

Synthesis of 1,8,11,12-Tetrachlorotricyclo[6.2.2.0^{2,7}]dodec-2-ene-4,5:9,10-bis(dicarboximides)

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Abstract—1,8,11,12-Tetrachlorotricyclo[6.2.2.0^{2,7}]dodec-11-ene-4,5:9,10-bis(dicarboximides) containing similar and different substituents on the nitrogen atoms were selectively synthesized by reactions of the corresponding dianhydride and imide anhydrides with aliphatic and aromatic amines in dimethylformamide. The structure of the resulting diimides was confirmed by independent synthesis via Diels–Alder reaction of N-substituted 1,2,3,4-tetrachlorobicyclo[4.4.0]deca-2,4-diene-8,9-carboximide with substituted maleimides.

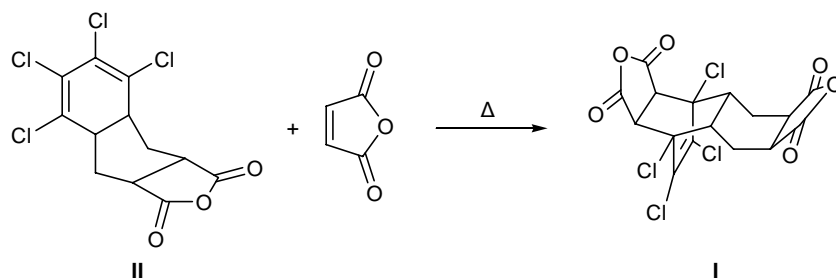
Halogen-containing dianhydrides derived from tetracarboxylic acids with a fixed steric structure are promising compounds from the viewpoint of their reactions with amines to obtain monomers having an imide ring with a reactive functional group in the substituent on the nitrogen; polycondensation of such monomers with other difunctional monomers should lead to formation of fire- and temperature-resistant polymeric materials [1].

We previously reported [2] on the synthesis of polychlorinated polycyclic tetracarboxylic acid dianhydride **I** having a specified steric structure by stereospecific Diels–Alder reaction of bicyclic anhydride **II** with maleic anhydride (Scheme 1). The steric structure of compound **I** was determined by measuring its dipole moment [3]. In continuation of these studies, the present communication reports on the synthesis of 1,8,11,12-tetrachlorotricyclo[6.2.2.0^{2,7}]dodec-11-ene-

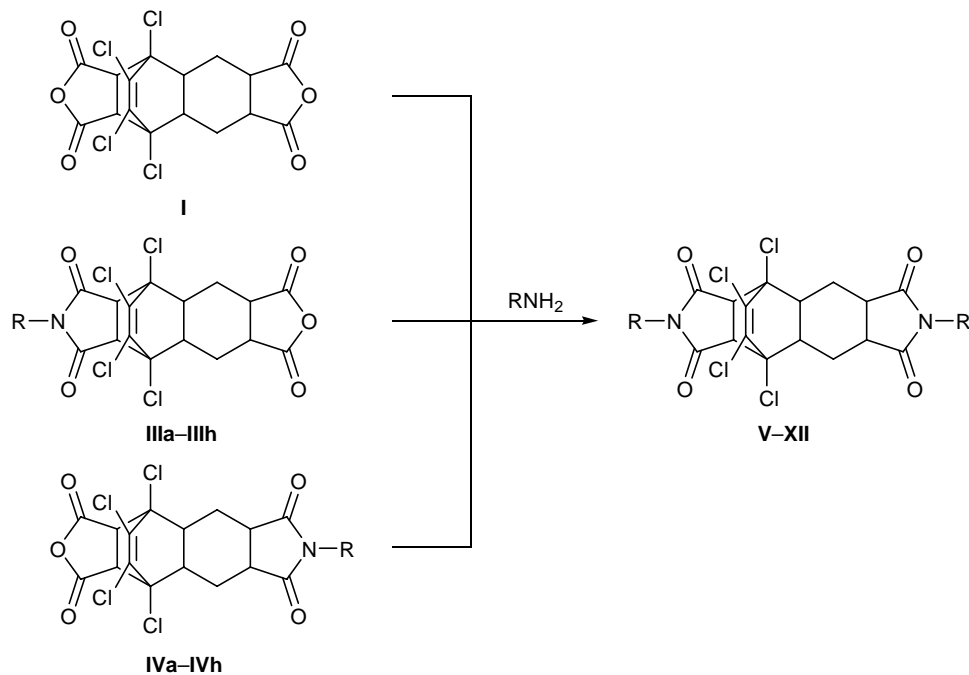
Yields, melting points, R_f values, and elemental analyses of 1,8,11,12-tetrachlorotricyclo[6.2.2.0^{2,7}]dodec-2-ene-4,5:9,10-bis(dicarboximides) **V–XIX**

Comp. no.	Yield, %	mp, °C (solvent)	R_f	Found, %				Formula	Calculated, %			
				C	H	Cl	N		C	H	Cl	N
V	86.0	260 (ethanol)	0.62	43.51	2.51	32.02	6.03	C ₁₆ H ₁₂ Cl ₄ N ₂ O ₄	43.83	2.74	32.42	6.39
VI	96.0	200 (ethanol)	0.56	42.99	2.62	25.13	4.88	C ₂₀ H ₁₆ Cl ₄ N ₂ O ₈	43.32	2.89	25.63	5.05
VII	97.0	300 (benzene)	0.50	56.60	3.00	23.78	4.31	C ₂₈ H ₂₀ Cl ₄ N ₂ O ₄	56.95	3.38	24.07	4.74
VIII	88.0	398 (ethanol)	0.58	52.96	2.55	20.39	3.81	C ₃₀ H ₂₀ Cl ₄ N ₂ O ₈	53.10	2.95	20.94	4.13
IX	88.0	341 (benzene)	0.59	53.86	2.91	22.31	4.08	C ₂₈ H ₂₀ Cl ₄ N ₂ O ₆	54.02	3.21	22.83	4.50
X	85.0	298 (benzene)	0.57	57.88	3.61	22.64	4.15	C ₃₀ H ₂₄ Cl ₄ N ₂ O ₄	58.25	3.88	22.98	4.53
XI	88.0	310 (benzene)	0.65	55.00	3.52	21.49	4.00	C ₃₀ H ₂₄ Cl ₄ N ₂ O ₆	55.38	3.69	21.84	4.31
XII	86.0	368 (ethanol)	0.71	61.91	5.00	15.61	6.01	C ₄₆ H ₄₂ Cl ₄ N ₄ O ₆	62.16	4.73	15.99	6.30
XIII	91.0	269 (ethanol)	0.64	51.12	3.21	25.11	4.88	C ₂₄ H ₂₀ Cl ₄ N ₂ O ₅	51.61	3.58	25.45	5.02
XIV	94.0	281 (ethanol)	0.64	51.10	3.30	25.08	4.90	C ₂₄ H ₂₀ Cl ₄ N ₂ O ₅	51.61	3.58	25.45	5.02
XV	90.0	300 (ethanol)	0.66	49.39	2.96	24.31	4.71	C ₂₄ H ₁₈ Cl ₄ N ₂ O ₆	49.84	3.14	24.82	4.89
XVI	87.5	310 (ethanol)	0.68	54.66	2.88	22.10	4.12	C ₂₉ H ₂₀ Cl ₄ N ₂ O ₆	54.89	3.15	22.40	4.41
XVII	89.0	321 (ethanol)	0.68	54.70	2.78	22.00	4.13	C ₂₉ H ₂₀ Cl ₄ N ₂ O ₆	54.89	3.15	22.40	4.41
XVIII	85.0	360 (chloroform)	0.70	59.71	4.21	18.91	5.16	C ₃₇ H ₃₃ Cl ₄ N ₃ O ₅	59.92	4.45	19.16	5.66
XIX	86.0	372 (chloroform)	0.71	59.69	4.21	18.89	5.15	C ₃₇ H ₃₃ Cl ₄ N ₃ O ₅	59.92	4.45	19.16	5.66

Scheme 1.



Scheme 2.

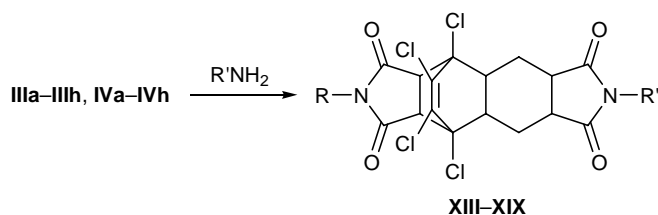


V, R = $\text{HO}(\text{CH}_2)_2$; VI, R = HOCOCH_2 ; VII, R = Ph; VIII, R = *p*- HOCOC_6H_4 ; IX, *p*- HOC_6H_4 ; X, R = *p*- MeC_6H_4 ;
 XI, R = *p*- MeOC_6H_4 ; XII, R = 4-(4-amino-3-methoxybenzyl)-2-methoxyphenyl.

4,5:9,10-bis(dicarboximides) containing similar and different substituents on the nitrogen atoms by acylation of aliphatic and aromatic amines with dianhydride I and imide anhydrides III and IV (Scheme 2). The

reactions were carried by heating the reactants in dimethylformamide (DMF) for 5–6 h, and the products were diimides V–XII (see table).

Scheme 3.



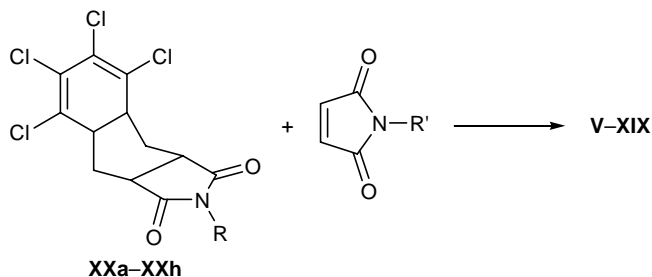
XIII, R = $\text{HO}(\text{CH}_2)_2$, R' = Ph; XIV, R = Ph, R' = $\text{HO}(\text{CH}_2)_2$;
 XV, R = Ph, R' = HOCOCH_2 ; XVI, R = Ph, R' = *p*- HOCOC_6H_4 ;
 XVII, R = *p*- HOCOC_6H_4 , R' = Ph; XVIII, R = Ph, R' = 4-(4-amino-3-methoxybenzyl)-2-methoxyphenyl;
 XIX, R = 4-(4-amino-3-methoxybenzyl)-2-methoxyphenyl, R' = Ph.

The proposed approach implies the possibility of obtaining diimides containing both similar and different substituents on the nitrogen atoms. By acylation of amines with compounds IIIa–IIIh and IVa–IVh [4] we obtained diimides XIII–XIX with different substituents on the nitrogen atoms (Scheme 3, see table).

The structure of diimides V–XIX was proved by the IR spectra and independent syntheses. The IR spectra of V–XIX contained absorption bands due to stretching vibrations of the carbonyl groups (1730 and 1780 cm^{-1}), C=C bond (1590 and 1601 cm^{-1}) and C–Cl bond (650 – 740 cm^{-1}). Diels–Alder reaction of *N*-aryl(alkyl)imides XXa–XXh with the corresponding

N-substituted maleimides (Scheme 4) gave expected compounds **V–XIX** which were identical to samples obtained as shown in Schemes 2 and 3.

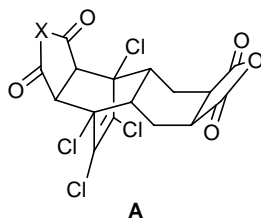
Scheme 4.



XXa–XXh

R = HO(CH₂)₂ (a), HOCOCH₂ (b), Ph (c), *p*-HOCOC₆H₄ (d), *p*-HOC₆H₄ (e), *p*-MeC₆H₄ (f), *p*-MeOC₆H₄ (g), 4-(4-amino-3-methoxybenzyl)-2-methoxyphenyl (h).

Analysis of the Stewart–Brigleb models showed that dianhydride **I** and imide anhydrides **III** and **IV** have structure **A**. Taking into account that replacement of the planar anhydride ring fused to the cyclohexane fragment by an analogous imide ring should not change steric structure, diimides **V–XIX** were also assigned structure **A**.



EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer from samples dispersed in mineral oil. The purity of the products was checked by thin-layer chromatography [5] using benzene–dichloroethane–acetic acid (4:1.5:1, by volume) as eluent; spots were visualized under UV light.

Initial anhydride **II** and N-substituted 2,3,4,5-tetrachlorobicyclo[4.4.0]deca-2,4-diene-8,9-dicarboximides

XXa–XXh were synthesized by the procedures reported in [6, 7]. 1,8,11,12-Tetrachlorotricyclo[6.2.2.0^{2,7}]dodec-11-ene-4,5:9,10-bis(dicarboxanhydride) was prepared as described in [2]. Imide anhydrides **IIIa–IIIh** were obtained according to [8].

1,8,11,12-Tetrachlorotricyclo[6.2.2.0^{2,7}]dodec-2-ene-4,5:9,10-bis(dicarboximides) V–XXI (general procedure). *a.* A mixture of 0.01 mol of dianhydride **I** and 0.02 mol of the corresponding aliphatic or aromatic amine in 50–60 ml of DMF was heated for 5–6 h. The mixture was cooled to room temperature and poured into ice water under stirring. The precipitate of diimide **V–XII** was filtered off, washed with water, and dried in air. Yield 88–91%.

b. A mixture of 0.01 mol of imide anhydride **IIIa–IIIh** or **IVa–IVh** and 0.01 mol of the corresponding amine in 50–60 ml of DMF was heated for 5–6 h. The mixture was then treated as described above in *a* to isolate 87–94% of diimide **V–XXI**.

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