Synthesis of Methoxalylferrocene

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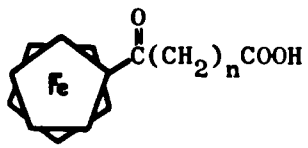
Synthesis of methoxalylferrocene, via treatment of methyl ferrocenylacetate with activated manganese dioxide at room temperature, is described.

THE SERIES of ω-ferrocenyl-ω-keto acids, represented by I (n = 0 to 4), were needed for evaluation of a projected study. Of these compounds, all except I (n = 0) were known (*1*). Synthesis of the first homolog—in the form of its methyl ester (II)—was, therefore, undertaken.

The choice to use ferrocenylacetic acid (III) (*2*) for preparation of methoxyalylferrocene (II) was dictated by a previous failure to obtain I (n = 0) via Friedel-Crafts acylation of ferrocene with oxalyl chloride (*3*).



I

Ferrocenylacetic acid (III) was converted to methyl ferrocenylacetate (IV) by treatment of the former with phosphorus trichloride (acid chloride not isolated) followed by methanolysis. In contrast to other ferrocene-substituted esters, IV was unstable. Slow but steady decomposition under ambient conditions occurred; nevertheless, this ester was smoothly converted into methoxalylferrocene (II) through mild oxidation with activated manganese dioxide (*4*) at room temperature in chloroform solution. Compound II was well characterized although it did decompose on alumina during attempts to purify it by elution chromatography. Purification was accomplished by means of molecular distillation. The keto-ester was also characterized through its 2,4-dinitrophenylhydrazone which was obtained as an unusual black-colored, crystalline solid.

EXPERIMENTAL

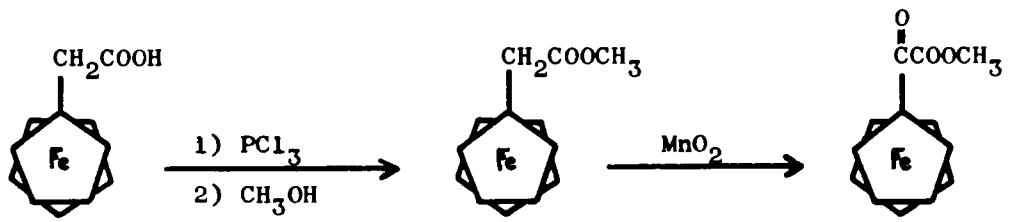
Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Infrared spectra were determined with a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were obtained with a Cary Model 14 spectrophotometer. All temperature readings are uncorrected.

Hydrolysis of ferrocenylacetonitrile (*5*), according to Lednicer, Lindsay, and Hauser (*3*), produced ferrocenylacetic acid (24.4 grams, 0.10 mole) which was contained in 150 ml. of phosphorus trichloride and heated under gentle reflux for two hrs. Excess phosphorus trichloride was then removed with a stream of nitrogen, and the dark-colored, viscous residue obtained was cooled while 150 ml. of absolute methanol was added. This mixture was refluxed for two hrs., and evaporated in vacuo to yield an oily residue which was suspended in 200 ml. of 5% aqueous sodium hydroxide solution. Exhaustive extraction with ether, followed by evaporation of the dry, combined ether extracts, gave 19.0 grams (74% yield) of methyl ferrocenylacetate as a orange-colored oil.

Attempts to prepare an analytical sample of this material by means of elution chromatography on alumina (Woelm, nonalkaline or Merck, acid-washed) failed since decompostion took place quite steadily during column development. Although molecular distillation in a Späth bulb [100–200° (0.2 mm. Hg), air bath] was smooth and yielded a condensate (m.p. 13–14°) which gave rise to an infrared spectrum (carbon tetrachloride) quite consistent with the methyl ester formulation (5.734μ, 7.95μ, and 8.15μ), the compound still decomposed steadily under ambient conditions. This situation precluded further characterization by combustion analysis since several days were required between sample preparation and analysis. Nevertheless, conversion to methoxalylferrocene left no doubt as to the presence of the desired compound.

Activated manganese dioxide (2.97 grams, 3.43×10^{-2} mole) was added to the methyl ester (1.77 grams, 6.86×10^{-3} mole in 25 ml. of chloroform); and, after it was magnetically stirred for 48 hrs. at room temperature, the mixture was passed through a paper filter in order to remove solids. Evaporation of the combined chloroform filtrate and washes left a viscous, dark red-colored oil which could not be induced to crystalline. This material was also found to decompose during elution chromatography on alumina. Three successive fractionations by means of molecular distillation, however, gave a condensate [115–125° (0.4 mm.), air bath] which slowly crystallized in the form of dark red-colored plates; 0.946 grams (42.4% yield), m.p. 65–8°.

An infrared spectrum (chloroform) of the purified product displayed the ester carbonyl band at 5.74μ as well as another intense band as 5.99μ which was indicative of the presence of the α-keto function. The ultraviolet spectrum (ethanol) of methoxalylferrocene is characterized



III IV II

by the following features: λ_{sh} 230μ (log ϵ = 3.87), λ_{min} 263mμ (log ϵ = 3.63), λ_{max} 288mμ (log ϵ = 3.69) and λ_{sh} 355 (log ϵ = 2.99).

Anal. Calcd. for $C_{13}H_{12}FeO_3$: C, 57.38; H, 4.45; Fe, 20.53. Found: C, 57.29; H, 4.58; Fe, 20.31.

Preparation of a 2,4-dinitrophenylhydrazone of methoxaylferrocene was achieved by adding 20 ml. of the reagent solution (*6*) to the keto-ester (0.544 grams, 2.00×10^{-3} mole) and allowing the reaction to take place at room temperature with stirring for one hr. The accumulated black, crystalline precipitate was collected by suction filtration and washed and dried. Three recrystallizations from hot benzene-hexane gave 0.728 grams (80% yield) of the crystalline, black-colored 2,4-dinitrophenylhydrazone of methoxalylferrocene, m.p. 226–227°.

Anal. Calcd. for $C_{19}H_{16}FeN_4O_6$: C, 50.47; H, 3.57; Fe, 12.35; N, 12.39. Found: C, 49.88; H, 3.73; Fe, 12.35; N, 12.40.

ACKNOWLEDGMENT

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Radical Addition of Perfluoroalkyl Iodides and Diiodides to Allyl Monomers

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The addition of perfluoropropyl iodide and symmetrical diiodohexafluoropropane to allyl alcohol and allyl chloride has produced intermediates from which a number of novel fluorine–containing compounds have been prepared. Synthesis methods are described, and physical properties of the resultant compounds are tabulated.

THE FREE radical-catalyzed addition of perfluoroalkyl iodides to olefins has been reported by numerous authors (*5*). The work presently reported successfully extends this reaction to the use of a typical perfluoroalkyl diiodide. In addition, this work uses the iodide-addition reaction to prepare several new mono- and difunctional entities containing fluorine. The fluorinated compounds prepared during the course of this work are presented in Table I, and the properties of these compounds are presented in Table II.

Perfluoropropyl iodide was prepared by the Hunsdiecker reaction on perfluoropropionic acid and subsequently was added to allyl alcohol or allyl chloride using ultraviolet irradiation. The adducts thus prepared were reacted further using conventional organic synthesis techniques to produce the mono-functional fluorine-containing entities described in Tables I and II.

In a similar manner, 1,3-diiodohexafluoropropane was prepared from perfluoroglutaric acid. The yield of this diiodide was greatly improved over the 18% reported in the literature (*2*) by the use of a large excess of iodine during the Hunsdiecker reaction. This diiodide subsequently was added to allyl alcohol or allyl chloride. However, despite long periods of irradiation, monoadducts were obtained as the principal reaction products. Yields of diadducts were considerably improved by adding mercury to the irradiated solution. In this manner, the diadducts were obtained as the principal products and were reacted further to produce the difunctional fluorine-containing entities described in Tables I and II.

Many of the compounds listed in Table I have not previously been reported in the literature. In addition to reporting these new compounds, the work presently reported presents an overall reaction scheme capable of inserting methylene groups between a perfluorinated cluster and a functional group as demonstrated by the conversion of hexafluoroglutaric acid to symetrical hexafluoroazelaic acid, etc.

EXPERIMENTAL

Silver Heptafluorobutyrate. This compound was prepared by the method of Hauptschein and Grosse (*2*) from commercially available heptafluorobutyric acid in yields of 96–98%.

I. I was prepared by the method of Hauptschein and Grosse (*2*) in yields of 78–82%.

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