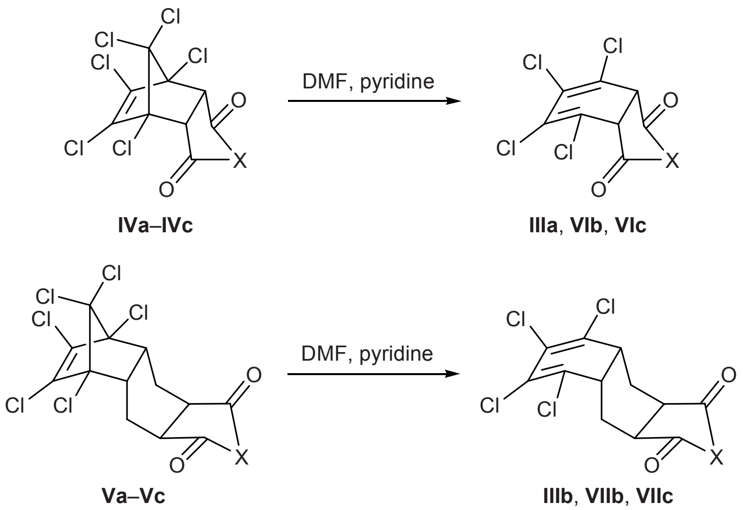


Ia



Ib

Scheme 2.



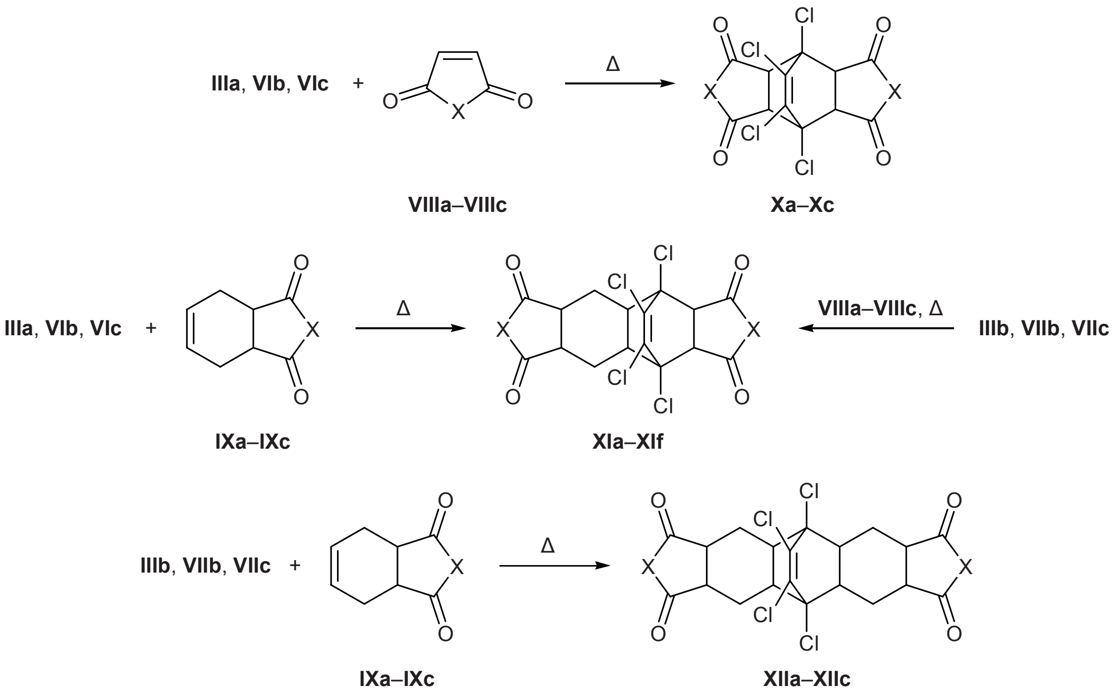
IIIa, **IIIb**, **IVa**, **Va**, X = O; **IVb**, **IVc**, **Vb**, **Vc**, **VIb**, **VIc**, **VIIb**, **VIIc**, X = NR; **IV**–**VII**, R = $H_2NCH_2CH_2$ (**b**), 4-(4-H_2N-3-$MeOC_6H_3CH_2$)-2-$MeOC_6H_4$ (**c**).

chlorotricyclo[6.2.1.$0^{2,7}$]undec-9-ene-4,5-dicarboxylic anhydrides and dicarboximides **IVa**–**IVc** and **Va**–**Vc**, by treatment with pyridine in dimethylformamide (Scheme 2). The presence of a primary amino group in molecules of initial imides **IVb**, **IVc**, **Vb**, and **Vc** did not affect their reaction with pyridine.

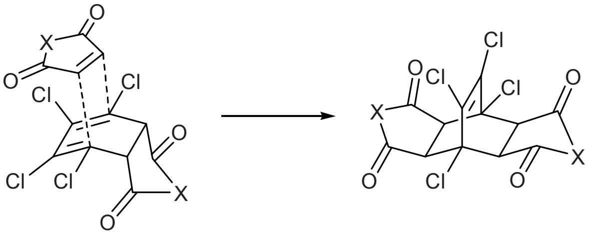
The structure of compounds **IIIa**, **IIIb**, **VIb**, **VIc**, **VIIb**, and **VIIc** was confirmed by the IR spectra which contained absorption bands at 1600–1601 cm^{-1} typical of stretching vibrations of C=C bonds, high- and medium-intensity carbonyl absorption bands in the region 1710–1780 cm^{-1}, and absorption bands at 680–800 cm^{-1} due to vibrations of C–Cl bonds.

Compounds **IIIa**, **IIIb**, **VIb**, **VIc**, **VIIb**, and **VIIc** displayed in the UV spectra absorption maxima at λ 246 nm (**IIIa**, **VIb**, **VIc**) and 285–287 nm (**IIIb**, **VIIb**, **VIIc**), which are typical of cisoid homoannular diene systems [8].

Scheme 3.



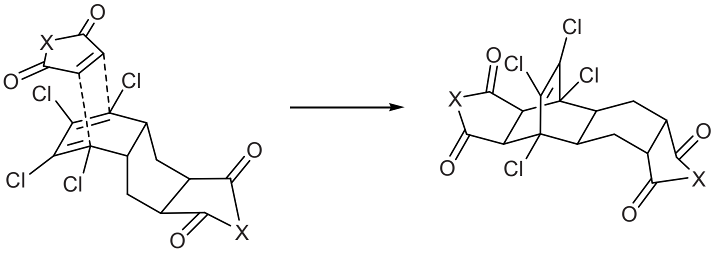
Scheme 4.



IIIa, **VIb**, **VIc** **Xa**–**Xc**

X = O (**a**), $H_2NCH_2CH_2N$ (**b**), 4-(4-H_2N-3-$MeOC_6H_3CH_2$)-2-$MeOC_6H_4N$ (**c**).

Scheme 5.



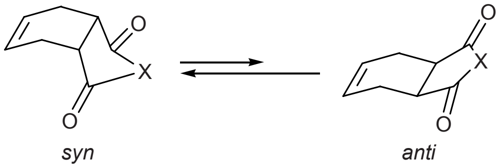
IIIb, **VIIb**, **VIIc** **XIa**–**XIc**

The presence of a conjugated double bond system in **IIIa**, **IIIb**, **VIb**, **VIc**, **VIIb**, and **VIIc** was confirmed by their Diels–Alder reactions with maleic and tetrahydrophthalic anhydrides and imides **VIIIa**–**VIIIc** and **IXa**–**IXc**. We showed previously [9] that anhydrides **IIIa** and **IIIb** readily react with maleic anhydride (**VIIIa**) to give the corresponding dianhydrides **Xa**–**XIIa**. Our present study has shown that anhydrides **IIIa** and **IIIb** and imides **VIb**, **VIc**, **VIIb**, and **VIIc** also readily react not only with maleic acid derivatives **VIIIa**–**VIIIc** but also with tetrahydrophthalic anhydride and imides **IXa**–**IXc**. The Diels–Alder reactions of **IIIa**, **VIb**, and **VIc** with tetrahydrophthalic anhydride (**IXa**) and imides **IXb** and **IXc** and of compounds **IIIb**, **VIIb**, and **VIIc** with maleic anhydride (**VIIIa**) and imides **VIIIb** and **VIIIc** gave adducts **XIa**–**XIf** having the same molecular constitution but different melting points (Scheme 3).

Taking into account *endo* orientation of the addends and the possibility for maleic acid derivatives to approach the diene system in **IIIa**, **VIb**, **VIc** at both *syn* and *anti* side, the bicyclic fragment in the adduct should have *exo*,*exo* configuration (**Xa**–**Xc**; Scheme 4). As shown previously with the aid of Stewart–Briegleb models [10, 11], the tricyclic fragment in **XIa**–**XIf** should have *exo*,*exo*,*endo* (**XIa**–**XIc**; Scheme 5) or *endo*,*exo*,*exo* structure (**XId**–**XIf**).

According to the NMR data [6, 8], tetrahydrophthalic anhydride (**IXa**) and imides **IXb** and **IXc** exist as equilibrium mixtures of two conformations *syn*- and *anti*-*boat* (Scheme 6).

Scheme 6.

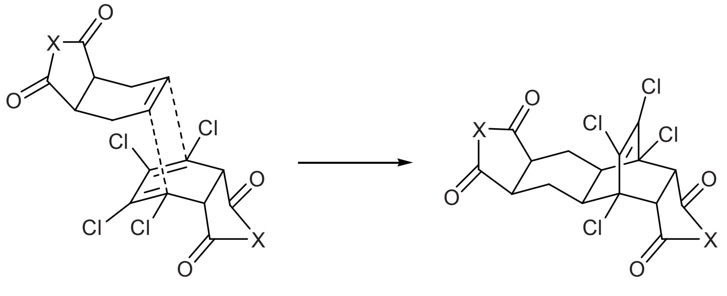


In the reactions with anhydrides **IIIa** and **IIIb** or imides **VIb**, **VIc**, **VIIb**, and **VIIc**, both conformers of dienophiles **IXa**–**IXc** are equally accessible for the formation of *endo*-oriented complex; therefore, attack on diene **IIIa**, **VIb**, or **VIc** by anhydride or imide **IXa**–**IXc** should involve mainly the *syn* conformer to give *endo*,*exo*,*exo*-adduct **XId**–**XIf** (Scheme 7), whereas analogous Diels–Alder adducts **XIa**–**XIc** obtained from dienes **IIIb**, **VIIb**, and **VIIc** should have *exo*,*exo*,*endo* configuration. Compounds **XIIa**–**XIIc** should be formed as *endo*,*exo*,*exo*,*endo* isomers (Scheme 8).

EXPERIMENTAL

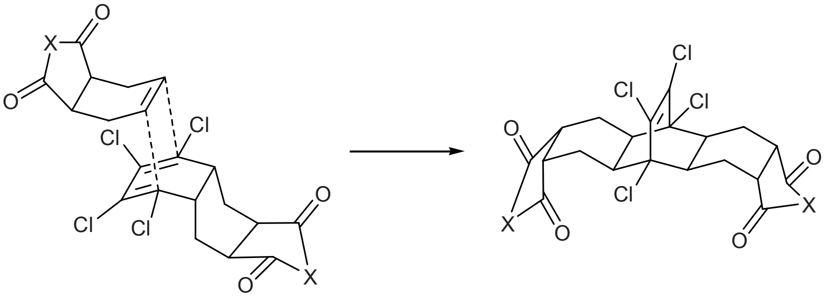
The UV spectra were recorded on a Specord-UV spectrophotometer from solutions in methanol with a concentration of 3.0×10^{-4} M. The NMR spectra were measured on a Tesla BS-487C spectrometer at 80 MHz

Scheme 7.



IIIa, **VIb**, **VIc** **XId**–**XIf**

Scheme 8.



IIIb, **VIIb**, **VIIc** **XIIa**–**XIIc**

using carbon tetrachloride as solvent and hexamethyldisiloxane as internal reference. The purity of the products was checked by thin-layer chromatography on Silufol plates using benzene–dichloroethane–acetic acid (4 : 1.5 : 1, by volume) as eluent; spots were detected under UV light [12].

1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**IVa**) [13], 1,8,9,10,11,11-hexachlorotricyclo[6.2.1.0^{2,7}]undec-9-ene-4,5-dicarboxylic anhydride (**Va**) [14], anhydrides **VIa** and **VIIa** [15, 16], N-substituted maleimides **VIIIb** and **VIIIc** [13], and tetrahydrophthalimides **IXb** and **IXc** [15] were synthesized by known methods.

***endo*-3,4,5,6-Tetrachlorocyclohexa-3,5-diene-1,2-dicarboxylic anhydride (IIIa) and imides VIb and VIc (*general procedure*).** Pyridine, 3 ml, was added dropwise to a solution of 0.1 mol anhydride **IVa** or imide **IVb** or **IVc** in 20 ml of DMF at room temperature. The mixture spontaneously warmed up to 35°C. It was allowed to cool down to 20°C and poured into ice water under stirring. The precipitate was filtered off and washed with water until neutral washings.

Compound **IIIa**. Yield 86%, mp 138–139°C (from methanol), R_f 0.85. Found, %: C 32.91; H 0.51; Cl 48.88. *M* 287.5. $C_8H_2Cl_4O_3$. Calculated, %: C 33.33; H 0.69; Cl 49.30. *M* 288.0.

Compound **VIb**. Yield 78%, mp 90–91°C (from chloroform–hexane), R_f 0.87. Found, %: C 35.91; H 2.01; Cl 42.77; N 8.01. *M* 329.0. $C_{10}H_8Cl_4N_2O_2$. Calculated, %: C 36.36; H 2.42; Cl 43.03; N 8.48. *M* 330.0.

Compound **VIc**. Yield 80%, mp 165–167°C (from chloroform–hexane), R_f 0.90. Found, %: C 51.99; H 3.10; Cl 26.31; N 5.04. *M* 526.0. $C_{23}H_{18}Cl_4N_2O_4$. Calculated, %: C 52.27; H 3.41; Cl 26.89; N 5.30. *M* 528.0.

***endo*,*exo*-7,8,9,10-Tetrachlorobicyclo[4.4.0]deca-7,9-diene-3,4-dicarboxylic anhydride (IIIb) and imides VIIb and VIIc** were synthesized in a similar way from 0.1 mol of anhydride **Va** and imides **Vb** and **Vc**, respectively, using 5 ml of pyridine.

Compound **IIIb**. Yield 90%, mp 160–162°C (from benzene), R_f 0.90. Found, %: C 32.91; H 0.51; Cl 48.88. *M* 341.0. $C_8H_2Cl_4O_3$. Calculated, %: C 33.33; H 0.69; Cl 49.30. *M* 342.0.

Compound **VIIb**. Yield 98%, mp 120–122°C (from methanol), R_f 0.91. Found, %: C 43.28; H 3.14; Cl 36.41; N 7.04. *M* 382.5. $C_{14}H_{14}Cl_4N_2O_2$. Calculated, %: C 43.75; H 3.64; Cl 36.98; N 7.29. *M* 384.0.

Compound **VIIc**. Yield 92%, mp 226–228°C (from acetone), R_f 0.92. Found, %: C 55.10; H 3.91; Cl 23.98; N 4.30. *M* 580.0. $C_{27}H_{24}Cl_4N_2O_4$. Calculated, %: C 55.67; H 4.12; Cl 24.40; N 4.81. *M* 582.0.

***exo*,*exo*-1,4,7,8-Tetrachlorobicyclo[2.2.2]oct-7-ene-2,3 : 5,6-tetracarboxylic dianhydride (Xa) and diimides Xb and Xc (*general procedure*).** A mixture of 0.01 mol of anhydride **IIIa** or imide **VIb** or **VIc** and 0.01 mol of maleic anhydride **VIIIa** or maleimide **VIIIb** or **VIIIc**, respectively, was dissolved in 20 ml of acetone. The mixture spontaneously warmed up to 38°C and was left to stand for 12 h. The precipitate was filtered off and dried at room temperature.

Compound **Xa**. Yield 96%, mp 260–263°C (from methanol), R_f 0.98. Found, %: C 36.98; H 0.89; Cl 36.29. *M* 385.0. $C_{12}H_4Cl_4O_6$. Calculated, %: C 37.30; H 1.04; Cl 36.79. *M* 386.0.

Compound **Xb**. Yield 97%, mp 184–185°C (from chloroform–hexane), R_f 0.96. Found, %: C 40.19; H 3.08; Cl 30.00; N 11.37. *M* 469.0. $C_{16}H_{16}Cl_4N_4O_4$. Calculated, %: C 40.85; H 3.40; Cl 30.41; N 11.91. *M* 470.0.

Compound **Xc**. Yield 98%, mp 201–202°C (from chloroform–hexane), R_f 0.97. Found, %: C 58.01; H 4.07; Cl 16.00; N 14.04. *M* 865.0. $C_{42}H_{36}Cl_4N_4O_8$. Calculated, %: C 58.20; H 4.15; Cl 16.40; N 14.78. *M* 866.0.

***exo*,*exo*,*endo*-1,8,11,12-Tetrachlorotricyclo-[6.2.2.0^{2,7}]dodec-11-ene-4,5:9,10-tetracarboxylic dianhydride (XIa) and diimides XIb and XIc (*general procedure*).** *a*. A mixture of 0.01 mol of anhydride **IIIb** or imide **VIIb** or **VIIc** and 0.01 mol of maleic anhydride (**VIIIa**) or maleimide **VIIIb** or **VIIIc**, respectively, was dissolved in 20 ml of acetone. The solution spontaneously warmed up to 38°C and was left to stand for 12 h. The precipitate was filtered off and dried.

Compound **XIa**. Yield 91%, mp 225°C (from diethyl ether), R_f 0.80. Found, %: C 43.00; H 1.97; Cl 31.87. *M* 439.0. $C_{16}H_{10}Cl_4O_6$. Calculated, %: C 43.64; H 2.27; Cl 32.27. *M* 440.0.

Compound **XIb**. Yield 90%, mp 88–90°C (from chloroform–hexane), R_f 0.81. Found, %: C 44.48; H 4.01; Cl 26.90; N 12.00. *M* 522.0. $C_{20}H_{22}Cl_4N_4O_4$. Calculated, %: C 43.72; H 3.24; Cl 28.74; N 12.21. *M* 524.0.

Compound **XIc**. Yield 90%, mp 125–127°C (from diethyl ether), R_f 0.80. Found, %: C 59.80; H 4.21; Cl 15.04; N 13.21. *M* 919.0. $C_{46}H_{42}Cl_4N_4O_8$. Calculated, %: C 60.00; H 4.56; Cl 15.43; N 13.91. *M* 920.0.

b. A solution of 0.01 mol of anhydride **IIIa** or imide **VIb** or **VIc** and 0.01 mol of 1,2,3,6-tetrahydrophthalic anhydride (**IXa**) or imide **IXb** or **IXc**, respectively, in 20 ml of benzene was heated for 2 h under reflux. After cooling, the precipitate was filtered off and dried at room temperature.

***endo*,*exo*,*exo*-1,8,11,12-Tetrachlorotricyclo-[6.2.2.0^{2,7}]dodec-11-ene-4,5:9,10-tetracarboxylic anhydride (XId) and imides XIe and XIf** were synthesized in a similar way from anhydride **IIIa** and imides **VIb** and **VIc**.

Compound **XId**. Yield 90%, mp 173–175°C (from diethyl ether), R_f 0.78. Found, %: C 43.10; H 1.89; Cl 31.88. *M* 439.0. $C_{16}H_{10}Cl_4O_6$. Calculated, %: C 43.64; H 2.27; Cl 32.27. *M* 440.0.

Compound **XIe**. Yield 90%, mp 166–168°C (from chloroform–hexane), R_f 0.80. Found, %: C 43.91; H 3.00; Cl 28.33; N 11.92. *M* 523.0. $C_{20}H_{22}Cl_4N_4O_4$. Calculated, %: C 43.72; H 3.24; Cl 28.74; N 12.21. *M* 524.0.

Compound **XIf**. Yield 91%, mp 116–118°C (from diethyl ether), R_f 0.81. Found, %: C 59.68; H 4.00; Cl 14.98; N 13.71. *M* 918.0. $C_{46}H_{42}Cl_4N_4O_8$. Calculated, %: C 60.00; H 4.56; Cl 15.43; N 13.91. *M* 920.0.

***endo*,*exo*,*exo*,*endo*-1,8,15,16-Tetrachlorotetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadec-15-ene-4,5:11,12-tetracarboxylic dianhydride (XIIa) and imides XIIb and XIIc.** A solution of 0.01 mol of compound **IIIb**, **VIIb** or **VIIc** and 0.01 mol of anhydride **IXa** or imide **IXb** or **IXc**, respectively, in 20 ml of benzene was heated for 2 h under reflux. The mixture was then treated as described above.

Compound **XIIa**. Yield 90%, mp 162–164°C (from chloroform–hexane), R_f 0.81. Found, %: C 48.04; H 2.88; Cl 28.21. *M* 493.0. $C_{20}H_{16}Cl_4O_6$. Calculated, %: C 48.58; H 3.24; Cl 28.74. *M* 494.0.

Compound **XIIb**. Yield 91%, mp 80–82°C (from chloroform–hexane), R_f 0.88. Found, %: C 44.04; H 4.01; Cl 21.91; N 8.18. *M* 641.0. $C_{24}H_{28}Cl_4N_4O_4$. Calculated, %: C 44.41; H 4.34; Cl 22.11; N 8.72. *M* 642.0.

Compound **XIIc**. Yield 88%, mp 160–162°C (from chloroform–hexane), R_f 0.90. Found, %: C 61.05; H 4.43; Cl 14.02; N 12.98. *M* 973.5. $C_{50}H_{48}Cl_4N_4O_8$. Calculated, %: C 61.60; H 4.93; Cl 14.58; N 13.14. *M* 974.5.

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