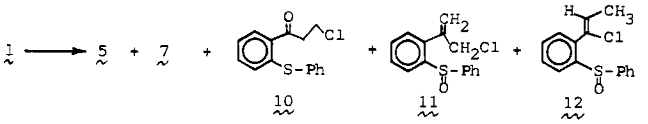
fashion. Sulfurane 2 exhibits an ^{1}H NMR spectrum that is noticeably broad in the cyclopropyl region 0.6–1.7 ppm when $CDCl_3$ purified by passage down a short column of basic alumina is used as the solvent. With a drop of dry HCl-laden $CDCl_3$, the broadening increases, or with a drop of dry pyridine, the broadening is eliminated. This acid-catalyzed process is akin to the racemization observed previously for 2.[11]

Under strictly anhydrous conditions, 1 decomposes as shown:



Products 10–12 have been identified tentatively. A full description of the chemistry of 1 will be presented in a future publication. At present, the rate enhancement of 1 over 2 is an intriguing result, regardless of the explanation ultimately accepted.

Acknowledgment. We acknowledge an Auburn University Intramural Grant-In-Aid (80-168) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

Registry No. 1, 86064-62-2; 5, 86046-43-7; 6, 86046-44-8; 1-ethoxycyclopropanol, 13837-45-1; 2-bromodiphenylsulfide, 15861-48-0.

Supplementary Material Available: Experimental data for 1, 2, 5, and 6 and experimental procedures for preparation of compounds used in this study (3 pages). Ordering information is given on any current masthead page.

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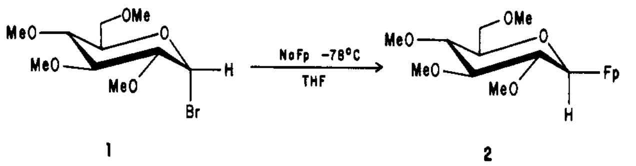
Preparation of a Stable Glucopyranosyliron Compound[1]

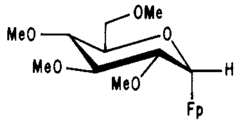
Summary: α-D-Glucopyranosyl bromide 1 reacts with sodium (η^5-cyclopentadienyl)dicarbonylferrate at low temperature to afford the stable, stereochemically pure (β-D-glucopyranosyl)iron compound 2.

Sir: The use of organo-transition-metal chemistry to solve selectivity problems in organic synthesis has been amply demonstrated in recent years.[2] The application of this technology to the carbohydrate field where regioselectivity and stereoselectivity problems are often severe, however, has been rather limited.[3-7] Only a few organo-transition-metal derivatives of carbohydrates have been isolated and characterized.[2a,5b,8] A recent report[9] on the preparation of a series of pyranos-6-yliron compounds and their use in the synthesis of chain-extended sugars prompts us to report our preliminary results on the organoiron chemistry of carbohydrates. We have focused our attention on pyranose derivatives substituted with iron at the anomeric center (C-1). We herein report the preparation and characterization of an unusually stable glucopyranosyliron compound (2).

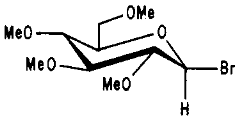


1 2

Fp ≡ (η_5-C_5H_5)Fe(CO)$_2$



3



4

2,3,4,6-Tetra-*O*-methyl-α-D-glucopyranosyl bromide (1)[10] in THF reacted immediately when it was added to a solution of sodium (η^5-cyclopentadienyl)dicarbonylferrate (NaFp)[11] (1.2 equiv) in THF at −78 °C.[12] After the THF was removed, the residual crude product was chromatographed on silica gel (ethyl acetate/benzene, 1:2) and then distilled (140 °C (0.2 torr)) to give stereochemically pure (2,6,4,6-tetra-*O*-methyl-β-D-glucopyranosyl)(η^5-cyclopentadienyl)iron dicarbonyl (2) as a yellow, crystalline solid (47%). Recrystallization from boiling hexane afforded yellow needles (mp 76–77.5 °C). The structure of 2 was established on the basis of the following spectroscopic and analytical data: NMR ($CDCl_3$) δ 4.80 (s, 5 H), 4.56 (d, 9.3 Hz, 1 H), 3.64 (s, 3 H), 3.57 (s, 3 H), 3.52 (s, 3 H), 3.50 (m, 2 H), 3.39 (s, 3 H), 3.04 (m, 4 H); IR (KBr) cm^{-1} 2008, 1950; high-resolution mass spectrum, *m/z* 340.0948 ($C_{15}H_{24}O_5Fe$, $(M - 2CO)^+$, calcd 340.0972). Anal. Calcd C, 51.53; H, 6.11. Found: C, 51.78; H, 6.08. The ^{13}C NMR spectrum exhibited the expected pair of resonances (δ 216.82 and 216.63) for the diastereotopic carbonyls. Pure, crystalline 2 can be handled for short periods of time in air and is stable indefinitely when stored under argon. Solutions of 2 are rapidly attacked by atmospheric oxygen, particularly in the presence of light.

When the glucosylation of NaFp by 1 was carried out at 25 °C and worked up as described above, a comparable yield of product was obtained. The product was shown by NMR to be a 5:1 mixture of 2 and a new, similar compound whose key spectral features (δ 6.54 (d, 5.4 Hz 1 H)

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(1) Contribution No. 3158 from E. I. du Pont de Nemours & Co., Inc.

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(12) All operations were carried out under an argon atmosphere by using standard Schlenk techniques.

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and 4.87 (s, 5 H)) are consistent with the α-anomer **3**. The mixture could not be chromatographically resolved. This apparently reduced stereospecificity at 25 °C can be explained by the well-known anomerization of glucopyranosyl halides in the presence of free halide.[13] If anomerization of the starting α-bromide (**1**) (by bromide ion released in the initial stages of the reaction) is sufficiently rapid to compete with direct displacement by NaFp, then the less thermodynamically stable but more reactive β-bromide (**4**) will be kinetically trapped, resulting in the appearance of the net retention product (**3**). This effect has been exploited in the preparation of α-glucopyranosides from α-glucopyranosyl halides.[14]

The (β-D-glucopyranosyl)iron compound **2** is notable in that it is exceptionally robust. It can be distilled in vacuo at 140 °C without decomposition. Similarly, only trace amounts of decomposition could be detected when **2** was heated to 100 °C in *p*-xylene for 3.5 h. *sec*-Alkyl(η^5-cyclopentadienyl)iron dicarbonyl (*sec*-alkyl-Fp) complexes have been reported to be only modestly stable and typically decompose at temperatures above 60 °C.[11,15,16] This instability has generally been attributed to facile "β-hydride elimination". In spite of the availability of a cis β-hydrogen (H-2), decomposition of **2** by this mode appears to be strongly retarded. Similar stabilization has been observed for ring-attached cobalt and palladium σ-complexes of glucose.[3a,6b] In contrast, (glucopyranos-6-yl)(η^5-cyclopentadienyl)iron dicarbonyl complexes in which the iron is not attached directly to the ring are reported to be unstable.[9]

Complex **2** shows reduced susceptibility to oxidatively induced carbon monoxide insertion. *sec*-Alkyl-Fp complexes ordinarily react rapidly at 0 °C with an excess of cupric chloride in alcohol under a CO atmosphere to replace iron with an alkoxycarbonyl substituent.[17] Complex **2** is unreactive under these conditions. At elevated temperatures (50 °C), **2** is slowly consumed, but the product mixture is complex.

(β-D-Glucopyranosyl)iron complex **2** can serve as a model system for the study of selective, transition-metal-mediated modification of carbohydrates at the anomeric and adjacent centers. The examination of organoiron chemistry in the highly functionalized and stereodefined carbohydrate environment should prove to be of fundamental interest as well. The elaboration of the chemistry of **2** and its extension to more suitably protected analogues are in progress and will be reported in due course.

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Registry No. 1, 51705-30-7; 2, 86120-31-2; 3, 86161-72-0; Fp, 12152-20-4.

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