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 improve[34] 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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[33] 2,5-Dialkoxybenzoquinones are readily distinguished from 2,6-dialkoxybenzoquinones by infrared: Thomson, R. H. "Naturally Occurring Quinones", 2nd ed.; Academic Press: New York, 1971; p 64-69.

[34] We have recently observed a significant increase in the regioselectivity of quinone formation from 1-hexyne and complex **4d** when the reaction was conducted at room temperature in the presence of $SnCl_4$. Under these conditions a 10:1 ratio of regioisomers was formed favoring the same isomer as that shown in Table I.

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

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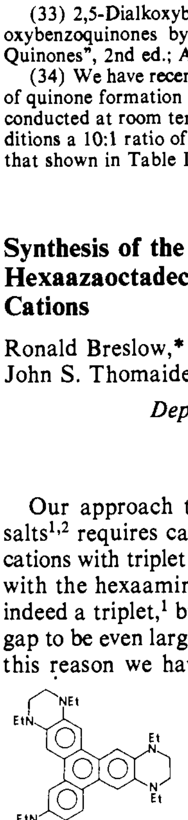
Our approach to the preparation of ferromagnetic organic salts[1,2] requires cation radicals that are easily oxidizable to dications with triplet ground states. This approach is being pursued with the hexaaminotriphenylene derivative I, whose dication is indeed a triplet,[1] but one would expect the 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 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.



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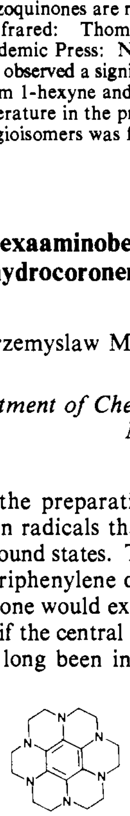
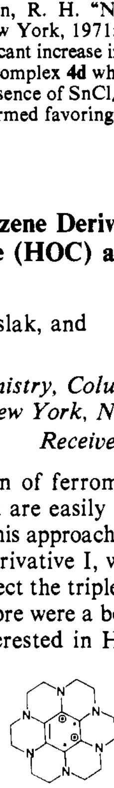
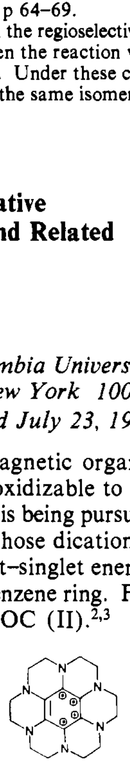


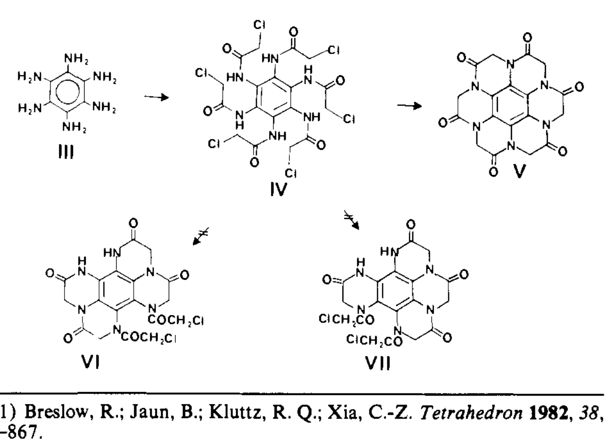
HOC(II)



HOC^{2+}



HOC^{4+}



Catalytic hydrogenation (10% Pd/C, EtOAc) of 2,4,6-trinitro-1,3,5-triaminobenzene[4] afforded crude hexaaminobenzene (III)[5] in ca. 80% yield. The air-sensitive substance was directly converted to the hexaamide IV[6] with chloroacetyl chloride in 59% overall yield based on the trinitro compound, and IV was cyclized with 0.4 M NaOEt in $EtOH/Me_2SO$ 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 akylation would make it easier to alkylate in the neighboring position. This is indeed the case. The yield of V[6] 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 M^{2+} at 162. Cyclic voltammetry of II in CH_3CN 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 HOC^{4+}, 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 I_2, Br_2, or $NO^+SbF_6^-$) as a deep green species, λ_{max} (ϵ) 716 (10400), 373 (8300), 304 nm (27000). The ESR spectrum showed 23–25 lines. The dication HOC^{2+} was prepared by oxidation of HOC in CH_2Cl_2 with 2 equiv of $NO^+SbF_6^-$ in CH_3CN. 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 I[1] 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 HOC^{2+} 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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[5] Backer et al. (Backer, H. J.; van der Baan, Sj. *Recl. Trav. Chim. Pays-Bas* **1937**, *56*, 1175-1186) and ref 4 report this compound by reduction with phenylhydrazine. We find that catalytic hydrogenation is much superior.

[6] Characterized by MS, ^1H NMR, IR, and combustion analysis.

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Registry No. II, 92187-27-4; III, 4444-26-2; IV, 92187-32-1; V, 92187-33-2; HOC^{+}, 92187-28-5; HOC^{2+}, 92187-29-6; HOC^{3+}, 92187-30-9; HOC^{4+}, 92187-31-0; 2,4,6-trinitro-1,3,5-benzenetriamine, 3058-38-6.

Lifetime of a Conformationally Constrained Norrish II Biradical. Photochemistry of *cis*-1-Benzoyl-2-benzhydrylcyclohexane

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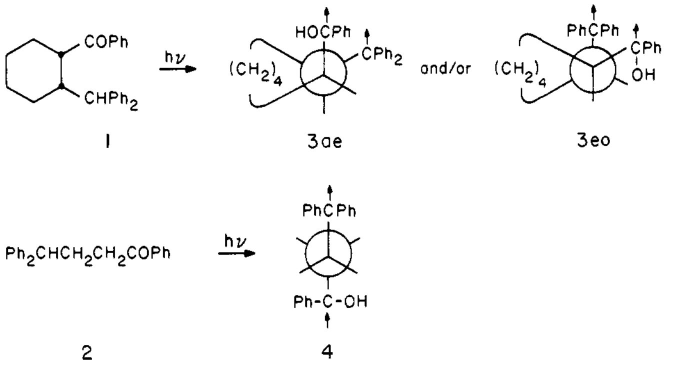
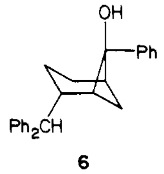
Interminal distance and orbital orientation have been suggested[1] as potentially significant factors in determining intersystem crossing rates and thus lifetimes of triplet biradicals. Scaiano[2] has suggested that a conformational dependence of intersystem crossing rate (gauche faster than trans) and a solvent-dependent conformational distribution will account for the increase of Norrish II biradical lifetimes in hydrogen-bond-accepting solvents and that the strikingly short lifetime of a Norrish II biradical with termini constrained cis on a cyclopropyl ring also may be a result of proximity of the termini. We also previously made a similar interpretation.[3] We now have prepared *cis*-1-benzoyl-2-benzhydrylcyclohexane (**1**) and compared its photochemistry and transient spectroscopy to that of γ,γ-diphenylbutyrophenone (2). Even though **1** affords a gauche-locked biradical **3** and **2** affords an anti-biased biradical **4**, the lifetimes (i.e., isc rates) are quite similar; in methanol, the lifetime of **3** is even longer than that of **4**. Our evidence thus suggests that the role of conformation in determining lifetimes of 1,4 biradicals may be small.



1 3ae 3eo

2 4

Photolysis of **1**,[4,5] mp 121–122 °C (250 mg in 50 mL of hexane, Pyrex, 450-W medium-pressure mercury lamp, 75 min), and column chromtography afforded sequentially 8 mg (3.2%) of 2-benzydryl-6-*exo*-phenylbicyclo[3.1.1]heptan-6-ol (**6**),[5] mp 215–216 °C, 15 mg (6%) of recovered **1**, and 190 mg (76%) of *cis*-7,8,8-triphenylbicyclo[4.2.0]octan-7-*endo*-ol (**7**),[5] mp 139–140 °C. Further elution afforded ca. 15 mg (6%) of polymeric material. Irradiation in methanol was incomplete in 4.5 h. In this case, elution of **6** (12 mg, 4.8%), **1** (85 mg, 34%), and **7** (90 mg, 36%) was preceded by a mixture of dienes (ca. 50 mg, 30%) with spectral properties expected for secondary photolysis products of the acyclic photofragmentation products from **1**. Quantum yields for **7** were 0.26 in hexane–benzene (4:1) and 0.12 in methanol.



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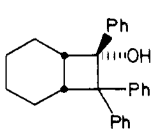

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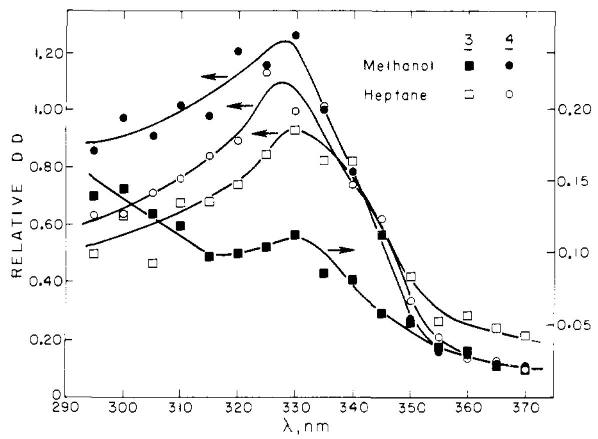

Figure 1. Transient spectra extrapolated from ca. 0.4–1 half-life back to the laser peak. OD (266 nm) = 2.06–2.14 cm^{-1}. Spectra were further normalized to the same laser dose. Note OD scale change for **3** in methanol.

In contrast, the photolysis of **2** (250 mg) afforded only the fragmentation products 1,1-diphenylethylene (120 mg, 80%) and acetophenone (80 mg, 80%) in hexane (Pyrex). Protracted elution afforded no further material; we believe that as much as 5% of a cyclobutanol would have been detected. Quantum yields for $Ph_2C{=}CH_2$ and $PhCOCH_3$ were identical and were 0.32 in hexane–benzene and 1.03 in methanol.

Transient spectroscopy was studied with a Q-switched Nd-YAG laser (266- nm fourth harmonic, 5–20 mJ/pulse, fwhm 10 ns). The transient spectra (Figure 1) are similar for **1** in heptane and **2** in both heptane and methanol. For **1** in methanol, the spectrum is much weaker and contains relatively much stronger end absorption (λ_{max} <300); however, the expected[3,6] λ_{max} 325–330 for the benzhydryl terminus is present as in the other spectra.

For **2**, assignment of the spectrum to biradical **4** from the products of photolysis is unambiguous. For **1** in heptane, assignment to biradical **3** is strongly indicated by the λ_{max} and by the high yield and quantum yield of **7**. For **1** in methanol, the altered spectral shape may reflect the intervention of an increased amount of ring hydrogen abstraction, leading to a valerophenone-like biradical absorbing at shorter wavelength.[3] The decreased intensity could be rationalized by a decreased quantum yield of biradical **3** due to the partitioning between the several H-abstraction pathways, quenching of the ketone excited states by a remote phenyl,[7] or both. In any case, the substantial yield of **7** affords confidence that lifetime measurements at an appropriate wavelength ($\lambda \geq 330$ nm) at which absorption of ring hydrogen abstraction derived biradicals is minimal[8] will give the lifetime of **3** in methanol.

Biradical lifetimes at 330 nm (nanoseconds, $\pm 2\sigma$) were, in methanol, 242 ± 14 (**3**) and 166 ± 3 (**4**) and, in heptane, 69 ± 5 (**3**) and 84 (**4**). The lifetimes for **3** are necessarily those for

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(3) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629.

(4) Reaction of cyclohexene (3 days, 110 °C) with diphenylketene afforded *cis*-8,8-diphenylbicyclo[4.2.0]octan-7-one, cleavage of which in refluxing ethylene glycol with KOH afforded 2-benzhydrylcyclohexanecarboxylic acid, mp 151–152 °C. The acid with PhLi at −77 °C in dry ether afforded **1**. The trans isomer **5**,[5] mp 154–155 °C, of **1** could be obtained by equilibration (**1**:**5** = 67.5:32.5) in 5% methanolic KOH.

(5) The proposed structure is suported by NMR and IR spectra, chromatographic homogeneity, and elemental analysis.

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(8) In both heptane and methanol the lifetime observed for biradical **3** is some 15% shorter at 290 nm than at 340 nm, consistent with qualitative expectation based on the shorter lifetime[3,9] of the valerophenone-derived biradical. The lifetime of **4** is independent (±2%) of wavelength in this range.

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