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 polychlorinatedcyclic 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 possibility to obtain on their basis a variety of valuable products of synthetic and structure 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-NO2C6H4 (b), p-NO2C6H4 (c), 2,4-(NO2)2C6H4 (g), p-CIC6H5 (d), M-CIC6H5 (e), 3,4-Cl2C6H4 (s), 2,5-Cl2C6H4 (s).

Scheme 2: R=Ph (a), m-NO2C6H4 (b), p-NO2C6H4 (c), 2,4-(NO2)2C6H4 (g), p-CIC6H5 (d), M-CIC6H5 (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 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 (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 AAA'BB'1С system of aromatic protons.

The five-spin AAA'BB'1С 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 [6.2.1.1.0²,10] decene-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 [6.2.1.1.0²,10] decene-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 110°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 70°C. The yield is 1.05 g (90%). Cinnamonic crystals, well soluble in benzene, toluene, acetone, chloroform, DMF, N-methylpyrrolidone, m.p. 178-180°C. IR spectrum, n cm⁻¹: 1748.1831 (CO), 1114.1385 (C-N); 1122.1144 (NO), 737 (C-Cl). 1 H, δ ppm. 7.31 (Ph); 2.89 (2H6.9); 2.20 and 1.26 (2H2). Found: C, 41.29; H, 1.85; Cl, 49.81; N, 2.45. C₂₀H₁₈Cl₂N₂O₂. 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 [6.2.1.1.0²,10] decene-2-ene-7,8-dicarboxylic acid, Acid (b). Yields 1.13 g (91%) m.p. 199-201°C. IR spectrum, n cm⁻¹: 1740.1830 (CO), 1112.1384 (C-N); 1120.1140 (NO), 736 (C-Cl). 1 H, δ ppm. 7.41, 6.54 (Ph); 2.89 (2H6.9), 1.93 and 1.51 (2H2). Found: C, 38.34; H, 1.60; Cl, 45.37; N, 4.47.  

N-(p-Chlorophenyl) imide endo-exo-1,2,3,4,7,8,11,11-octachlorotetracyclo [6.2.1.1.0²,10] decene-2-ene-7,8-dicarboxylic acid, Acid (c). Yield 1.24 g (95%) m.p. 145-147°C. IR spectrum, n cm⁻¹: 1753-1705 (C=O), 1342 (=N-), 839 (CH₃), 735 (C-Cl). 1 H, 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. C₂₀H₁₆Cl₂N₂O₂. Calculated, % C, 37.21; H, 1.40; Cl, 54.26; N, 2.17.  

**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.