

chloroform, *i.e.*, the polymer is a right-handed  $\alpha$  helical; (iii) the spectrum of PBLA in TMP has a lower intensity especially in the parallel  $\pi-\pi^*$  band. The perpendicular  $\pi-\pi^*$  band lies at 196 nm.

All these peculiarities may find their origin in structures slightly distorted with respect to that of a regular  $\alpha$  helix. A contribution of the side chains to the rotatory properties of PBLA cannot be excluded.

If CD spectra of PBLA in TMP are recorded at temperatures higher than 100° the dichroic bands are characteristic of a coil conformation having a negative maximum at  $\sim 200$  nm.

PBLA dissolves readily in DMSO. ORD measurements on these solutions gave  $b_0$  values around  $-100$ , which is the value found for PBLA in the random coil conformation.<sup>11</sup>

Also the films that we obtained from PBLA solutions in DMSO by evaporating the solvent gave ir spectra similar to those reported in Figure 1 for a right-handed  $\alpha$  helix.

All these results point out the importance of the solvent in stabilizing the overall conformation of a polypeptide and in making one sense of spiralization energetically more favorable than the other, at least when the difference in internal potential energy between the two is not large, as appears to be the case for PBLA chains.<sup>12</sup>

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(11) E. M. Bradbury, C. Crane-Robinson, V. Giaccotti, and R. M. Stephens, *Polymers*, in press.

(12) J. F. Yan, G. Vanderkooi, and H. A. Scheraga, *J. Chem. Phys.*, **49**, 2713 (1968).

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## The Reaction of Benzo[2.2]paracyclophane with Singlet Oxygen

Sir:

We have recently described the reactions of singlet oxygen with [2.2](2,5)-furanophane,<sup>1</sup> [2.2](2,5)-furanoparacyclophane,<sup>2</sup> and *anti*-[2.2](1,4)naphthalenophane.<sup>3,4</sup> In the above cases, initial oxygen uptake was followed by a second-stage intramolecular Diels-Alder addition forming cage-like oxygenated derivatives. We now report that the reaction of singlet oxygen in methanol with the cyclophane III results in oxygenation of the naphthalene ring accompanied by a rearrangement to the metaparacyclophane system.

Benzo[2.2]paracyclophane (III),<sup>5</sup> prepared by a

(1) H. H. Wasserman and A. Doumaux, *J. Amer. Chem. Soc.*, **84**, 4611 (1962).

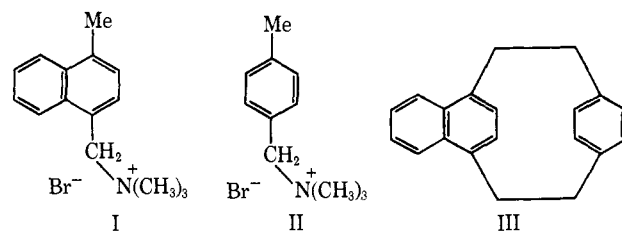
(2) H. H. Wasserman, A. Doumaux, and R. E. Davis, *ibid.*, **88**, 4517 (1966).

(3) H. H. Wasserman and P. M. Keehn, *ibid.*, **88**, 4522 (1966).

(4) P. M. Keehn, Ph.D. Dissertation, Yale University, 1969.

(5) A previous preparation of III was reported by D. J. Cram, C. K. Dalton, and G. R. Knox (*J. Amer. Chem. Soc.*, **85**, 1088 (1963)) through a route involving annelation of the benzo ring to a [2.2]paracyclophane nucleus. Our product gave a satisfactory C and H analysis and ex-

pyrolytic route,<sup>6</sup> was subjected to photooxidation in the standard way, using a 150-W (G.E.) floodlamp as light source, methylene blue as sensitizing dye, and a



mixture of methanol and benzene (1:1) as solvent. After bubbling oxygen through this mixture for 12 days, the solvent was removed, yielding a mixture of materials containing mostly III and two new products (*ca.* 15%), a solid (A), and an oil (B).<sup>7</sup>

Product A is a crystalline material. The mass spectrum contains a weak parent peak at  $m/e$  288, and strong peaks at 184, 169, and 154 as well as a weak peak at 104. The appearance of peaks at  $m/e$  184 and 104 corresponding to the rupture of the ethylene bridges is typical of the fragmentation observed in the cyclophane series,<sup>4,10</sup> and clearly shows that the methoxyl group is located on the naphthalene ring. The infrared spectrum contains no hydroxyl band, but absorption ( $\text{cm}^{-1}$ , KBr) at 1610, 1385 (strong), and 1103. The ultraviolet spectrum has  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  at 296 ( $\epsilon$  5190) and 236 nm ( $\epsilon$  45,200). The nmr spectrum ( $\text{CDCl}_3$ ) contains peaks at  $\tau$  2.02, (m, 2 H), 2.5 (m, 2 H), 2.77 (m, 2 H), 4.48 (s, 1 H), 4.49 (q, 2 H,  $J = 8$  Hz), 6.04 (s, 3 H), and a multiplet centered at 7.3 (8 H). *Anal.* Calcd for  $\text{C}_{21}\text{H}_{20}\text{O}$ : C, 87.46; H, 6.99. Found: C, 87.37; H, 6.84.

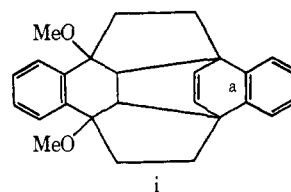
The above spectroscopic evidence is in complete agreement with the assignment of structure IX to the methoxylated product A. Its formation is outlined in the sequence IV  $\rightarrow$  IX (Scheme I). Of particular importance in distinguishing between IX and the alternative system X is the appearance of the low-field nmr spectrum of A which corresponds in detail remarkably closely to the spectrum of 1-methoxy-2,4-dimethyl-

hibited spectroscopic properties identical with those described by the above workers.

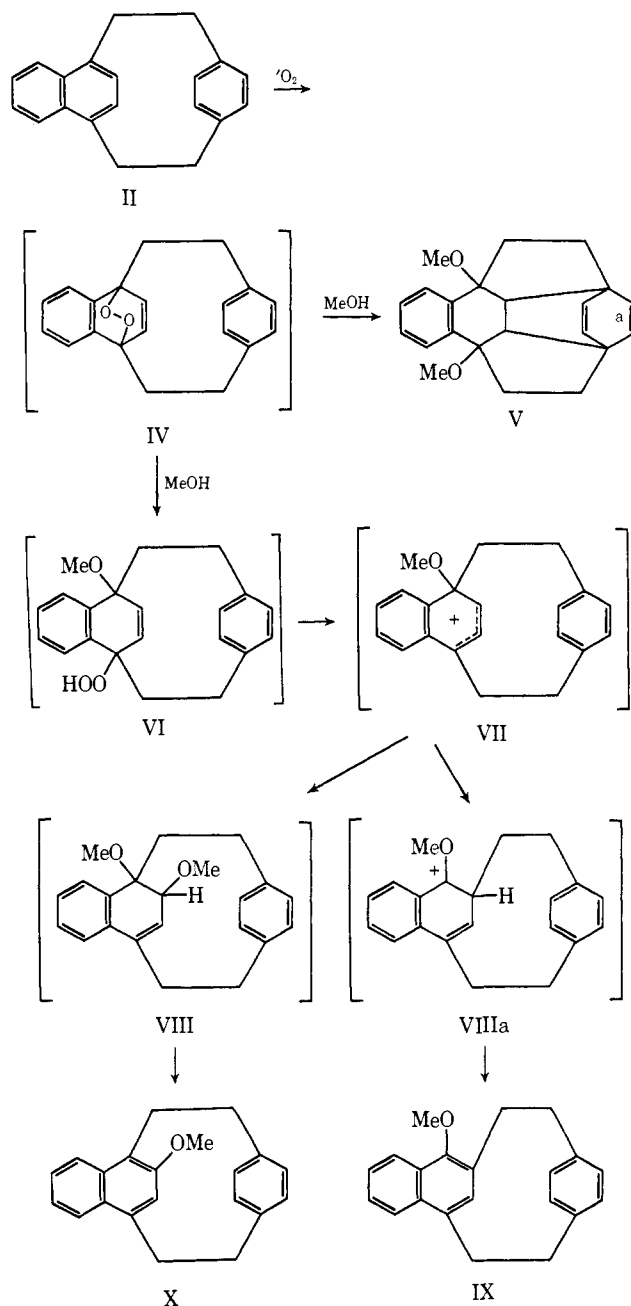
(6) By heating a mixture of quaternary ammonium bromides I and II in boiling xylene for 10 hr, followed by chromatography on silica gel.

(7) Compound B has an nmr spectrum showing aromatic absorption in the region  $\tau$  2.85, and sharp singlets at 3.64 (2 H), 4.47 (2 H), and 7.14 (6 H). This material was quite labile, and on warming, underwent rapid change to an unstable product which did not exhibit the sharp nmr singlets at  $\tau$  3.64 and 4.47. On treatment with HI, it readily reverted to III. Based on the nmr evidence and analogies with related reactions,<sup>3</sup> we have assigned structure V to the labile compound, B. This product appears to result from the transannular peroxide, IV, by solvolysis in methanol followed by an internal Diels-Alder reaction (see Scheme I).<sup>8</sup>

(8) The stability of i<sup>3</sup> relative to V may be associated with the presence of the aromatic ring in the place of a double bond at position a. Compound V most probably undergoes a ready thermal reversal of the intramolecular Diels-Alder reaction.



Scheme I



naphthalene,<sup>9</sup> and is unlike that of 1,4-dimethyl-2-methoxynaphthalene.

Strong additional support for the assignment of the metaparacyclophane structure IX to the oxidation product A was obtained from high-temperature nmr studies which are known to distinguish between metaparacyclophane and paracyclophane systems.<sup>10-18</sup> As would be expected for the metaparacyclophane structure IX (but not for X), we have observed a pronounced

(9) M. Fetizon and Nguyen Trong Anh, *Bull. Soc. Chim. Fr.*, 3208 (1966). We thank Dr. Fetizon for providing us with the 60-Hz nmr spectrum of 1-methoxy-2,4-dimethylnaphthalene.

(10) S. Akabori, S. Hayashi, M. Nawa, and K. Shiomi, *Tetrahedron Lett.*, 3727 (1969).

(11) D. T. Hefelfinger and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 1073 (1970).

(12) H. J. Reich and D. J. Cram (*ibid.*, **91**, 3517 (1969)), have shown that racemization of (-)-4-carbomethoxy[2.2]paracyclophane takes place only above 200°, and then by a radical process involving cleavage of the ethylene bridge.

(13) T. Sato, S. Akabori, M. Kainosho, and K. Hata, *Bull. Chem. Soc. Jap.*, **41**, 218 (1968).

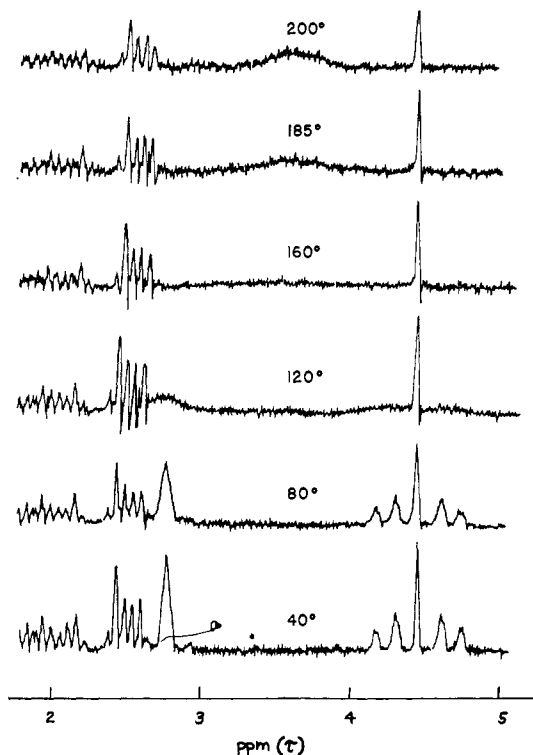
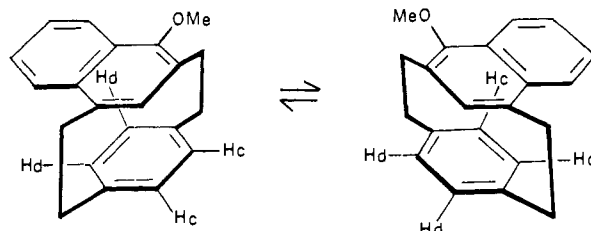


Figure 1. The nmr spectrum (60 MHz) of compound A (IX) in hexachloro-1,3-butadiene as a function of temperature.

temperature dependence of the nmr spectrum of A over the range 25–200° (see Figure 1). The multiplet observed at  $\tau$  2.77 and the quartet at 4.49 (at room temperature) gradually broaden on heating and disappear completely at 150°, giving rise, at 180°, to a new signal midway between these peaks (*ca.*  $\tau$  3.63). This new peak, quite pronounced at 200°, represents the coalescence of the Hc and Hd protons in IX and, as illustrated below, may be associated with the rapid inversion of the naphthalene ring in the [2.2]metaparacyclophane system, permitting exchange of the Hc and Hd proton environments.



In a control experiment, we have examined the nmr spectrum of benzo[2.2]paracyclophane (III) from 25 to 200° and have observed no change in the absorption over this temperature range, in accord with previous findings<sup>12</sup> on the absence of ring inversion in the [2.2]-paracyclophane series.

Formation of IX in the oxygenation of III illustrates an unusual transformation<sup>14</sup> of a [2.2]paracyclophane system to a meta, para isomer under relatively mild conditions. A previous example of such a rearrangement under stronger conditions (Lewis acids) was recently reported by Cram,<sup>15</sup> who suggested that a

(14) B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y., 1964, p 245.

(15) (a) D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *J. Amer. Chem. Soc.*, **88**, 1324 (1966); (b) M. H. Delton, R. E. Gilman, and D. J. Cram, *ibid.*, **93**, 2329 (1971).

driving force for the change may be the relief of strain associated with the lessening of the  $\pi$ - $\pi$  repulsion of the overlapping aromatic rings.

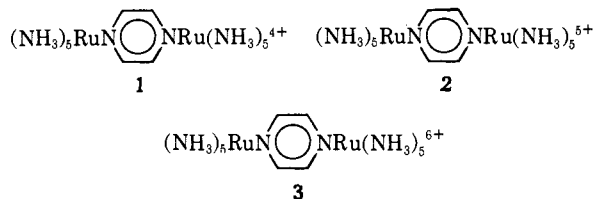
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### Ligand-Bridged Ruthenium Complexes

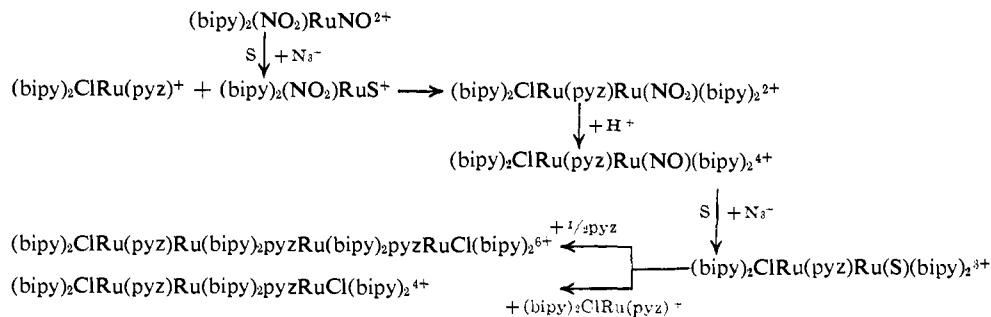
Sir:

Creutz and Taube<sup>1</sup> have characterized the pyrazine bridged dimer, compound **1**, and its oxidized forms



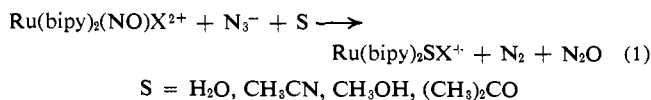
compounds **2** and **3** (see above). We have developed a general synthetic route to ligand bridged bis(2,2'-bipyridine)ruthenium complexes. The syntheses are

**Scheme I**



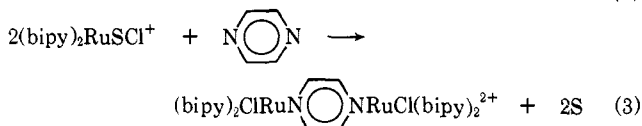
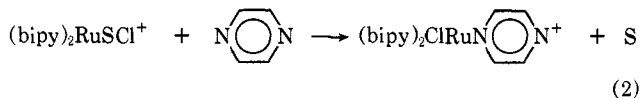
based on our earlier work on reactions of NO and NO<sub>2</sub><sup>-</sup> coordinated to ruthenium. It appears that with an appropriate combination of reactions, long-chain molecules can be obtained with synthetic control at each step. We report here cases of two, three, and four ruthenium atoms linked by bridging ligands. We have also investigated the oxidation-reduction properties of these complexes electrochemically.

Azide ion reacts with Ru(bipy)<sub>2</sub>(NO)X<sup>2+</sup> (X = Cl, NO<sub>2</sub>)<sup>2,3</sup> in water or nonaqueous solvents giving solvent complexes.

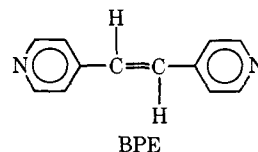


The acetone and methanol complexes are useful synthetic intermediates because of the lability of the coordinated solvent molecule.<sup>3</sup> With dibasic ligands both 1:1 and 2:1 complexes can be isolated. We have used reactions 2 and 3 to prepare 1:1 and 2:1

(1) C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, **91**, 3988 (1969).  
(2) F. J. Miller and T. J. Meyer, *ibid.*, **93**, 1294 (1971).  
(3) S. A. Adeyemi, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, in press.



complexes with pyrazine (pyz), 4,4'-bipyridine (4,4'-bipy), and *trans*-1,2-bis(4-pyridyl)ethylene (BPE). The



coordination at the ruthenium in all cases is presumably *cis*.<sup>3,4</sup>

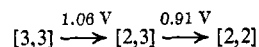
The bipyridine complexes are remarkably versatile synthetically. Coordinated nitrite is converted into nitrosyl by acids,<sup>4,5</sup> e.g.



By combining reactions like 1, 2, 3, and 4, we have prepared more highly linked systems (S is acetone or methanol; pyz is pyrazine) (Scheme I). With the exception of the solvent complexes, all of the intermediates and products have been isolated as PF<sub>6</sub><sup>-</sup> salts and characterized by elemental analyses. Examples

follow. *Anal.* Calcd for [(bipy)<sub>2</sub>ClRu(py<sub>z</sub>)RuCl(bipy)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·2H<sub>2</sub>O: C, 40.53; H, 3.10; N, 10.74; Cl, 5.44; F, 17.49; Found: C, 40.43; H, 2.91; N, 10.27; Cl, 5.68; F, 17.74. Calcd for [(bipy)<sub>2</sub>ClRu(py<sub>z</sub>)Ru(bipy)<sub>2</sub>(py<sub>z</sub>)RuCl(bipy)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·3H<sub>2</sub>O: C, 38.78; H, 2.94; N, 10.64; Cl, 3.37. Found: C, 38.38; H, 2.76; N, 10.80; Cl, 3.25. We are currently extending the uses of these reactions synthetically in the preparation of higher polymers, mixed metal polymers, and of polymers with mixed ligand bridges.

Voltammetric and cyclic voltammetric measurements on (bipy)<sub>2</sub>ClRu(py<sub>z</sub>)RuCl(bipy)<sub>2</sub><sup>2+</sup> [2,2] in acetonitrile show that it also has two oxidized forms, (bipy)<sub>2</sub>ClRu(py<sub>z</sub>)RuCl(bipy)<sub>2</sub><sup>3+</sup> [2,3] and (bipy)<sub>2</sub>ClRu(py<sub>z</sub>)RuCl(bipy)<sub>2</sub><sup>4+</sup> [3,3]. The reduction potentials<sup>6</sup> relating the three are



(4) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471 (1971).

(5) J. B. Godwin and T. J. Meyer, *ibid.*, **10**, 2150 (1971).

(6) All electrochemical measurements were made at platinum electrodes at 22 ± 2° using 0.1 M (*n*-bu)<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> as the supporting electrolyte. Potential values are reduction potentials *vs.* the saturated sodium chloride calomel electrode and are uncorrected for junction potentials. Ep refers to peak potentials from cyclic voltammetry measurements.