also express our gratitude to Professor J. Baldwin for communication of his method of β-lactam synthesis prior to publication and to Professor Baldwin and Professor D. Evans for valuable discussions.

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(6) This structure was defined by x-ray crystallography by Dr. N. Jones and Dr. M. Chaney of the Lilly Research Laboratories.

(7) For a total synthesis, see T. Kamiya, "Recent Advances in the Chemistry of β-Lactam Antibiotics", Chemical Society, Cambridge, England, 1976.

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G. A. Koppel,* L. McShane,* F. Jose, R. D. G. Cooper*
The Lilly Research Laboratories, Eli Lilly and Company
Indianapolis, Indiana 46206

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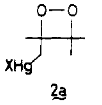
Mercuric Trifluoroacetate Catalyzed Decomposition of an Allylic Hydroperoxide via a Mercury-Substituted 1,2-Dioxetane[1]

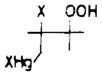
Sir:

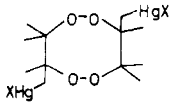
Peroxymercuration and cycloperoxymercuration have been studied extensively;[2] however, to the best of our knowledge allylic hydroperoxides have not been employed for this purpose. Attempted cyclomercuration of the allylic hydroperoxide **1** led to acetone, the expected Hock cleavage product,[3] but with chemiluminescence. Since 1,2-dioxetanes are likely precursors to this chemiluminescence,[4] we searched for and confirmed the intervention of the mercury-substituted 1,2-dioxetane **2**. Presently we communicate our unusual findings because they constitute (1) a rare example of four-membered-ring formation in cyclomercuration,[5] in particular the first example of the formation of the labile four-membered-ring cyclic peroxides via mercuration, (2) a novel synthetic entry into functionalized 1,2-dioxetanes, and (3) an intriguing allylic mercuration as major process.

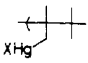
Treatment of 2,3-dimethyl-3-hydroperoxy-1-butene (**1**) with mercuric trifluoroacetate in $CDCl_3$ at 35 °C under rigorously anhydrous conditions gave 75% acetone and 100% trifluoroacetic acid within 1 h. When $CDCl_3$ solutions of the reagents were mixed at -40 °C, ^1H NMR monitoring revealed that mercuration was essentially instantaneous. Although the ^1H NMR spectrum of the reaction was complex, the proton of trifluoroacetic acid was immediately visible at δ 8.7 ppm, but the methyl protons of acetone at δ 2.1 ppm grew in slowly only on warmup and was accompanied by light emission. In fact, the rates of acetone production and light emission were the same within the experimental error, but much slower than trifluoroacetic acid formation. Unfortunately the mercurated 1,2-dioxetane **2a** intermediate could as yet not be isolated by low temperature silica gel chromatography, but the following chemical trapping experiments convincingly demonstrate its intervention.

Since $LiAlH_4$ cleanly reduces 1,2-dioxetanes to their respective 1,2-diols,[6] reduction of the mercurated reaction mixture of the allylic hydroperoxide **1** in $CFCl_3$ at -70 °C afforded the expected pinacol in ~15% yield (by VPC). Such pinacol formation suggested that **2a** was formed in the mercuration of **1**, but the noncyclic mercurial **3**, the cyclodimer **4**, and the polymer **5** are all plausible precursors to pinacol on $LiAlH_4$ reduction. However, since it was not possible to isolate a pure sample of the postulated mercurated 1,2-dioxetane intermediate **2a**, it was difficult to differentiate among these alternatives.


2a
X = CF_3CO_2


3

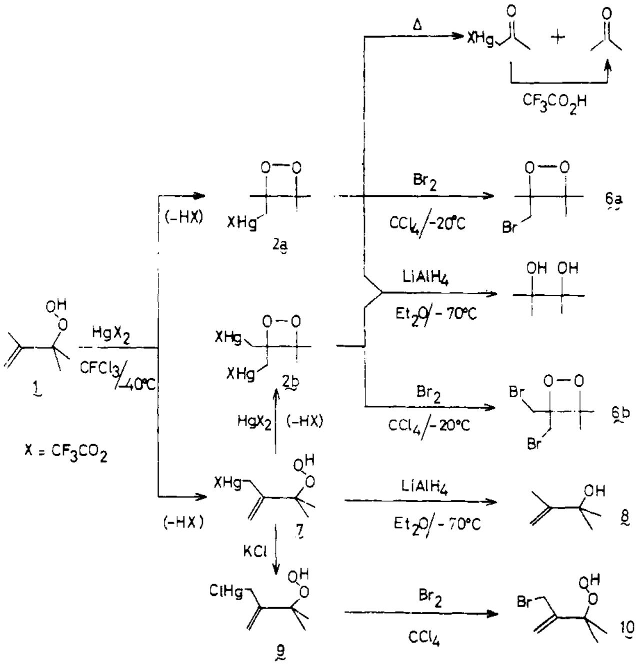

4


5

Consequently, bromodemercuration of **2a** was performed. On treatment of the mercurated reaction mixture with Br_2 in CCl_4 at -20 °C, followed by silica gel chromatography at -45 °C eluting with CH_2Cl_2, the chemiluminescent fractions were collected, rotaevaporated, and rechromatographed at -45 °C eluting with n-pentane/CH_2Cl_2 (6:4), affording the bromo-1,2-dioxetanes **6a**[7] and **6b**[8] in ~10 and ~8% yields, respectively. The new dioxetane **6a** was identical with an authentic sample prepared via the Kopecky route[6] by bromination of the allylic hydroperoxide **1** and cyclization of the resulting dibromide with silver trifluoroacetate.[9]

Formation of the dibromodioxetane **6b** implies that the unusual dimercurio-1,2-dioxetane **2b** was also formed. A reasonable pathway to **2b** is cycloperoxymercuration of **7** which is formed from **1** by allylic mercuration[10] (Scheme I). Several lines of evidence confirm that allylic mercuration was the major process in the reaction of **1** with mercuric trifluoroacetate. First of all, $LiAlH_4$ reduction of the mercurated reaction mixture at -40 °C in $CFCl_3$ gave ~80% allylic alcohol **8**. That **8** was not derived from unreacted **1** was easily ruled out since the ^1H NMR spectrum of the mercurated reaction mixture showed that the proton of trifluoroacetic acid was formed at the expense of the allylic protons of **1**. Furthermore, the allylic

Scheme I



and vinylic protons broadened out extensively presumably through fluxional isomerism in the allylic mercurial **7**.[11] Treatment of the mercurated reaction mixture with aqueous KCl solution at −20 to 0 °C and silica gel chromatography at −50 °C gave an ~40% yield of hydroperoxy mercurial **9** which on subsequent treatment with bromine gave the allylic bromohydroperoxide **10**, but not **6a** nor **6b**.

The novel mercurio-1,2-dioxetanes **2a** and **2b** reported here are the first examples of an unprecedented cycloperoxymercuration leading to four-membered rings.[5] Regioselectivity[5] and the Baldwin rules[12] predict that formation of the 1,2-dioxetane ring should be preferred over the 1,2-dioxolane ring in the mercuration of **1**; however, in view of the ring strain in **2a** and **2b** the major process is allylic mercuration. Work is in progress to suppress this menacing side reaction by cyclomercurating allylic hydroperoxides **1** without allylic hydrogens.

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(7) Distilled at 20 °C (0.01 mm); yellow liquid which solidifies at −20 °C, but could not be recrystallized; ^{1}H NMR (CCl_4, Me_4Si) δ 1.53 (s, CH_3, 6 H), 1.61 (s, CH_3, 3 H), and 3.30 and 3.97 ppm (AB q, J = 10 Hz, CH_2, 2 H); IR (CCl_4) 3030, 2980, 1456, 1387, 1380, 1373, 1232, 797, and 740 cm^{-1}. On heating at 80 °C **6a** decomposes quantitatively into acetone and bromoacetone.
(8) Yellow liquid; ^{1}H NMR (CCl_4, Me_4Si) δ 1.61 (s, CH_3, 6 H) and 3.82 and 4.08 ppm (AB q, J = 11 Hz, CH_2, 4 H); IR (CCl_4) 2990, 2965, 1430, 1383, 1370, and 1295 cm^{-1}. On heating at 80 °C **6b** decomposes quantitatively into acetone and 1,3-dibromo-2-propanone.
(9) The dibromohydroperoxide, prepared by bromination of **1**, was added to silver trifluoroacetate in CH_2Cl_2 at 0 °C under stirring. After workup a yellow oil was obtained and separated by silica gel chromatography at −35 °C to afford **6a** in 30% yield.
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Waldemar Adam,*[13] Katsumasa Sakanishi[14]
Department of Chemistry, University of Puerto Rico
Río Piedras, Puerto Rico 00931

Received January 20, 1978

A Low Spin Manganocene and Its Novel Anionic Derivative. Synthesis and Characterization of Decamethylmanganocene Complexes

Sir:

Manganocene is unique among the first row transition metal metallocenes in that it has a high spin ($^6A_{1g}$) ground electronic configuration, behaves antiferromagnetically as a crystalline solid, and undergoes reactions characteristic of ionic cyclopentadienide complexes.[1,2] Detailed EPR and magnetic studies of 1,1′-dimethylmanganocene in both solution[3a] and the solid state[3b] indicate an equilibrium between high spin (S = 5/2) and low spin (S = 1/2) electronic states, with the low spin configuration predominating at lower temperature. It was inferred that manganocene is close to the high spin–low spin crossover point and that the substitution of an electron-donating methyl group on each ring sufficiently increases the donor character of the ligand to stabilize the low spin configuration.

We wish to report our synthetic and initial physical studies of decamethylmanganocene (**1**). The reaction of lithium pentamethylcyclopentadienide[4] in tetrahydrofuran (THF) with anhydrous manganese(II) chloride, followed by vacuum sublimation (100 °C (10^{-5} Torr)) and recrystallization from hexane, gave good yields of pure **1** as air-sensitive, red-orange crystals.[5]

Magnetic susceptibility measurements on solid samples of **1** from 4 to 116 K indicate simple Curie behavior (Ci = 0.59) with a $\mu_{\mathrm{eff}} = 2.16 \pm 0.1\ \mu_B$ at 116 K. In toluene solution at 313 K, a $\mu_{\mathrm{eff}} = 1.97 \pm 0.1\ \mu_B$ was determined using the Evans NMR method.[6] These results are consistent with the formulation of a low spin (S = 1/2) electronic configuration for **1**, with no evidence for thermal population of the high spin (S = 5/2) state up to room temperature. These data, in conjunction with infrared, NMR,[7] EPR, and preliminary x-ray crystallographic[8] results indicate that **1** is a normal metallocene, and is isostructural and isoelectronic with the ferricenium ion.

This analogy suggests that **1** might be readily reduced to a d^6, manganese(I) anionic derivative that is isoelectronic with ferrocene and π-benzene-π-cyclopentadienylmanganese.[9] No such metallocene anions have been isolated and it has been suggested[10] that they might be too "electron rich" to be readily isolable. While the electrochemical reduction of nickelocene, cobaltocene, chromocene, and vanadocene has recently been reported,[11] the resulting anions were neither isolated nor characterized in solution. The closed-shell, 18-electron sandwich complex, bis(η-benzene)vanadium(−I) anion, has been characterized in solution by ^{1}H NMR spectroscopy.[12] An EPR spectrum of the 19-electron (η-cyclopentadienyl)(η-cycloheptatrienyl)chromium anion has also been reported.[13] However, neither of these reduced species were sufficiently stable to allow isolation.

The cyclic voltammogram of **1** exhibits both a reversible one-electron reduction and oxidation.[14] The reaction of **1** with 1 equiv of sodium naphthalide in THF yielded a dark red solution of the decamethylmanganocene anion (**2**). From this solution, an orange, crystalline sodium salt of **2** containing coordinated THF was isolated. This material readily loses THF at room temperature in vacuo to yield $Na[(C_5Me_5)_2Mn]$ as a pyrophoric orange powder.[15a] The ^{1}H and ^{13}C NMR spectra[15b] of **2** are consistent with the formulation of a diamagnetic, closed-shell metallocene.

In its reactions with protic acids and alkyl halides, **2** behaves as a strong one-electron reducing agent to yield only **1** with no evidence of products derived from addition of electrophile to the ring. Reaction of **2** with excess $FeCl_2$ in THF gives only **1**, with no detectable amount of decamethylferrocene. This indicates that both **1** and **2** are inert toward ring exchange reactions that are characteristic of manganocene.[1]

These preliminary results suggest that the addition of five electron-donating methyl substituents to the cyclopentadienyl ligands results in a significantly increased crystal field splitting in planar metallocenes. Detailed spectral and structural studies of complexes **1** and **2** are underway in an effort to more completely describe their electronic structures.[16] These, and related studies on other decamethylmetallocenes,[16] will be important in assessing the *electronic* effects of methyl substitution on the structure and reactivity of coordinatively unsaturated and highly reduced derivatives of the early transition metals.

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