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Some Transformations of the Substitutive Recyclization Product Obtained from Tetrachlorocyclopentadiene Dimer and Diethylamine

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Abstract—1,1a,2,3,3a,4,5-Heptachloro-*N*,*N*-diethyl-6-oxo-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalene-1-carboxamide reacts with hydroxide ion and N-centered nucleophiles following exclusively the Ad_NE scheme with replacement of the 4-chlorine atom. Its reactions with methylmagnesium iodide and diethyl malonate sodium salts involve simultaneous substitution, 1,2-addition at the carbonyl group, and aromatization. Oxidation of 1,1a,2,3,3a,4,5-heptachloro-*N*,*N*-diethyl-6-oxo-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalene-1-carboxamide with potassium permanganate under conditions of phase-transfer catalysis is accompanied by cleavage of the cyclopentenone fragment with formation of 2,3,4,5,6-pentachloro-6-diethylcarbamoylbicyclo[3.1.0]hex-3-ene-1,2-dicarboxylic acid.

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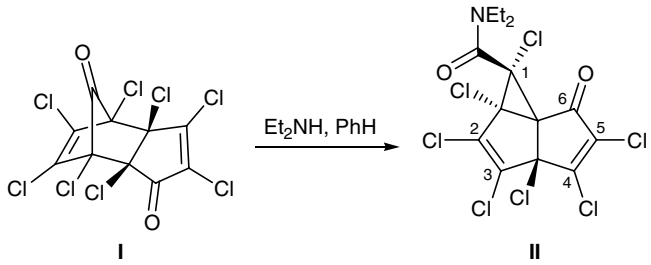
We recently reported on a new transformation of the 2,3,4,5-tetrachlorocyclopentadien-1-one dimer (**I**) [1] in reactions with primary and secondary amines, which led to the formation of tricyclic amides [2, 3] (Scheme 1). In the present work we examined the hydrolysis, substitution reactions, and oxidation of one of the obtained amides, compound **II**.

Scheme 1.



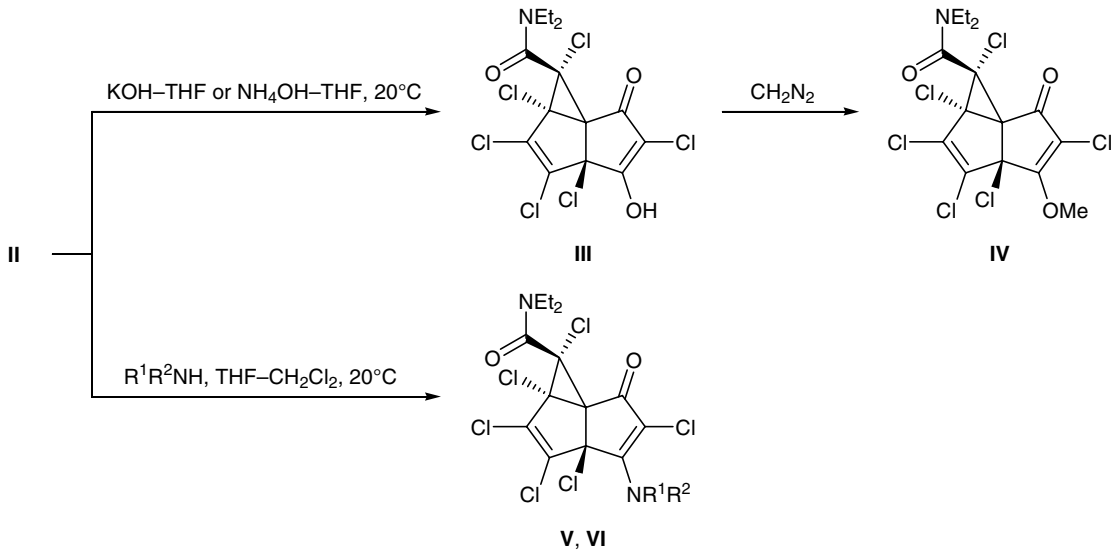
I **II**

The carboxamide group in molecule **II** remained unchanged under alkaline conditions, while replacement of the activated chlorine atom at the sp^2-hybridized C^4 atom by hydroxy group occurred (Ad_NE substitution pattern) [4]. Keto enol **III** thus formed (Scheme 2) was smoothly converted into the corresponding enol ether **IV** by treatment with diazomethane. The same result, i.e., the formation of enol **III**, was obtained when amide **II** was kept in a mixture of aqueous ammonia with THF. The reactions of **II** with morpholine and diethylamine lead to the corresponding Ad_NE-substitution products **V** and **VI** via replacement of the vinylic 4-Cl atom in the cyclopentenone fragment [5] (Scheme 2).

The reaction of compound **II** with a hard nucleophile, methylmagnesium iodide, was accompanied by profound structural reorganization. The process involved aromatization, 1,2-addition of the Grignard reagent to the C=O group in the cyclopentenone fragment, and partial replacement of the chlorine atom on C^4. As a result, an approximately equimolar mixture of compounds **VII** and **VIII** was formed (according to the ^{1}H NMR data; Scheme 3); we failed to separate this mixture by chromatography on silica gel.

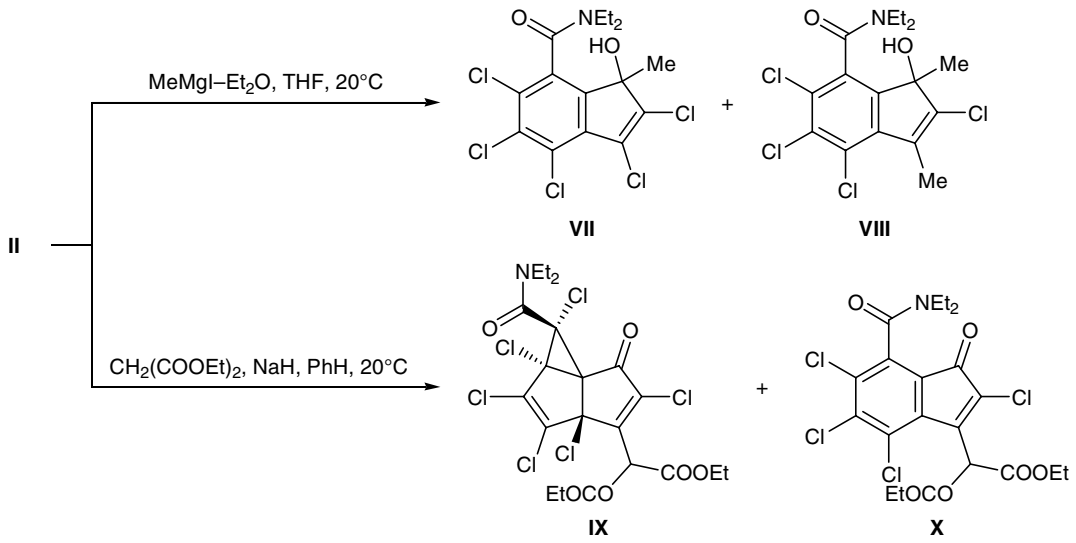
In the reaction of adduct **II** with a softer nucleophile, diethyl malonate sodium salt, we succeeded in isolating product **IX** resulting from Ad_NE substitution of the chlorine atom on C^4; however, the reaction was accompanied by formation of indenone derivative **X** (Scheme 3). After chromatographic separation in a column charged with silica gel, the ratio of the substitution and substitution–aromatization products **IX** and **X** was ~6:5.

Scheme 2.



V, R^1R^2N = morpholino; **VI**, $R^1 = R^2$ = Et.

Scheme 3.



We believe that the key precursors of indene derivatives **VII**, **VIII**, and **X** are intermediates **A** and **B**, respectively; their formation is facilitated due to intramolecular assistance of the β-hydroxy and oxo groups to opening of the cyclopropane ring (Scheme 4).

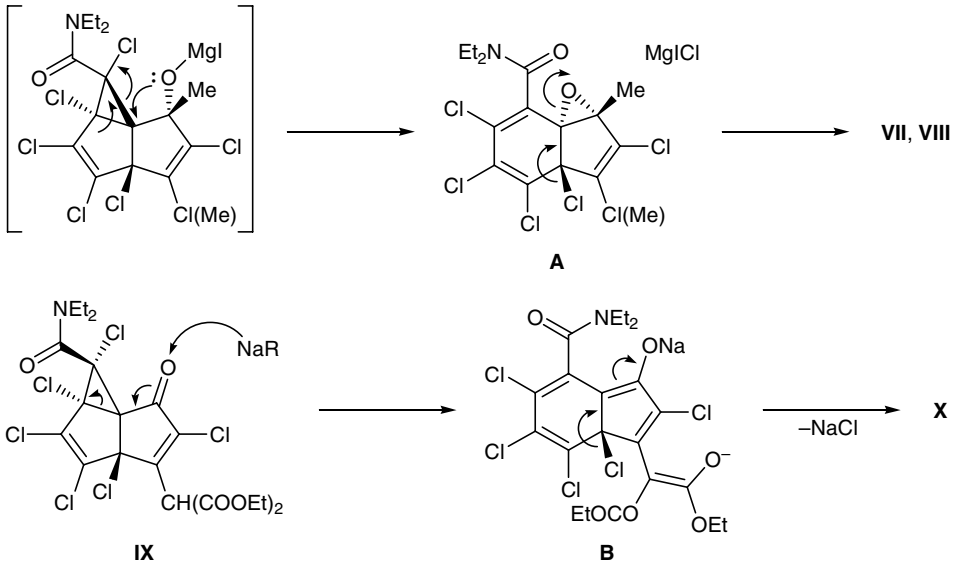
An interesting example of anomalous oxidative cleavage was revealed while studying the reaction of enone **II** with potassium permanganate. The oxidation with $KMnO_4$ in a two-phase system in the presence of benzyltrimethylammonium chloride as phase-transfer catalyst [6] was chemoselective; it occurred at the cyclopentenone fragment with loss of one carbon atom and formation of dicarboxylic acid **XI** (Scheme 5).

The described transformations of 2,3,4,5,6,7,8-heptachloro-*N*,*N*-diethyl-9-oxotricyclo[4.3.0.0^{1,3}]nona-4,7-diene-2-carboxamide open synthetic routes to new polyfunctionalized derivatives of tricyclo[4.3.0.0^{1,3}]-nonadiene, indene, and bicyclo[3.1.0]hex-2-ene.

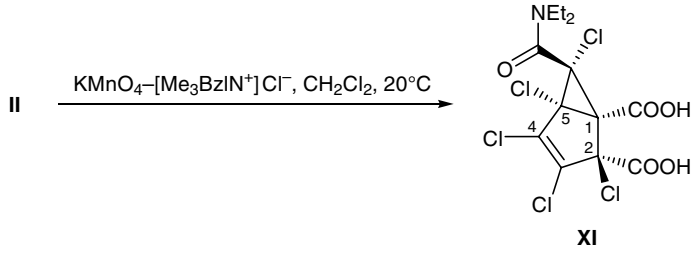
EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord M-80 spectrophotometers from samples dispersed in mineral oil. The NMR spectra were measured from solutions in $CDCl_3$ on a Bruker AM-300 spectrometer at 300.13 (^{1}H) and 75.47 MHz (^{13}C). Sorbfil plates (Russia) were used for thin-layer chro-

Scheme 4.



Scheme 5.



matography; spots were detected by calcination or by treatment with iodine vapor and subsequent wetting with water.

(1*S,1a*S**,3a*S**,6a*R**)-1,1a,2,3,3a,5-Hexachloro-*N*,*N*-diethyl-4-hydroxy-6-oxo-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalene-1-carboxamide (III).** A solution of 0.2 g (3.57 mmol) of KOH in 6 ml of water was added to a solution of 0.3 g (0.64 mmol) of compound **II** in 10 ml of THF, and the mixture was stirred for 24 h. Tetrahydrofuran was evaporated, the residue was acidified with 5% hydrochloric acid, the product was extracted into chloroform, and the extract was dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate–petroleum ether (1:1) as eluent. Yield 0.13 g (43%), colorless powder, mp 179–182°C (decomp.). IR spectrum, ν, cm^{-1}: 1576, 1654, 1696, 3412. ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.00 t (3H, CH_3, J = 7.0 Hz), 1.23 t (3H, CH_3, J = 7.0 Hz), 3.20 d.q (2H, NCH_2, ^2J = 14.0, ^3J = 7.0 Hz), 3.40 d.q (1H, ^2J = 14.0, ^3J = 7.0 Hz) and 3.70 d.q (1H, NCH_2, ^2J = 14.0, ^3J = 7.0 Hz), 4.35 br.s (1H, OH). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 10.89 (CH_3), 12.19 (CH_3), 39.14 (NCH_2), 44.02 (NCH_2), 46.49 (C^{6a}), 58.43 (C^1), 58.52 (C^{1a}), 75.53 (C^{3a}), 104.80 (C^5), 129.39 and 133.40 (C^2, C^3), 160.51 (C=O, amide), 178.15 (C^4), 180.93 (C=O). Found, %: C 36.80; H 2.64; Cl 46.29; N 2.92. $C_{14}H_{11}Cl_6NO_3$. Calculated, %: C 37.04; H 2.44; Cl 46.86; N 3.09.

(1*S,1a*S**,3a*S**,6a*R*)-1,1a,2,3,3a,5-Hexachloro-*N*,*N*-diethyl-4-methoxy-6-oxo-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalene-1-carboxamide (IV).** Compound **III**, 0.08 g (1.76 mmol), was dissolved in 5 ml of a 1:1 MeOH–Et_2O mixture, the solution was cooled to 0°C, and 30 ml of a solution of diazomethane prepared from 1.94 g (18.84 mmol) of *N*-nitroso-*N*-methylurea was slowly added under stirring. The mixture was stirred for 1 h at 0°C, several drops of acetic acid were added to decompose excess diazomethane, the mixture was evaporated, and the residue was subjected to chromatography on silica gel using ethyl acetate–petroleum ether 1:8) as eluent. Yield 0.05 g (60%), colorless oily substance. IR spectrum, ν, cm^{-1}: 712, 766, 790, 832, 982, 1008, 1084, 1198, 1588,

1618, 1654, 1732. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.08 t (3H, CH_3, J = 7.1 Hz), 1.27 t (3H, CH_3, J = 7.1 Hz), 3.26 d.q (2H, NCH_2, ^2J = 14.5, ^3J = 7.0 Hz), 3.42 d.q (1H, ^2J = 13.9, ^3J 7.1 Hz) and 3.66 d.q (1H, NCH_2, ^2J = 13.9, ^3J = 7.1 Hz), 4.53 s (3H, OCH_3). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 12.16 (CH_3), 13.49 (CH_3), 39.65 (NCH_2), 44.28 (NCH_2), 47.07 (C^{6a}), 59.17 (C^1), 59.52 (C^{1a}), 74.73 (C^{3a}), 110.88 (C^5), 127.95 and 135.77 (C^2, C^3), 159.25 (C=O, amide), 172.48 (C^4), 180.11 (C=O).

(1*S,1a*S**,3a*S**,6a*R**)-1,1a,2,3,3a,5-Hexachloro-*N*,*N*-diethyl-4-morpholino-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalene-1-carboxamide (V).** A solution of 0.13 g (1.5 mmol) of morpholine in 5 ml of THF was added to a solution of 0.3 g (0.64 mmol) of compound **II** in 10 ml of a 3:1 THF–CH_2Cl_2 mixture, and the mixture was stirred for 4 h and evaporated. The residue was dissolved in methylene chloride, the solution was washed with a solution of sodium chloride, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography on silica gel using ethyl acetate–petroleum ether (1:5) as eluent. Yield 0.10 g (30%), colorless powder, mp 166–169°C (decomp.). IR spectrum, ν, cm^{-1}: 910, 1122, 1243, 1470, 1576, 1611, 1660, 1715. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.07 t (3H, CH_3, J = 7.1 Hz), 1.28 t (3H, CH_3, J = 7.0 Hz), 3.14 m (2H, NCH_2, J = 7.3 Hz), 3.47 m (1H, J = 7.0 Hz) and 3.71 m (1H, NCH_2, J = 7.0 Hz), 3.82 m (4H, NCH_2, morpholine), 3.90 m (2H, OCH_2), 4.09 m (2H, OCH_2). ^{13}C NMR spectrum, δ_C, ppm: 11.54 and 12.91 ($2CH_3$), 40.17 and 44.82 ($2NCH_2$), 49.82 (C^{6a}), 51.76 ($2NCH_2$, morpholine), 57.81 and 60.02 (C^1, C^{1a}), 67.06 ($2OCH_2$), 111.44 (C^{3a}, C^5), 126.63, 139.44 (C^2, C^3), 160.34 (C^4), 161.74 (C=O, amide), 179.90 (C=O). Found, %: C 40.87; H 3.64; Cl 40.29; N 5.52. $C_{14}H_{11}Cl_6NO_3$. Calculated, %: C 41.33; H 3.47; Cl 40.67; N 5.36.

(1*S,1a*S**,3a*S**,6a*R**)-1,1a,2,3,3a,5-Hexachloro-4-diethylamino-*N*,*N*-diethyl-6-oxo-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalene-1-carboxamide (VI)** was synthesized as described above for compound **V** from 0.3 g (0.64 mmol) of compound **II** and 0.11 g (1.5 mmol) of diethylamine. Yield 0.08 g (25%), oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.09 t (3H, CH_3, amine, J = 7.1 Hz), 1.29 t (3H, CH_3, amine, J = 7.1 Hz), 1.20 t (3H, CH_3, amide, J = 7.2 Hz), 1.23 t (3H, CH_3, amide, J = 7.3 Hz), 3.13 m (2H, J = 7.1 Hz) and 3.44 d.q (2H, NCH_2, amine, J = 7.0 Hz), 3.58 q (2H, NCH_2, amide, J = 7.2 Hz), 3.70 d.q (1H, J = 7.3 Hz) and 4.19 d.q (1H, NCH_2, amide, J = 7.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.45 and 12.81 ($2CH_3$, amide); 13.68 and 13.79 ($2CH_3$, amine); 40.02 and 44.71 ($2NCH_2$, amide); 46.80 and 47.15 ($2NCH_2$, amine); 49.58 (C^{6a}); 57.63 and 59.91 (C^1, C^{1a}); 112.59 (C^{3a}); 126.20, 131.22, and 132.22 (C^2, C^3, C^5); 162.28 (C^4); 162.98 (C=O, amide); 179.90 (C=O).

2,3,4,5,6-Pentachloro-*N*,*N*-diethyl-1-hydroxy-1-methyl-1*H*-indene-7-carboxamide (VII) and 2,4,5,6-tetrachloro-*N*,*N*-diethyl-1-hydroxy-1,3-dimethyl-1*H*-indene-7-carboxamide (VIII). A solution of 0.34 g (0.73 mmol) of amide **II** in 14 ml of THF was added dropwise under nitrogen to a solution of 2.98 mmol of MeMgI in 10 ml of diethyl ether while stirring at 0°C. After 1 h, an additional portion of MeMgI, 2.98 mmol, in 1 ml of diethyl ether was added, and the mixture was stirred for 1 h until compound **II** disappeared (according to the TLC data). The mixture was treated with a saturated solution of ammonium chloride and extracted with CH_2Cl_2 (3×30 ml), the extracts were combined, dried over $MgSO_4$, and evaporated, and the residue was subjected to column chromatography on silica gel using ethyl acetate–petroleum ether (1:4), followed by recrystallization from CH_2Cl_2–petroleum ether (1:3). As a result, 0.10 g of a mixture of compounds **VII** and **VIII** at a ratio of ~1:1 (according to the ^{1}H NMR data) was isolated. Colorless powder, mp 229.5–234.5°C (decomp.). IR spectrum, ν, cm^{-1}: 1115, 1222, 1295, 1370, 1383, 1455, 1475, 1535, 3330.

Compound **VII**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.19 t (3H, CH_3, amide, J = 7.0 Hz), 1.34 m (3H, CH_3, amide, J = 7.0 Hz), 1.51 s (3H, CH_3), 3.28 m (2H, NCH_2, J = 6.9 Hz), 3.81 m (2H, NCH_2, J = 6.7 Hz), 5.10 br.s (1H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.07 and 13.25 ($2CH_3$, amide); 22.49 (CH_3); 39.11 and 43.20 ($2NCH_2$); 78.68 (C^1); 126.39, 127.31, 128.90, 130.49, 133.59, 134.95 (C^9, C^3, C^5, C^6, C^4, C^7); 142.48, 143.52 (C^8, C^2); 165.62 (C=O, amide).

Compound **VIII**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.15 t (3H, CH_3, amide, J = 6.7 Hz), 1.33 m (3H, CH_3, amide), 1.53 s (3H, CH_3), 2.35 s (3H, CH_3), 3.28 m (2H, NCH_2, J = 6.9 Hz), 3.53 m (2H, NCH_2, J = 6.7 Hz), 5.10 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 12.28 and 13.25 ($2CH_3$, amide); 18.42 (CH_3); 22.39 (CH_3); 39.22 and 43.37 ($2NCH_2$); 78.85 (C^1); 126.54, 126.83, 130.06, 132.62, 133.87, 134.41 (C^9, C^3, C^4, C^5, C^6, C^7); 142.94, 144.21 (C^8, C^2); 168.36 (C=O, amide).

Diethyl (1*S,1'a*S*,3'a*S**,6a*S**)-2-(1,1a,2,3,3a,5-hexachloro-1-diethylcarbamoyl-6-oxo-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalen-4-yl)malonate**

(IX) and diethyl 2-(2,4,5,6-tetrachloro-7-diethylcarbamoyl-1-oxo-1*H*-inden-3-yl)malonate (X). A solution of 0.30 g (0.65 mmol) of amide **II** in 10 ml of benzene was added dropwise while stirring under nitrogen to a suspension of 0.21 g (1.32 mmol) of diethyl malonate and 0.04 g (1.67 mmol) of sodium hydride in 10 ml of benzene. The mixture was stirred for 1 h until compound **II** disappeared (according to the TLC data), treated with a saturated solution of NH_4Cl, and extracted with methylene chloride (3×30 ml), the extracts were combined, dried over $MgSO_4$, and evaporated, and the residue was separated by column chromatography on silica gel using ethyl acetate–petroleum ether (1:4) as eluent to isolate 0.12 g (30%) of compound **IX** and 0.08 g (25%) of **X**.

Compound **IX**. Colorless powder, mp 122.0–124.5°C. IR spectrum, ν, cm^{-1}: 740, 930, 1040, 1165, 1440, 1610, 1660, 1750. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.09 t (3H, J = 7.1 Hz) and 1.24 t (3H, $2CH_3$, amide, J = 7.0 Hz), 1.29 t (3H, J = 7.2 Hz) and 1.32 t (3H, $2CH_3$, J = 7.2 Hz), 3.15 d.q (1H, ^2J = 6.8, ^3J = 13.8 Hz) and 3.25 d.q (1H, NCH_2, ^2J = 7.0, ^3J = 14.0 Hz), 3.46 d.q (1H, ^2J = 6.9, ^3J = 14.0 Hz) and 3.64 d.q (1H, NCH_2, ^2J = 6.9, ^3J = 14.0 Hz), 4.25 q (2H, J = 6.9 Hz) and 4.31 q (2H, $2OCH_2$, J = 7.1 Hz), 4.98 s (1H, CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.58, 12.76 ($2CH_3$, amide); 13.78 and 13.89 ($2CH_3$); 40.24 and 44.59 ($2NCH_2$); 48.17 (C^{6a}); 50.52 (CH); 60.86, 61.71, 62.01 (C^1, C^{1a}, C^{3a}); 62.89 and 62.99 ($2OCH_2$); 127.49 and 136.32 (C^2, C^3); 139.64 (C^5); 155.22 (C^4); 159.32 (C=O, amide); 163.34 and 163.86 ($2\mathbf{C}O_2Et$); 181.83 (C^6).

Compound **X**. Pale yellow powder, mp 160–162°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.09 t (3H, J = 7.2 Hz), 1.35 t (3H, $2CH_3$, amide, J = 7.1 Hz), 1.29 t (3H, J = 7.1 Hz) and 1.31 t (3H, $2CH_3$, J = 7.1 Hz); 3.13 q (1H, J = 7.2 Hz) and 3.14 q (1H, NCH_2, J = 7.2 Hz); 3.55 d.q (1H, ^2J = 7.1, ^3J = 14.1 Hz) and 3.71 d.q (1H, NCH_2, ^2J = 7.1, ^3J = 14.1 Hz), 4.29 q (2H, J = 7.1 Hz) and 4.30 q (2H, $2OCH_2$, J = 7.1 Hz), 5.29 s (1H, CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.09 and 13.67 ($2CH_3$, amide); 13.95 (CH_3); 39.04 and 42.79 ($2NCH_2$); 50.69 (CH); 62.85 (OCH_2); 123.91, 127.36, 131.75, 133.26, 133.61 (C^9, C^4, C^5, C^6, C^7); 138.75, 139.34 (C^2, C^8); 146.95 (C^3); 162.21 (C=O, amide); 164.40 and 164.68 ($2\mathbf{C}O_2Et$); 184.36 (C^1). Found, %: C 47.72; H 4.12; Cl 26.49; N 2.92. $C_{14}H_{11}Cl_6NO_3$. Calculated, %: C 48.02; H 4.03; Cl 27.00; N 2.67.

2,3,4,5,6-Pentachloro-6-diethylcarbamoylbicyclo-[3.1.0]hex-3-ene-1,2-dicarboxylic acid (XI). A solution of 0.50 g (1.07 mmol) of compound **II** in 10 ml of methylene chloride was cooled to 0°C, a solution 0.1 g (1.79 mmol) of potassium hydroxide in 12 ml of water and 0.32 g (1.73 mmol) of benzyltrimethylammonium chloride were added under stirring, and 0.38 g (2.38 mmol) of potassium $KMnO_4$ was added in small portions. The mixture was stirred for 4 h, the brown precipitate was filtered off, and the organic phase was separated, washed with a saturated aqueous solution of sodium chloride, dried over $MgSO_4$, and evaporated. The residue was recrystallized from methylene chloride to isolate 0.16 g of initial amide **II** and 0.2 g (62% on the reacted amide **II**) of dicarboxylic acid **XI** as a colorless powder with mp 134.5–136.5°C. IR spectrum, ν, cm^{-1}: 952, 1036, 1126, 1156, 1240, 1270, 1348, 1378, 1456, 1558, 1636, 1750, 3484. ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.06 t (3H, CH_3, J = 7.1 Hz), 1.27 t (3H, CH_3, J = 7.0 Hz), 3.23 m (2H, NCH_2, J = 6.7 Hz), 3.52 m (1H, J = 7.0 Hz) and 3.84 m (1H, NCH_2, J = 7.2 Hz), 10.38 s (1H, COOH), 10.72 s (1H, COOH). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 10.61 and 12.13 ($2CH_3$), 39.40 and 44.05 ($2NCH_2$), 49.14 (C^1), 57.69 and 59.82 (C^5, C^6), 76.86 (C^2), 127.47 and 135.41 (C^3, C^4), 159.93 (C=O, amide), 161.79 and 164.35 (2COOH). Found, %: C 35.25; H 2.78; Cl 39.98; N 3.26. $C_{13}H_{12}Cl_5NO_5$. Calculated, %: C 35.53; H 2.75; Cl 40.33; N 3.19.

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