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SHORT COMMUNICATIONS

Synthesis of 2,3-Dichlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid N-Carboxyphenylimides

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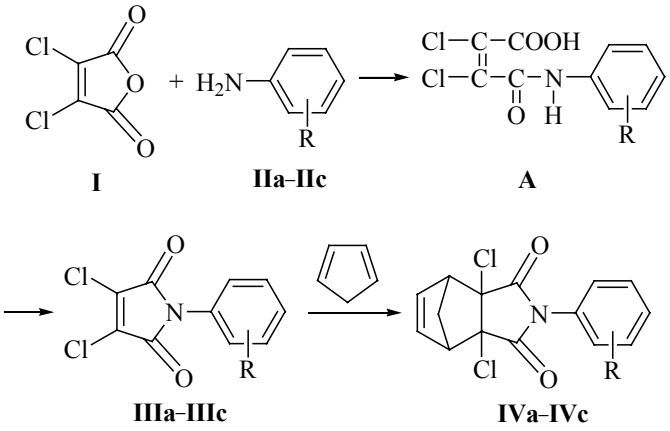
Compounds of bicyclo[2.2.1]hept- and [2.2.2]oct-5-ene series exhibit a wide range of biologic and physiologic action [1–6]. They are synthesized using primary amines and cyclopentadiene and 1,3-cyclohexadiene as dienes.

We formerly studied the synthesis of similar compounds using as primary amines various functionally substituted amines: aminonitriles, nitramines etc. [2, 4–8]. Here we report on the syntheses of new mono- and bicyclic compounds proceeding from *o*-, *m*-, and *p*-aminobenzoic acids.

First we investigated the reaction of dichloromaleic anhydride (**I**) and aminoacids **IIa–IIc** giving N-arylimides of dichloromaleic acid **IIIa–IIIc**. In the first stage of the process amidoacids **A** are formed [6] which under the reaction condition undergo further cyclization into the corresponding imides. Judging from the yields of compounds **IIIa–IIIc** the reactivity of isomeric aminobenzoic acids decreses in the series *para*-, *meta*-, *ortho*- due to the growing steric hindrance to the formation of the planar dichloromaleic acid N-arylimide [9].



I **IIa–IIc** **A**

IIIa–IIIc **IVa–IVc**

R = *o*-COOH (**a**), *m*-COOH (**b**), *p*-COOH (**c**).

The composition and structure of synthesized compounds **IIIa–IIIc** were confirmed by the elemental analysis, IR and ^{1}H NMR spectroscopy. The formation of the assumed structure is indicated by the presence of groups =CO, –COOH, chlorine and tertiary nitrogen atoms. In the ^{1}H NMR spectra of compounds **IIIa–IIIc** the proton signals are registered in the following regions, δ, ppm: 10.3 and 11.5 (COOH), 7.20 and 7.99 (C_6H_4).

Synthesized dichloromaleic acid N-arylimides **IIIa–IIIc** possess four electron-acceptor groups resulting in their high reactivity in the diene synthesis involving cyclopentadiene.

The composition and structure of synthesized adducts were confirmed by the elemental analysis, IR and ^{1}H NMR spectroscopy. In the IR spectrum of adduct **IVb** the absorption bands were present of the vibration of the benzene ring at 1630–1536 cm^{-1} and also of the stretching and bending vibrations of the C–H bond (3000, 1440 cm^{-1}). The bands in the region of 2950–2880 [δ(=CH)] and 960–820 cm^{-1} [δ(C–H)] indicate the presence in the molecule of a strained double bond.

In the ^{1}H NMR spectrum of imide **IVc** the protons of the six-membered ring of the norbornene fragment form a spin system AA^1XX^1 where A and A^1 are protons $H^{1,4}$, δ 3.44 ppm, and X and X^1 are protons $H^{5,6}$, δ 6.45 ppm. The bridging methylene protons are nonequivalent and appear as an AB system with $\delta(H^A)$ 2.19, $\delta(H^B)$ 2.50 ppm,

$^2J_{AB}$ 9.6 Hz. Each component of the *AB* system possesses an additional fine structure originating from the spin-spin coupling of the bridging protons with the protons $H^{1,4-6}$. In the downfield region (7.39 and 8.04 ppm) the spectrum contains multiplet resonances corresponding to the five-spin system AA^1BB^1C of aromatic protons.

The testing of the biological properties of imide **IVc** showed that it exhibits herbicidal, fungicidal, bactericidal, and biocidal action.

Dichloromaleic acid N-*m*-carboxyphenylimide (IIIb). To a dispersion of 16.7 g (0.1 mol) of anhydride **I** in 60 g of glacial acetic acid was added dropwise 13.7 g (0.1 mol) of *m*-aminobenzoic acid. The mixture was stirred for 30 min at 80°C and 90 min at 108°C. Then the reaction mixture was cooled to 10°C, the precipitate was filtered off, dried in a vacuum at 60°C. Yield 25.74 g (90%). Colorless crystals, well soluble in benzene, toluene, acetone, chloroform. DMF, dioxane, mp >250°C. IR spectrum, ν, cm^{-1}: 1750–1705 (C=O), 1630, 985–900 (C=C), 1505, 1330–1305 (=N–), 1480–1400 (C–H), 1130–1120 (COH), 835–760 (C_6H_4), 690–650 (C–Cl). Found, %: C 46.44; H 2.01; Cl 24.85; N 4.96. $C_{11}H_5Cl_2NO_4$. Calculated, %: C 46.15; H 1.79; Cl 24.83; N 4.90.

Compounds **IIIa, IIIc** were prepared similarly

Dichloromaleic acid N-*o*-carboxyphenylimide (IIIa). Yield 80%, mp >240°C. IR spectrum, ν cm^{-1}: 3260, 2700, 1750, 1505, 1480–1400, 1305–1300, 1130, 940, 780, 690, 650. Found, %: C 46.37; H 1.99; Cl 24.89; N 4.86. $C_{11}H_5Cl_2NO_4$. Calculated, %: C 46.15; H 1.79; Cl 24.83; N 4.90.

Dichloromaleic acid N-*p*-carboxyphenylimide (IIIc). Yield 26.6 g (93%), mp >250°C. IR spectrum, ν, cm^{-1}: 3260, 2800, 2650, 1750, 1705, 1605, 1480–1440, 1330–1305, 985, 835, 690, 670. Found, %: C 46.42; H 1.96; Cl 24.84; N 4.93. $C_{11}H_5Cl_2NO_4$. Calculated, %: C 46.15; H 1.79; Cl 24.83; N 4.90.

2,3-Dichlorobicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic acid N-*p*-carboxyphenylimide (IVc). To a solution of 0.704 g (2 mmol) of imide **IIIc** in 10 ml of benzene at 40°C was added dropwise within 15 min a solution of 0.165 g (2.5 mmol) of freshly distilled cyclopentadiene in 3 ml of benzene, the mixture was kept for 4 h and evaporated on a water bath. The residue was recrystallized from a mixture benzene–hexane, 1:1, dried at 90°C. Yield 0.662 g (94%). Colorless powder, stable, nonhygroscopic, nonexplosive, well soluble in DMF, dioxane, N-methylpyrrolidone, acetone, mp 268–270°C. IR spectrum, ν, cm^{-1}: 3000–1440 (C–H); 2950, 2885 (=CH); 2880, 2744 (=N–); 1750, 1710 (C=O); 1640, 820 (C=C); 1630, 1536 (C_6H_4); 1380, 1210 (CON); 1090 (O–H), 1005 (C–O), 680 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 2.19 m (1H, H^A), 2.50 m (1H, H^B), 3.44 m (2H, $H^{1,4}$), 6.45 m (2H, $H^{5,6}$), 7.39–8.04 m (4H, C_6H_4). Found, %: C 54.39; H 3.19; Cl 19.87; N 4.11. $C_{16}H_{11}Cl_2NO_4$. Calculated, %: C 54.55; H 3.13; Cl 20.17; N 3.98.

Compounds **IVa, IVb** were analogously prepared.

2,3-Dichlorobicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic acid N-*o*-carboxyphenylimide (IVa). Yield 83%, mp 223–225°C. IR spectrum, ν, cm^{-1}: 3350, 2950–2800, 2765, 2735, 1740, 1710, 1600, 1500, 1300, 1230, 1090, 940, 800, 725, 675. ^{1}H NMR spectrum, δ, ppm: 2.14 m (1H, H^A), 2.46 m (1H, H^B), 3.45 m (2H, $H^{1,4}$), 6.46 m (2H, $H^{5,6}$), 7.47–8.09 m (4H, C_6H_4). Found, %: C 54.66; H 2.98; Cl 20.56; N 3.92. $C_{16}H_{11}Cl_2NO_4$. Calculated, %: C 54.55; H 3.13; Cl 20.17; N 3.98.

2,3-Dichlorobicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic acid N-*p*-carboxyphenylimide (IVb). Yield 0.641 г (91%), mp 278–280°C. IR spectrum, ν, cm^{-1}: 3300–3200, 2980–2800, 2770, 2740, 1750, 1710, 1605–1505, 1475, 1370, 1320, 1120, 950, 880, 685. ^{1}H NMR spectrum, δ, ppm: 2.17 m (1H, H^A), 2.49 m (1H, H^B), 3.48 m (2H, $H^{1,4}$), 6.48 m (2H, $H^{5,6}$), 7.50–8.12 m (4H, C_6H_4). Found, %: C 54.47; H 3.02; Cl 20.56; N 3.76. $C_{16}H_{11}Cl_2NO_4$. Calculated, %: C 54.55; H 3.13; Cl 20.17; N 3.98.

IR spectra were recorded on a spectrophotometer Specord M-80 from pellets with KBr. ^{1}H NMR sperctra were taken on a spectrometer Tesla BS-484 (80 MHz) in $(CD_3)_2CO$, internal reference TMS. Initial reagents and solvents were prepared by procedures [2, 10].

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