[4 + 2] Cycloadditions of Substituted Homobenzoquinones with Cyclopentadiene

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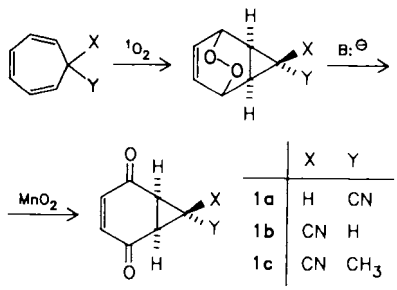
The Diels-Alder reaction of homobenzoquinones with cyano-substituted cyclopropane rings and cyclopentadiene affords the *endo/anti* and the *exo/syn* cycloadducts, the former preferred by four- to fivefold. X-ray structure analyses and nuclear Overhauser enhancements (NOE) were necessary to define the stereochemistry of these products. The lower reactivity and stereoselectivity compared to *p*-benzoquinone is attributed to unfavorable steric effects.

[4 + 2]-Cycloadditionen substituierter Homobenzochinone mit Cyclopentadien

Diels-Alder-Reaktionen von Homobenzochinonen, die am Cyclopropanring Cyan-Substituenten tragen, und Cyclopentadien führen zu *endo/anti*- und zu *exo/syn*-Cycloaddukten, wobei das erste in etwa vier- bis fünffachem Überschuß gebildet wird. Die Stereochemie dieser Produkte konnte mit Hilfe von Röntgenstrukturanalysen und Nuklear-Overhauser-Experimenten definiert werden. Die niedrigere Reaktivität und schlechtere Stereoselektivität dieser Reaktionen, verglichen mit *p*-Benzochinon, wird auf ungünstige sterische Effekte zurückgeführt.

The chemistry of homoquinones **1** is relatively little explored, mainly because these synthetically potentially useful dienophiles are not readily available[1]. A convenient preparative route to these compounds was worked out recently by us[2], starting from appropriately 7,7-disubstituted cycloheptatrienes and employing singlet oxygen as key reagent (Eq. 1).



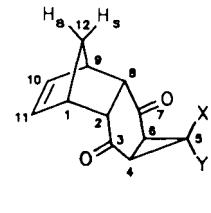
	X	Y
1a	H	CN
1b	CN	H
1c	CN	CH_3

(Eq. 1)

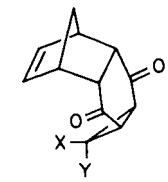
In this way, sufficient amounts of these useful building blocks with defined stereochemistry are conveniently accessible. Presently we report on the Diels-Alder reaction of the homoquinones **1a–c** with cyclopentadiene.

In principle four stereoisomers are possible, namely *endo/anti*-**2**, *endo/syn*-**2**, *exo/anti*-**2**, and *exo/syn*-**2**, but presumably for steric reasons only the *endo/anti* and *exo/syn* isomers are produced, with the *endo/anti* configuration dominating. The results are summarized in Table 1.

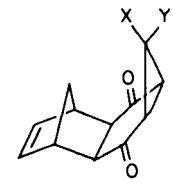
While the structures proposed for the cycloadducts **2** were in good accord with the spectral data (IR, ^1H and ^{13}C NMR, MS; cf. Experimental Section), ambiguities persisted con-



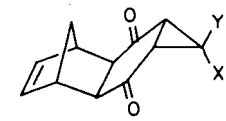
endo/anti-**2**



endo/syn-**2**



exo/syn-**2**



exo/anti-**2**

Table 1. Product yields in the [4 + 2] cycloaddition of homobenzoquinones **1** with cyclopentadiene[a]

Homobenzoquinone	Product balance[b] (%)	Relative yields (%)[c] *endo,anti*-**2**	*exo,syn*-**2**
1a	56	83	17
1b	94	83	17
1c	76	80	20

[a] Run in benzene at 79°C for 3 h. – [b] After silica gel chromatography, except for **1b**. – [c] Determined by ^1H NMR (400 MHz) of the crude reaction mixture; normalized to 100%.

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cerning their stereochemical assignments. Fortunately, crystal structure determinations were successful for the major isomers *endo/anti*-**2a** and *endo/anti*-**2c** (cf. Figure 1 and Tables 2–4). This also defined unequivocally the stereochemistry of the major isomer *endo/anti*-**2b**. However, the minor stereoisomers **2**, which could not be isolated in pure form even by preparative HPLC, required differential ^{1}H-NMR nuclear Overhauser enhancement (NOE) studies directly on the crude reaction mixture.

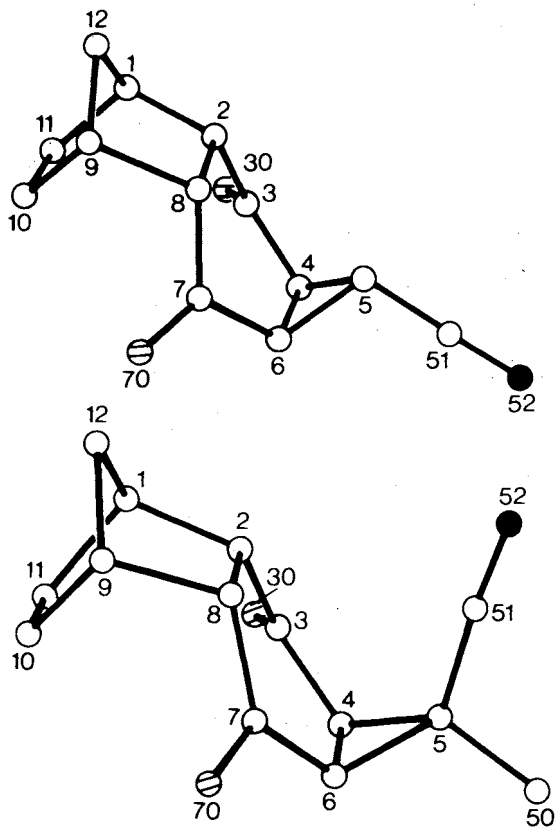

Figure 1. Perspective drawings of the molecular structures of the *endo/anti* cycloadduct **2a** (top) and **2c** (bottom); the numbering of the atoms corresponds to that of Tables 3 and 4, respectively. Open, solid, and hatched circles are carbon, nitrogen, and oxygen atoms, respectively

In the major isomer *endo/anti*-**2a** the cyclopropane protons 4,5,6-H give rise to an AB_2 system, easily recognized in the $\delta = 2.6-2.8$ region. Irradiation of 5-H at $\delta = 2.77$ induces a 5.4% enhancement of a multiplet at $\delta = 3.12$, which is assigned to the zero-bridge protons 2,8-H. The reverse experiment brings about a 14.2% enhancement of the 5-H signal. Also the perturbation of 2,8-H induces positive 6.1% and negative −1.1% enhancements of the signals of the methano protons 12s-H and 12a-H, respectively. 2,8-H are, therefore, *exo* oriented in the major adduct **2a** derived from *endo* addition to cyclopentadiene. The strong interactions between 5-H and 2,8-H and the absence of any between cyclopropane and olefinic protons reveal that the cyclopropane ring is *exo* oriented with respect to the norbornene moiety.

In the minor isomer *exo/syn*-**2a** the cyclopropane 4,5,6-H signals are nearly degenerate and are located at $\delta = 2.85-2.86$. Irradiation in this region causes 7.5% enhancement of a doublet at $\delta = 2.39$, to be attributed to the zero-bridge protons 2,8-H. Their perturbation

Table 2. X-ray operations and results of the *endo/anti* cycloadducts **2a** and **2c**

Crystallographic Section		
Empirical formula	$C_{13}H_{11}NO_2$	$C_{14}H_{13}NO_2$
Molecular mass	213.24	227.26
a [pm]	1779.5(18)	978.5(3)
b [pm]	992.6(9)	1495.0(7)
c [pm]	631.2(11)	787.0(2)
β [deg]	105.13(12)	
V [pm$^3 \cdot 10^{-6}$]	1076(8)	1151.3(5)
Z	4	4
d (calcd) [g · cm^{-3}]	1.316	1.290
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Data Collection		
Diffractometer	Syntex P3	
Radiation	Mo-K_α	
Monochromator	graphite	
Crystal size [nm]	0.3 × 0.7 × 0.1	0.4 × 0.7 × 0.3
Data collection mode	ω-scan	
Theta range [deg]	1.75–27.5	
Recip. latt. segment	$h = 0-23$	0–12
	$k = 0-12$	0–19
	$l = \bar{8}-8$	0–10
No. refl. measd.	1751	1444
No. unique refl.	1638	1429
No. refl. $F > 3\sigma(F)$	1374	1375
Lin. abs. coeff. [cm^{-1}]	0.84	0.82
Abs. correction	ψ-scan	
Structural Analysis and Refinement		
Solution by	direct methods	
Method of refinement [a]		
Parameter/F_o ratio	0.106	0.112
R,R_w	0.064	0.061
Program used	SHELXTL [b]	

[a] Anisotropic block diagonal least squares; hydrogen positions were calculated and considered isotropically. — [b] H. M. Sheldrick: SHELXTL, Universität Göttingen, 1985, unpublished results.

Table 3. Positional [× 10^4] and thermal [pm^2 × 10^{-1}] parameters of the atoms of the cycloadduct *endo/anti*-**2a**. For numbering of the atoms cf. Figure 1; the standard deviations are given in parentheses

	x	y	z	U
C(50)	92(6)	10821(3)	11813(7)	55(2)*
C(7)	-480(5)	8287(3)	10823(6)	42(1)*
C(3)	647(5)	9243(3)	7893(6)	43(1)*
O(30)	1425(4)	9412(3)	6750(5)	73(2)*
C(10)	188(6)	6872(3)	8371(7)	54(2)*
C(5)	-266(4)	10037(3)	10662(6)	39(1)*
C(6)	306(5)	9135(3)	11135(6)	42(1)*
O(70)	-493(6)	7715(3)	11897(5)	79(2)*
C(1)	-391(6)	7894(3)	6316(6)	50(2)*
C(2)	-610(5)	8660(3)	7608(5)	37(1)*
C(4)	894(4)	9614(3)	9632(6)	41(1)*
C(11)	730(5)	7298(4)	7058(8)	57(2)*
C(51)	-1624(5)	10124(3)	9912(6)	43(1)*
N(52)	-2670(4)	10248(3)	9360(7)	64(2)*
C(8)	-1222(4)	8172(3)	9173(6)	36(1)*
C(12)	-1668(5)	7327(4)	6702(8)	59(2)*
C(9)	-1287(5)	7179(3)	8569(7)	47(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 4. Positional [$\times 10^4$] and thermal [$pm^2 \times 10^{-1}$] parameters of the atoms of the cycloadduct *endo/anti*-**2c**. For numbering of the atoms cf, Figure 1; the standard deviations are given in parentheses

	x	y	z	U
O(70)	2799(2)	5831(3)	2584(5)	68(1)*
C(8)	3009(2)	3691(4)	1157(6)	45(1)*
O(30)	1964(2)	3728(4)	-4672(4)	85(1)*
C(7)	2527(2)	4863(4)	1511(6)	47(1)*
C(6)	1669(2)	4791(4)	469(6)	50(1)*
C(11)	3653(2)	4602(5)	-2259(8)	67(2)*
C(3)	2037(2)	3638(4)	-2727(6)	54(1)*
C(10)	3877(2)	5141(5)	-268(8)	65(2)*
C(4)	1412(2)	4133(4)	-1741(6)	54(1)*
C(1)	3496(2)	3129(5)	-1999(7)	62(2)*
C(2)	2749(2)	3029(4)	-1170(6)	48(1)*
N(52)	-87(2)	3266(5)	808(7)	90(2)*
C(5)	1298(2)	3434(4)	243(6)	49(1)*
C(51)	515(2)	3346(5)	535(7)	62(2)*
C(9)	3877(2)	4035(5)	1358(7)	60(2)*
C(12)	4110(2)	2826(5)	169(8)	72(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

induces 6.7% enhancement of the cyclopropane signal and 2.2% enhancement of the olefinic 10,11-H signals at $\delta = 6.19$ (2.1% enhancement of 2,8-H in the reverse experiment). The 2,8-H protons, therefore, point toward the *endo* direction in the *exo* adduct to cyclopentadiene. The degeneracy of the 4,5,6-H protons prevents assigning the orientation of the cyclopropane ring, i.e. the observed interaction with 2,8-H could be due to the proximity of the 4,6-H protons in *endo/anti*-**2a** or to that of the 5-H protons in *exo/syn*-**2a**.

The *exo* and *endo* orientations of the 2,8-H protons in *endo/anti*- and *exo/syn*-**2a**, respectively, agree with the coupling patterns[3], as determined by a series of decoupling experiments. In the *endo/anti*-**2a** isomer $J_{1,2} = J_{8,9} = 2.1$ Hz was measured, but no coupling of 2,8-H with 12a-H was detected. In the *exo/syn*-**2a** isomer the long-range W-couplings $J_{2,12a} = J_{8,12a} = 1.8$ Hz were observed, but no coupling between the zero-bridge 2,8-H and bridgehead 1,9-H protons.

By comparison with **2a**, the zero-bridge protons 2,8-H of the major isomer *endo/anti*-**2b** can be identified with the multiplet at $\delta = 3.35$. Their saturation induces positive 5.3% and negative −0.9% enhancements of the 12s-H and 12a-H protons, respectively. The 2,8-H protons are, therefore, *exo* oriented.

In the minor isomer *exo/syn*-**2b** the 2,8-H protons can be identified as a doublet at $\delta = 2.65$. From their saturation there follows 2.0% enhancement of the olefinic protons 10,11-H (1.8% enhancement of the 2,8-H protons in the reverse experiment). Therefore, the zero-bridge protons 2,8-H point toward the *endo* direction. In this isomer the cyclopropane protons are separated sufficiently (5-H at $\delta = 2.51$ and 4,6-H at $\delta = 2.74$) allowing selective saturation. No effect is induced on other multiplets. This suggests that the minor isomer has the *exo/syn* configuration **2b**.

In the case of the major isomer *endo/anti*-**2c**, saturation of the zero-bridge protons 2,8-H at $\delta = 3.36$, gives positive 5.4% and negative −0.9% enhancement of the 12s-H and 12a-H signals respectively, and the protons are, therefore, *exo* oriented. The cyclopropane methyl protons at $\delta = 1.58$ and the 4,6-H protons at $\delta = 2.34$ interact reciprocally upon saturation (2.1% enhancement of methyl group and 9.0% enhancement of the 4,6-H protons), but do not perturb the remaining system.

The zero-bridge 2,8-H proton signals in the minor isomer *exo/syn*-**2c** are located at $\delta = 2.65$. Upon irradiation in this region, a 2.2% enhancement of the olefinic 10,11-H signals is observed, revealing the *endo* orientation of the former protons. The methyl group at $\delta = 1.63$ interacts only with the 4,6-H protons at $\delta = 2.55$ (2.1% enhancement of methyl group, 8.7% enhancement of 4,6-H protons). Because of the spectral proximity of the 4,6-H and 2,8-H protons, their possible interaction cannot be detected. However, in the *exo/syn* configuration **2c**, the methyl group and the 4,6-H and 2,8-H protons are quasi linearly arranged; upon saturation of the methyl protons no negative enhancement of the 2,8-H protons was discerned. These findings suggest that the minor isomer has the *exo/syn* configuration **2c**.

With respect to the stereochemical course of this [4 + 2] cycloaddition, the *endo* isomer predominates for all three homobenzoquinones **1** by ca. four- to fivefold. Preference for the *anti* versus *syn* stereochemistry of the cyclopropane moiety derives undoubtedly from steric interactions between the incipient carbon−carbon double bond and the X,Y-substituents in the transition state for cycloaddition. Thus, it is not surprising that the *endo/anti*-**2** stereoisomers are the major products for all three homobenzoquinones. This steric repulsion is evidently sufficiently large that the *exo/syn*-**2** stereoisomer (the minor product) is preferred over the *endo/syn* configuration.

An additional point of significance for synthetic utilization concerns the reactivity of these substituted homobenzoquinones compared to *p*-benzoquinone. Clearly, the homobenzoquinones are considerably less reactive as dienophiles. While the cycloaddition of homobenzoquinones with cyclopentadiene proceeds at a reasonable rate in refluxing benzene, with 1,3-cyclohexadiene the reaction must be carried out in an autoclave at 120−130°C to achieve a reasonable rate of conversion. A complex reaction mixture resulted with at least three stereoisomers which could not be separated by preparative HPLC or GC.

The reduced dienophilicity of the homobenzoquinones compared to *p*-benzoquinone derives undoubtedly from steric repulsion with the cyclopropane moiety, but also from diminished stabilization of the cycloaddition transition state through secondary orbital interaction[4]. Furthermore, the LUMO−HOMO gap is unquestionably larger for the homobenzoquinone and thus its dienophilicity lower. Unless high-pressure autoclave reactions are employed, only the most reactive 1,3-dienes will be useful for cycloaddition with the homobenzoquinones **1**. In this context it should be mentioned that catalysis by Lewis acids such as aluminium trichloride proved ineffective.

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Experimental

Melting points are uncorrected and taken on a Reichert Thermovar Kofler apparatus. – Infrared spectra (IR) were obtained from a Beckman Acculab 4 instrument. – ^{1}H-NMR spectra were run either on a Hitachi-Perkin-Elmer R 24 B (60 MHz), Varian EM 360 (90 MHz) or on a Bruker WM 400 (400 MHz) instrument, using TMS as internal standard. – ^{13}C-NMR spectra were taken on a Bruker WM 400 (100.6 MHz) instrument, using $CDCl_3$ as

internal standard. The chemical shifts are reported in δ values. – Mass spectra (MS) were measured on a Varian MAT CH 7. – Combustion analyses for elemental composition were either obtained in-house or from Prof. G. Maiers' staff at the Institute of Organic Chemistry (Gießen). – Thin-layer chromatography (TLC) was run on Polygram SIL/G/UV (40 × 80 mm) from Macherey-Nagel & Co. Column chromatography utilized silica gel (70–230 mesh ASTM, activity III), using an adsorbent–substrate ratio of ca. 100:1. – For analytical HPLC a Kontron liquid chromatograph (Pump 414, UV Detector Uvikon 720 LC, Anacomp Computer) was used, supplied with a LiChrosorb Si 60 (5 μm) column (250 mm × 4 mm).

Commercial reagents and solvents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. Known compounds were prepared according to literature procedures and purified accordingly.

Crystallographic Work on the endo/anti Cycloadducts **2a** *and* **2c**: The operations and results are summarized in Table 2, the positional and thermal parameters in Tables 3 and 4, respectively, for **2a** and **2c**, and the structures exhibited in Figure 1. Further details of the structure determination are deposited at the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (FRG). These data are available on request with quotation of the registry number CSD 52716, the authors, and the reference to this publication.

Nuclear Overhauser Spectroscopy of the Cycloadducts **2a–c**: The NOE experiments were carried out with a Bruker WP 200 SY instrument. The sample (in $CDCl_3$) was freed from oxygen through sonication under N_2 gas purging. The usual procedure for gated irradiation experiments was modified[5] and the selected resonance was saturated by an 8-s cyclic perturbation of all lines with a 38–40-dB attenuation of a nominal 0.2-W decoupling power. The enhancements (in %) were obtained from the multiplier of the reference spectrum by bringing the observed multiplet to exact matching with the corresponding multiplet in the perturbed spectrum. Errors are ca. 0.3%. By careful choice of the multiplier, in most cases it was possible in the differential mode to single out a pure multiplet from a bunch of overlapping signals.

General Procedure for the Cycloadditions of Homobenzoquinones and Cyclopentadiene: Mixtures of the homobenzoquinones **1a–c** and a fourfold excess of freshly distilled cyclopentadiene in ca. 10 ml of absol. benzene were refluxed while stirring vigorously. The consumption of starting materials was monitored by ^1H NMR. The solvent and excess of cyclopentadiene were removed by roto-evaporation (ca. 40°C at 20 Torr) and the residue was purified by flash chromatography on silica gel or by recrystallization.

Cycloaddition of Homobenzoquinone **1a**[2b]: Following the general procedure, 70.0 mg (0.480 mmol) of homobenzoquinone **1a** and 130 mg (1.97 mmol) of cyclopentadiene in 10 ml of benzene were refluxed for 3 h. Flash chromatography with CH_2Cl_2 as eluant gave 100 mg (0.469 mmol) of a mixture of the cycloadducts *endo/anti*-**2a** and *exo/syn*-**2a** (R_f = 0.21) in a ratio of ca. 83:17. Repeated recrystallization (ca. 10 ×) from ethyl acetate/petroleum ether (1:1) gave 40.0 mg (0.188 mmol) of cycloadduct *endo/anti*-**2a** as colorless needles, m.p. 211–212°C. – IR (KBr): 3050 cm^{-1}, 3005, 2995, 2985, 2965, 2930, 2250, 1700, 1260, 720. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.23 (dtt, $J_{12s,12a}$ = 8.9 Hz, $J_{1,12s}$ = $J_{9,12s}$ = 1.5 Hz, $J_{10,12s}$ = $J_{11,12s}$ = 0.6 Hz, 1H, 12s-H), 1.46 (dt, $J_{1,12a}$ = $J_{9,12a}$ = 1.9 Hz, 1H, 12a-H), 2.66 (m, $J_{4,5}$ = $J_{5,6}$ = 5.0 Hz, 2H, 4,6-H), 3.12 (m, $J_{1,2}$ = $J_{9,8}$ = 2.1 Hz, 2H, 2,8-H), 3.44 (m, 2H, 1,9-H), 6.08 (m, $J_{9,10}$ = $J_{1,11}$ = 1.5 Hz, 2H, 10,11-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ 10.3 (d, C-5), 35.6 (d, C-4,6), 45.0 (d, C-2,8), 46.3 (t, C-12), 48.4 (d, C-1,9), 115.7 (s, CN), 136.9 (d, C-10,11), 199.8 (s, C-3,7). – MS (70 eV): *m/z* (%) = 213 (3, M^+), 185 (1), 91 (8), 66 (100, $C_5H_6^+$), 39 (11).

$C_{13}H_{11}NO_2$ (213.2) Calcd. C 73.23 H 5.19 N 6.57
Found C 73.14 H 5.08 N 6.74

Its X-ray structure is exhibited in Figure 1 (top), the data are collected in Tables 2 and 3.

Cycloadduct exo/syn-**2a**: ^1H NMR ($CDCl_3$, 200 MHz; crude reaction mixture): δ = 0.79 (br. d, $J_{12a,12s}$ = 9.5 Hz, $J_{1,12s}$ = $J_{9,12s}$ = 1.5 Hz, $J_{10,12s}$ = $J_{11,12}$ = 0.6 Hz, 1H, 12s-H), 1.34 (dquint, $J_{1,12a}$ = $J_{9,12a}$ = 1.9 Hz, 1H, 12a-H), 2.39 (d, $J_{2,12a}$ = $J_{8,12a}$ = 1.8 Hz, 2H, 2,8-H), 2.89 (m, 2H, 4,6-H), 3.56 (m, 2H, 1,9-H), 6.19 (m, $J_{9,10}$ = $J_{1,11}$ = 1.9 Hz, 2H, 10,11-H).

Cycloaddition of Homobenzoquinone **1b**[2b]: Following the general procedure, 250 mg (1.70 mmol) of homobenzoquinone **1b** and 360 mg (5.40 mmol) of cyclopentadiene in ca. 10 ml of benzene were refluxed for 3 h. The brown residue, 340 mg (1.59 mmol) of a mixture of the cycloadducts *endo/anti*-**2b** and *exo/syn*-**2b** (ratio ca. 83:17), was sublimed at 140°C/15 Torr. Repeated recrystallization (ca. 10 ×) from CH_2Cl_2/petroleum ether (1:1) gave 130 mg (0.598 mmol) of cycloadduct *endo/anti*-**2b** as colorless prisms, m.p. 186–187°C. – IR (KBr): 3070 cm^{-1}, 3050, 3005, 2990, 2980, 2975, 2970, 2945, 2260, 1705, 1690, 1170, 720. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.34 (dtt, $J_{12s,12a}$ = 9.0 Hz, $J_{1,12s}$ = $J_{9,12s}$ = 1.4 Hz, $J_{10,12s}$ = $J_{11,12s}$ 0.6 Hz, 1H, 12s-H), 1.48 (dt, $J_{1,12a}$ = $J_{9,12a}$ = 1.9 Hz, 1H, 12a-H), 2.43 (m, $J_{4,5}$ = $J_{5,6}$ = 8.7 Hz, 1H, 5-H), 3.35 (m, $J_{1,2}$ = $J_{9,5}$ = 2.0 Hz, 2H, 2,8-H), 3.54 (m, 2H, 1,9-H), 6.13 (m, $J_{9,10}$ = $J_{1,11}$ = 1.7 Hz, 2H, 10,11-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 9.6 (d, C-5), 35.2 (d, C-4,6), 46.6 (d, C-2,8), 47.0 (t, C-12), 51.1, (d, C-1,9), 116.2 (s, CN), 137.3 (d, C-10,11), 200.9 (s, C-3,7). – MS (70 eV): *m/z* (%) = 213 (7, M^+), 185 (5), 91 (12), 66 (100, $C_5H_6^+$), 39 (15).

$C_{13}H_{11}NO_2$ (213.2) Calcd. C 73.23 H 5.20 N 6.57
Found C 73.02 H 5.30 N 6.41

Cycloadduct exo/syn-**2b**: ^1H NMR ($CDCl_3$, 200 MHz, crude reaction mixture): δ = 0.90 (br. d, $J_{12s,12a}$ = 9.5 Hz, $J_{1,12s}$ = $J_{9,12s}$ = 1.7 Hz, $J_{10,12s}$ = $J_{11,12s}$ = 0.5 Hz, 1H, 12s-H), 1.35 (dquint, $J_{1,12a}$ = $J_{9,12a}$ = 1.8 Hz, 1H, 12a-H), 2.51 (m, $J_{4,5}$ = $J_{5,6}$ = 8.6 Hz, 1H, 5H), 2.65 (d, $J_{2,12a}$ = $J_{8,12a}$ = 1.8 Hz, 2H, 2,8-H), 2.74 (m, 2H, 4,6-H), 3.63 (m, 2H, 1,9-H), 6.25 (m, $J_{9,10}$ = $J_{1,11}$ = 1.8 Hz, 2H, 10,11-H).

Cycloaddition of Homobenzoquinone **1c**[6]: Following the general procedure, 200 mg (1.24 mmol) of homobenzoquinone **1c** and 130 mg (2.00 mmol) of cyclopentadiene in ca. 10 ml of benzene were refluxed for 3 h. Flash chromatography with CH_2Cl_2/petroleum ether/ethyl acetate (1:6:3) as eluant gave 220 mg (0.968 mmol) of a mixture of the cycloadducts *endo/anti*-**2c** and *exo/syn*-**2c** (R_f = 0.30) in a ratio of ca. 80:20. Thick-layer chromatography on silica gel, eluting with CH_2Cl_2/petroleum ether/ethyl acetate (20:1:4) and repeated recrystallization (ca. 8 ×) from CCl_4, gave 20.0 mg (0.088 mmol) of cycloadduct *endo/anti*-**2c** as colorless plates, m.p. 159–160°C. – IR (KBr): 3070 cm^{-1}, 3040, 2995, 2985, 2970, 2960, 2240, 1700, 1680, 1140, 720. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.33 (dtt, $J_{12s,12a}$ = 8.9 Hz, $J_{1,12s}$ = $J_{9,12s}$ = 1.5 Hz, $J_{10,12s}$ = $J_{11,12s}$ = 0.5 Hz, 1H, 12s-H), 1.46 (dt, $J_{1,12a}$ = $J_{9,12a}$ = 1.9 Hz, 1H, 12a-H), 1.58 (s, 3H, CH_3), 2.34 (s, 2H, 4,6-H), 3.36 (m, $J_{1,2}$ = $J_{9,8}$ = 2.2 Hz, 2H, 2,8-H), 3.53 (m, 2H, 1,9-H), 6.11 (m, $J_{9,10}$ = $J_{1,11}$ = 1.5 Hz, 2H, 10,11-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.6 (s, C-5), 22.4 (q, CH_3), 43.3 (d, C-4,6), 46.7 (d C-2,8), 47.0 (t, C-12), 50.7 (d, C-1,9), 118.4 (s, CN), 137.1 (d, C-10,11), 200.9 (s, C-3,7). – MS (70 eV): *m/z* (%) = 227 (5, M^+), 199 (6), 184 (1), 91 (8), 66 (100, $C_5H_6^+$), 39 (11).

$C_{14}H_{13}NO_2$ (227.3) Calcd. C 73.99 H 5.76 N 6.16
Found C 74.23 H 5.97 N 5.83

Its X-ray structure is exhibited in Figure 1 (bottom), the data are collected in Tables 2 and 4.

*Cycloadduct exo/syn-***2c**: ^{1}H NMR ($CDCl_3$, 200 MHz, crude reaction mixture): δ = 0.88 (br. d, $J_{12s,12a}$ = 9.3 Hz, $J_{1,12s}$ = $J_{9,12s}$ = 1.7 Hz, 1H, 12s-H), 1.32 (dquint, $J_{1,12a}$ = $J_{9,12a}$ = 1.8 Hz, 1H, 12a-H), 1.63 (s, 3H, CH_3), 2.55 (s, 2H, 4,6-H), 2.65 (d, $J_{2,12a}$ = $J_{8,12a}$ = 1.8 Hz, 2H, 2,8-H), 3.60 (m, 2H, 1,9-H), 6.25 (m, $J_{9,10}$ = $J_{1,11}$ = 1.9 Hz, 2H, 10,11-H).

CAS Registry Numbers

1a: 72612-77-2 / **1b**: 72612-78-3 / **1c**: 113088-04-3 / *endo/anti-***2a**: 113088-05-4 / *exo/syn-***2a**: 113158-80-8 / *endo/anti-***2b**: 113158-81-9 / *exo/syn-***2b**: 113158-82-0 / *endo/anti-***2c**: 113088-06-5 / *exo/syn-***2c**: 113158-83-1 / cyclopentadiene: 542-92-7

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