onances. The improved resolution of peaks close to the diagonal is apparent, as is the suppression of t_1 noise associated with the HDO signal at 4.68 ppm. Particularly impressive are the cross-peaks between the terminal 5′ and 5″ protons at $\omega_2 = 3.7$ ppm. These are resolved neither in the 1D spectrum nor via NOESY. It should be pointed out that all of the cross-peaks in the region are relatively intense; where weakly coupled protons of similar chemical shift exist, the advantage of the diagonal-supression pulse sequence over NOESY will be amplified. In a forthcoming paper[14] we shall discuss in more depth the pulse sequence and its applications in both solution and the solid state.

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Synthesis and Deuteration of (η-Thiophene)Ru(η-C_5H_5)$^+$: A Model for Adsorption and Deuterium Exchange of Thiophene on Hydrodesulfurization Catalysts

George H. Spies and Robert J. Angelici*

Department of Chemistry and Ames Laboratory[1]
Iowa State University, Ames, Iowa 50011

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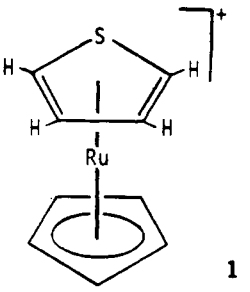
While the hydrodesulfurization (HDS) of thiophene on heterogeneous catalysts has been studied extensively,[2] the complexity of this reaction has left most important mechanistic questions unanswered. For other heterogeneously catalyzed reactions, important mechanistic concepts have been developed by studying homogeneous reactions of model compounds.[3] Few model studies of thiophene HDS have been reported.[4] Indeed, it has not been established whether thiophene adsorbs to the surface by coordination to a metal site through the sulfur atom only[5] or via the sulfur and the unsaturated carbon atoms (i.e., as a π-complex).[6] Recently, Harris and Chianelli[7] concluded, on the basis of SCF-Xα molecular orbital calculations of metal sulfides, that the initial interaction of thiophene with second-row, catalytically active transition metals was most likely via the S atom only. They noted that the preference for S atom coordination by second-row metals was important for the higher HDS activity of these metals, including Ru. Supporting the conclusion that second-row metals preferred S atom coordination were the facts that there were no known π-thiophene complexes of the second- and third-row transition metals and that the only reasonably well-characterized S-bound thiophene complex was of Ru, namely, $Ru(NH_3)_5(SC_4H_4)^{2+}$.[8,9] In this paper, we report the first example of a π-thiophene complex, $(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)^+$ (**1**), of a second- or third-row transition metal (Figure 1). The thiophene is strongly coordinated and readily exchanges its 2,5-protons in the presence of bases or Al_2O_3; this latter observation suggests an explanation for the known exchange of these protons when thiophene and D_2 are passed over HDS catalysts.



1

Figure 1.

The $[(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)]BF_4$ (**1**) complex was prepared by refluxing $(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl$[10] (1.00 g, 1.38 mmol), thiophene (20 mL), $AgBF_4$ (0.290 g, 1.52 mmol) in 10 mL of MeOH for 72 h under N_2. Isolation of **1** was accomplished by removing the volatiles from the reaction mixture in vacuo, extracting the residue with CH_2Cl_2, and precipitating the product by slowly adding Et_2O. Successive recrystallizations yielded the pure air- and water-stable **1** as a pale brown powder in 60% yield.[11] The π-thiophene ligand is strongly bound to the Ru as shown by its slow rate of displacement (only 33% after 4.5 h) from **1** (10 mg) by $(n\text{-}Bu)_3P$ (7 equiv) in acetone (0.35 mL) at room temperature.

The stability of **1** suggests that thiophene could adsorb to HDS catalysts in the π-bonded form. This form may account for the observed exchange of the 2,5-protons of thiophene when it is passed with D_2 over several catalysts (e.g., Mo/Al_2O_3,[12] $Mo\text{-}Co/Al_2O_3$,[12] MoS_2,[13-15] and M_xMoS_2[15]). From ^1H NMR studies we find that the 2,5-protons of the thiophene ligand in **1** readily undergo exchange in the presence of bases. Thus, the 2,5-protons in **1** (0.003 mmol) completely exchange with deuterium (CD_3OD solvent 0.35 mL) in the presence of KOH (0.01 mmol) in less than 4 min.[16] Deuteration at the 2,5-positions was established by displacing the exchanged thiophene from **1** with *tert*-butyl isocyanide and noting the almost complete disappearance of the 2,5-proton resonance of free thiophene.[17] There was no evidence for exchange of the 3,4-protons. Treatment of **1** (0.017 mmol) in CD_3OD (0.35 mL) with Et_3N (0.04 mmol) resulted in approximately 50% exchange after 20 min. No exchange is observed

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under these conditions when **1** is dissolved in CD_3OD in the absence of base. The base-catalyzed proton exchanges presumably occur by deprotonation of the 2- or 5-position followed by rapid deuterium transfer from the CD_3OD solvent to give the deuterated product.

In order to probe the possibility that basic sites on Al_2O_3, used as a support in catalytic HDS studies, would facilitate exchange of surface protons with **1**, we prepared Al_2O_3 with surface OD groups by stirring γ-alumina[18] with D_2O for 1 day. After filtration and drying *in vacuo* for 16 h at room temperature, the powder (300 mg) was added to a solution of **1** (20 mg) in 0.5 mL of CD_2Cl_2; most of the complex adsorbed to the alumina. After 2 h, the CD_2Cl_2 was decanted and **1** was extracted from the Al_2O_3 with Me_2SO-d_6.[19] A ^1H NMR spectrum of the Me_2SO-d_6 solution indicated that approximately 10% of the 2,5-positions in **1** had been deuterated. Thus, surface OD groups on Al_2O_3 are capable of exchanging deuterium with adsorbed $[(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)]BF_4$; this exchange is probably catalyzed by basic oxygen groups on the Al_2O_3 surface.

Others have explained[12,13] the preferential exchange of the 2,5-protons on HDS catalysts by assuming that thiophene adsorbs to the surface via the S atom only; this form of attachment places the 2,5-protons near the catalyst surface. There are, however, no model studies that support such an exchange mechanism. The results reported herein suggest that a more likely mechanism involves π-bound thiophene. By forming a π-complex with the transition metal of the catalyst, the thiophene would be susceptible to deprotonation by basic sites on the Al_2O_3 or MoS_2 which would facilitate exchange with OD or SD groups present on the catalyst surface.

(18) Alumina, Grade E, Test No. 52452, Ketjen Catalysts, Armak Catalysts Div., Pasadena, TX.

(19) **1** does not undergo deuteration in CD_2Cl_2 or Me_2SO-d_6 and no deuteration of **1** was observed when undeuterated Al_2O_3 was used.

Total Synthesis of (-)-Upial

Michael J. Taschner* and Abdulsadeh Shahripour

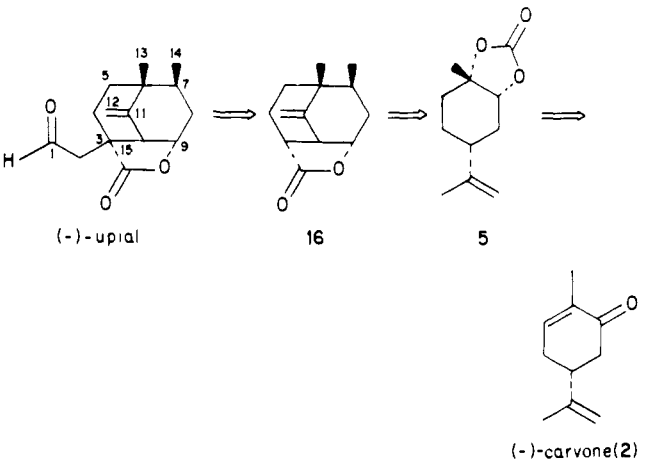
Department of Chemistry, The University of Akron
Akron, Ohio 44325

Received April 26, 1985

In 1979, Scheuer and co-workers isolated (+)-upial (**1**) from the Kaneohe Bay, Oahu, sponge *Dysidea fragilis*. Upial was found to be a nonisoprenoid sesquiterpene aldehyde lactone that contained the rare bicyclo[3.3.1]nonane skeleton. Its structure was assigned on the basis of elemental composition and spectral properties of the natural product and a number of degradation products. A large portion of evidence comes from the high-field NMR spectrum of upial and a lanthanide-induced-shift study of the $NaBH_4$ reduction product, upiol.[1] The structural assignment has yet to receive confirmation by X-ray crystallography or total synthesis. In this report we wish to delineate the *enantioselective* synthesis of (-)-upial. The synthesis, which is efficient and stereocontrolled, serves to confirm for the *first time* the structural assignment, as well as establish the absolute configuration for upial.

In our strategic analysis, we envisioned upial as ultimately being derivable from one of the carvones. We chose the less expensive (-)-carvone (**2**), since at the time we initiated our assault on this architechturally unique sesquiterpene the absolute configuration was unknown.[2]

Our synthesis (Scheme I) begins with the reductive alkylation of (-)-carvone (**2**) with ethyl bromoacetate utilizing the lithium–bronze conditions[3] to give an inseparable mixture of keto esters



3a and **3b** (83:17, respectively).[4,5] The mixture of esters was hydrolyzed to the keto acids **4a** and **4b**. Ketone reduction[6] and lactonization afforded lactone **5** [53% overall from **2**, $[\alpha]_D$ -9.0° (c 47.6, $CHCl_3$)].[5,7]

With lactone **5** in hand, we turned our attention to the introduction of the C14 methyl group (upial numbering system). We planned to take advantage of the concave–convex nature of lactone **5** and utilize the known propensity for reagents to add to the convex face of such systems.[7a] To this end, the lithium enolate of **5** was generated (LDA/THF) and alkylated with CH_3I to furnish the monomethylated lactone **6** as a single isomer [$[\alpha]_D$ 22.4° (*c* 50.0, $CHCl_3$)].[5,8]

Having controlled the relative configuration between the C13 and C14 methyls, we set about to elaborate lactone **6** into the bicyclic hydroxy ketone **10**. This was most effectively accomplished by first reducing lactone **6** to diol **7**.[5,9] A double-Swern oxidation[10] (2.2 equiv) transformed diol **7** into the sensitive keto aldehyde **8**, which was immediately subjected to the homologation reaction. Selective homologation of the aldehyde was accomplished by treating keto aldehyde **8** with (methoxymethylene)triphenylphosphorane[11,12] (1.05 equiv) to afford enol ether **9**[5] as mixture of double-bond isomers. Hydrolysis of the enol ethers was accompanied by concomitant intramolecular aldol cyclization[13] to furnish the hydroxy ketone **10** [mp 109–110 °C, $[\alpha]_D$ +67 (*c* 36.1, $CHCl_3$)].[5,14]

After assembling the bicyclo[3.3.1]nonane ring system,[15] some minor cosmetic surgery was required to transform the appropriately placed functionality on the bicyclic skeleton for ultimate conversion to tricyclic lactone **16**. The hydroxy ketone **10** was reacted with 2.5 equiv of CH_3MgBr to provide diol **11** [mp 139–140 °C, $[\alpha]_D$ +3.83° (*c* 30.0, $CHCl_3$)].[5] It was anticipated that the stereochemistry of the newly introduced methyl group

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(15) For other bicyclo[3.3.1]nonane syntheses, see: Schultz, A. G.; Dittami, J. P. *J. Org. Chem.* **1983**, *48*, 2318 and references therein.

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