such as Bu^{t}O$^\bullet$ that do not have a preference for addition reactions, react quite readily with [1.1.1]propellane in an S_H2 type of displacement. In a recent related study, we have demonstrated that diphenylcarbene also adds readily to [1.1.1]propellane with a rate constant of 6.7×10^6 M^{-1} s^{-1} to yield a 1,4-biradical.[26]

Experimental Section

[1.1.1]Propellane was prepared following the method of Szeimies et al.[27] and purified by preparative gas chromatography. Di-*tert*-butyl peroxide (MC&B) was passed through an alumina column to eliminate traces of hydroperoxide present as an impurity. Cyclohexane (Aldrich, Spectro grade) was used as received, and Freon-113 (Fluka) was passed through an alumina column to eliminate acid impurities. Diphenyl disulfide (Aldrich) was recrystallized from cyclohexane, and diphenylmethanol (Aldrich) from ethanol. The samples were excited with the pulses from a Lumonics TE860-2 excimer Laser (308 nm, 5 ns, <20 mJ/pulse) in the case of the disulfide and a Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, <9 mJ/pulse) for the peroxide. Further details of our laser photolysis system have been reported elsewhere.[28]

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance, to Professor J. Michl for the communication of unpublished results, and to the Natural Sciences and Engineering Research Council of Canada for partial support of this work.

Registry No. Bu^{t}O$^\bullet$, 3141-58-0; PhS$^\bullet$, 4985-62-0; propellane, 35634-10-7.

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5,10,15,20-Tetrakis($\alpha,\alpha,\alpha,\alpha$-*o*-(*N*-*tert*-butylcarbamoyl)phenyl)porphyrin: Synthesis and Redox Properties of Zinc(II) and Copper(II) Complexes

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In metalloporphyrins, various chemical and steric factors, such as the substitution of the macrocycle and its microenvironment, control the ligand binding or the electronic-state changes of their central ion. Considering this, superstructures covalently linked to the macrocycle have been used to modulate the reactivity of the metallic center, and they have received considerable attention in the past decade.[1] Thus, it has been reported that the location of secondary amide groups (PhNHCO) in "picket fence" and "basket handle" porphyrins, in the vicinity of the metallic ion, induces unusual behavior in redox and coordination chemistry. This includes stabilization of dioxygen and negatively charged species, due to either hydrogen bonds or dipole–dipole interactions, as well as multiple-electron transfer.[2,3]

To obtain a deeper insight into the effects of the environmental chemical factors, we synthesized 5,10,15,20-tetrakis($\alpha,\alpha,\alpha,\alpha$-*o*-(*N*-*tert*-butylcarbamoyl)phenyl)-porphyrin (**1**). It was expected that the main consequence of the presence of the "reversed" amide groups (PhCONH) would be the stabilization of positively charged species compared to that observed with Collman's "picket fence" porphyrin (TpivPP,[4] Scheme I).

The key intermediate to the porphyrin **1** was the tetrakis(*o*-carboxyphenyl)porphyrin (**3**). Initial attempts to obtain the latter from *o*-carboxybenzaldehyde failed due to the existence of an intramolecular equilibrium with the 3-hydroxyphthalimide form. On the other hand, condensation of *o*-carbomethoxybenzaldehyde with pyrrole, following Rothemund's method,[5] gave porphryin **5** with a weak yield (2%). The successful approach to obtain porphyrin **3** (Scheme II) involves the preparation of 5,10,15,20-tetrakis(*o*-cyanophenyl)porphyrin (**2**) from the cyclization of *o*-cyanobenzaldehyde with pyrrole, following the same method (11%). On treatment with H_2SO_4 in acetic acid, this tetracyano derivative was hydrolyzed to the desired porphyrin **3**, in a quantitative yield.

Esterification of **3** was accomplished in order to separate the four atropisomers. The tetra-acid chloride **4** was obtained by the use of oxalyl chloride, and it was then quantitatively converted to the tetramethyl ester **5**, with methanol. After $\alpha,\alpha,\alpha,\alpha$-atropisomer enrichment, under the conditions described by Lindsey,[6] atropisomers were separated by column chromatography on silica gel. The desired $\alpha,\alpha,\alpha,\alpha$-atropisomer was isolated as the most polar compound, eluted with methylene chloride, in a 32% yield. The identification of the four atropisomers of **5** was also supported by ^{1}H NMR analysis, based on their molecular symmetries (Table I). The spectrum of the $\alpha,\alpha,\alpha,\alpha$-atropisomer shows a single resonance for the eight pyrrolic protons, confirming their equivalence. The double peak for these protons of the $\alpha,\alpha,\beta,\beta$-atropisomer is explained by the presence of a symmetry plan and a conversion axe, through the pyrrolic nitrogen atoms. The spectrum of the $\alpha,\alpha,\alpha,\beta$-atropisomer shows several resonances for the same protons, indicating the absence of symmetry in the molecule. Furthermore the three signals of relative intensity 1,1,2 for the methyl ester protons are in perfect agreement with their statistic distribution on both faces of the macrocycle.

On treatment with basic aqueous ethanol, $\alpha,\alpha,\alpha,\alpha$-**5** was saponified to tetraacid **3**, which was then converted to the corresponding tetra-acid chloride, as previously. Subsequent final treatment with an excess of *tert*-butylamine afforded the desired 5,10,15,20-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-(*N*-*tert*-butylcarbamoyl)phenyl)porphyrin (**1**), in a 56% yield, after purification on preparative silica gel chromatography and crystallization. ^{1}H NMR spectral data ($CDCl_3$) were in complete agreement with the indicated structure (Figure 1). The most significant feature of this spectrum is an upfield shift of methyl protons (at 0.1 ppm) arising from the ring current of the porphyrin ring. The amide protons were observed at 5.4 ppm, a position similar to the chemical shift of the same protons in (*tert*-butylcarbamoyl)-phenyl, taken as reference. This shift indicated the absence of ring-current effect on the amide protons, corresponding to their outer position.

Zinc and copper insertion into the porphyrin **1** was accomplished by using zinc(II) and copper(II) chloride, under argon, at 50 °C, in dry tetrahydrofuran, in the presence of 2,6-dimethylpyridine.

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(4) Collman, J. P.; Gagne, R. R.; Reed, T. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427.
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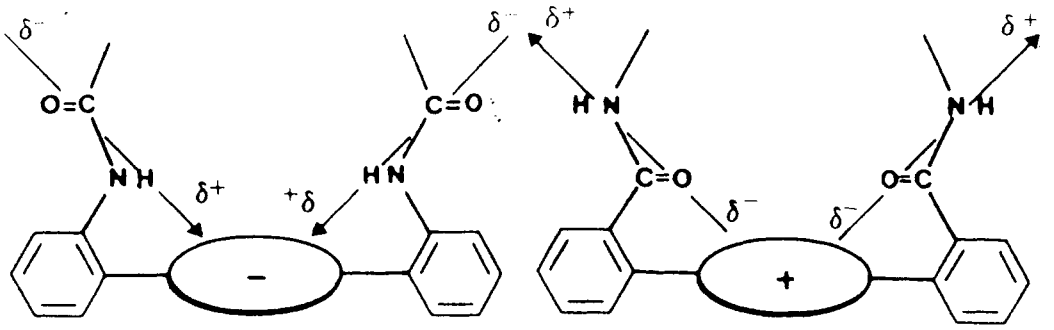
0022-3263/89/1954-6135$01.50/0

Scheme I



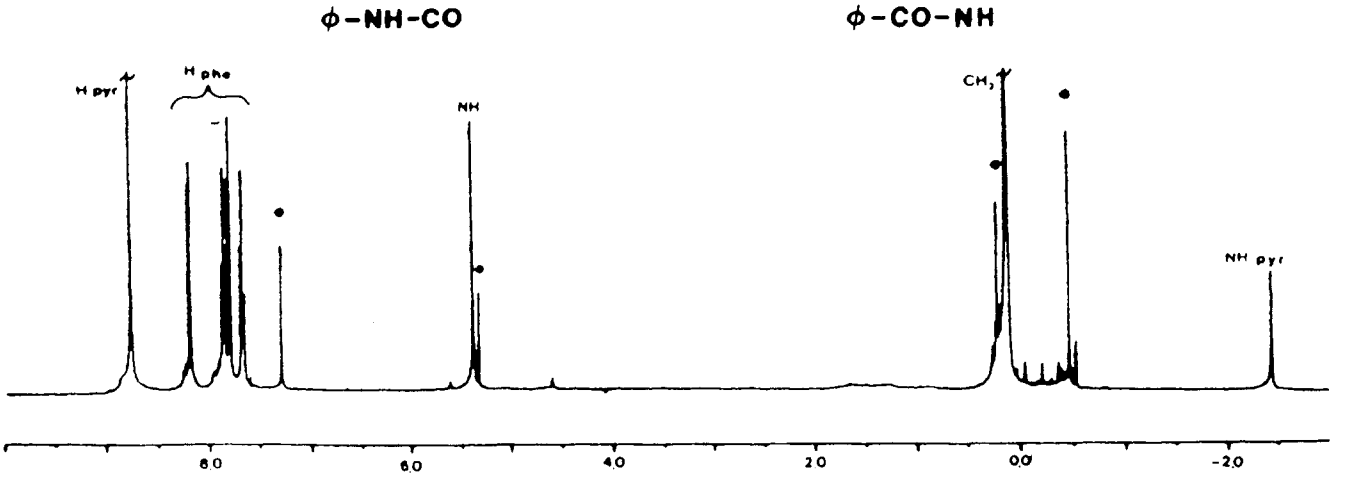


Figure 1. The 400-MHz ^1H NMR spectrum of porphyrin 1 in $CDCl_3$ at 27 °C.

Table I. Proton NMR Shifts (in ppm from TMS) for the Four Isomers of Porphyrin 5[a]

		H_{phenyl}					
atropisomers	H_{pyr}	ortho (d)	meta' (d)	meta (t)	para (t)	CH_3 (s)	NH_{pyr} (s)
α,α,α,α	8.60 (s)	8.39	8.07	7.86	7.80	2.90	−2.44
α,α,β,β	8.61 (d)	8.39	8.17	7.89	7.83	2.72	−2.42
α,α,α,β	8.60 (m)	8.37	8.15	7.89	7.83	2.90, 2.78, 2.60	−2.42
α,β,α,β	8.59 (s)	8.37	8.18	7.89	7.83	2.90	−2.42

[a] s, singlet; d, doublet; t, triplet; m, multiplet.

Table II. Half-Wave Potentials (V vs SCE) at 20 °C, in the Presence of 0.1 M NBu_4BF_4 on Glassy Carbon Electrode in Dry CH_2Cl_2

porphyrin	E (P^-/P^{2-})	E (P/P^-)	E (P/P^{2+})
Zn-(1)	−1.54	−1.22	0.75
Zn-(TpivPP)	−1.49	−1.06	1.00
Cu-(1)	−1.52	−1.11	1.06
Cu-(TpivPP)	−1.59	−1.03	1.28

To reveal the effects of "reversed" amide groups, electrochemical behaviors of zinc and copper complexes of compound 1 were examined and compared to those of Collman's "picket fence" porphyrin. We began our study by determining the cyclic voltammograms of these derivatives and thus establishing the reduction and oxidation half-wave potentials, $E_{1/2}$, of both compounds. Two reduction and one oxidation waves were observed in methylene chloride solution (Figure 2). The half-wave potentials, $E_{1/2}$ (vs saturated calomel electrode, SCE) are reported in Table II. It can be clearly seen that the reverse of the secondary amide groups of "pickets" in the new compounds significantly decreases the first reversible reduction waves corresponding to the formation of monoanion radicals, relative to those of Zn- and Cu-TpivPP,

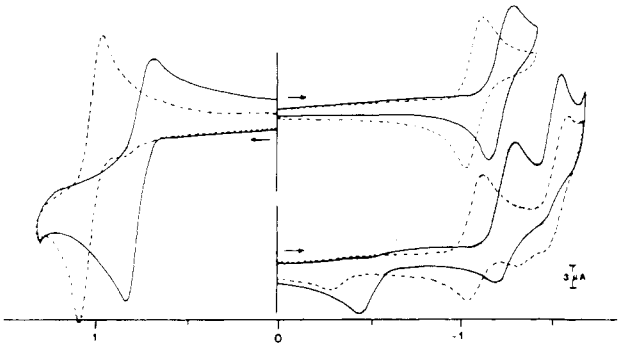
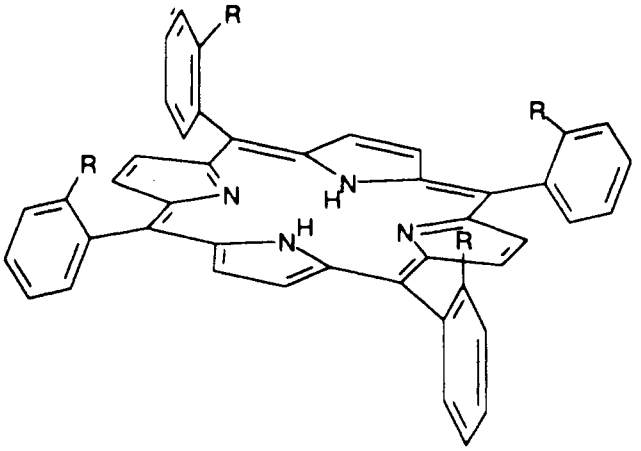


Figure 2. Cyclic voltammetry of Zn-1 (—) and Zn-TpivPP (---) in dry CH_2Cl_2, in the presence of 0.1 M NBu_4BF_4 at 20 °C. $E_{1/2}$, potentials in V vs KCl SCE; sweep rate, 0.1 V s^{-1}.

by a value of 160 and 80 mV, respectively. The second cathodic peak corresponds to an irreversible process resulting from a chemical reaction of the dianion with the solvent. The two steps are one-electron transfers.[7] On the contrary, in the oxidation process, single two-electron

(7) Lanese, J. G.; Wilson, G. *J. Electrochem. Soc.* **1972**, *119*, 1039.

Scheme II



(1) R = CO-NH-C(CH_3)$_3$
(2) R = CN
(3) R = CO_2H
(4) R = COCl
(5) R = CO_2CH_3

waves were observed, featuring the direct formation of the dication species from the starting complexes of Zn–1 and Cu–1. The two electrons per molecule stoichiometry was confirmed by comparison of the peak intensities of the oxidation and the first reduction waves (e.g., i_{ox}/i_{red} = 7.20/3.66, for Zn–1. This electrochemical behavior is similar to that observed with the same metallic complexes of TpivPP and amide "basket handle" porphyrins. For the latter the two-electron transfer was also confirmed by coulometry.[8] A more negative electrochemical shift was also found by comparing the oxidation $E_{1/2}$ of the analogous complexes. A 250-mV difference was found in the case of zinc complexes, in an almost reversible process.

In conclusion, tetrakis(*o*-cyanophenyl)porphyrin appears to be a suitable compound for efficient preparation of tetrakis(*o*-carboxyphenyl)porphyrin. This latter can be useful for many applications in the field of superstructured porphyrins, in which superstructures would be linked to the macrocycle by ester or secondary amide groups. The porphyrin 1 of one of these two new series of compounds appears to be able to provide a new means of modulation in the molecular environment effects on the reactivity of the metallic center. The presence of "reversed" amide groups (PhCONH) in the vicinity of the reacting center gives a systematic cathodic potential shift, which is indicative of a greater stabilization of positively charged species, in comparison to the opposite phenomena observed in amide series (PhNHCO).[3]

Further investigations on the chemical reactivity of iron derivatives, related to both coordination and redox properties, compared to Collman's "picket fence" and "basket handle" porphyrins will be reported in a future publication.

Experimental Section

All chemicals used were of reagent grade and were purchased from Aldrich. Tetrahydrofuran (THF) was distilled from sodium–benzophenone and immediately used. Merk silica gel (40–60 μm) or 60 M (15 μm) was used for column chromatography. Pure porphyrins were obtained by preparative high-pressure liquid chromatography (HPLC) with a Jobin Yvon apparatus. Merk precoated preparative plates (Silica gel 60, 2 mm) were used for thin-layer chromatography (TLC). Elemental analyses were carried out by the Service Central de Microanalyse du CNRS. Proton NMR spectra were obtained in $CDCl_3$ with a Brucker AM-400 instrument. Cyclic voltammetry studies were carried out with an EGG M 263 potentiostat. All potentials are referred to the saturated calomel electrode (SCE). The working electrode was a 3-mm-diameter glassy carbon disk. The counter electrode was a platinum wire. The temperature of all experiments was 20 °C. The solutions were purged with argon, and an argon atmosphere was maintained during the experiments.

5,10,15,20-Tetrakis(*o*-cyanophenyl)porphyrin (Four Atropisomers, 2). *o*-Cyanobenzaldehyde (16.25 g, 0.124 mol) was refluxed in a mixture of acetic acid (520 mL) and pyridine (130 mL). Pyrrole (9 mL, 0.134 mol) was then added dropwise for 10 min. After complete addition, the reaction mixture was stirred for another 2 h and cooled to room temperature. After evaporation under reduced pressure of the solvent to dryness, the solid residue was dissolved in methylene chloride and flash chromatographed on silica gel. Elution with methylene chloride followed by a mixture of methylene chloride–ether (10/3 v/v) gave porphyrin and corresponding chlorin. The solution was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The mixture of four atropisomers of **2** was purified by column chromatography (30 cm × 5 cm) on silica gel (CH_2Cl_2/ether 10/1 v/v) and then was crystallized by low evaporation of CH_2Cl_2/hexane (1/1 v/v, 2.5 g, 11.3%): IR 2224 cm^{-1} (CN). Anal. Calcd for $C_{48}H_{26}N_8$, H_2O: C, 78.67; H, 3.85; N, 15.29. Found: C, 78.84; H, 4.08; N, 15.09.

5,10,15,20-Tetrakis(*o*-carboxyphenyl)porphyrin (Four Atropisomers, 3). Porphyrin **3** (300 mg, 0.42 mmol) was refluxed under argon for 18 h in a mixture of water (20 mL), H_2SO_4 (20 mL), and acetic acid (20 mL). After this cooled, ethyl acetate (100 mL) and trifluoroacetic acid (1 mL) were added. The organic layer of dicationic porphyrin was then washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to dryness, giving the porphyrin **3**, which was directly used in the next reaction without further purification.

5,10,15,20-Tetrakis(*o*-carbomethoxyphenyl)porphyrin (Four Atropisomers, 5). Porphyrin **3** (1.3 g, 1.7 mmol) in dry methylene chloride (50 mL) was treated with oxalyl chloride (25 mL) at 40 °C for 1 h. Solvent and excess reagent were removed by evaporation under reduced pressure to dryness. The porphyrin was dissolved in dry CH_2Cl_2 (50 mL) and then treated with methanol (40 mL) at room temperature overnight. The solvent was removed with a rotary evaporator, and the residue dissolved in CH_2Cl_2 (50 mL). The solution was washed with water and aqueous saturated hydrogen carbonate and then dried (Na_2SO_4). After evaporation of the organic solvent, the title compound was crystallized by low evaporation of CH_2Cl_2/hexane (1/1 v/v, 1.4 g, 99%). Anal. Calcd for $C_{52}H_{38}N_4O_8$, H_2O: C, 72.21; H, 4.66; N, 6.48. Found: C, 72.75; H, 4.46; N, 6.52.

α,α,α,α-Atropisomer of Porphyrin 5. The crystalline mixture of the four atropisomers was heated under reflux in xylenes (120 mL)/acetone (2.5 mL) in the presence of silica gel (50 g) under argon for 20 h. The solvents were rotary evaporated, and the solid residue was loaded on the top of a HPLC silica gel column. Elution with methylene chloride gave four fractions. The fourth fraction corresponded to the most polar compound (R_f = 0.20) and was identified by ^1H NMR spectroscopy as the desired α,α,α,α-atropisomer of porphyrin **5** (31.8%).

5,10,15,20-Tetrakis(*o*-(*N*-*tert*-butylcarbamoyl)phenyl)porphyrin (1). α,α,α,α-Atropisomer of compound **3** (200 mg), obtained by saponification of **5** with 2 N KOH in ethanol 80%, was treated with oxalyl chloride (10 mL) in dry methylene chloride (20 mL), following the method described above for the preparation of compound **5**. The tetracarboxylic chloride porphyrin **4** was treated with terbutylamine (1 mL). After 2 h at room temperature with stirring, the reaction mixture was washed with water, dried (Na_2SO_4), and then evaporated under reduced pressure to dryness. The solid residue was purified by TLC on silica gel. The desired compound eluted with CH_2Cl_2/acetone (5/1 v/v), corresponding to the main band (R_f = 0.65), and was then crystallized by low evaporation of CH_2Cl_2/hexane (1/1 v/v, 142.7 mg, 55.6%). Anal. Calcd for $C_{64}H_{66}N_8O_4 \cdot 2H_2O$: C, 73.39; H, 6.73; N, 10.7. Found: C, 73.10, H, 6.11; N, 11.41. ^1H NMR ($CDCl_3$) δ 8.75 (s, 8 H, H_{pyr}),

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8.21 (d, 4 H, *o*-Ar), 7.85 (t, 4 H, *p*-Ar), 7.79 (d, 4 H, *m*-Ar), 7.66 (t, 4 H, *m'*-Ar), 5.38 (s, 4 H, NHCO), 0.10 (s, 36 H, CH_3), -2.44 (s, 2 H, NH pyr).

5,10,15,20-Tetrakis(*o*-pivalamidophenyl)porphyrin (TpivPP). This compound was synthesized following the procedure described by Collman et al.[4]

Zinc and Copper Complexes of Porphyrins. Insertion of zinc and copper into the free-base porphyrins was accomplished using $ZnCl_2$ and $CuCl_2$ in tetrahydrofuran, in the presence of 2,6-dimethylpyridine at 50-60 °C for 1 h. The crude metalloporphyrins were purified by TLC over silica gel plates with methylene chloride/acetone (5/1 v/v) as eluant and crystallized by low evaporation of CH_2Cl_2/hexane (1/2 v/v, 70%). Zn-1: λ_{max}/nm (ϵ/mmol L^{-1}) 425 (370.5), 555 (15.8), 605 (3.7); ^1H NMR (CD_2Cl_2) δ 8.68 (s, 8 H, H_{pyr}), 8.06 (d, 4 H, *o*-Ar), 7.78 (t, 4 H, *p*-Ar), 7.64 (d, 4 H, *m*-Ar), 7.56 (t, 4 H, *m'*-Ar), 6.20 (s, 4 H, NHCO), 0.33 (s, 36 H, CH_3).

Cu-1: λ_{max}/nm (ϵ/mmol L^{-1}) 419 (128.8), 542.5 (4.8), 577.5 (0.8).

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Registry No. 1, 123811-58-5; Zn-1, 123811-59-6; Cu-1, 123811-60-9; **2** ($\alpha,\alpha,\alpha,\alpha$ isomer), 123878-56-8; **2** ($\alpha,\alpha,\alpha,\beta$ isomer), 123878-57-9; **2** ($\alpha,\alpha,\beta,\beta$ isomer), 123878-58-0; **2** ($\alpha,\beta,\alpha,\beta$ isomer), 123878-59-1; **3** ($\alpha,\alpha,\alpha,\alpha$ isomer), 123878-60-4; **3** ($\alpha,\alpha,\alpha,\beta$ isomer), 123878-61-5; **3** ($\alpha,\alpha,\beta,\beta$ isomer), 123878-62-6; **3** ($\alpha,\beta,\alpha,\beta$ isomer), 123878-63-7; **4** ($\alpha,\alpha,\alpha,\alpha$ isomer), 123811-56-3; **4** ($\alpha,\alpha,\alpha,\beta$ isomer), 123878-64-8; **4** ($\alpha,\alpha,\beta,\beta$ isomer), 123878-65-9; **4** ($\alpha,\beta,\alpha,\beta$ isomer), 123878-66-0; **5** ($\alpha,\alpha,\alpha,\alpha$ isomer), 123811-57-4; **5** ($\alpha,\alpha,\alpha,\beta$ isomer), 123878-67-1; **5** ($\alpha,\alpha,\beta,\beta$ isomer), 123878-68-2; **5** ($\alpha,\beta,\alpha,\beta$ isomer), 123878-69-3; Zn-(TpivPP), 86782-69-6; Cu-(TpivPP), 86727-67-5; *o*-cyanobenzaldehyde, 7468-67-9; pyrrole, 109-97-7.

Site Selectivity of Diels-Alder Reactions of a Bicyclic, Heteroannular Dienone[1]

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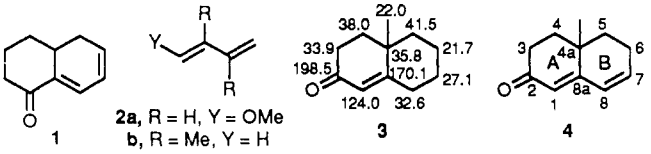
Received May 8, 1989

In a recent study of Diels-Alder reactions of cycloalkenones it was shown that the interaction of 3,4,4a,5-tetrahydronaphthalen-(2*H*)-1-one (**1**) with (*E*)-1-methoxy-1,3-butadiene (**2a**) under Yb(fod)$_3$ catalysis led exclusively to cycloaddition at the dienophile's α,β double-bond site and the formation of a spiro tricycle.[3] The absence of any adduct of the hydroanthracene type illustrated the sharp difference of reactivity of the two olefinic sites in the dienone.[3] This interesting result pointed to the need of exploration of Diels-Alder reactions of structurally varying dienones.



The present note reports on the cycloadditions of 4a-methyl-4,4a,5,6-tetrahydronaphthalen-2(3*H*)-one (**4**) with (*E*)-1-methoxy-1,3-butadiene (**2a**) and with 2,3-dimethyl-1,3-butadiene (**2b**). In view of dienone **4** containing a structure component of the 3-alkyl-2-cyclohexenone type—a system known not to undergo Diels-Alder reaction[4]—the the dienophile could be expected to behave differently from dienone **1** and perhaps show preference for addition across its γ,δ olefinic linkage. The reactive, electron-rich dienes **2** were chosen for the present study to compensate for the expected low reactivity of the reaction partner **4**.

Table I. Reaction Conditions of the Diels-Alder Reactions of Dienes 2 with Dienone 4[a]

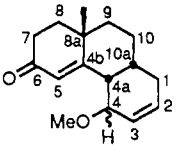
diene	diene/ketone[b]	temp, °C	time, h	products	product yield,[c] %
2a	4.5	170	69	2.7:1 **5a** and **5b**[g]	56
2b	12	170	96	**6**[g]	17
2a[d,e]	6	100	120	5.2:1 **5a** and **5b**	27
2b[d,f]	4.5	75	47	**6**	35

[a] In dry toluene. [b] Ratio of equivalents. [c] GC based. [d] Complexation time, 40 min;[4b] complexation temperature, 22 °C.[4b] [e] Yb(fod)$_3$/ketone equivalents ratio, 0.25; concentration, 0.2 M. [f] $AlCl_3$/ketone equivalents ratio, 0.5; concentration, 0.2 M. [g] Plus two products of unknown constitution accounting for 14 and 12% of the total product mixture from **2a** and **2b**, respectively.

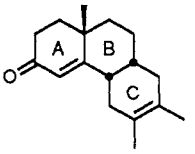
Diels-Alder Reaction Products

The cycloadditions of dienone **4**, prepared from 10-methyl-$\Delta^{1(9)}$-octal-2-one[5] (**3**) by dehydrogenation with chloranil,[6] were performed with various diene-dienophile combinations under thermal as well as acid-catalyzed (aluminum trichloride and ytterbium tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedioate)[7]) conditions, leading to adducts in 17-56% yields (Table I).

The product structures revealed the cycloaddition to have taken place exclusively on the side of dienone **4** opposite to its angular methyl group, methoxybutadiene **2a** leading to the formation of adducts **5a** and **5b** and dimethylbutadiene **2b** furnishing tricycle **6**. The methoxybutadiene reaction favored endo addition (the **5a**/**5b** ratio being ca. 3), which tendency was enhanced on Yb(fod)$_3$ catalysis (**5a**/**5b** ratio of ca. 5).



5a, 4β-H
b, 4α-H



6

The structures of the three products were determined in the following manner. The infrared carbonyl absorption band (ca. 1657 cm^{-1}) and the ^{13}C NMR signal of the carbonyl group (ca. 199 ppm), characteristic of a conjugated enone unit, show the cycloaddition to have occurred in ring B of dienone **4**. Furthermore, the strong similarity of the chemical shifts of the angular methyl group and the ring

(1) (a) Publication 17 of the series "Diels-Alder Reactions of Cycloalkenones. (b) For the previous paper see: Fringuelli, F.; Guo, M.; Minuti, L.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1989**, *54*, 710.

(2) (a) University of California. (b) Università di Perugia.

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