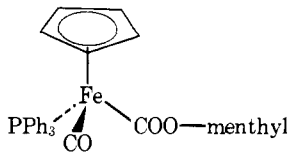
the observation that, whereas epimerization about the chiral iron center of the optically pure menthyl ester **7** does not occur upon heating in benzene, nonetheless only the racemate of the methyl ester **6a** was obtained upon transesterification of **7** by simple dissolution for a few minutes in methanol at room temperature.[18]



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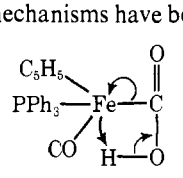
The reactions of the chloride salt of the bisphosphine cation **4c** are also surprising. No apparent reaction occurs between **4c** and aqueous NaOH. Passage of an aqueous solution of the chloride salt **4c** twice through a column of anion-exchange resin previously treated with excess NaOH, followed by addition of a concentrated NaOH solution to the eluate and extraction with ethyl acetate, afforded yellow needles of the ionic hydroxide **4c** (X = OH), mp 89–91 °C. The compound displays a single intense IR absorption at 1980 cm^{-1} identical with that seen for the corresponding chloride salt of **4c.** Treatment of **4c** (X = OH) with aqueous NaCl produces an immediate precipitate of the corresponding chloride (**4c**, X = Cl).

Even the BH_4^- anion does not readily react with the carbonyl groups of the cation **4c.** Thus, treatment of the chloride salt of **4c** with $NaBH_4$ gave an immediate yellow precipitate of the borohydride salt of the cation, as a yellow powder, mp 132–133 °C. This borohydride salt also possessed the strong absorption at 1980 cm^{-1} in the IR spectrum, characteristic of the cation **4c.** In aqueous methanol, the borohydride salt rapidly reduced acetone and benzaldehyde to isopropanol and benzyl alcohol respectively.

Finally, with respect to the mechanism of the decarboxylation of metallocarboxylic acids, we have observed that benzene solutions of the carboxylic acid **5b** rapidly decompose with liberation of CO_2 upon warming. In contrast, solutions of the potassium salt of the acid in dry formamide do not decompose upon heating to 100 °C. With this particular system, at least, a concerted elimination of CO_2, as shown in **8**, is indicated in preference to one involving loss of CO_2 via a metallocarboxylic anion. Both types of mechanisms have been proposed for other



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systems in which decarboxylation of intermediate metallocarboxylic acids is inferred.[9,19]

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for financial support.

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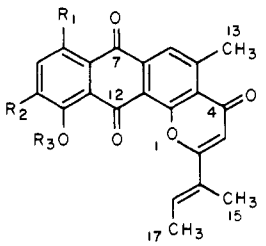
4*H*-Anthra[1,2-*b*]pyran Antibiotics. Total Synthesis of the Methyl Ether of Kidamycinone

Sir:

In connection with our studies toward development of new methods for synthesis of anthracycline antibiotics,[1-4] we have accomplished an efficient regioselective synthesis of the methyl ether of kidamycinone (**1b**), i.e., the methyl ether of the aglycone[5] (**1c**) of the anticancer antibiotic kidamycin (**1a**).[6]



1a. R_1 = angolosamine, R_2 = N,N-dimethylvancosamine, R_3 = H
1b. $R_1 = R_2 = H$, $R_3 = CH_3$
1c. $R_1 = R_2 = R_3 = H$

Kidamycin[6] (**1a**), neopluramycin,[7] pluramycin A,[7] hedamycin,[8] and indomycins[9] are a family of antibiotics which have a functionalized 4*H*-anthra[1,2-*b*]pyran nucleus as a common structural feature. Because of their complexity, full structural elucidation has been achieved only for **1a** and that required X-ray analysis.[6]

The synthetic plan followed for preparation of *O*-methylkidamycinone (**1b**) was regioselective construction of the hexasubstituted anthracene **4a,** followed by annelation of the pyrone portion from the *o*-hydroxyl and acetyl functionalities of **4a.** Efficient construction of anthracene **4a** was achieved using the synthetic strategy and complementary ring annelation methodologies previously reported by us.[1,3] The anion of 7-methoxy-3-phenylsulfonyl-1(3*H*)-isobenzofuranone (**2**)[3] (lithium diisopropylamide (LDA), tetrahydrofuran (THF), −78 °C) readily condensed with methyl crotonate to give, after methylation (K_2CO_3/dimethyl sulfate), regioselectively constructed naphthoate **3a**[10,11] as an oil in 83% yield. Reaction of **3a** with 1 equiv of *N*-bromosuccinimide in CCl_4 gave bromomethyl compound **3b** (mp 84–87 °C) which upon treatment with sodium thiophenoxide in ethanol yielded the corresponding sulfide **3c** (mp 91–92 °C) in 89% overall yield from **3a.** Oxidation (*m*-chloroperbenzoic acid/CH_2Cl_2, −78 °C)

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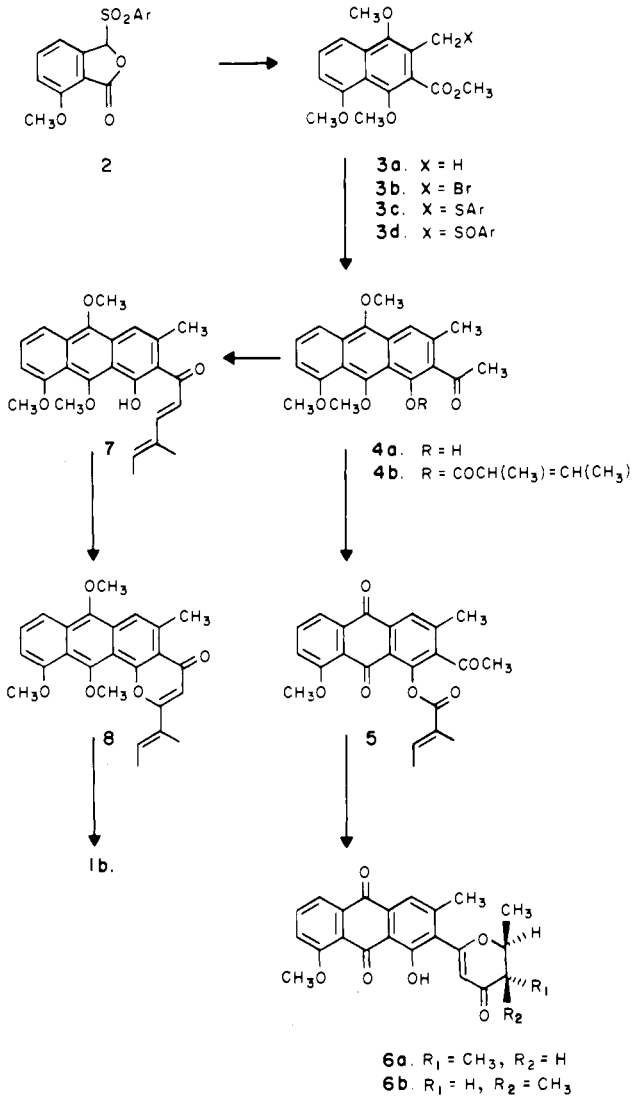

of sulfide **3c** to sulfoxide **3d** (mp 114–116 °C) was accomplished in 95% yield. The anion of sulfoxide **3d** (LDA/THF, −78 °C) was condensed with 3-penten-2-one to give, after thermal elimination of sulfenic acid, regioselectively constructed anthracene **4a**[11] in 71% yield (mp 132–134 °C). Construction of the pyrone portion of **1b** from the *o*-hydroxyl and acetyl functionalities present in anthracene **4a** was undertaken next. Attempted transfer of the acyl group of tigloyl ester **4b** to the methyl ketone using sodium hydride in dioxane was unsuccessful. Following oxidation ($CuBr_2$/THF) of **4b** to **5**, successful transfer of the tigloyl moiety was accomplished by base treatment (NaH/dioxane). The 1,3-diketone intermediate was immediately cyclized (HOAc/HCl). No **1b** resulted; instead, alternate cyclization products **6a** and **6b** were produced in 76 and 22% yield, respectively.

An alternative route to **1b** from **4a** was devised. Conversion of **4a** to a dilithium anion (2.2 equiv of LDA) followed by condensation with tiglaldehyde gave dienone **7**[11] in 75% yield. After a lengthy study, conditions were found (SeO_2/*tert*-amyl alcohol)[12] whereby dienone **7** underwent cyclization and dehydrogenation to **8** (mp 150–152 °C). The structure of **8** was confirmed from its ^1H NMR spectrum. The 5-methyl group was shifted from 2.38 ppm in **7** to 2.98 ppm in **8** as a consequence of its proximity and coplanarity with the deshielding cone of the carbonyl group at C-4. Further confirming features were the shift of the vinyl hydrogen of the propenyl side chain from 5.85 ppm in **7** to 7.29 ppm in **8** and the appearance in **8** of the C-5 hydrogen at 6.46 ppm. Oxidation[13] of **8** (AgO/HNO_3) cleaved the 7,12-dimethoxyl groups, furnishing *O*-methylkidamycinone **1b**[11,14] in 83% yield (mp 251–252 °C).

Acknowledgments: The authors express their appreciation to Dr. M. Furukawa, Daiichi Seiyaku Co., and Dr. Karl Dahm, Texas A&M University, for generously supplying spectral data on kidamycin and indomycins, respectively. This work was supported by the National Cancer Institute of the Department of Health, Education and Welfare, Grant No. CA 18141.

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A High-Field Mössbauer Study of the Iron Sites in Mixed-Valent Biferrocene Monocation

Sir:

In an attempt to elucidate the electron-exchange mechanisms and differences in apparent exchange rate in biferrocene(1+) and bis(fulvalene)diiron(1+) (BFDFe(1+)), we have studied biferrocene, biferrocene(1+), biferrocene(2+), and ferricenium ion using Mössbauer spectroscopy in external magnetic fields at low temperature. Our results are not consistent with the accepted view of biferrocene(1+) as consisting of a ferrocene-like Fe(II) and a ferricenium-like Fe(III)[1,2] and point to the need for a re-formulation of the electronic structure of these systems.

Biferrocene monocation and dication are paramagnetic,[3,4] with the formally mixed-valent (Fe(II),Fe(III)) monocation displaying intense absorption in the near-infrared region of the electronic spectrum, often attributed to intervalent charge

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