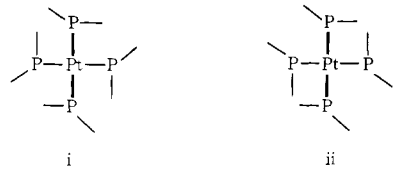
dynamic behavior below 210 K and has two separate rhodium-103 coupled signals in a 4:1 ratio at 190 K. These are attributed to conformational isomers in which the ligands exist in chair or boat form: P. A. Chaloner, unpublished work.

(11) The reasons for preference of a boat-chair conformation in **2** but a chair-chair conformation in **6** must be quite subtle. Both correspond to the schematic orientation i rather than ii and molecular models suggest that the latter suffers more extensive H–H repulsive interactions.



i ii

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Anionic Oxy-Cope Rearrangements with Aromatic Substrates in Bicyclo[2.2.1]heptene Systems. Facile Synthesis of *cis*-Hydrindanone Derivatives, Including Steroid Analogues[1]

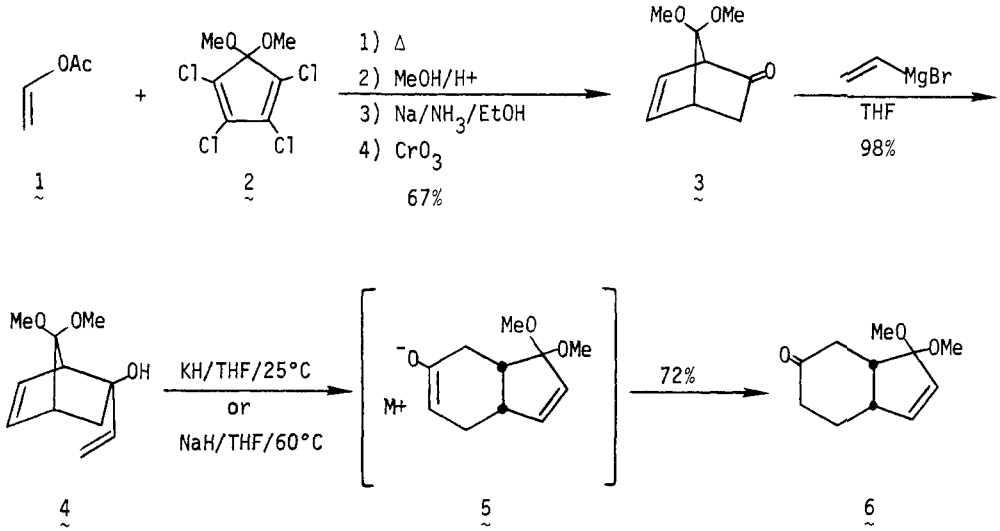
Sir:

Recently Evans[2] has greatly increased the usefulness of the oxy-Cope rearrangement, originally developed by Berson[3] and Viola[4] as a highly thermal process, by reporting that the rate of the [3,3]-sigmatropic shift is enhanced by up to a factor of 10^{17} by reaction of the anion of the allylic alcohol rather than the neutral compound. Similar rate enhancements have been observed in analogous reaction types.[5] We now report the base-catalyzed oxy-Cope rearrangement in highly substituted norbornene systems in which one of the olefinic omponents is an aromatic ring. The use of a naphthyl substituent in this procedure affords a very rapid synthesis of 18,19-bis norsteroids.

The bicyclic enone **3** is readily available in four steps from vinyl acetate **1** and dimethoxytetrachlorocyclopentadiene **2** in an overall yield of 67% (Scheme I).[6] To test the possibility of oxy-Cope rearrangements in these norbornenyl systems, **3** was reacted with vinylmagnesium bromide to afford only the exo alcohol **4** (NMR ($CDCl_3$) δ 6.12 (2 H, m), 4.9–5.9 (3 H, vinyl H), 4.47 (1 H, s), 3.33 (3 H, s), 3.20 (3 H, s), 3.0 (1 H, m), 2.63 (1 H, m), 1.75 (2 H, m); IR (liquid film) 3500 cm^{-1}) in 98% yield.[7,8] The exclusive endo attack of the organometallic reagent is expected since exo attack is sterically hindered by the *syn*-7-methoxy group. Treatment of **4** with KH in tetrahydrofuran (THF) at 25 °C or with NaH in THF at 66 °C for a few minutes afforded cleanly (presumably via the enolate **5**) the rearranged ketone **6** in 72% isolated yield after purification by filtration chromatography on neutral activity III alumina: NMR (CCl_4) δ 5.82 (2 H, br s), 3.12 (3 H, s), 3.08 (3 H, s), 1.5–2.6 (8 H, m); IR (liquid film) 1710 cm^{-1}; mass spectrum (70 eV) *m/e* 196 (M^+), 164 (M − MeOH), 150 (M − MeOMe). This is the first instance of the oxy-Cope rearrangement in bicyclo[2.2.1]heptene systems of this type. Although the structurally similar bicyclo[2.2.2]octene systems are well-known substrates in this process,[2,3] one might have expected some difficulties in reaching the transition state for rearrangement in the norbornenyl systems due to ring and angle strain. However, this does not appear to be the case.

With the demonstration of the feasibility of this type of anionic rearrangement in simple norbornenyl systems accomplished, attention was then directed to the possibility of utilizing aromatic rings as the olefinic component (Scheme II). At the outset of this research, there was only one example of the Cope rearrangement on an aromatic system in the literature, namely the pioneering work of Doering and Bragole.[9] Reaction of **3** with 1-naphthylmagnesium bromide[10] afforded the exo alcohol **7a** in 90% yield: mp 97–99 °C; NMR ($CDCl_3$) δ 7.2–7.8 (7 H, m), 6.0 (2 H, t, J = 2 Hz), 5.05 (1 H, s), 3.43 (3 H, s), 3.29 (3 H, s), 3.0 (2 H, m), 2.4–3.5 (2 H, m); IR (liquid film) 3400 cm^{-1}. The desired rearrangement was best effected by refluxing a mixture of **7a** and NaH in THF for 1 h. In this manner one can isolate (presumably via the enolate **8a**) a 75% yield of the tetracyclic ketone **9a**, which is again purified by filtering through neutral activity III alumina: NMR ($CDCl_3$) δ 6.9–7.3 (4 H, m), 5.8–6.3 (4 H, m), 3.17 (3 H, s), 3.09 (3 H, s), 2.3–3.5 (6 H, m); IR (liquid film) 1710 cm^{-1}; mass spectrum (70 eV) *m/e* 296 (M^+), 264 (M − MeOH), 262 (M − MeOH − H_2). Although we have not yet been able to definitely assign the stereochemistry of the C-8 and C-9 hydrogens (steroid numbering) in ketone **9a**,[11] we believe that it is probably the all-cis isomer shown. Examination of molecular models of the likely transition state indicates that the C-8 hydrogen should be syn to the hydrogens at the juncture of the six- and five-membered rings (C-13 and C-14). One would expect the hydrogen at C-9 to be mainly cis to that

Scheme I



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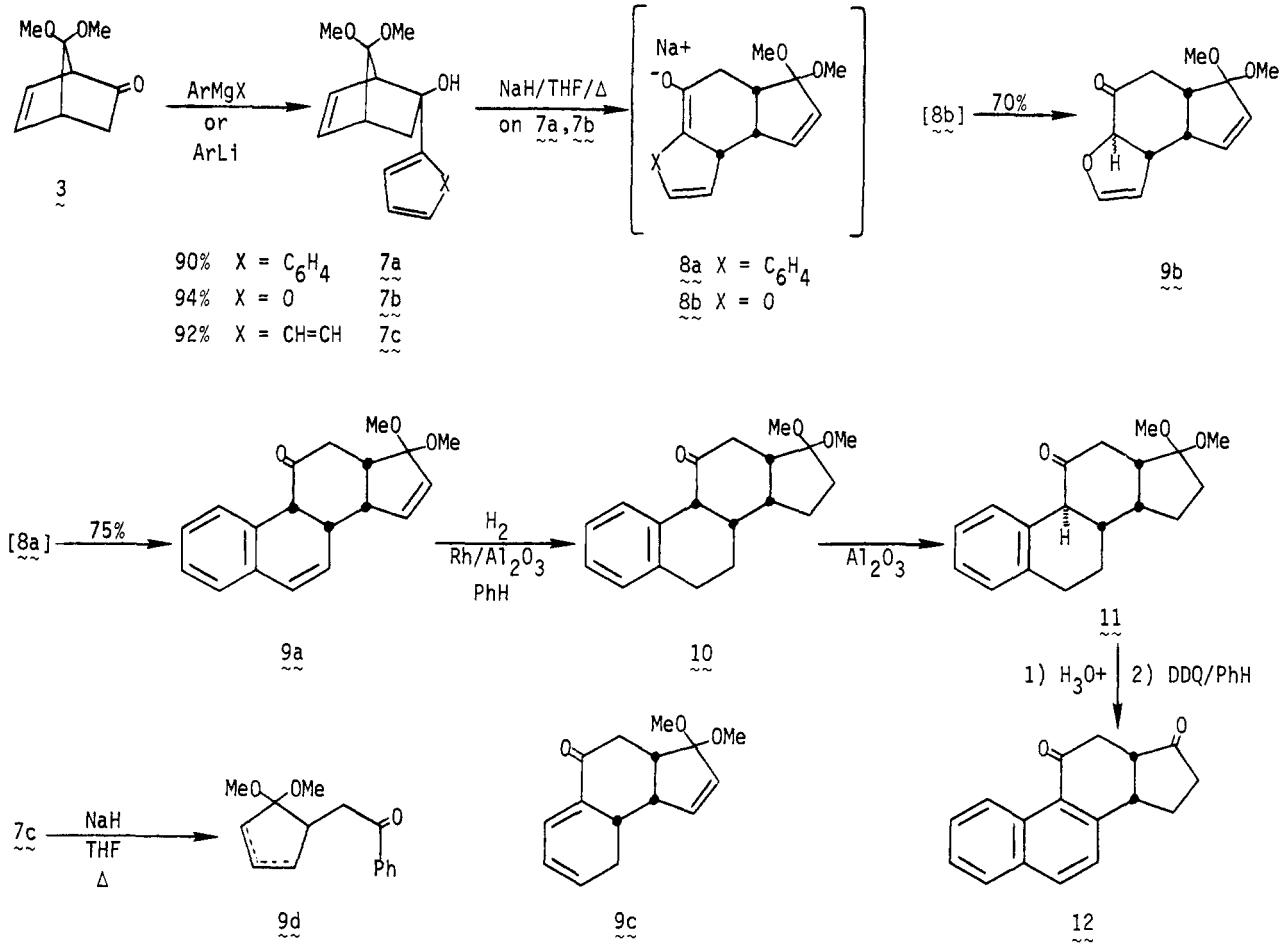
Scheme II



at C-8, since protonation of the enolate **8a** should occur from the less hindered face. Indirect evidence for this stereochemical assignment was obtained by examination of the 200-MHz NMR spectrum of the tetrahydro compound **10** (H_2, Rh/Al_2O_3, PhH, 5 h, 85%), which showed a broad singlet at δ 3.9, which should correspond to the all-cis stereochemistry. After chromatography on alumina, the 200-MHz NMR spectrum showed a doublet at δ 3.95 with a coupling constant of 10 Hz, which should correspond to the trans disposition of the hydrogens at C-8 and C-9, namely structure **11**. Confirmation of the gross structural assignment was obtained by the conversion of **11** into the dione **12** by hydrolysis and dehydrogenation. Dione **12** was identical (melting point, 200-MHz NMR, IR, TLC) with an authentic sample prepared from 2-acetylnaphthalene and furfural by a known procedure.[12]

The furyl aromatic system can also function as the olefinic component. For example, the exo alcohol **7b** (NMR ($CDCl_3$) δ 7.3 (1 H, br s), 6.0-6.3 (3 H, m), 5.6 (1 H, m), 4.5 1 H, s), 3.39 (3 H, s), 3.23 (3 H, s), 2.9-3.1 (2 H, m), 2.0 (2 H, m); IR (liquid film) 3450 cm^{-1}), prepared in 94% yield from the ketone **3** and 2-furyllithium,[13] upon treatment with NaH in THF at 66 °C for 1 h afforded (via **8b**) the tricyclic ketone **9b** in 70% yield: NMR ($CDCl_3$) δ 6.4 (1 H, t, J = 1 Hz), 5.92, (2 H, br s), 4.97 (1 H, t, J = 1 Hz), 4.62 (1 H, d, J = 12 Hz), 3.26 (3 H, s), 3.18 (3 H, s), 2.3-3.7 (5 H, m); IR (liquid film) 1720, 1610 cm^{-1}; mass spectrum (70 eV) m/e 236 (M^+), 204 (M − MeOH), 202 (M − MeOH − H_2).[14]

The success of the rearrangement in the naphthyl and furyl cases prompted the investigation of the phenyl analogue **7c**, in which the loss of aromaticity associated with the rearrangement would be much more severe in terms of energy than in **7a** or **7b**. Addition of phenylmagnesium bromide to **3** furnished a 92% yield of the exo alcohol **7c**: mp 72-73 °C; IR (liquid film) 3400 cm^{-1}. After many unsuccessful attempts, the following conditions were found to effect a rearrangement. Warming of a mixture of **7c** and NaH in THF at reflux for 1.25 h afforded a mixture of products, from which a compound assigned structure **9d** could be isolated in 10% yield by careful chromatography on neutral activity IV alumina: NMR ($CDCl_3$) δ 7.9 (2 H, m), 7.45 (3 H, m), 5.7 (2 H, br s), 3.27 (3 H, s), 3.2 (3 H, s), 2.5-3.5 (5 H, m); IR (liquid film) 1685 cm^{-1}.[15] None of the corresponding oxy-Cope rearrangement product **9c** was isolated from this reaction. Thus the driving force of the anionic oxy-Cope rearrangement does not seem to compensate for the loss of aromaticity in the phenyl system. Further work on substituted phenyl systems is necessary before precise limitations on the generality of the reaction can be fixed.

The conversion of the ketone **9a**, which contains carbonyl functionality at both C-11 and C-17 but has the epi configuration at C-14, into 11-functionalized estrone derivatives, as well as the possible use of more highly functionalized substrates in the key step, is currently underway in our laboratory.[16]

Acknowledgment. We acknowledge the partial support of this research, especially in its early stages, by a Frederick Cottrell grant from the Research Corporation. We also thank Eli Lilly and Co. for an unrestricted grant which has been used to support part of this research. The NMR spectrometer (Bruker WP-200) used in this work was purchased with funds provided by the National Science Foundation via a major equipment grant.

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(1) This work was presented in part at the 13th Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Oct 1977.
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(6) M. E. Jung and J. P. Hudspeth, *J. Am. Chem. Soc.*, **99**, 5508 (1977).
(7) All new compounds had spectral properties (NMR, IR, mass spectra) in complete accord with the assigned structures.
(8) The assignment of the exo stereochemistry to the alcohols **4**, **7a**, **7b**, and **7c** was based on several facts: the analogy of their NMR spectra to those of compounds with aryl groups in the endo position and, most importantly, the effect of the europium shift reagent, Eu(fod)$_3$, on the chemical shifts of the various protons in the molecules. In general, of all of the protons in the exo alcohols, those of the *syn*-7-methoxy group experienced the largest downfield shift by far, implying that this group is proximate to the coordinating alcoholic function. When the known endo alcohol corresponding to **3** (see ref 6) is treated with the same europium shift reagent, there is essentially no downfield shift of the *syn*-7-methoxy group.
(9) W. von E. Doering and R. A. Brazole, *Tetrahedron*, **22**, 385 (1966). Since the completion of this research, a recent paper has appeared in which the second example of an aromatic Cope rearrangement is reported, using 1-(*m*-hydroxyphenyl)-2-vinylcyclopropane as the substrate: E. N. Marvell and C. Lin, *J. Am. Chem. Soc.*, **100**, 877 (1978). In both of these examples, vigorous conditions are required to effect the desired rearrangement.
(10) M. Gilman, N. B. St. John, and F. Schulze, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 425.
(11) This ketone corresponds to 14-*epi*,18,19-bisnorestr-6,15-diene-11,17-dione 17-dimethyl ketal.
(12) A. Koebner and R. Robinson, *J. Chem. Soc.*, 1994 (1938), 566 (1941); R. Robinson, *ibid.*, 1390 (1938).
(13) C. H. Heathcock, L. G. Gulick, and T. Dehlinger, *J. Heterocycl. Chem.*, **6**, 141 (1969).
(14) The structure of **9b** was assigned on the basis of both its spectra data and mechanistic analogy to **9a**.
(15) Close examination of the 200-MHz NMR spectrum of **9d** did not allow one to determine the position of the double bond in **9d**. The broad singlet at δ 5.7 due to the olefinic protons was not defined enough to distinguish between the two possible isomers.
(16) For example, the use of the Grignard reagent from 6-methoxy-1-iodonaphthalene (readily available; see A. A. Akhrem and Y. A. Titov, "Total Steroid Synthesis", Plenum Press, New York, N.Y., 1970, p 861) would permit the introduction of the 3-methoxy substituent in the steroid system. Likewise the vinyl anion derived (via the vinyl bromide or the *N*-sulfonylhydrazone) from 6-methoxy-α-tetralone (readily available; see G. Stork, *J. Am. Chem. Soc.*, **69**, 576 (1947)) would also introduce oxygen functionality at the eventual C-3 position.

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Thiocarbonyl Complexes of Iron(II) Porphyrins. Formation by Thiophosgene Reduction

Sir:

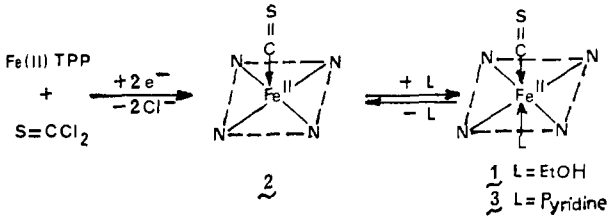
Carbon monoxide is a widely used ligand of metalloporphyrins and hemoproteins.[1] Some transition metal complexes of its analogue, carbon monosulfide, have been described; this ligand is a better σ donor and π acceptor leading to stronger bonds with electron-rich metals.[2] However, no thiocarbonyl complexes of metalloporphyrin have yet been described, perhaps because of the great unstability of free CS contrary to CO.

Since iron(II) porphyrins are able to reduce various halogenated compounds[3] and to form CX_2 carbene complexes from polyhalogenated methanes CX_4 in the presence of an excess of reducing agent,[4-6] we tried to prepare thiocarbonyl-iron(II) porphyrin complexes by in situ reduction of thiophosgene. This paper reports the isolation and characterization of some $Fe^{II}(TPP)(CS)$[7] complexes and compares some of their properties with those of the corresponding $Fe^{II}(TPP)(CO)$ or -(carbene) complexes.

Addition of deaerated thiophosgene to a DMF[7] solution of $Fe^{II}(TPP)$ results in an immediate oxidation of the iron, giving $Fe^{III}(TPP)(Cl)$. When the same experiment is done in the presence of an excess of iron powder as a reducing agent, with vigorous stirring, there is formation of a new species[8] characterized in visible spectroscopy by peaks at 420 and 539 nm. In a preparative experiment, thiophosgene (1 mmol) is added to a stirred CH_2Cl_2–MeOH (20:1) solution of $Fe^{III}(TPP)(Cl)$ (0.5 mmol) and $(CH_3S)_2CS$[8] (3 mmol) in the presence of iron powder and under argon. After reaction for 1 h, followed by filtration, evaporation of solvents, and crystallization from CH_2Cl_2–EtOH, a crystalline purple complex **1** is obtained (yield 90%). All of its characteristics indicate the structure $Fe^{II}(TPP)(CS)(EtOH)$: elemental analysis (C, H, Cl, N, S) in agreement with $C_{47}H_{34}FeN_4OS$;[9] ^1H NMR δ ($CDCl_3$, Me_4Si,[7] ppm) 8.83 (s, 8 H), 8.11 (m, 8 H), 7.71 (m, 12 H) for the protons of the porphyrin ring, and 3.61 (q, J = 6.6 Hz, 2 H), 1.21 (t, J = 6.6 Hz, 3 H), 1.06 (s, 1 H) for the protons of EtOH; ^{13}C NMR δ ($CDCl_3$, Me_4Si, ppm) 145.7, 141.7, 133.6, 132.5, 127.6, 126.7, 120.8 for the carbons of the porphyrin ring, 57.9 and 17.9 for the carbons of EtOH, and a sharp weak peak at 313.5. It is a low-spin iron(II) complex as indicated by its magnetic susceptibility (μ_{eff} = 0 at 33 °C, measured by the Evans method[10]), and by the positions and shapes of the signals of its ^1H and ^{13}C NMR spectra. The NMR data are also indicative of an axial symmetry. Carbon monosulfide is one ligand of iron(II) as shown by the elemental analysis, the ^{13}C NMR peak at 313.5 ppm, and the intense 1295-cm^{-1} IR band (KBr pellet) of complex **1**. These two spectroscopic data ($\delta_{C=S}$ and $\nu_{C=S}$) are in good agreement with those reported for thiocarbonyl complexes of iron(II).[11] Furthermore, the mass spectrum (100 eV, 200 °C) of complex **1** exhibits a peak at *m/e* 712 corresponding to Fe(TPP)(CS).

In solution, complex **1** is in equilibrium with the pentacoordinated complex Fe(TPP)(CS) (**2**) and free EtOH. At 25 °C, this equilibrium, when established from pure complex **1**, is almost completely displaced toward complex **2**. Accordingly, the signals of EtOH in the ^1H NMR spectrum of complex **1** (10^{-2} M in $CDCl_3$ at 35 °C) are those of free EtOH. Lowering the temperature down to −60 °C causes a progressive upfield shift of the methylene quartet (~1.7 ppm) and the methyl triplet (~1 ppm) of EtOH, indicating that the equilibrium is progressively driven toward the hexacoordinated complex **1**, the exchange between bound and free EtOH remaining always fast on the NMR time scale. The equilibrium constant (K = 6 L mol^{-1} at 25 °C) between the complexes **2**, λ 409 nm (ε 2.2 × 10^5), 523 (17 × 10^3), 550 (sh), and **1**, λ 419 nm (ε 2.3 × 10^5), 535 (14 × 10^3), has been calculated from the visible spectra of complex **1** in benzene containing increasing amounts of EtOH.

More basic ligands such as pyridine or *N*-methylimidazole exhibit a greater affinity for complex **2**. For instance, binding of pyridine leads to the Fe(TPP)(CS)(pyridine) complex **3**, λ 424 nm (ε 2.25 × 10^5), 543 (14 × 10^3) nm in benzene, with



an equilibrium formation constant of 5600 L mol^{-1} at 25 °C.

The Fe–CS bond in complexes **1**, **2**, or **3** is considerably stronger than the Fe–CO bond of known Fe(TPP)(CO)(L) complexes.[12] It is not dissociated upon dilution (2.10^{-8} M) or after heating complex **2** at 150 °C under 10^{-2} mmHg for 4 h. Moreover, solutions of complex **2** are remarkably stable to oxygen as shown by the lack of detectable oxidation after bubbling oxygen during 20 h. Complex **2** can thus be handled

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