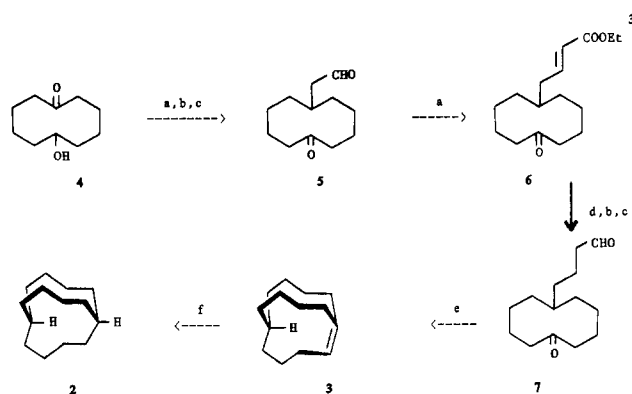


Scheme 1^a

^a (a) (EtO)₂P(O)CH₂COOEt, NaH, THF; (b) LiAlH₄, THF; (c) pyridinium chlorochromate, CH₂Cl₂, NaOAc; (d) H₂, Pd/C, ethanol; (e) TiCl₃, Zn-Cu, dimethoxyethane, Δ; (f) H₂, PtO₂, ether, 50 psi, 3 days.

aldehyde 7 taking place in 30% yield to give *in*-bicyclo[4.4.4]-1-tetradecene (3).⁷ In addition to *in*-isomer 3, a small amount of isomeric product—presumably the corresponding out isomer—was detected by GC/MS.

That the titanium-induced cyclization did indeed give the *in* isomer 3 rather than the alternative out isomer was confirmed by subsequent reactions. Thus, catalytic hydrogenation of 3 over Adams' catalyst proceeded slowly in ether solution to give *in*,*out*-bicyclo[4.4.4]tetradecane (2), which shows six signals in its ¹³C NMR spectrum and shows two unique one-proton absorptions at δ 2.50 and 0.81 in its ¹H NMR spectrum,⁸ assignable to the two different bridgehead protons. Since the resonance at δ 2.50 did not appear when the reduction was carried out with deuterium rather than hydrogen, we assign that signal to the outside hydrogen and the signal at δ 0.81 to the inside hydrogen. The unusually high upfield shift of the inside hydrogen is presumably due to anisotropic shielding by nearby C-C bonds.

One of the most intriguing chemical consequences of *in*,*out* bicycloalkane geometry is the possibility of intrabridgehead interactions.³ Treatment of olefin 3 with trifluoroacetic acid in CDCl₃ at room temperature yielded a stable solution that showed a broad one-proton singlet at δ -3.5 in its ¹H NMR spectrum and contained only three peaks at δ 18.7, 40.8, and 139.3 in its ¹³C NMR spectrum. When deuterated trifluoroacetic acid was used, the recovered olefin contained 11 deuterium atoms. These data are consistent with the μ -hydrido-bridged structure 8, in which



the inside hydrogen bears a partial negative charge and is symmetrically disposed between the two positively charged bridgehead carbons.⁹ Confirmation of the assignment as a static hydrido-bridged structure rather than as a pair of rapidly equilibrating degenerate cationic structures was obtained by using the Saunders isotopic perturbation technique.¹⁰ Introduction of a deuterium atom into the cation by treatment of 3 with deuterated fluoro-

(7) ¹H NMR (300 MHz, CDCl₃) δ 5.42 (br dd, 1 H), 3.35 (br dd, 1 H) 2.54 (dd, 1 H), 2.34 (q, 1 H), 2.18 (m, 2 H), 2.1-0.85 (m, 18 H); ¹³C NMR (CDCl₃) δ 143.0, 131.7, 36.3, 36.0, 35.1, 33.7, 33.6, 32.3, 29.7, 28.9, 27.5, 26.4, 25.8, 23.1; mass spectrum, *m/z* M⁺ 192.

(8) Mp 159-161 °C (sealed tube); ¹H NMR (CDCl₃) δ 2.50 (m, 1 H), 1.73 (dd, 6 H), 1.53 (m, 12 H), 1.13 (dd, 6 H), 0.81 (m, 1 H); ¹³C NMR (CDCl₃) δ 36.1, 31.0, 29.7, 28.7, 25.0, 7.7; mass spectrum, *m/z* M⁺ 194.

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sulfonic acid at -92 °C, and observation of the resultant ¹³C NMR spectrum, indicated a small splitting of the peak at δ 136.7 into two peaks at δ 137.1 and 136.3. Were two rapidly equilibrating structures involved, a much larger splitting would be expected.¹⁰

We are continuing our study of the intrabridgehead chemistry of the *in*,*out*-bicyclo[4.4.4]tetradecane system.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Experimental section with preparation and spectra of 2 and 3 (2 pages). Ordering information is given on any current masthead page.

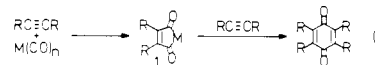
Convergent, High-Yield, Regioselective Synthesis of Substituted Benzoquinones from Maleoylcobalt Complexes and Alkynes

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Treatment of stoichiometric transition-metal carbonyl reagents with alkynes often produces benzoquinones or benzoquinone complexes.²⁻¹⁵ The generation of these organic products has been rationalized in terms of an initial maleoylmatal complex formation, 1, followed by subsequent reaction with an alkyne to give a benzoquinone (eq. 1).^{16,17} Early work by Maitlis provided strong



support for this pathway to quinones.⁷ Our studies on the synthesis of analogous phthaloylmatal complexes^{18,19} and their reaction with

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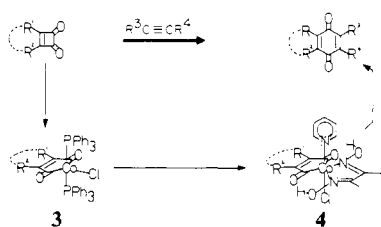
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Scheme I



alkynes to give naphthoquinones^{19,20} confirmed the latter half of the reaction shown in eq 1 and gave us a powerful method for the synthesis of naphthoquinone-derived natural products.^{21,22} We now report that readily available cyclobutenediones **2a-c** react with $ClCo(PPh_3)_3$ to give high yields of stable, crystalline maleoylcobalt complexes **3a-d**, which, after ligand exchange to 6-coordinate dimethylglyoxime complexes **4**, react with a wide variety of alkynes to provide high yields of substituted benzoquinones in a convergent and regioselective manner (Scheme I).²⁶

Our current results are listed in Table I. Reaction of cyclobutenediones **2a-d** with $ClCo(PPh_3)_3$ (1.5–2.5 equiv) proceeded in benzene between room temperature and 60 °C, depending on the substrate, and gave the air-stable maleoylcobalt complexes **3a-d** in yields of 90%, 99%, 86%, and 63%, respectively, after crystallization. Trigonal bipyramidal structures with trans diaxial PPh_3 ligands were assigned on the basis of spectroscopic data (supplementary material) and analogy with our earlier studies of phthaloylcobalt complexes.^{18,19} As in our previous investigations of the phthaloylcobalt analogues,^{19,20} treatment of the bisphosphine complexes **3** with an alkyne in the presence of $AgBF_4$ gave good yields of benzoquinones (i.e., **3a** + 3-hexyne \rightarrow 2,3-diethyl-5,6-dimethylbenzoquinone, 70%; **3d** + 3-hexyne \rightarrow 2,3-diethyl-5-methoxy-6-methylbenzoquinone, 77%). However, in concurrent studies with phthaloylcobalt complexes directed at eliminating the need for $AgBF_4$ in this chemistry, we discovered that the simple expedient of treating the bis(triphenylphosphine)cobalt complexes with 1 equiv of dimethylglyoxime in pyridine at room temperature gave very high yields of dimethylglyoxime complexes which reacted

Table I. Conversion of Cyclobutenediones into Benzoquinones

cyclobutenedione ^a	% 3 ^b	% 4 ^b	alkyne	benzoquinone (isomer ratio ^c , yield ^d)
2a				
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone (81%) ^e
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone (85%) ^e
2b				
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone (85%) ^e
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone (79%) ^e
2c				
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone (88%) ^e
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone (84%) ^e
2d				
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone (80%) ^f
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone + regioisomer (5:1, 81%) ^f
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone + regioisomer (3:7, 1, 89%) ^f
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone + regioisomer (2:8, 1, 73%) ^f
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone + regioisomer (3:7, 1, 64%) ^{f,g}
			\equiv	1,8-dimethyl-2,3-dimethyl-5,6-dimethylbenzoquinone + regioisomer (13:5, 1, 81%) ^f

^aReference 23. ^bYields refer to purified, recrystallized material.

^cRatios were determined by integration of the 270-MHz spectra and by capillary gas-liquid chromatography. ^dYields refer to isolated material purified by chromatography. ^eReactions were performed 0.1 M in acetone at 80 °C for 90 min using 1.5 equiv of alkyne and 1.0 equiv of $CoCl_2 \cdot 6H_2O$ to coordinate any liberated pyridine or dimethylglyoxime. ^fReactions were performed 0.1 M in CH_2Cl_2 at 100 °C for 6 h by use of 2.0 equiv of alkyne. ^gPartial reduction to the hydroquinone occurred.

with alkynes on heating *without added* $AgBF_4$ and produced high yields of quinones.²⁸ Similar treatment of maleoylcobalt complexes **3a-d** provided the air-stable dimethylglyoxime variants **4a-d** in 83%, 90%, 86%, and 87% yields, respectively. The maleoylcobalt complexes from cyclobutenediones **2a-c** were heated with 3-hexyne and 1-hexyne (1.5 equiv, 0.1 M in acetone, 1 equiv of $CoCl_2 \cdot 6H_2O$,²⁹ 80 °C, 90 min) and gave, after chromatography, the corresponding benzoquinones in very good yields (Table I). Reaction of complex **4d** was surveyed with a wider variety of alkynes in order to assess the inherent regiochemical preference of this complex (2.0 equiv of alkyne, 0.1 M in CH_2Cl_2 , 6 h, 100 °C).³⁰ Reaction of **4d** with propyne gave a 5.2:1 mixture (81%) of 2-methoxy-3,5-dimethylbenzoquinone and 3-methoxy-2,5-dimethylbenzoquinone identified after separation (SiO_2 , 5:1 hexane/ether, four passes) by comparison of IR, UV, and mp of the separate isomers with data available in the literature.^{31,32} The major/minor quinone regioisomers produced from reaction of 1-hexyne and 3,3-dimethyl-1-butene with **4d** showed the same chromatographic trends (major isomer less polar) and 270-MHz ¹H NMR spectroscopic trends (vinyl H of major isomer absorbed upfield of minor isomer) as the propyne derived regioisomers, and structural assignments were made accordingly. Ethyl tetrolate, an alkyne that failed to react in the $AgBF_4$ system, produced a

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(27) A simple, large-scale, reproducible preparation of this material is described in ref 19.

(28) The rationale behind and full details of this ligand modification will be discussed in: Liebeskind, L. S.; Baysdon, S. L.; Goedken, V., manuscript in preparation.

(29) Addition of $CoCl_2 \cdot 6H_2O$ to the reaction mixture gave higher yields of product in shorter reaction times perhaps by coordinating any free pyridine or dimethylglyoxime.²⁸ Further studies are under way to clarify the role of $CoCl_2 \cdot 6H_2O$ in this chemistry.

(30) The resulting methoxymethylbenzoquinone substitution pattern is found in many naturally occurring quinones. Added $CoCl_2 \cdot 6H_2O$ was found to diminish the regioisomeric ratio for at least one alkyne and therefore was not used in this preliminary screening.

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64% yield of product regioisomers (3.7:1 ratio) and the major regioisomer was identified by conversion into 2,4-dimethyl-3,5,6-trimethoxybenzyl alcohol, which was identical with an authentic sample prepared from 2,6-dimethylbenzoquinone (see supplementary material). Finally, very high regioselectivity was achieved in the reaction of 1-ethoxypropyne with cobalt complex **4d** to predominate the 2,5-dialkoxybenzoquinone regioisomer (13.5:1, 81% yield).³³

Efforts to improve³⁴ and further explore the regiochemistry of this highly convergent route to quinones are under way as a prelude to the use of this method in the total synthesis of quinone-based natural products.

Acknowledgment. This investigation was supported by PHS Grant CA 26374 awarded by the National Cancer Institute, DHHS.

Supplementary Material Available: Experimental procedures for and physical properties of new compounds (18 pages). Ordering information is given on any current masthead page.

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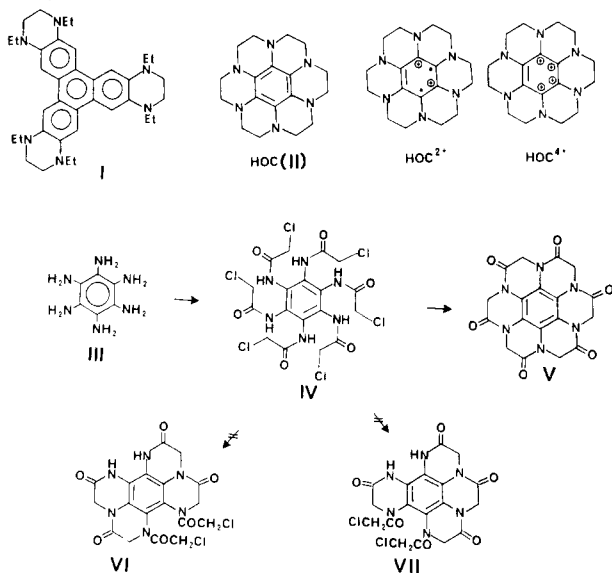
Synthesis of the Hexaaminobenzene Derivative Hexaazaoctadecahydrocoronene (HOC) and Related Cations

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Our approach to the preparation of ferromagnetic organic salts^{1,2} requires cation radicals that are easily oxidizable to dication radicals with triplet ground states. This approach is being pursued with the hexaaminotriphenylene derivative **I**, whose dication is indeed a triplet,¹ but one would expect the triplet-singlet energy gap to be even larger if the central core were a benzene ring. For this reason we have long been interested in HOC (II).^{2,3} A



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benzene ring with six simple dimethylamino substituents was not easily oxidized to the dication,³ apparently because the substituents are twisted by steric interaction. We now wish to report the synthesis and preliminary study of HOC (II), in which the nitrogen atoms can fully contribute to the stabilization of higher oxidation states of the benzene ring. As expected, a variety of cations of II can be prepared or detected. Furthermore, the dication of II is indeed in a triplet electronic state, with the correct spectroscopic properties.

Catalytic hydrogenation (10% Pd/C, EtOAc) of 2,4,6-trinitro-1,3,5-triaminobenzene⁴ afforded crude hexaaminobenzene (III)⁵ in ca. 80% yield. The air-sensitive substance was directly converted to the hexaamide IV⁶ with chloroacetyl chloride in 59% overall yield based on the trinitro compound, and IV was cyclized with 0.4 M NaOEt in EtOH/Me₂SO at room temperature. If the cyclization steps were completely random, the desired product V should have been formed in only 46% yield. The formation of V requires that all the alkylations be, e.g., in a clockwise sense, and any counterclockwise process should block its formation. If the cyclizations had been random but complete as far as possible, they should also have formed products VI and VII. However, we hoped that cyclization might propagate, so that the first alkylation would make it easier to alkylate in the neighboring position. This is indeed the case. The yield of V⁶ is 80%, and other cyclization isomers (VI and VII) are not detected. When only 2 equiv of NaOEt are used with IV, the fully cyclized desired product V is formed in 99% of the theoretical (33%) yield, and IV is recovered in 94% of the theoretical (67%) yield. Presumably the neighboring alkylation is faster when the first cyclization forces a chloroacetyl group into the plane, or possibly cyclization increases the NH acidity.

Reduction of V with borane affords HOC (II) in 77% yield as an air-sensitive solid. The ¹H NMR spectrum of II shows a signal at 3.1 ppm. The EI mass spectrum (70 V) shows M⁺ at 324 and M²⁺ at 162. Cyclic voltammetry of II in CH₃CN at 600 mV/s shows four reversible waves at -0.11, 0.36, 0.87, and 1.25 V vs. SCE. It is interesting that the fourth wave corresponds to the formation of HOC⁴⁺, a tetracation with two π electrons instead of six (ignoring the nitrogen electrons, which of course contribute much to the stability of these cations). The third and fourth waves indicate formation of the first reported derivatives of benzene trication and tetracation.

The cation radical HOC^{•+} was formed by oxidation (with air or I₂, Br₂, or NO⁺SbF₆⁻) as a deep green species, λ_{max} (ε) 716 (10400), 373 (8300), 304 nm (27000). The ESR spectrum showed 23-25 lines. The dication HOC²⁺ was prepared by oxidation of HOC in CH₂Cl₂ with 2 equiv of NO⁺SbF₆⁻ in CH₃CN. It gave a purple solution, λ_{max} (ε) 525 (15000), 360 sh, 316 nm (28000). The frozen solution showed a typical triplet ESR spectrum, with $\Delta m = 2$ at 1485, z lines at 2545 and 3805, and x, y lines at 2825 and 3560 G. From this the value of E is zero, and the value of the zero-field splitting parameter D is 0.059 cm⁻¹, larger than the 0.022 cm⁻¹ for the triplet dication of I¹ but smaller than the 0.101 cm⁻¹ of hexachlorobenzene dication.⁷ The intensity of the $\Delta m = 2$ transition follows the Curie 1/ T law over the temperature range 100-150 K, as expected if the triplet is the ground state.

Further work will be needed to characterize the HOC²⁺ triplet species completely, and to establish whether it can be used to construct an organic ferromagnet. The easy synthesis devised for HOC should make it possible to explore the properties of all the cations that electrochemistry indicates to be accessible.

Acknowledgment. This work has been supported by the National Science Foundation.

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