

Synthesis of New Halogen-Containing Norbornene Adducts Based on N-Substituted Imides of 2,3-Dichlorobicyclo [2.2.1] Hept-5-ene-2,3-Dicarboxylic Acids and Hexachlorocyclopentadiene

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Abstract

Diene condensation of N-substituted 2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid imides with hexachlorocyclopentadiene proceeds regioselectively through the double bond of dienophile, resulting in the corresponding polychlorinated cyclic adducts with endo configuration.

Keywords: Double bond; Functional groups; Organic compounds

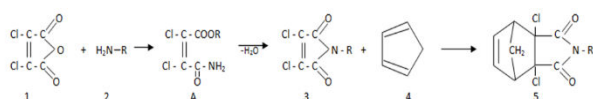
Introduction

Polychlorocyclic compounds containing functional groups in the side chain have a variety of biological and physiological effects [1-10], are used as flame retardants to increase the fire resistance of polymeric materials [4,10], are of interest as synthones in the purposeful synthesis of many classes of organic and element organic compounds [11-14].

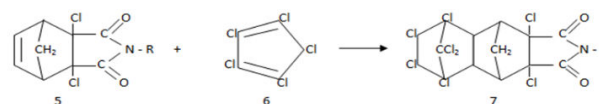
The availability of norbornene derivatives has increased as a result of the improvement of the Diels-Alder reactions and due to the preparation of cyclopentadiene, 1,3-cyclohexadiene and hexachlorocyclopentadiene on their basis.

Previously, we investigated the diene condensation of N-substituted imidates of dichloromaleic acid with cyclopentadiene and 1,3-cyclohexadiene, leading to the formation of bicyclic adducts. The structure and properties of the synthesized compounds were studied, as well as certain patterns of reactions [15-20].

The N-substituted imidates of 2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid contains reactive groups that make it possible to obtain on their basis a variety of valuable products of fine organic synthesis. In this work, studies are continued in this direction and the results of studying the diene condensation of N-substituted imides of 2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid and hexachlorocyclopentadiene [21]. The reactions were carried out at a molar ratio of the reacting components (diene: dienophile=1:1) (Schemes 1 and 2).



Scheme 1: R=Ph (a), m-NO₂C₆H₅ (b), p-NO₂C₆H₅ (c), 2,4-(NO₂)₂C₆H₄ (g), p-ClC₆H₅ (d), M-ClC₆H₅ (e), 3,4-Cl₂C₆H₄ (x), 2,5-Cl₂C₆H₄ (s).



Scheme 2: R=Ph (a), m-NO₂C₆H₅ (b), p-NO₂C₆H₅ (c), 2,4-(NO₂)₂C₆H₄ (g), p-ClC₆H₅ (d), M-ClC₆H₅ (e), 3,4-Cl₂C₆H₄ (g), 2,5-Cl₂C₆H₄ (s).

The composition and structure of the synthesized products were confirmed by IR, ¹H NMR spectroscopy and elemental analysis data. The compounds 7 (a-x) obtained are solid crystalline substances. The reactions were carried out at 110-120°C for 8-10 h at a 1: 1 diene-dienophile mole ratio. Under similar conditions, the reaction of [4+2]-cycloaddition of hexachlorocyclopentadiene to other substituted 2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid imides 5 (b-g) was carried out. The yield of adducts 7 (a-x) varies within the limits of 78-97%, with the highest yield observed for compound 7 b (97%), and the lowest yield for N-(m-Chlorophenyl) imide endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.05,10]-decene-2-ene-7,8-dicarboxylic acid (e).

In the IR spectrum of the adduct 7 (a-e), vibrational bands of the substituted benzene ring at 1630-1536; 1790-1730 (C=O), 745-735 cm⁻¹ (C-Cl) are observed, as well as bands of valence and deformation of the C-H bond vibration (3000, 1440 cm⁻¹). The absorption bands in the region 2950-2880 [δ (=CH)] and 960-820 [δ (C-H)] indicate the presence of a strained double bond in the molecules. In the ¹H NMR spectrum of imide 6 (a-b), the protons of the six-membered cycle of the norbornene fragment form a spin system AA'XX', in which A and A' are protons H1.4, (δ 2.81 md), and HX' protons H 5.6 δ 5.61 md. Bridged methylene protons are not equivalent and represent the spectrum of the system AB with δ (HA) 1.35, δ (HB) 2.22 ppm. 2 J_{AB} 9.6 Hz. Each component of the spectrum AB has an additional fine structure due to the spin-spin interaction of the bridge protons with protons H 1.4-6. In the low-field region (6.54 and 7.41 ppm), the spectrum contains multiple resonance signals corresponding to the five-spin AA'BB'CC' system of aromatic protons.

The resulting heterocyclic compounds are crystalline substances. The chemical composition and structure of N-phenylimide-endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.05,10] -dodec-2-ene-7.8-dicarboxylic acid are established by elemental analysis and methods of PMR, IR spectroscopy, as well as X-ray diffraction analysis (7a). It has been found that the product 7a obtained has an endo-configuration.

Experimental part

N-Phenylimide-endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.05,10]-dodec-2-ene-7.8-dicarboxylic acid (a). A solution of 0.546 g (2 mmol) hexachlorocyclopentadiene in 5 ml of toluene was added dropwise to a solution of 0.616 g (2 mmol) of the adduct (7a) in 15 ml of toluene at 1100°C for 15 minutes. The reaction mixture was stirred for 10 hours at the boiling point of toluene. The mass was then cooled to 100°C, the precipitate was filtered off, washed with water, and dried in vacuo at 700°C. The yield is 1.05 g (90%). Cinnamon crystals, well soluble in benzene, toluene, acetone, chloroform, DMF, N-methylpyrrolidone, m.p. 178-180°C. IR spectrum, cm^{-1} : 3000-1442 (C-H); 2882, 2742 (=N-); 1632.1638 (C_6H_4); 1382.1212 (SON); 682 (C-Cl). Nuclear Magnetic Resonance Spectrum ^1H , δ ppm. 7.31 (Ph); 2.89 (2H6.9); 2.20 and 1.26 (2H2). Found: C, 41.29; H 1.85; Cl 48.91; N 2.45. $\text{C}_{20}\text{H}_{11}\text{Cl}_8\text{NO}_2$. Calculated, % C, 41.31; H, 1.89; Cl, 48.88; N, 2.41.

N-(m-Nitrophenyl) imide endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.05,10] -dodec-2-ene-7.8-dicarboxylic acid, Acid (b). Yield 1.13 g (91%) m.p. 199-201°C. IR spectrum, cm^{-1} : 1740.1830 (CO), 1112.1384 (C-N); 1120.1140 (NO), 736 (C-Cl). ^1H , δ ppm. 7.41, 6.54 (Ph); 2.89 (2H6.9); 2.20 and 1.26 (2H₂). Found: C, 38.37; H, 1.56; Cl, 45.39; N, 4.44. $\text{C}_{20}\text{H}_{10}\text{Cl}_8\text{N}_2\text{O}_4$. Calculated, % C, 38.34; H, 1.60; Cl, 45.37; N, 4.47.

N-(p-Nitrophenyl) imide endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.05,10] -dodec-2-ene-7.8-dicarboxylic acid, Acid (in). Yield 1.214 g (97%) m.p. 203-205°C. IR spectrum, cm^{-1} : 1750.1830 (CO); 1360.1400 (C-N); 1100.1120 (NO); 736 (C-Cl). NMR spectrum ^1H , δ ppm. 7.31 (Ph); 2.89 (2H6.9); 2.20 and 1.26 (2H₂). Found: C, 38.46; H, 1.52; Cl, 45.32; N, 4.51. $\text{C}_{20}\text{H}_{10}\text{Cl}_8\text{N}_2\text{O}_4$. Calculated, % C, 38.34; H, 1.60; Cl, 45.37; N, 4.47.

N-(2,4-Dinitrophenyl) imido-endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.05,10] -decene-2-ene-7.8-dicarboxylic acid (g). Yield 1.21 g (90%) m.p. 196-198°C. IR spectrum, cm^{-1} : 1748.1831 (CO), 1114.1385 (C-N); 1122.1144 (NO), 737 (C-Cl). ^1H , δ ppm. 7.43, 6.56 (Ph); 2.87 (2H6.9); 2.19 and 1.25 (2H₂). Found: C, 35.67; H, 1.36.

N-(p-Chlorophenyl) imid-endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.05,10]- dodec-2-ene-7.8-dicarboxylic acid, Acid (e). Yield 1.102 g (95%) m.p. 168-170°C. IR spectrum, cm^{-1} : 1745-1705 (C=O), 1336 (=N-), 832 (C_6H_4), 737 (C-Cl). ^1H , δ ppm. 6.93 (Ph); 2.83 (2H6.9), 1.95 and 1.51 (2H₂). Found: C, 38.95; H, 1.59; Cl, 51.87; N, 2.23. $\text{C}_{20}\text{H}_{10}\text{Cl}_9\text{NO}_2$. Calculated, % C 38.99; H 1.61; Cl, 51.91; N, 2.27.

N-(m-Chlorophenyl) imide endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.05,10] -dodec-2-ene-7.8-dicarboxylic acid, Acid (e). Yield 1.07 g (92%) m.p. 166-168°C. IR spectrum, cm^{-1} : 1750-1707 (C=O), 1334 (=N-), 835 (C_6H_4), 735 (C-Cl). ^1H , δ ppm. 6.91 (Ph); 2.84 (2H6.9), 1.93 and 1.52 (2H₂). Found: C, 38.91; H, 1.62;

Cl, 51.94; N, 2.29. $\text{C}_{20}\text{H}_{10}\text{Cl}_9\text{NO}_2$. Calculated, % C 38.99; H 1.61; Cl, 51.91; N, 2.27.

N-(3,4-Dichlorophenyl) imide endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.05,10] -dodec-2-ene-7.8-dicarboxylic acid, Acid (E). Yield 1.21 g (93%) m.p. 142-144°C. IR spectrum, cm^{-1} : 1751-1707 (C=O), 1340 (=N-), 837 (C_6H_4), 737 (C-Cl). ^1H , δ ppm. 6.90 (Ph); 2.82 (2H6.9), 1.92 and 1.50 (2H₂). Found: C, 37.35; H, 1.39; Cl, 54.37; N, 2.21. $\text{C}_{20}\text{H}_9\text{Cl}_{10}\text{NO}_2$. Calculated, % C, 37.21; H, 1.40; Cl, 54.26; N, 2.17.

N-(2,5-Dichlorophenyl) imide endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.05,10] -decene-2-ene-7.8-dicarboxylic acid (G). Yield 1.24 g (95%) m.p. 145-147°C. IR spectrum, cm^{-1} : 1753-1705 (C=O), 1342 (=N-), 839 (C_6H_4), 735 (C-Cl). ^1H , δ ppm. 6.90 (Ph); 2.82 (2H6.9), 1.92 and 1.50 (2H₂). Found: C, 37.31; H, 1.37; Cl, 54.22; N, 2.19. $\text{C}_{20}\text{H}_9\text{Cl}_{10}\text{NO}_2$. Calculated, % C, 37.21; H, 1.40; Cl, 54.26; N, 2.17.

The IR spectra were recorded on a Nikolet IS10 spectrophotometer in KBr Thermo Scientific USA. ^1H NMR spectra were recorded on a Tesla BS-484 (80MHz) spectrometer in $(\text{CD}_3)_2\text{CO}$, the internal standard was TMS. Initial reagents and solvents were prepared according to the methods described [22].

Conclusion

Diene condensation of N-substituted imides of 2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid with hexachlorocyclopentadiene proceeds regioselectively over double bond of dienophile.

The resulting polychlorinated bicyclic adducts have an endo-configuration.

The reaction of hexachlorocyclopentadiene with N-substituted 2,3-dichlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid imides proceeds according to a classical type of diene condensation "diene-acceptor, dienophile-donor".

The X-ray diffraction analysis has shown that the obtained product has endo-configuration.

A crystalline structure of the resulting heterocyclic compounds has been established.

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