H_2SO_4 as the proton source. As seen in Figure 2 the supported catalyst is even more resistent to deactivation at 90 °C than it was at 70 °C when compared to the homogeneous system.

The inactivity of homogeneous organosulfide complexes in catalysis (outside of electron-transfer roles) is a direct result of sulfide's strong bridging ability which effectively eliminates necessary coordination sites. The demonstration of (1) the stability of the monomeric organosulfide rhodium carbonyl complexes reported here (with respect to dimerization) in cases of effective site isolation on silica gel, (2) the ability of the [SG]-SH supported Rh(I)-Cu(II) system to effectively catalyze the oxidation of 1-hexene, and (3) the inhibition of catalyst decomposition by site isolation of Rh(I) serve as yet another example of the unique role which may be served by functionalized polymers as supports for transition-metal complexes.[12] The greater resistance to catalyst deactivation with the site isolated monomeric III compared to either the dimer II or the homogeneous I may be a result of a stabilizing influence of the sulfide ligand to irreversible monomeric rhodium oxidation and/or the effectiveness of rhodium site isolation in inhibiting multiordered decomposition mechanisms. We are currently investigating the role of Cu(II) in this sytem by further diluting the silica gel surface in organosulfide to achieve site- separation of Rh(I) and Cu(II). The most dilute samples reported here (0.025 mmol of S per gram of [SG]) most likely allow some Rh(I)-Cu(II) interaction. A drop in supported catalyst activity with further dilution would implicate the need for the direct interaction of Rh(I) and Cu(II) in the reaction mechanism.

Acknowledgment. We gratefully acknowledge the support of this research by the Office of Naval Research.

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[12] One of the best examples is the demonstration of effective site isolation. See, for example: (a) Gubitosa, G.; Boldt, M.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1977**, *99*, 5174. (b) Wild, F. R. W. P.; Gubitosa, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1978**, *148*, 73. (c) Drago, R. S.; Gaul, J. H. *Inorg. Chem.* **1979**, *18*, 2019. (d) Grubbs, R.; Lau, C. P.; Cukier, R.; Brubaker, C., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4517. (e) Teal, O.; Anderson, D. L.; Bowman, R. G.; Basolo, F.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 5125.

Synthesis and Molecular Structure of μ^4-Carbido-μ^2-carbonyl-dodecacarbonyltetrairon, a Neutral Iron Butterfly Cluster Bearing an Exposed Carbon Atom

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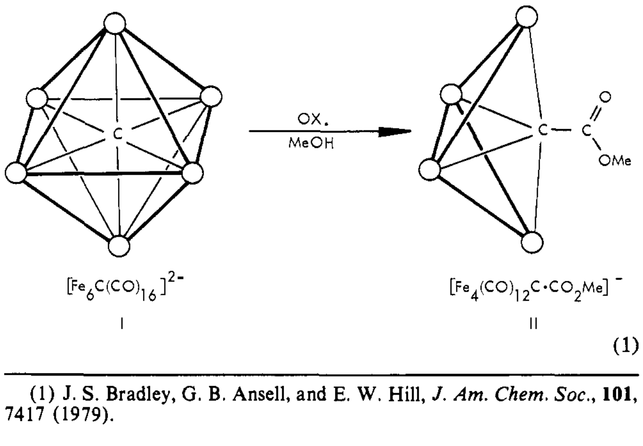
We recently reported[1] the first observation of the chemical reactivity of a cluster bound carbon atom in the synthesis from $Fe_6C(CO)_{16}^{2-}$ (I) of the butterfly (carbomethyoxy)methylidyne cluster $Fe_4(CO)_{12}CCO_2CH_3^-$ (II) in an oxidative fragmentation of the octahedral dianion I in methanol (eq 1).



(1)

The remarkable reactivity of the hitherto encapsulated carbon atom in I when exposed by loss of two vertices from the original cluster is of immediate relevance to current conceptions of the hydrogenation of carbon monoxide on metal surfaces,[2] which propose the formation of surface carbon atoms via dissociative adsorption of CO. Our observation[1] of the facile assembly of a carbomethoxy group on such a carbon atom when its coordination number is reduced to four demonstrated for the first time the reactivity of cluster bound carbon atoms with low coordination number. This phenomenon has also been utilized by Muetterties et al. in the synthesis of $HFe_4(CO)_{12}CH$ from $Fe_4(CO)_{12}C^{2-}$. The hydrogenation of II to methyl acetate[1] provided a unique synthetic pathway to an organic oxygenate from CO and hydrogen mediated by a cluster reaction site, and we have continued our investigation into the promising reactivity of cluster bound carbon atoms.

We suggested a possible mechanism for the formation of II via carbonylation of the carbon atom in a μ^4-carbide intermediate to yield a ketenediyl cluster, $Fe_4(CO)_{12}CCO$, which then reacted with solvent methanol to yield II. We report here the results of our efforts to obtain evidence supporting this postulate and further investigations in the iron carbide system which have led to the isolation of $Fe_4(CO)_{13}C$, a tetranuclear iron species containing a carbon atom bound to four metal atoms.[4]

Our first aim was to establish the intermediacy of a ketenediyl cluster in the formation of II. In view of the reaction of a related (carbomethoxy)methylidynetricobalt cluster with acid to yield the corresponding acylium ion[5] (eq 2), we investigated the protonation of $Fe_4(CO)_{12}CCO_2CH_3^-$ as a route to $Fe_4(CO)_{12}CCO$.

$$Co_3(CO)_9CCO_2R \xrightarrow{HPF_6} Co_3(CO)_9CCO^+ \qquad (2)$$

When trifluoromethanesulfonic acid (1.0 mL) was added to a suspension of $Et_4N[Fe_4(CO)_{12}CCO_2CH_3]$ (1.0 g) in methylcyclohexane, under nitrogen, the green-black starting material dissolved in the acid layer immediately. Addition of degassed water and gentle warming resulted in the total extraction of the dark brown product into the organic phase, which was decanted via cannula onto molecular sieves. Filtration and evaporation under reduced pressure yielded a black, gummy solid which was extracted into hexane. Slow evaporation under nitrogen yielded the product (0.45 g) as a black, air-sensitive crystalline solid (III).

The infrared spectrum of III [cyclohexane, 2062 (s), 2051 (s), 2040 (s), 2035 (s), 2015 (w), 2000 (w), 1990 (m), 1901 (m) cm^{-1}] confirmed the removal of the carboxylic ester function from II [$\nu_{CO}(CO_2CH_3)$ 1655 cm^{-1}), a conclusion confirmed by the absence of ^1H resonances in the 90-MHz NMR spectrum of III. The ^{13}C NMR spectrum (22.5 MHz, CD_2Cl_2) of III contained only two resonances (30 °C), at 469 and 208 ppm (Me_4Si) in an intensity ratio of 1:13.[6] The prospect of a fluxional process averaging Fe-CO and C=CO environments in the target molecule $Fe_4(CO)_{12}CCO$ seemed unlikely, if intriguing, but the presence of 13 carbonyls and a unique carbon atom, confirmed by a parent ion at m/e 600 ($Fe_4C(CO)_{13}^+$) in the mass spectrum of III, suggested either a ketenediyl structure or one in which all the carbonyls were bound to iron atoms and a lone carbon atom was present.

Since the spectroscopic evidence was insufficient to establish unambiguously the identity of III, an X-ray structure determination[7] was performed on a single crystal grown by repeated

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[1] J. S. Bradley, G. B. Ansell, and E. W. Hill, *J. Am. Chem. Soc.*, **101**, 7417 (1979).

[2] V. Ponec, *Catal. Rev.-Sci. Eng.*, **18**, 151 (1978); P. Bileon, J. N. Helle, W. M. H. Sachtler, *J. Catal.*, **58**, 95 (1978).

[3] (a) M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, **102**, 4541 (1980). (b) M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *ibid.*, **102**, 4542 (1980).

[4] The structural characterizations of two other examples of Fe_4C clusters have recently been reported: $HFe_4(CO)_{12}C^-$ (D. F. Shriver and E. Holt, *J. Organomet. Chem.*, in press) and $Fe_4(CO)_{12}C^{2-}$ (J. H. Davis, M. A. Beno, J. M. Williams, J. Zimmie, M. Tachikawa, and E. L. Muetterties, *Proc. Natl. Acad. Sci. U.S.A.* **78**, 668 (1981)).

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[6] ^{13}C NMR spectra were obtained with samples prepared from ^{13}CO enriched $Fe(CO)_5$ as before.

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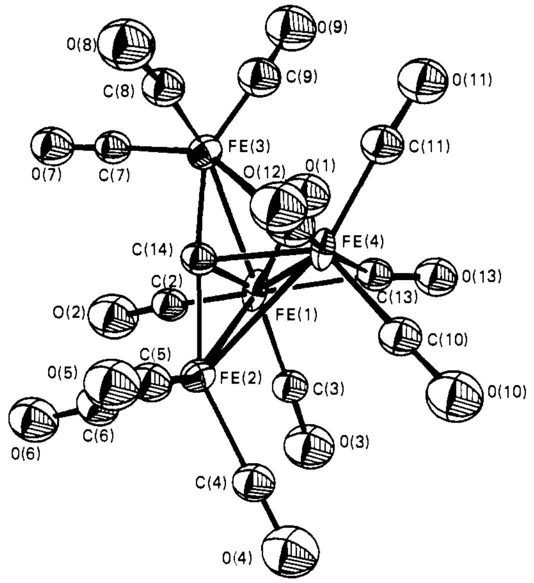

Figure 1. Structure of $Fe_4(CO)_{13}C$. Fe(1)–Fe(2) = 2.642 (1), Fe(1)–Fe(3) = 2.637 (1), Fe(1)–Fe(4) = 2.545 (1), Fe(2)–Fe(4) = 2.647 (1), Fe(3)–Fe(4) = 2.640 (1), Fe(1)–C(14) = 1.998 (4), Fe(2)–C(14) = 1.799 (4), Fe(3)–C(14) = 1.779 (4), Fe(4)–C(14) = 1.987 (3) Å; Fe(2)C(14)Fe(3) = 175°. Dihedral at Fe(1)(4) = 101°.

recrystallization at low temperature from hexane solution and sealed in a capillary under inert atmosphere. The cluster crystallizes ($Z = 4$) in the monoclinic space group $P2_{1/n}$ with $a = 9.337$ (2), $b = 21.440$ (5), $c = 9.519$ (1) Å; $\beta = 98.73$ (1)°; $V = 1883$ (1) Å^3. The final conventional residual was $R_1 = 0.045$ and the weighted residual, $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.055$;[9] all atoms were refined anisotropically.[10] The final difference Fourier synthesis displayed a uniform background density of 0.4 e Å^{-3} throughout the unit cell.

The molecule (Figure 1) comprises a butterfly configuration of four iron atoms similar to that which we reported for II.[1] The dihedral angle between the two triangular planes Fe(1,2,4) and Fe(3,2,4) is 101°, compared with 130° in II. Each of the four iron atoms bears three terminal carbonyl ligands, but the 13th carbonyl [C(13)O(13)] does not form part of the expected ketenediyl function but rather bridges Fe(1) and Fe(4). The most dramatic feature of the molecule is the μ^4-carbon atom, C(14), a close molecular analogue to the proposed surface carbon atoms formed on metal surfaces in the dissociative adsorption of carbon monoxide.[2,4]

The Fe(3)–C(14)–Fe(2) angle is 175° (cf. 147° in II) and the Fe(2,3)–C(14) bonds are significantly shorter (1.80 Å) than the analogous bonds in II (2.02, 2.03 Å) (see Figure 2), suggesting multiple bond character between Fe(2,3) and C(14). A shortening of 0.25 Å has been reported in alkylidene-metal bonds when compared with alkyl-metal bonds.[11]

It is interesting to compare the electronic and geometric structures of $[Fe_4(CO)_{12}CCO_2CH_3]^-$ and $Fe_4(CO)_{13}C$ (Figure 2). Application of Wade's electron counting rules[12] for $Fe_4(CO)_{13}C$ results in seven skeletal bonding pairs—four from the four $Fe(CO)_3$ units, two from the carbon atom, and one from the extra carbonyl ligand. These electrons are accomodated in an arachno structure corresponding to four vertices and seven electron pairs, i.e., a butterfly. The lone carbon atom C(14) does not occupy a vertex in this polyhedron and lies only 0.06 Å above the Fe(2)–Fe(3) vector (∠Fe(2)CFe(3) = 175°).

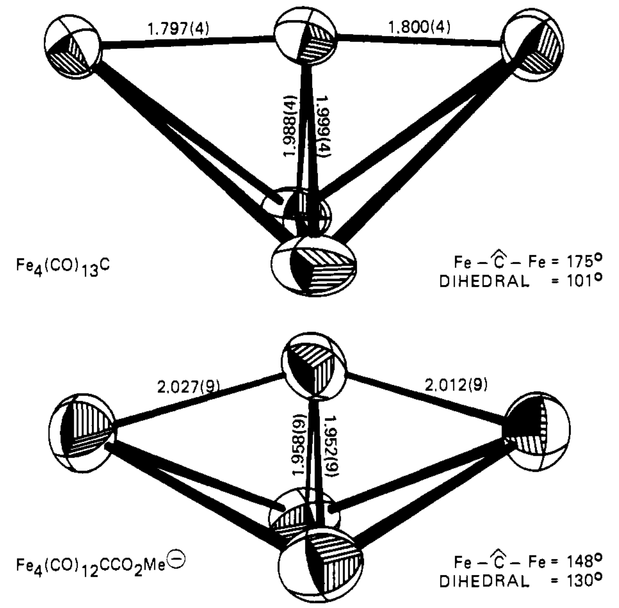

Figure 2. Comparison of core geometries of $Fe_4(CO)_{13}C$ and $[Fe_4(CO)_{12}CCO_2CH_3]^-$.

In the case of the anionic ester $Fe_4(CO)_{12}CCO_2CH_3^-$ a similar treatment results in six bonding pairs—four from the $Fe(CO)_3$ units and two from the methylidyne group plus negative charge. Although it has been suggested[3b] that the cluster is thus electron deficient as an arachno four vertex polyhedron, we feel that it is more appropriate to consider this structure as a *closo* trigonal bipyramid (which requires only six skeletal electron pairs) in which an equatorial vertex is occupied by the μ^4-methylidyne carbon which projects significantly (0.56 Å) from the Fe(2)–Fe(3) vector (∠FeCFe = 148°). If allowance is made for the distortion from a regular trigonal bipyramid necessitated by the differing sizes of the iron and carbon atoms, the cluster is structurally consonant with the predictions of Wade's rules.

Of the various carbidocarbonyl clusters so far structurally characterized, there was until recently none with a carbon atom bonded to less than five metal atoms,[4,13] a fact which has apparently precluded the development of the chemistry of the cluster bound carbon atom. An example of the reactivity of such species was provided by confirmation of the intermediacy of III in the synthesis of II from I (eq 1). Immediate reaction of III with methanol occurs at 25 °C to yield a dark green solution with infrared absorptions similar to those of II. Addition of triethylamine results in the isolation of $Et_3NH[Fe_4(CO)_{12}CCO_2CH_3]$, presumably via deprotonation of the conjugate acid. It is interesting to note that evaporation of methanol prior to base addition results in the quantitative regeneration of III; the mobility of CO between the iron core and the peripheral carbon atom is striking.[14]

The parent Fe_4C cluster $Fe_4(CO)_{13}C$ is now readily accessible. We are actively investigating the chemistry of the exposed cluster bound carbon atom and anticipate a rapid expansion in this intriguing aspect of CO related cluster chemistry.

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(7) Data (4127) were examined by using an 8–28 scan with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) on an Enraf–Nonius CAD 4 diffractometer. Of the independent data, 2566 were regarded as observed $[I > 3\sigma(I)]$.[8] No absorption correction was made [μ(Mo Kα) = 3.12 nm^{-1} with a calculated density of 2.12 g cm^{-3}]. Periodically monitored check reflections revealed no significant variation in intensity throughout the experiment.

(8) $I = S(C - RB)$ and $I = [S^2(C + R^2B) + (kI)^2]^{1/2}$; C is the total count recorded during the scan, $R = 2.0$ is the ratio of the scanning time to the total background B, S is the scan rate, and $k = 0.05$ is a factor introduced to reflect instrument instability.

(9) $\omega = \sigma(F_o)^{-2}$; $|F_o| = I/(LP)$ and $\alpha(F_o) = I/(2|F_o|LP)$ where L and P are the Lorentz and polarization corrections.

(10) All calculations were performed by using the Enraf–Nonius structure determination package and integrated set of crystallographic computer programs for PDP II series computers.

(11) See, for example, R. R. Schrock, *Acc. Chem. Res.*, **12**, 98 (1979).

(12) K. Wade, *Inorg. Nucl. Chem. Lett.*, **8**, 559 (1972).

(13) M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.*, in press.

(14) The original isolation of II by oxidation of I in methanol[1] but without addition of base may have been due to deprotonation by some basic byproduct or impurity in the reaction mixture. We have observed a higher yield and greater reproducibility in this synthesis if 1 equiv of base, such as KOH in methanol, is added to the reaction mixture prior to workup.

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Acknowledgment. We thank Professor D. F. Shriver, Northwestern University, and Professor E. L. Muetterties, University of California, Berkeley, for information on their studies in this area prior to publication.

Supplementary Material Available: A list of atomic coordinates and thermal parameters for $Fe_4(CO)_{13}C$ (2 pages). Ordering information is given on any current masthead page.

Novel Bay-Region Diol Epoxides from Benzo[*c*]phenanthrene

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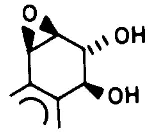
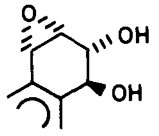
Received May 14, 1981

Diol epoxides in which the epoxide group forms part of a sterically hindered bay region of the molecule have been identified as ultimate carcinogenic metabolites of a number of polycyclic aromatic hydrocarbons.[1] Two diastereomers are possible in which the benzylic hydroxyl group is either cis (series **1**) or trans (series **2**) to the epoxide oxygen. In the absence of unusual steric effects, the diol epoxide **1** diastereomers prefer the conformation in which their hydroxyl groups are quasi-diaxial, whereas the diol epoxide **2** diastereomers prefer the quasi-diequatorial conformation.[2] Only the quasi-diequatorial diol epoxide **2** diastereomers have shown high tumorigenic activity.[3] In the case of benzo[*e*]pyrene, whose bay-region diol epoxide **1** and **2** diastereomers prefer the quasi-diaxial conformation for steric reasons,[4] neither diastereomer displayed strong tumorigenic activity.[5] The 3,4-diol 1,2-epoxides **1a** and **2a** derived from benzo[*c*]phenanthrene were synthesized for the present study in the hope that the highly hindered bay region between carbons 1 and 12 (referred to as a fjord region[6]) would cause **1a** to adopt the presently unknown quasi-diequatorial conformation for a diol epoxide **1** diastereomer.

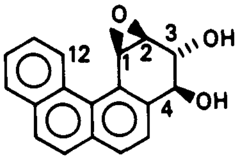


series 1

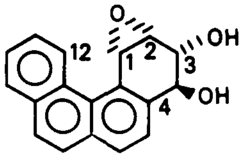


series 2

a, benzo[*c*]phenanthrene
b, chrysene
c, benzo[*a*]pyrene
d, phenanthrene

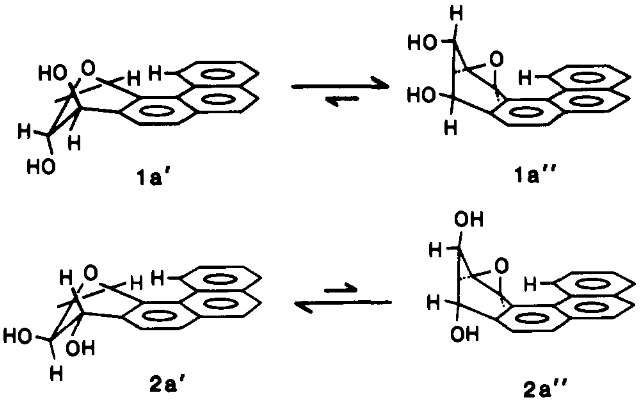


1a



2a

Scheme I



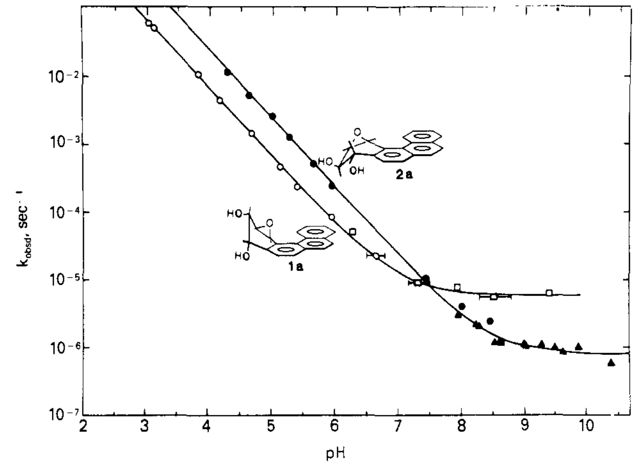


Figure 1. Dependence of pseudo-first-order rate constants for hydrolysis of **1a** and **2a** on pH in 10:90 (v/v) dioxane-water, ionic strength 0.1 M ($NaClO_4$) at 25 °C. Circles designate rate constants determined spectrophotometrically (271 nm) under pseudo-first-order conditions, triangles, rate constants determined from measurement at 271 nm of initial rate, and squares, rate constants determined by HPLC assay of reactant (as the mercaptoethanol adduct) in aliquots of the reaction mixture (see supplementary material for details).

Conformation and Activity. Procedures used with other dihydrodiols[2,7] cleanly converted *trans*-3,4-dihydroxy-3,4-dihydrobenzo[*c*]phenanthrene[8] into diol epoxide **1a** via an intermediate bromohydrin and into **2a** via direct epoxidation. The large values of the coupling constant $J_{3,4}$ (J_{diol}) of 9.0 Hz for **1a** and of 8.0 Hz for **2a** in the ^1H NMR spectra of the diol epoxides[9] indicate that the predominant conformation is that in which the hydroxyl groups are quasi-diequatorial for both diastereomers (**1a**″ and **2a**′, Scheme I). Thus **1a** is the first example in the diastereomer-**1** series in which the quasi-diequatorial conformation is preferred. Relief of steric hindrance between H_1 and H_{12} in **1a**′ and a possible intramolecular H bond between the hydroxyl groups in **1a**″ favor **1a**″. Although the adverse interaction between H_1 and H_{12} is

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(1) For a recent review and leading references, see: Nordqvist, M.; Thakker, D. R.; Yagi, H.; Lehr, R. E.; Wood, A. W.; Levin, W.; Conney, A. H.; Jerina, D. M. in "Molecular Basis of Environmental Toxicity"; Bhatnagar, R. S., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; pp 329-357.

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(7) Yagi, H.; Thakker, D. R.; Hernandez, O.; Koreeda, M.; Jerina, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 1604-1611.

(8) Croisy-Delcey, M.; Ittah, Y.; Jerina, D. M. *Tetrahedron Lett.* **1979**, 2849-2852.

(9) The 100-MHz ^1H NMR spectra (Me_2SO) are as follows. **1a**: δ 4.32 (H_1), 3.87 (H_2), 3.60 (H_3), 4.64 (H_4), 5.82 (C-OH_3 and C-OH_4), 7.50-8.10 (aromatic protons H_5-H_{11}), 9.05 (H_{12}), ($J_{12} = 4.0$, $J_{2,3} \sim 1.0$, $J_{3,4} = 9.0$, and $J_{OH_3,H_3} = J_{OH_4,H_4} = 6.3$ Hz). **2a**: δ 4.71 (H_1), 3.69 (H_2), 3.76 (H_3), 4.60 (H_4), 5.59 (C-OH_3), 5.78 (C-OH_4), 7.50-8.10 (aromatic protons H_5-H_{11}), and 8.60 (H_{12}), ($J_{1,2} = 4.2$, $J_{2,3} = 2.0$, $J_{3,4} = 8.0$, $J_{OH_3,H_3} = 6.3$, and $J_{OH_4,H_4} = 4.9$ Hz).

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