The g_F spectra measured are thus qualitatively consistent with expectations based on fluorescence quenching results. In the future, it may be possible to provide more detailed interpretation of the spectra. This could be done by analogy with spectra measured for tryptophans in known environments. For example, the spectra of ACTH and glucagon may prove to be typical of tryptophan in a random coil. However, this will require measuring a library of spectra. An alternative approach is to compare measured spectra with those generated theoretically from an assumed conformation. Woody has made such calculations for tyrosine and phenylalanine but points out they are more difficult for tryptophan.[26] Several weak transitions are apparent in the g_F spectra reported here, indicating that it will be important to consider them in any such calculations.

The results reported here demonstrate that FDCD spectra can be measured for a single fluorescent tryptophan in a protein. The 2-PMT detection geometry essentially eliminates artifacts due to imperfect circularly polarized light. This is especially important above 250 nm where the fluorescence is significantly polarized. While this polarization must be considered in making the measurement, it is reasonable to neglect it in analyzing the spectra reported here. However, this will not always be the case. Spectra were limited to wavelengths above 220 nm by signal-to-noise problems. Nevertheless, the g_F spectra are clearly sensitive to conformation. Several of them show indications of an additional strong band below 220 nm, which should also be conformationally sensitive. Thus FDCD provides a selective method for monitoring structural changes near fluorescent tryptophans.

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Acknowledgment. This work was supported by NIH Grant GM22939. E.W.L. was an NIH Predoctoral Trainee (Grant 5T32GM07230).

Supplementary Material Available: Figures showing ellipticity vs. wavelength for HSA; ellipticity vs. wavelength for glucagon, monellin, ribonuclease T1, and ACTH; absorbance spectrum of HSA; and absorbance spectrum of glucagon, monellin, ribonuclease T1, and ACTH (4 pages). Ordering information is given on any current masthead page.

Communications to the Editor

Synthesis of Bridging Vinylideneiron Dimers Using 1,1-Dichlorocyclopropanes. Cyclopropenes as Intermediates

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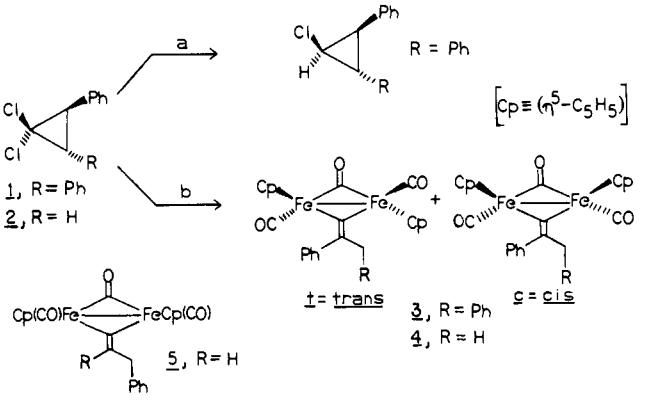
Received February 2, 1981

Bridging alkylidene,[1] alkylidyne,[2] and vinylidene[3] transition-metal complexes have received intense interest recently because of their relationship to various reactions catalyzed on heterogeneous metal surfaces.[4] It would be extremely helpful in studying these model compounds if general and reliable routes for their syntheses were available, especially for a series of substituted derivatives. The use of alkyl substituted examples would aid in the isolation and identification of the organic and organometallic intermediates and products. We report here a general one-step synthesis of substituted bridging vinylideneiron dimers using an unusual new reaction.

In our studies related to the reducing ability of sodium η^5-cyclopentadienyl(dicarbonyl)ferrate (NaFp), we have found that Fp^- can be used as a selective reducing agent in the conversion of 1,1-dichlorocyclopropanes to 1-chlorocyclopropanes.[5] An attempt was made to simplify the procedure by eliminating the need to produce the Fp^- from Fp_2 and sodium amalgam in THF. The reaction was performed instead under typical phase-transfer conditions[6] ($NaOH-H_2O$ (50:50), THF, n-$Bu_4N^+HSO_4^-$) by using Fp_2 directly with *trans*-1,1-dichloro-2,3-diphenylcyclopropane (**1**). Previous work by Alper seemed to indicate this procedure may be an alternate source of Fp^-.[7] The homogeneous reaction of NaFp with **1** produced a good yield of the 1-chloro-2,3-diphenylcyclopropane; however, none was observed with Fp_2 under the heterogeneous conditions although all of **1** was consumed. Analysis of the product mixture showed the presence of a deep purple iron-containing substance which transformed on standing to a new red compound. The more easily purified red complex was subsequently identified as **3c** by spectral[8] and X-ray structural

Scheme I[a]



[a] Reagents: (a) NaFp/THF. (b) $NaOH-H_2O$ (50:50)/THF/Bu_4NHSO_4/Fp_2.

† Initial work was performed while on leave from the Technical University of Berlin, 1978. Current address: Facultät für Chemie, Universität Bielefeld, Postfach 8640, D-4800 Bielefeld 1, Germany.

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(8) **3c**: IR (heptane) 2000 s, 1968 m, 1809 s cm^{-1}; ^1H NMR (CS_2, 100 MHz) δ 4.26 (s, 5 H, Cp_a), 4.51 (s, 2 H, CH_2), 4.80 (s, 5 H, Cp_b), 6.9-7.3 (m, 10 H, 2-Ph). **3t**: IR (heptane) 1976 sh, 1962 s, 1809 m cm^{-1}; ^1H NMR (CS_2, 100 MHz) δ 4.27 (s, 5 H, Cp_a), 4.57 (d, 1 H, J = 16 Hz, benzylic H), 4.72 (s, 5 H, Cp_b), 4.83 (d, 1 H, J = 16 Hz, other benzylic H), 7.9-7.5 (m, 10 H, 2-Ph).

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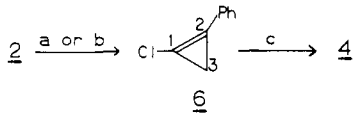
Scheme II[a]



[a] Reagents: (a) NaOH-H_2O (50:50)/THF/Bu_4NHSO_4. (b) KOBu-*t*/THF/12 °C. (c) Fp_2/NaOH-H_2O (50:50)/THF/Bu_4NHSO_4.

analysis[9] (see Scheme I). Initial difficulty in assigning the correct structure for **3c** was attributed to the unusual opening of the cyclopropane ring (vide infra) and the ^1H NMR spectrum which exhibited significantly different η^5-C_5H_5 (Cp) resonances. Also, an AB pattern would be predicted for the benzylic hydrogens, while a singlet was observed. Knowing the correct structure, one can attribute the large Cp chemical-shift difference to the anisotropic nature of the central phenyl group which shields the *cis*-Cp and the 2 H singlet to accidental equivalence of the benzylic hydrogens.

The initial purple compound (isolated in 17% yield) was assigned structured **3t** on the basis of its spectral[8] properties and thermal conversion to **3c** ($K_{eq} \sim$ 20:1, cis–trans; $t_{1/2} \simeq$ 5 h at 80 °C). The anticipated AB pattern for the benzylic hydrogens was indeed observed (J = 16 Hz).

Information related to a possible mechanism for the formation of **3** deserves attention at this time. First, the reaction is general for dichlorocyclopropanes possessing an aryl group in the 2 position.[10] However, a hydrogen must also be present on carbon 2, since 1,1-dichloro-2-methyl-2-phenylcyclopropane fails to yield a vinylidene dimer. Second, 1,1-dichloro-2-phenylcyclopropane (**2**) yields **4**[11] in 28% yield and none of the isomeric **5**. Third, when **1** was reacted in NaOD/D_2O, one deuterium was incorporated into the benzylic position of **3t**. All of these facts are consistent with a base promoted elimination of HCl from the dichlorocyclopropanes to produce chlorocyclopropanes as key intermediates in the reaction.[12] In fact, **2** was found to rapidly produce the known[13] 1-chloro-2-phenylcyclopropene (**6**) under the phase-transfer conditions but in the absence of Fp_2. When all of **2** was consumed under these conditions and then Fp_2 added, comparable yields of **4** were obtained. Production of **6** from **2** by using potassium *tert*-butoxide[13a] and subsequent phase-transfer reaction as above gave **4** (see Scheme II). Therefore, the chlorocyclopropenes are strongly implicated as the key intermediates.

Cleavage of the cyclopropene ring must occur at the C_1–C_3 bond in **6** to produce **4**. The mechanism for such a cleavage may involve a cyclopropene to vinylcarbene rearrangement[14] or a transition-metal insertion into that bond.[17] Studies are in progress to differentiate between these two processes and further define the mechanism.[18] A detailed examination of a variety of bridging vinylidene complexes and their chemistries is also under way.

Acknowledgment. Partial support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation is gratefully acknowledged. E.V.D. acknowledges support from the University of Oklahoma/Technical University of Berlin Chemistry Exchange Program and technical assistance by J. Soufi.

(9) Crystal data at −135 °C: $C_{28}H_{22}O_3Fe_2 \cdot C_4H_{10}O$; M_r 592.3; triclinic, $P\bar{1}$; a = 12.792 (7), b = 15.514 (5), c = 7.021 (16) Å; α = 93.37 (6), β = 80.93 (9)°, γ = 96.12 (3)°; V = 1366.8 Å^3; Z = 2; D_c = 1.439 g cm^{-3}; μ (Mo $K\alpha$) = 11.1 cm^{-1}. R = 0.072 for all 5613 reflections ($2\theta \leq 53°$, Mo $K\alpha$ radiation). Full details of the structural analysis will be submitted elsewhere.

(10) Other cyclopropanes found to give similar adducts: 1,1-dichloro-2-phenylcyclopropane; *trans*-1,1-dichloro-2-methyl-3-*p*-tolylcyclopropane; *trans*-1,1-dichloro-2-methyl-3-*p*-anisylcyclopropane; 1,1-dichloro-2,2-dimethyl-3-phenylcyclopropane; 1,1-dichloro-2,2-dimethyl-3-*p*-tolylcyclopropane.

(11) **4c**: IR (heptane) 2000 s, 1969 m, 1808 s cm^{-1}; ^1H NMR (CS_2, 100 MHz) δ 2.82 (s, 3 H, CH_3), 4.40 (s, 5 H, Cp_a), 4.88 (s, 5 H, Cp_b), 7.1–7.6 (m, 5 H, Ph). **4t**: IR (heptane) 1971 sh, 1960 s, 1808 m cm^{-1}; ^1H NMR (CS_2, 100 MHz) δ 2.92 (s, 3 H, CH_3), 4.25 (s, 5 H, Cp_a), 4.79 (s, 5 H, Cp_b), 7.1–7.6 (m, 5 H, Ph).

(12) The reaction of **1** with NaOD/D_2O confirms that one hydrogen is replaced with solvent deuterium. This labeling experiment is consistent with the proposed base promoted elimination of HCl from **1** to form the cyclopropene. The external deuterium found in the product is introduced at a later, yet undefined, step in the mechanism.

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(14) Previous kinetic studies on the cyclopropene to vinylcarbene rearrangement have shown activation energies in the 30–40 kcal/mol region.[15] The high activation energy would seem to rule out this possibility for the current reaction which proceeds readily at room temperature. However, the compounds that were studied in the thermal reactions were mainly hydrocarbons, and no systemic examination of substituent effects, especially with heteroatoms, has been reported.[16] A cyclopropene to vinylcarbene rearrangement was used to explain ring-opened products in the reaction of 1-chlorocyclopropenes with methoxide ion in methanol at room temperature.[13b] Appropriately substituted cyclopropenes, such as those encountered in the current work, may indeed rearrange to vinylcarbenes at or near room temperature. Therefore, vinylcarbenes cannot be ruled out as possible intermediates at this time.

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End-to-End Cyclization of Hydrocarbon Chains. Photochemical and Computer Simulation Studies

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Received March 10, 1981

Hydrocarbon chains are essential components of a multitude of systems including micelles, microemulsions, and biological membranes which depend upon chain flexibility for their unique properties.[1] As a consequence, the factors which influence hydrocarbon chain conformation have been the topic of current concern, both among theoretical chemists and experimentalists.[2] Of particular importance to the development of this field are instances where conformationally dependent experimental phenomena can be simulated by means of theoretical models, since this not only provides a test of the model and its parameters but permits new insights into the experimental results themselves.[3]

Since the classic paper by Kuhn[4] in 1934, models of increasing sophistication have been used to examine the factors which influence the shape of polymethylene chains in solution. The most successful of these are various forms of the rotational isomeric state (RIS) model, whose development was pioneered largely by Flory and his co-workers.[2] The model is "realistic" in that it treats the chains as a sequence of CH_2 groups in the geometries of gauche and trans rotational states at each bond. While many chain

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