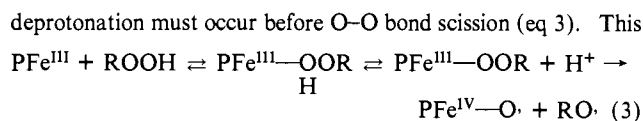ROOH and ClFe^{III}TPP by both initial rate and pseudo-first-order methods. In Figure 1, the log k_{ROOH} values are plotted against pK_a for the corresponding leaving group (ROH). For comparative purposes, we also examined the oxygen-transfer rates of several other often used oxidants (Table I). Iodosobenzenediacetate reacts with a rate constant similar to the peracids while the rate of oxygen transfer from p-cyano-N,N-dimethylaniline N-oxide is 2× that of the most reactive hydroperoxide.

The slope of the linear free energy plot in Figure 1 shows a break at a pK_a for ROH of 11. This behavior is highly suggestive of a change in mechanism or a change in rate-limiting step. In the transfer of an oxygen atom from ROOH to a tertiary amine, an alkyl sulfide, and iodide, plots of log k_{ROOH} vs. pK_a(ROH) exhibited a negative slope with no break.[15] Likewise, a negative slope with no break was observed in a plot of log k_{ROOH} vs. pK_a(ROH) for oxygen transfer to (tetraphenylporphyrin)chromium chloride (ClCr^{III}TPP).[16] Since the reactions of protohemin[11] and ClFe^{III}TPP with peracids have been shown to involve heterolytic O–O bond cleavage, we suggest that, for hydroperoxides with a pK_a < 11 for the corresponding leaving group (ROH), the mechanism of oxygen transfer to ClFe^{III}TPP involves a heterolytic cleavage of the O–O bond. For hydroperoxides of lower acidity, we propose the mechanism of oxygen transfer involves a homolytic cleavage of the O–O bond. We are unable to rationalize the data in Figure 1 by assuming a heterolytic mechanism and a change in rate-determining step.

The calculated slope (β_{1g}) for oxygen transfer to ClFe^{III}TPP via the proposed heterolytic cleavage of ROOH is –0.35. This is identical with the value obtained for oxygen atom transfer to ClCr^{III}TPP[16] and may be compared to β_{1g} = –0.6 for oxygen atom transfer to thioxane, N,N-dimethylbenzylamine, and iodide.[15] The less negative β_{1g} for heterolytic cleavage of ROOH by ClFe^{III}TPP and ClCr^{III}TPP as compared to the classical nucleophiles, :S<, :N<, and I$^-$, can be loosely interpreted as an earlier transition state for the former. Interestingly, the absolute magnitude of the rate constants for oxygen transfer to ClFe^{III}TPP is greater than for the three classical nucleophiles studied earlier. This forces one to consider a "positively" charged iron(III) porphyrin a relatively strong nucleophile toward peroxide oxygen. The nucleophilicity of the iron center is conceivably due to the pairing of electrons in an axially oriented d orbital. The magnitude of the rate constant may be influenced by low-lying d orbitals capable of reducing electron–electron repulsion by forming a π bond in the transition state.[17]

As expected for homolytic cleavage of an O–O bond, the hydroperoxides of lowest acidity show small variations in k_{ROOH} with the pK_a of ROH.[18] We have also briefly examined the sensitivity of k_{ROOH} for $tert$-butyl hydroperoxide and diphenylhydroperoxyacetonitrile with ClFe^{III}TPP toward hydrogen ion activity in pure methanol. $tert$-Butyl hydroperoxide shows a large negative dependence on hydrogen ion concentration in the range 10^{-4} to 10^{-9} M (values were obtained by adding calculated amounts of NaOCH$_3$ or methanolic HCl). In contrast, k_{ROOH} for diphenylhydroperoxyacetonitrile exhibits the reverse hydrogen ion sensitivity in this concentration range. It appears that in the homolytic cleavage of a hydroperoxide bound to an iron porphyrin

deprotonation must occur before O–O bond scission (eq 3). This

$$PFe^{III} + ROOH \rightleftharpoons PFe^{III}\underset{H}{-}OOR \rightleftharpoons PFe^{III}-OOR + H^+ \rightarrow$$

$$PFe^{IV}-O\cdot + RO\cdot \quad (3)$$

differs significantly from the heterolytic mechanism where the proton must be transferred to the oxygen atom of the leaving group.[11]

We feel our results help to clarify much of the controversy in the current literature concerning the reaction mechanism of simple iron(III) porphyrins with peracids and hydroperoxides. In examples where the mechanism of O–O bond cleavage differs from the prediction, additional catalysis could be invoked. The observed heterolysis of H$_2$O$_2$ by the peroxidases is a case in point.[19] For cytochrome P-450, our results suggest that indeed both homolytic and heterolytic mechanisms can be operative depending on the structure of the oxidant.

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Electron-Transfer Reactions of Trivalent Uranium. Preparation and Structure of (MeC$_5$H$_4$)$_3$U=NPh and [(MeC$_5$H$_4$)$_3$U]$_2$[μ-η^1,η^2-PhNCO]

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In contrast to the large number of d-metal organoimides,[1]

$$\overset{+}{M}{-}\overset{-}{N}R \leftrightarrow M{=}\overset{\cdot\cdot}{N}R \leftrightarrow \overset{-}{M}{\equiv}\overset{+}{N}R$$
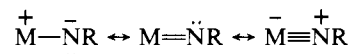
only one f-metal organoimide, Cp$_3$UNC(Me)C(H)PPh$_2$Me,[2a] prepared by insertion of acetonitrile into Cp$_3$U(CH)PPh$_2$Me,[2b] has been reported. The U–N distance of 2.06 (1) Å and the U–N–C angle of 163 (1)° suggest that the U–N bond order is between 2 and 3. Organoimides are of considerable interest relative to structure[3] and reactivity studies[4] and rational synthetic reactions need to be developed before the reaction chemistry can be explored systematically. Reaction of a trivalent uranium compound with either an organic azide or isocyanate to give a pentavalent uranium organoimide derivative with evolution of either nitrogen or carbon monoxide, respectively, is a rational and potentially general synthetic reaction for these interesting complexes.[1,5] In this paper we describe the reaction of U-(C$_5$H$_4$Me)$_3$(THF) with organic azides to give U(C$_5$H$_4$Me)$_3$NR

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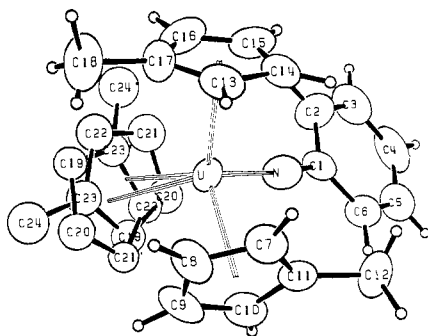(18) Benson, S. W.; Shaw, R., ref 17, pp 105–139.

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Figure 1. ORTEP diagram for $(MeC_5H_4)_3UNPh$. One MeC_5H_4 ring is disordered, see ref 9 and the supplementary material. The averaged U–C(7–11) = 2.758 ± 0.024, U–C(13–17) = 2.734 ± 0.023, and U–C-(19–23) = 2.759 ± 0.036 Å (for the 63% occupancy ring). The averaged U–ring centroid distance is 2.48 Å. There is no bond between C(2) and C(14), the line from C(2) is the bond to hydrogen.

or organoisocyanates to give $[U(C_5H_4Me)_3]_2[PhNCO]$.

The uranium metallocene, $U(C_5H_4Me)_3(THF)$,[6] reacts with Me_3SiN_3 or PhN_3 in diethyl ether at room temperature with evolution of nitrogen over 30 min to give red $U(C_5H_4Me)_3UNR$, R = Me_3Si[8] or Ph,[9] on crystallization from hexane in ca. 50% isolated yield. The $Cp_3UNSiMe_3$ was prepared similarly and crystallized from diethyl ether.[10] An ORTEP diagram for the phenylimide complex is shown in Figure 1. The most important feature is the presence of the imido functional group with a U–N distance of 2.019 (6) Å and a U–N–C(1) angle of 167.4 (6)°. The U–N distance is the shortest U–N distance ever reported. The U–N (single) bond distance in tricyclopentadienyluranium complexes ranges from 2.29 (1) Å in Cp_3UNPh_2[11a] to an average of 2.38 (1) Å in Cp_3U(pyrazolate).[11b] If we assume a standard U–N single-bond distance of 2.30 Å, then the U–N distance in the organoimide of 2.02 Å is 0.28 Å or 12% shorter. Similar shortening is observed in comparing M—NR_2 relative to M=NR or M≡NR distances in the transition-metal series.[1,12] The essentially linear UNC angle suggests that both lone pairs of electrons on the nitrogen atom are involved in bonding to uranium and the U–N bond is best viewed as a triple bond.

(6) Prepared from UCl_3[7] and NaC_5H_4Me in THF, followed by crystallization from hexane/THF (50:1) as dark (black) needles in 33% yield, mp 136–140 °C. Analytical data for all new compounds is in supplementary material. ^{1}H NMR (C_6D_6, δ 7.15, 27.5 °C): δ–11.6 (br, 6 H), –14.0 (4 H), –14.4 (6 H), –15.6 (9 H), –31.1 (4 H). The second and fifth resonances undergo exchange with added THF showing that these resonances are due to coordinated THF.

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(8) Mp 132–140 °C; ^{1}H NMR (C_6D_6, 36 °C) δ 6.72 ($\nu_{1/2}$ = 11 Hz, 9 H), 3.03 ($\nu_{1/2}$ = 10 Hz, 9 H), –1.96 ($\nu_{1/2}$ = 37 Hz, 6 H), –10.4 ($\nu_{1/2}$ = 29 Hz, 6 H); ^{13}C{^{1}H} NMR δ 121.0, 117.4, 100.9, 73.26, –2.28. The first three resonances and the last resonance are due to the MeC_5H_4 carbon atoms.

(9) M$^+$, 566 amu, mp 108–110 °C; ^{1}H NMR (C_6D_6, +32 °C) δ 18.5 ($\nu_{1/2}$ = 15 Hz, 2 H), 4.20 ($\nu_{1/2}$ = 2 Hz, t, J = 7 Hz, 1 H), 3.67 ($\nu_{1/2}$ = 19 Hz, 9 H), –2.40 ($\nu_{1/2}$ = 8 Hz, 2 H), –3.39 ($\nu_{1/2}$ = 45 Hz, 6 H), –10.8 ($\nu_{1/2}$ = 45 Hz, 6 H); ^{13}C{^{1}H} NMR the methylcyclopentadienyl carbons appear at δ 118, 99.3, 82.0, and –3.9, the phenyl carbons appear at δ 122.7, 97.6, and 108.4, and the *ipso* carbon resonance was not observed. Crystal Data (–95 ± 5 °C), orthorhombic, a = 8.4113 (14) Å, b = 10.0701 (19) Å, c = 22.9639 (33) Å, space group $P2_12_12_1$, F_w = 566.5, V = 1945.1 (10) Å^3, ρ(calcd) = 1.93 g cm^{-3}, Z = 4, μ(Mo Kα) = 79.2 cm^{-1}, λ = 0.71073 Å. The final residuals for 231 variables refined against 26 constraints and the 1405 data for which F^2 > $3\sigma(F^2)$ were R = 0.0212, R_w = 0.0293, and GOF = 1.803. The R value for all 1484 data was 0.0248. The occupancy factor of the majority component of Cp(3) refined to 0.63.

(10) M$^+$ = 520 amu, mp = 207–208 °C, μ = 1.98 μ_B (4–300 K); ^{1}HNMR (C_6D_6, 32 °C) δ 6.96 ($\nu_{1/2}$ = 8 Hz, 9 H), –6.47 ($\nu_{1/2}$ = 30 Hz, 15 H); ^{13}C{^{1}H} NMR δ 108.1 (d, J = 150 Hz), 72.27 (q, J = 118 Hz.).

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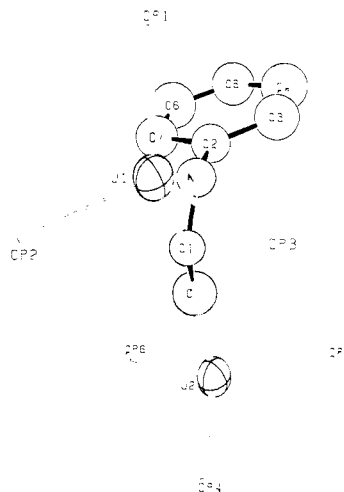

Figure 2. ORTEP diagram for $[(MeC_5H_4)_3U]_2[PhNCO]$. MeC_5H_4 groups are labeled Cp (1···6) for clarity. The averaged U(1)–C(Cp 1–3) and U(2)–C (Cp 4–6) distances are 2.80 (3) and 2.76(2) Å, respectively. The averaged U(1)–ring centroid (Cp(1–3)) and U(2)–ring centroid (Cp(4–6)) distances are 2.53 and 2.48 Å, respectively, and the averaged ring centroid–U(1)–ring centroid and ring centroid–U(2)–ring centroid angles are 113.8 and 116.5°, respectively. C(1)–N(1) = 1.31 (2) Å, C(1)–O = 1.36 (2) Å, U(1)–N–C(2) = 152.3 (13)°, C(1)–N–C(2) = 130.1 (16)°, N(1)–C(1)–O = 118.9 (16)°, U(1)–C(1)–O = 168.1 (13)°, C(1)–O–U(2) = 164.0 (12)°. The torsional angle Cp(1)–U(1)–U(2)–Cp(4) is 176.0° and C(2)–N–U(1)–Cp(1) is –8.7°.

We can account for the bonding in a very crude symmetry orbital picture in the following way.[13] Assume that the molecule has C_{3v} symmetry and that the 5f, 6d, and 7s orbitals on uranium are available for bonding to the Cp and NR functional groups. Assume further that the 7p orbitals are too high in energy for useful bonding interactions.[13c,d] The e_1 (pπ) orbitals of the three Cp rings give rise to four SALC's that transform as a_1, a_2, and 2 × e, and the a_1 (pπ) orbitals of the three Cp rings rise to two SALC's that transform a_1 and e. The metal AO's transform as a_1 [s, z^2, z^3, and $x(x^2 - 3y^2)$], a_2 [$y(3x^2 - y^2)$], and e [xy, $x^2 - y^2$, xz, yz, xz^2, yz^2, xyz, $z(x^2 - y^2)$]. If we let the nine Cp orbitals overlap with the a_1 [s, z^2, $x(x^2 - 3y^2)$], a_2, and e [xy, $x^2 - y^2$, xz, yz, xyz, $z(x^2 - y^2)$] metal AO's, then we have left over the $2a_1$ + e AO's to overlap with the a_1 + e set on the NR fragment. In this way we can account for the M–NR triple bond since the six electrons on the $(NR)^{2-}$ unit are donated into the $2a_1$ + e AO's of the $(Cp_3U)^{2+}$ unit which contains one electron.

In contrast to the reaction of the organoazides with the trivalent metallocene $U(C_5H_4Me)_3(THF)$, reaction of phenyl isocyanate does not give the phenylimide with evolution of carbon monoxide but gives the red 2:1 complex $[(C_5H_4Me)_3U]_2[[\mu-\eta^1,\eta^2-PhNCO]]$.[14] An ORTEP drawing is shown in Figure 2. The structural feature of most interest is the $[PhNCO]^{2-}$ unit that is bridging the two tetravalent uranium, $U(C_5H_4Me)_3$, fragments in an $\eta^1[U(2)-O]$, $\eta^2[U(1)NC(1)]$ fashion. The U(1)–N distance of 2.36 (2) Å is similar to that found in Cp_3U(pyrazolate)[11b] of 2.38 (1) Å, the U(1)–C(1) distance of 2.42 (2) Å is similar to

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(14) μ = 3.58 μ_B (90–300 K) per molecule; ^{1}H NMR (C_7D_8, 29 °C) inequivalent C_5H_4Me resonances δ 12.6 (6 H), 4.39 (6 H), –3.14 (9 H), –7.86 (6 H), –18.6 (6 H), –21.7 (9 H), phenyl resonances δ 6.40 (1 H, t, J = 7 Hz), 3.06 (2 H, m), –24.9 (2 H, d, J = 7 Hz). The width at half height is 1–2 Hz for all of the resonances. Crystal data (25 °C), monoclinic, a = 17.596 (6) Å, b = 13.882 (3) Å, c = 16.312 (6) Å, β = 113.11 (3)°, space group $P2_1/c$ (No. 14), F_w = 1069.9, V = 3665 (4) Å^3, ρ(calcd) = 1.94 g cm^{-3}, Z = 4, μ(Mo Kα = 84.0 cm^{-1}, λ = 0.71073 Å, crystal size 0.09 × 0.21 × 0.25 mm. In the final cycles of least squares the uranium atoms were refined with anisotropic thermal parameters and all other atoms with isotropic thermal parameters. The final residuals for 199 variables refined against 2089 data for which F^2 > $3\sigma(F^2)$ were R = 0.0435, R_w = 0.0483, and GOF = 1.254. The R value for all of the 4810 data was 0.124.

that found in Cp₃U(*n*-Bu) of 2.43 (2) Å,[15a] and the U(2)–O distance of 2.11 (1) Å is similar to that found in [(Me₅C₅)₂U-(OMe)]₂PH of 2.05 (1) Å.[15b] The bond-length data support the view that the uranium atoms in the U(C₅H₄Me)₃ units are tetravalent and that the bridging phenyl isocyanate is best represented by the valence bond structure
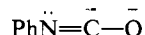
$$PhN = C - O$$

the result of a one-electron transfer from each (MeC₅H₄)₃U molecule. The PhNCO complex does not liberate CO on heating to 80 °C, nor do the nonequivalent MeC₅H₄ groups undergo site exchange.

Supplementary Material Available: Complete listing of bond lengths and angles for both crystal structures and positional and thermal parameters and all analytical data (11 pages). Ordering information is given in any current masthead page.

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Stereocontrolled Syntheses of (*E*)- and (*Z*)-γ-Bisabolene 8,9-Epoxide

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γ-Bisabolene (**1**) is a naturally occurring sesquiterpene hydrocarbon[1] which on a speculative level is considered an important early intermediate in the biosynthesis of a variety of natural sesquiterpenoids.[2] However, only a few experimental works have been done in order to confirm either the *E* or *Z* isomeric forms of γ-bisabolene (**1a,b**) as real biogenetic intermediates,[3] or to exclude them as such,[4] which may be due to the fact that, despite the abundance of sesquiterpenes in nature and the variety of structural types, few compounds possessing the γ-bisabolene skeleton have been found in nature until recently. Chemical reports that permit a differentiation of both isomers, or which include an independent synthesis of each, have been published[5] and, as a result of these definitive studies,[5c] the proper identification of γ-bisabolene in natural systems can now be made.

The biosynthetic origin of the complex halogenated chamigrenes and related skeletal rearranged sesquiterpenes isolated from marine

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sources[6] has been the subject of recent discussions,[7] and pathways involving bromonium ion induced ring closure of γ-bisabolene (**1**) or γ-bisabolene 8,9-epoxide (**2**) have been proposed.[7d] As a part

1a   **1b**   **2a**   **2b**
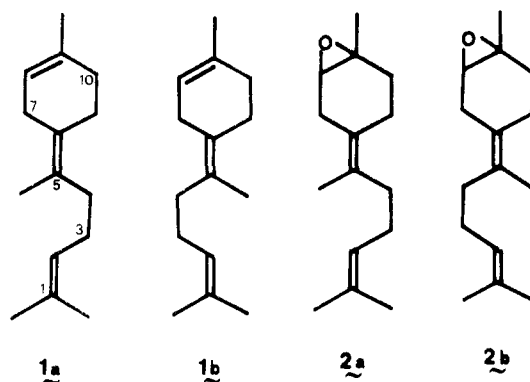
of our program on the synthesis of intermediates in terpene biogenesis and constituents of marine organisms, we have developed and record herein the first differentiated synthesis of the naturally found (*E*)-γ-bisabolene 8,9-epoxide (**2a**)[8] and its geometrical (*Z*)-isomer (**2b**), a discussion of which is the subject of this communication.

Neighboring group participation[9] is an established tool for reactivity control. It has been used for stereoselective introduction of functional groups,[10] selective protection,[11] double-bond transposition,[12] and to induce molecular conformational changes.[13] Racemic 8,9-trans-disubstituted (*E*)- and (*Z*)-γ-bisabolenes are synthesized here with regio- and stereocontrol by using simple forms of bridged intermediates (Scheme I). The control elements "X" and "Y" are inherent to the molecular organization of the starting material and are converted to *vicinal* groupings having defined stereochemistry in the final products. The stereochemistry of the tetrasubstituted olefinic bonds is controlled by bridging delivery from C₅ and C₆ positions.

The synthesis of (±)-**2a** (Scheme II) was initiated from the (±)-β-hydroxy acid **3a**, available[5c] on a large scale from 4-methyl-3-cyclohexenecarboxylic acid and 6-methyl-5-hepten-2-one in 85% yield, followed by fractional recrystallization of the diastereoisomeric **3a,b** mixture. Reaction of the diisopropylamine salt of **3a** with iodine in dichloromethane produced the iodo lactone **4a**[14] in 97% yield. Treatment of **4a** in THF with 1.5 equiv of aqueous potassium hydroxide at 0 °C for 2 h and isolation of the acidic product provided the unstable epoxy acid **5a** in 98% yield, which without further purification was treated with a catalytic amount of *p*-toluenesulfonic acid in methylene chloride to produce

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