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5-Nitro[2.2]paracyclophanepyran-6-one—building block for the synthesis of [2.2]paracyclophanes containing condensed benzofuran subunits

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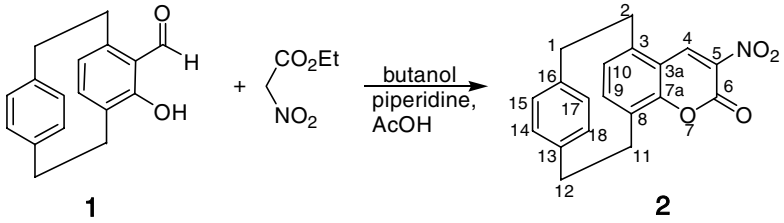
Abstract—The 5-nitro[2.2]paracyclophanepyran-6-one **2** has been synthesized. DBN treatment of the Diels–Alder cycloadducts of **2** followed by DDQ oxidation unexpectedly led to [2.2]paracyclophanes containing a condensed benzofuran subunit.

Coumarins are important molecules that are well known for their biological and therapeutic activities,[1] as well as for their use in laser dyes and organic light-emitting diodes (LEDs) due to their fluorescence.[2] Coumarins can also be considered as versatile building blocks and intermediates for the synthesis of various interesting compounds (e.g., benzo- and dibenzofurans,[3] fluorescent triazole-coumarins[4] and polycyclic coumarins[5]).

In view of the increasing interest in the [2.2]paracyclophane derivatives due to their potential applications as new materials (e.g., organic semiconductor, emissive layer in OLEDs)[6] and in light of our continued interest in angularly fused polycyclic [2.2]paracyclophanes incorporating heterocyclic rings,[7] we decided to study the synthesis of α-substituted [2.2]paracyclophanepyranones. Such molecules can be considered as a new type of coumarin derivative containing the three-dimensional π-electron system of phanes. It was envisaged that these molecules themselves might have interesting biological and/or optoelectronic properties and could be converted into new [2.2]paracyclophanes containing fused benzochromene or benzofuran subunits.

Here, we report (i) the preparation of the 5-nitro[2.2]paracyclophanepyran-6-ones (**2**) (Scheme 1) (ii) the study of the Diels–Alder reactions of **2** with 1,3-butadienes **3** and (iii) the conversion of the relative cycloadducts **4** in [2.2]paracyclophanes containing a fused benzofuran subunit **5** (Scheme 2).

Synthesis of the 5-nitro[2.2]paracyclophanepyran-6-one (**2**) was carried out optimizing a procedure previously reported for the synthesis of coumarins starting from



1 2

Scheme 1.

Keywords: [2.2]Paracyclophanes; Coumarins; Benzofuran; High pressure; Diels–Alder cycloaddition; 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN).
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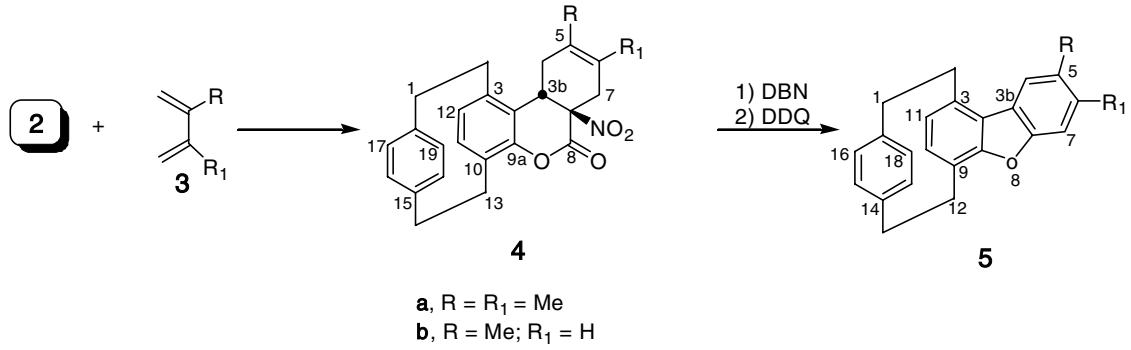

Scheme 2.

salicylaldehyde.[4] When 4-formyl-5-hydroxy[2.2]paracyclophane[8] (**1**) was treated with ethylnitroacetate in *n*-butanol and in the presence of piperidine/AcOH at 110 °C, compound **2** was obtained in 72% yield (Scheme 1).[9] The structure of **2** was supported mainly by ^{1}H and ^{13}C NMR spectra. The shifts of H(4) (singlet at 8.55 ppm) and the paracyclophane methylenic protons (multiplets at 2.8–3.2 ppm), as well as the carbon shifts of C(5) and C(6) at 143.8 and 154.9 ppm, respectively, were diagnostic for the structure assignment.

The Diels–Alder cycloadditions between the nitrocoumarin **2** and dienes **3** (Scheme 2) were studied at atmospheric and under high pressure.[10]

The cycloadduct **4a** was obtained in low yield (30%) when the cycloaddition reaction of **2** with 2,3-dimethyl-1,3-butadiene (**3a**) was carried out under normal pressure conditions at reflux temperature in toluene. A nearly quantitative yield (98%) was obtained when this cycloaddition was carried out at 8 kbar, in CH_2Cl_2 solution and at 65 °C; in this case **4a** was obtained practically pure at the end of the reaction, after simple evaporation of the solvent and residual diene.

When the cycloaddition of **2** was extended to isoprene (**3b**), no reaction occurred under normal pressure conditions at reflux temperature in toluene. On the contrary, under hyperbar activation (8 kbar) and at 65 °C, the cycloaddition led regioselectively to the cycloadduct **4b** in good yield (80%).[10] The structures of **4a**,**b** were assigned by ^{1}H and ^{13}C NMR spectroscopy. The configuration of the C(3b) carbon was supported by ^{1}H–{^{1}H} NOE experiments. Selective pre-irradiation of H(3b) resonance ($\delta = 4.04$ and 4.12 ppm for **4a** and **4b**, respectively) resulted in signal enhancement of the resonances attributed to H(2) and H(19), thus confirming that H(3b) points toward the unsubstituted arene ring of the [2.2]paracyclophane unit in both compounds. In the case of **4b**, the regiochemistry of the methyl group at C(5) was supported by the long-range hetero-correlations observed between the methyl protons and C(4) and between H(3b) and the quaternary carbon C(5).

In an attempt to prepare [2.2]paracyclophanes containing a fused chromenone subunit by aromatization of the cyclohexene ring of the cycloadducts **4a**,**b**, firstly we submitted **4a**,**b** to treatment with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) to achieve HNO_2 elimination. Treatment of **4a** with DBN in dry THF solution for 22 h at 22 °C under nitrogen led to a complex mixture. Careful TLC and GC–MS monitoring of this reaction showed that two dihydroderivatives of **5a** were the early products (M+ at *m*/*z* 328), which were partially converted into **5a** (M+ at *m*/*z* 326) throughout the course of the reaction. All attempts to separate these compounds were unsuccessful. The crude mixture was then submitted directly to 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation in benzene at reflux temperature for 1 h to afford the benzofuran derivative **5a** in 28% yield.[11]

The same reactions sequence was then applied on **4b**. When this cycloadduct was treated with DBN under the same experimental conditions, it afforded a mixture of **5b** and its dihydroderivative, from which no product could be isolated. The presence of the dihydroderivative of **5b** was tentatively assigned by the mass spectrum (M^{+} at *m*/*z* 314) and by ^{1}H NMR spectrum, which revealed the presence of the C(5) methyl protons (singlet 1.88 ppm). This mixture was then submitted to DDQ oxidation to afford, after chromatographic purification, **5b** in 20% yield.[11]

Structural confirmation of compounds **5a**,**b** follows mainly from the ^{1}H–{^{1}H} NOE observed between H(4) and H(2), as well as from the long-range heterocorrelations observed between proton H(4) and carbons C(3a) and C(7a). In the case of **5b**, irradiation of H(4) gave long-range heterocorrelations with the methyl group and the C(6) and C(7a) carbons, thus confirming the regiochemistry of the methyl group at C(5).

It was previously reported that nitrotetrahydrobenzo[*c*]chromenones, originating from Diels–Alder reaction of 3-nitro-2-coumarins with 1,3-butadienes, were converted into dihydrobenzo[*b*,*d*]furans in water, via one-pot hydrolysis/decarboxylation reactions under strong basic conditions followed by in situ Nef/cyclodehydration reactions in acidic medium.[3a]

Our results were unexpected since we only carried out the DBN reaction in dry conditions to avoid hydrolysis of the lactonic ring of **4a**,**b**; furthermore, the occurrence

of the Nef reaction can be excluded since it generally requires strong acid conditions. Based on the results obtained we have observed that in one-step DBN converts the nitro-tetrahydrochromenone units of cycloadducts **4** into dihydrobenzofurans, which are subsequently oxidized to benzofurans **5** by treatment with DDQ. Currently, we cannot suggest the sequence of events that led to compounds **5**. To our knowledge, there is no precedence for DBN behaving in this manner.

When the adducts **4a**,**b** were submitted separately to hydrolysis/decarboxylation reaction with 3 M NaOH, followed by in situ Nef-cyclodehydration reaction in 3.75 M H_2SO_4, according to the previously reported procedure,[3a] **5a** and **5b** were obtained in 32% and 30% overall yield, respectively.

In conclusion, 5-nitro[2.2]paracyclophanepyran-6-one (**2**) has been prepared, which is the first example of a coumarin derivative incorporating the [2.2]paracyclophane unit. A new synthetic route to [2.2]paracyclophanes containing angularly condensed benzofuran subunits has been reported, based on Diels–Alder reaction of **2** followed by DBN treatment and DDQ oxidation. Since the 4-formyl-5-hydroxy[2.2]paracyclophane can be easily prepared in enantiomerically pure form,[12] this approach opens a route for synthesizing new enantiopure [2.2]paracyclophanepyranones and [2.2]paracyclophanes bearing a condensed tetrahydrochromenone or benzofuran subunit. Further studies along these lines are currently in progress in our laboratory.

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9. Preparation of 5-nitro[2.2]paracyclophanepyran-6-one (**2**). A mixture of 4-formyl-5-hydroxy[2.2]paracyclophane[8] (**1**) (0.45 g, 1.78 mmol), molecular sieves (3 mg), piperidine (49 μl), acetic acid (98 μl), ethylnitroacetate (0.2 ml, 1.78 mmol) and *n*-butanol (10 ml) was heated at 110 °C for 23 h under nitrogen. The mixture was then cooled at room temperature, then concentrated in vacuo and the residue was submitted to short chromatography on silica gel. Elution with CH_2Cl_2 afforded pure compound **2** as a bright yellow solid (0.41 g, 72%) and unreacted hydroxyaldehyde **1** (78 mg, 17%).
A small amount of **2** was recrystallized from CH_2Cl_2 to give an analytical sample: mp 242–243 °C; IR 1758 (s, C=O), 1582 (s, C–NO_2) cm^{-1}; ^1H NMR δ 2.82 (ddd, 1H, $J = 13.4$, 10.4, 6.1 Hz, H-11), 2.92 (ddd, 1H, $J = 12.2$, 11.3, 5.3 Hz, H-1), 3.10–3.28 (m, 4H, H-1, H-2, H-12), 3.53 (ddd, 1H, $J = 13.1$, 11.2, 1.7 Hz, H-2), 3.66 (ddd, 1H, $J = 13.4$, 9.7, 3.4 Hz, H-11), 6.13 (dd, 1H, $J = 7.9$, 2.0 Hz, H-17), 6.48 (dd, 1H, $J = 7.9$, 1.8 Hz, H-14), 6.53 (dd, 1H, $J = 7.9$, 1.8 Hz, H-18), 6.58 (dd, 1H, $J = 7.9$, 2.0 Hz, H-15), 6.76 (d, 1H, $J = 7.7$ Hz, H-10), 6.96 (d, 1H, $J = 7.7$ Hz, H-9), 8.55 (s, 1H, H-4); ^{13}C NMR δ 30.1 (C-11), 32.4 (C-2), 34.1 (C-12), 35.4 (C-1), 118.6 (C-3a), 126.9 (C-18), 128.7 (C-8), 130.8 (C-17), 131.0 (C-10), 133.5 (C-15), 133.7 (C-14), 133.9 (C-3), 137.8 (C-16), 140.0 (C-4), 140.2 (C-13), 143.9 (C-5), 144.7 (C-9), 152.1 (C-7a), 154.9 (C-6). Anal. Calcd for $C_{19}H_{15}NO_4$: C, 71.02; H, 4.71; N, 4.36. Found: C, 70.98; H, 4.73; N, 4.39.
10. General procedure for the high pressure Diels–Alder reaction of 5-nitro[2.2]paracyclophanepyran-6-one (**2**) with dienes **3a**,**b**. A solution of compound **2** (0.48 g, 1.5 mmol) and diene **3a** or **3b** (9 mmol) in 15 ml of CH_2Cl_2 in the presence of a small amount of hydroquinone was kept at 8 kbar at 65 °C for 20 h. After depressurising, the solvent was evaporated in vacuo to give a pale yellow residue.
Compound **4a** was obtained pure in 98% yield; mp 185–186 °C (EtOAc); IR 1768 (s, C=O), 1560 (C–NO_2) cm^{-1}; ^1H NMR δ 1.48 (s, 3H, 5-Me), 1.58 (s, 3H, 6-Me), 1.97 (ddd, 1H, $J = 17.2$, 6.7 Hz, H-4), 2.27 (dd, 1H, $J = 17.2$, 7.2 Hz, H-4), 2.72 (ddd, 1H, $J = 13.9$, 10.2, 4.0 Hz, H-13), 2.81 (d, 1H, $J = 17.2$ Hz, H-7), 2.88 (d, 1H, $J = 17.2$ Hz,

H-7), 2.94–3.21 (m, 6H, H-1, H-2, H-14), 3.35 (ddd, 1H, $J = 13.9$, 10.2, 4.1 Hz, H-13), 4.04 (dd, 1H, $J = 7.2$, 6.7 Hz, H-3b), 6.32 (d, 1H, $J = 7.8$ Hz, H-12), 6.39 (d, 1H, $J = 7.8$ Hz, H-11), 6.42 (dd, 1H, $J = 8.3$, 1.5 Hz, H-19), 6.54 (dd, 1H, $J = 8.3$, 1.6 Hz, H-20), 6.60 (m, 1H, H-16), 6.63 (m, 1H, H-17); ^{13}C NMR δ 18.4 (6-Me), 18.5 (5-Me), 29.3 (C-13), 33.3 (C-2), 34.4 (C-14), 34.9 (C-1), 35.9 (C-4), 36.0 (C-7), 37.3 (C-3b), 90.2 (C-7a), 121.4, 123.8 (C-5, C-6), 122.7 (C-3a), 127.5 (C-10), 130.0 (C-19), 130.3 (C-20), 132.5 (C-12), 132.9 (C-16, C-17), 135.5 (C-11), 138.4 (C-15 or C-18), 139.0 (C-3), 139.9 (C-15 or C-18), 148.7 (C-9a), 161.5 (C-8). Anal. Calcd for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.25; N, 3.47. Found: C, 74.48; H, 6.22; N, 3.49.

Compound **4b**: obtained pure in 80% yield by short column chromatography eluting with CH_2Cl_2; mp 138–139 °C (hexane/EtOAc); IR 1770 (s, C=O), 1550 (C–NO_2) cm^{-1}; ^{1}H NMR δ 1.57 (d, 3H, $J = 1.5$ Hz, 5-Me), 1.99 (ddd, 1H, $J = 18.4$, 7.1, 0.8 Hz, H-4), 2.27 (ddd, 1H, $J = 18.4$, 6.6, 1.0 Hz, H-4), 2.76 (ddd, 1H, $J = 13.8$, 10.3, 4.0 Hz, H-13), 2.93 (dd, 1H, $J = 16.0$, 3.7 Hz, H-7), 2.95–3.26 (m, 6H, H-1, H-2, H-14), 2.98 (dd, 1H, $J = 16.0$, 4.1 Hz, H-7), 3.38 (ddd, 1H, $J = 13.8$, 10.2, 4.2 Hz, H-13), 4.12 (dd, 1H, $J = 7.1$, 6.6 Hz, H-3b), 5.30 (m, 1H, H-6), 6.35 (d, 1H, $J = 7.8$ Hz, H-12), 6.41 (d, 1H, $J = 7.8$ Hz, H-11), 6.44 (dd, 1H, $J = 8.1$, 1.8 Hz, H-19), 6.57 (dd, 1H, $J = 8.1$, 1.7 Hz, H-20), 6.63–6.66 (m, 2H, H-16, H-17); ^{13}C NMR δ 22.9 (5-Me), 29.3 (C-13), 30.7 (C-7), 33.4 (C-2), 34.3 (C-4), 34.4 (C-14), 35.0 (C-1), 37.2 (C-3b), 89.4 (C-7a), 115.8 (C-6), 122.5 (C-3a), 127.5 (C-10), 130.1 (C-19), 130.4 (C-20), 131.9 (C-5), 132.6 (C-12), 132.8 (C-16, C-17), 135.7 (C-11), 138.4 (C-15 or C-18), 138.9 (C-3), 140.0 (C-15 or C-18), 148.8 (C-9a), 161.5 (C-8). Anal. Calcd for $C_{24}H_{23}NO_4$: C, 74.02; H, 5.95; N, 3.60. Found: C, 73.97; H, 5.99; N, 3.62.

Diels–Alder reaction of **2** with dienes **3a**,**b** under normal pressure. A solution of **2** (0.16 g, 0.5 mmol) and diene **3a** (3 mmol) in toluene (5 ml) was heated in an oil bath at reflux temperature for 30 h. After cooling, the solvent was evaporated in vacuo to give a residue that was chromatographed on silica gel eluting with CH_2Cl_2 to give pure **4a** in 30% yield and unreacted **2** in 52% yield. In the case of the reaction **2**–**3b**, no reaction occurred under the same experimental conditions and only unreacted **2** was recovered.

11. Preparation of compounds **5**. A solution of **4a** or **4b** (0.5 mmol) in dry THF (6 ml) was treated with DBN (1.5 mmol) for 22 h at 22 °C under nitrogen, then poured into water and extracted with diethylether. The organic layer was washed with brine, dried (Na_2SO_4) and evaporated in vacuo to afford a residue, which was submitted directly to DDQ oxidation. A benzene solution (5 ml) of the above residue and DDQ (0.7 g) was heated at reflux temperature for 1 h. After cooling the solvent was evaporated in vacuo and the residue chromatographed on silica gel eluting with 95:5 hexane/EtOAc.

Compound **5a** was obtained as a white crystalline solid in 28% overall yield; mp 167–168 °C (*n*-hexane/EtOAc); ^{1}H NMR δ 2.45 (s, 6H, 5-Me, 6-Me), 2.90 (m, 1H, H-12), 2.95–3.15 (m, 5H, H-1, H-2, H-13), 3.61 (ddd, 1H, $J = 13.3$, 10.1, 3.2 Hz, H-12), 3.82 (ddd, 1H, $J = 13.3$, 11.6, 5.7 Hz, H-2), 5.46 (dd, 1H, $J = 7.8$, 1.9 Hz, H-18), 6.01 (dd, 1H, $J = 7.8$, 1.9 Hz, H-19), 6.40 (dd, 1H, $J = 7.9$, 1.9 Hz, H-16), 6.46 (dd, 1H, $J = 7.9$, 1.9 Hz, H-15), 6.54 (d, 1H, $J = 7.7$ Hz, H-11), 6.62 (d, 1H, $J = 7.7$ Hz, H-10), 7.37 (s, 1H, H-7), 7.68 (s, 1H, H-4); ^{13}C NMR δ 20.4, 21.0 (5-Me, 6-Me), 30.1 (C-12), 33.2 (C-2), 33.6 (C-13), 34.5 (C-1), 112.5 (C-7), 122.8 (C-4), 123.5 (C-3b), 124.5 (C-3a), 126.3 (C-19), 127.1 (C-9), 127.3 (C-18), 128.8 (C-11), 131.3 (C-5), 131.9 (C-10), 132.4 (C-15), 132.5 (C-16), 135.7 (C-6), 136.1 (C-3), 137.9 (C-17), 139.0 (C-14), 154.6 (C-7a), 155.8 (C-8a); MS, *m/e* (rel. intens.) 326 (M^+, 24), 223 (18), 222 (base), 221 (12), 207 (8), 179 (4). Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.35; H, 6.76.

Compound **5b** was obtained as a white crystalline solid in 20% overall yield; mp 98–99 °C (*n*-pentane); ^{1}H NMR δ 2.55 (s, 3H, 5-Me), 2.90 (m, 1H, H-12), 2.95–3.15 (m, 4H, H-1, H-13), 3.00 (m, 1H, H-2), 3.62 (ddd, 1H, $J = 13.2$, 10.1, 3.2 Hz, H-12), 3.85 (m, 1H, H-2), 5.43 (dd, 1H, $J = 7.7$, 2.0 Hz, H-18), 6.02 (dd, 1H, $J = 7.7$, 1.9 Hz, H-19), 6.40 (dd, 1H, $J = 7.9$, 2.0 Hz, H-16), 6.47 (dd, 1H, $J = 7.9$, 1.9 Hz, H-15), 6.57 (d, 1H, $J = 7.7$ Hz, H-11), 6.65 (d, 1H, $J = 7.7$ Hz, H-10), 7.26 (dd, 1H, $J = 8.3$, 1.9 Hz, H-6), 7.47 (d, 1H, $J = 8.3$ Hz, H-7), 7.72 (d, 1H, $J = 1.9$ Hz, H-4); ^{13}C NMR δ 21.8 (5-Me), 30.1 (C-12), 33.2 (C-2), 33.6 (C-1), 34.5 (C-13), 111.4 (C-7), 122.5 (C-4), 123.6 (C-3a), 126.3 (C-19), 126.7 (C-3b), 126.9 (C-9), 127.4 (C-18), 127.6 (C-6), 128.9 (C-11), 132.3 (C-5), 132.3_9, 132.4_2, 132.4_5 (C-10, C-15, C-16), 136.5 (C-3), 137.9 (C-17), 139.0 (C-14), 154.1 (C-7a), 155.2 (C-8a); MS, *m/e* (rel. intens.) 312 (M^+, 24), 209 (16), 208 (base), 178 (6), 165 (5), 104 (3). Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.39; H, 6.48.

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