(20 mmol) of **19** was added at once. The dry ice–acetone cooling bath was removed. After stirring the solution for 8 h under ammonia reflux, the ammonia was evaporated under a continuous stream of N_2. The residue was dissolved in 25 mL of water, and the pH of the solution was adjusted to 4–5 by addition of 0.5 M H_2SO_4. The unreacted **19** which precipitated was removed by filtration. The filtrate was concentrated in vacuo, and the residue was crystallized from H_2O–EtOH three times to give 0.42 g (10%) of **20**: mp 168 °C dec; ^{1}H NMR (D_2O) δ 2.2 (m, 2, $-CH_2-$), 2.6 (broad m, 2, $-SCH_2-$), 3.0 (m, 2, $-CH_2S-$), 4.4 (m, 3, OCH–), 5.93 (d, 1, J = 4 Hz, NCHO–), 6.27 (t, 1, J = 52 Hz, CHF_2), 8.20 and 8.03 (two s, 2 (NCH=N); UV$_{max}$ (H_2O) 259 nm (ϵ 13700); TLC (system C) 0.21.

Anal. Calcd for $C_{15}H_{20}N_6O_5S{\cdot}H_2O$: C, 39.82; H, 4.90; N, 18.57. Found: C, 39.90; H, 4.80; N, 18.20.

***S*-Adenosyl-α-(difluoromethyl)methionine (15l).** A mixture of 2 mL of AcOH, 2 mL of HCO_2H, 100 mg (0.2 mmol) of **20**, and 1.5 g (10.6 mmol) of methyl iodide was stirred in the dark for 5 days and then quenched with 10 mL of ice–water. The reaction mixture was extracted with ether (3 × 10 mL). Lyophilization of the aqueous phase gave the unstable mixture of diasteroisomers **15l** contaminated with about 25% of starting material: electrophoresis, Schleicher and Schuell (Dassel, G.F.R.) silica gel G 1500 plate; 0.5 M pyridium acetate buffer pH 4.8; 600 V, 3 h; ninhydrin staining 2 spots, *Rf* 0.5 and 0.3 (corresponding to **20**); ^{1}H NMR (D_2O + DCl) δ 2.6, 3.6, and 4.1 (three m, $CH_2SCH_2CH_2$), 3.08 and 3.11 (two s, $^+SCH_3$), 4.4 (m, OCH–), 6.0 (d, J = 3 Hz, NCHO), 6.3 (t, J = 52 Hz, CHF_2), 8.3 and 8.5 (two s, N=CHN). No analysis.

Decarboxylation of 15e. To a solution of 0.11 g of **15e** and 24 mg of pyridoxal hydrochloride in 3 mL of phosphate buffer (0.5 M, pH 6.5) was added 10 mL of benzene. The mixture was heated at 80–85 °C under N_2 for 18 h. The organic phase was separated, washed with brine, and dried over $MgSO_4$. Concentration in vacuo gave 63 mg of analytically pure 1-fluoro-3-phenylacetone (**18**) identified by comparison with an authentic sample prepared from 2-phenylacetyl chloride according to the method described by Olah and Welch.[24]

Acknowledgments. The authors wish to express their thanks to Dr. J. Wagner for determining the pK_a values of the α-amino group of the α-(halogenomethyl)-α-amino acids and also for measuring the rate of hydrolysis of the α-(chloromethyl)-α-amino acids in aqueous solution. They are also indebted to Miss J. Barth and Mrs. F. Ramaharobandro for valuable technical assistance.

Registry No. 2a, 16975-24-9; **2a**·HCl, 70470-89-2; **2b**·HCl, 69955-50-6; **2c**·HCl, 70470-90-5; **2e**, 70470-91-6; **2f**, 69955-07-3; **2g**, 70470-92-7; **2g**·HBr, 70470-93-8; **2h**, 70470-94-9; **2i**, 70470-95-0; **2i**·HBr, 70470-96-1; **4** (Y = CH_2F), 70470-97-2; **4** (Y = CH_2OH), 69955-53-9; **4** (Y = CH_2Cl)·HCl, 69955-54-0; (+)-**4** (Y = CHF_2)·HCl, 69955-41-5; (−)-**4** (Y = CHF_2)·HCl, 69961-02-0; (±)-**4** (Y = CHF_2), 70470-98-3; (−)-**4** (Y = CHF_2) (−)-binaphthylphosphoric acid salt, 70471-00-0; (+)-**4** (Y = CHF_2) (−)-binaphthylphosphoric acid salt, 70471-40-8; **6a**, 40216-71-5; **6b**, 69955-51-7; **6c**, 69955-44-8; **6d**, 40216-74-8; **6e**, 40216-77-1; **6f**, 69955-04-0; **6g**, 70471-01-1; **6h**, 70471-02-2; **6i**, 69356-05-4; **7a** (M = Na), 70471-03-3; **7f** (M = Li), 70471-37-3; **8a**, 67654-60-8; **8b**, 70471-04-4; **8c**, 69955-48-2; **8d**, 70471-05-5; **8e**, 70471-06-6; **8f**, 69955-05-1; **8g**, 70471-07-7; **8h**, 70471-08-8; **8i**, 70471-09-9; **9a**, 67654-61-9; **9b**, 70471-10-2; **9c**, 69955-45-9; **9d**, 70471-11-3; **9e**, 70471-12-4; **9f**, 70471-13-5; **9g**, 69955-02-8; **9i**, 70471-14-6; **10a**, 67654-67-5; **10b**, 70471-15-7; **10e**, 70471-16-8; **11a**, 67654-66-4; **12a**·HCl, 67654-62-0; **12c**·2HCl, 69955-49-3; **12d**·HCl, 70471-17-9; **12e**·HCl, 70471-18-0; **12f**·HCl, 70471-19-1; **12g**·HCl, 70471-20-4; **12h**·HCl, 70471-21-5; **12i**·2HCl, 70471-22-6; **13a**·HCl, 67654-63-1; **13b**·4HCl, 70471-23-7; **13c**·2HCl, 70471-24-8; **13d**·HCl, 70471-25-9; **13e**·HCl, 70471-26-0; **13g**·HCl, 69955-20-0; **13i**·4HCl, 70471-27-1; **14a**·HCl, 70471-28-2; **14b**·2HCl, 70471-29-3; **14e**, 70471-30-6; **14e**·HCl, 70471-31-7; **15a**, 67654-65-3; **15b**·HCl, 70050-56-5; (+)-**15b**·HCl, 70050-55-4; (−)-**15b**·HCl, 69955-42-6; **15c**·HCl, 69955-47-1; **15d**, 69955-35-7; **15e**, 70471-32-8; **15f**, 70471-33-9; **15g**, 69955-03-9; **15i**·HCl, 69937-69-5; **15j**, 69955-56-2; **15k**, 69955-43-7; **15l**, 70471-34-0; **16a**, 679-79-8; **16b**·HCl, 70494-47-2; **16e**, 70471-35-1; **17**, 32418-99-8; 18, 1524-06-7; **19**, 892-48-8; **20**, 69955-37-9; ornithine methyl ester dihydrochloride, 40216-82-8; benzaldehyde, 100-52-7; chlorobromomethane, 74-97-5; chlorodifluoromethane, 75-45-6; chlorofluoromethane, 593-70-4; dibromodifluoromethane, 75-61-6; α-(hydroxymethyl)ornithine methyl ester dihydrochloride, 69955-52-8; 2-(difluoromethyl)-2-amino-3-(3,4-dimethoxyphenyl)propionic acid, 70471-36-2; methyl 2-amino-3-(3,4-dimethoxyphenyl)propionate hydrochloride, 70494-48-3; methyl *N*-benzylideneglycinate, 66646-88-6; methyl 2-amino-2-(3,4-dimethoxyphenyl)methyl-3-(3,4-dimethoxyphenyl)propionate, 70471-38-4; benzyl chloride, 100-44-7.

The Reaction of Some Carbohydrate α-Enones with Iron Carbonyls[1a,b]

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The reactions of the carbohydrate α-enones and ethyl 2,3-dideoxy-α-D-*erythro*-hexenopyranosid-4-ulose (**6a**) and its tritylated derivative (**6b**) with $Fe_2(CO)_9$ give tetracarbonyl complexes **7** (**a** and **b**) and **8** (**a** and **b**), respectively. There is no evidence for the formation of dienic tricarbonyl complexes such as **3**. The structures of the products were established by examination of their IR, Mössbauer, NMR, and mass spectra. From the IR spectra, it is evident that each enone gives two diastereomers representing the two possible orientations of complexation. Because of the instability of the complexes, it was not possible to make definite assignments of these diastereomers.

The chemical modification of sugars by employing reactions of α-enone derivatives has been a focus of attention in our laboratory for a number of years.[2] In the past, our emphasis has been mainly on the addition of nucleophilic[3] and photochemically generated[4] species, and some interesting syntheses have resulted from these studies.[5,6] Electrophilic substitution could conceivably open alternative pathways for modifying the pyranose ring, and

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[1] (a) Work supported by grants from the National Research Council of Canada. (b) Taken from the Ph.D. thesis of M.B.Y., University of Waterloo, 1976. (c) Holder of N.R.C.C. studentships 1972–1975.

[2] (a) B. Fraser-Reid, A. McLean, E. W. Usherwood, and M. Yunker, *Can. J. Chem.*, **48**, 2877 (1970); (b) N. L. Holder and B. Fraser-Reid, *ibid.*, **51**, 3357 (1973); (c) B. Fraser-Reid, D. L. Walker, S. Y-K. Tam, and N. L. Holder, *ibid.*, **51**, 3950 (1973); (d) M. B. Yunker and B. Fraser-Reid, *ibid.*, **56**, 2221 (1978).

[3] M. B. Yunker, D. E. Plaumann, and B. Fraser-Reid, *Can. J. Chem.*, **55**, 4002 (1977).

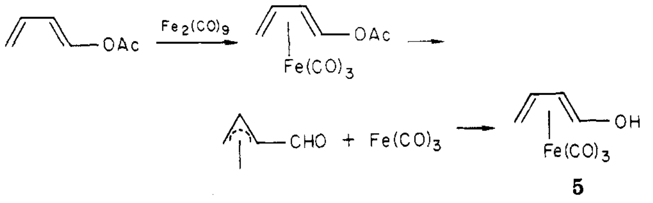
[4] B. Fraser-Reid, N. L. Holder, D. R. Hicks, and D. L. Walker, *Can. J. Chem.*, **55**, 3978 (1977); B. Fraser-Reid, R. C. Anderson, D. R. Hicks, and D. L. Walker, *ibid.*, **55**, 3986 (1977).

[5] D. L. Walker and B. Fraser-Reid, *J. Am. Chem. Soc.*, **97**, 6251 (1975).

[6] D. E. Plaumann, M.Sc. Thesis, University of Waterloo, 1977.

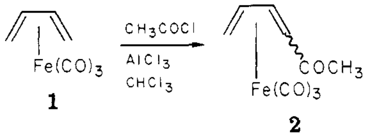
0022-3263/79/1944-2742$01.00/0

Scheme I

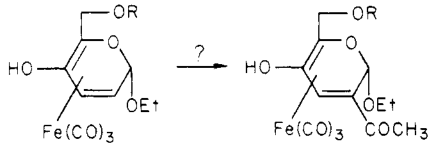


consequently studies designed to explore this area were initiated.

The approach adopted by us was based on the fact that tricarbonyl (diene) iron complexes such as **1** undergo



1 **2**



3 **4**

Friedel–Crafts acylation giving **2**,[7-9] the reaction being 3800 times faster than the one with benzene.[7,8] The question therefore arose as to whether a complex such as **3** would give rise to a product such as **4**. Although terminal substitution of the dienic moiety is known to decrease its reactivity markedly,[7] it was surmised that the electron-rich nature of the 2,3 double bond of **3** might reverse this tendency.

We therefore set out to see whether a complex such as **3** could be obtained from the corresponding enone. Our expectations were based on the well-known propensity of iron carbonyls to form complexes with conjugated dienes. Thus 1,4-dienes are readily isomerised to conjugated isomers,[10,11] and structures which are otherwise remarkably unstable may be isolated, e.g., the enol of crotonaldehyde (**5**) from the enol acetate[12] (Scheme I). This sequence also shows that the tendency for complexation of a diene is so strong that other ligands (e.g., CO) may be displaced from the iron carbonyl reagent.

In this report, we describe our attempts to prepare the iron carbonyl complex, **3**.

Results and Discussion

The enone **6a** and 2 equiv of diiron nonacarbonyl[13] were dissolved in purified benzene and allowed to react under an atmosphere of nitrogen for 16 h. Some starting material still remained, but this could not be remedied by prolonged reaction times, nor by the use of a larger excess of $Fe_2(CO)_9$. The products were isolated (see Experimental Section) and chromatographed under nitrogen on a column of degassed silica gel using highly purified solvents.

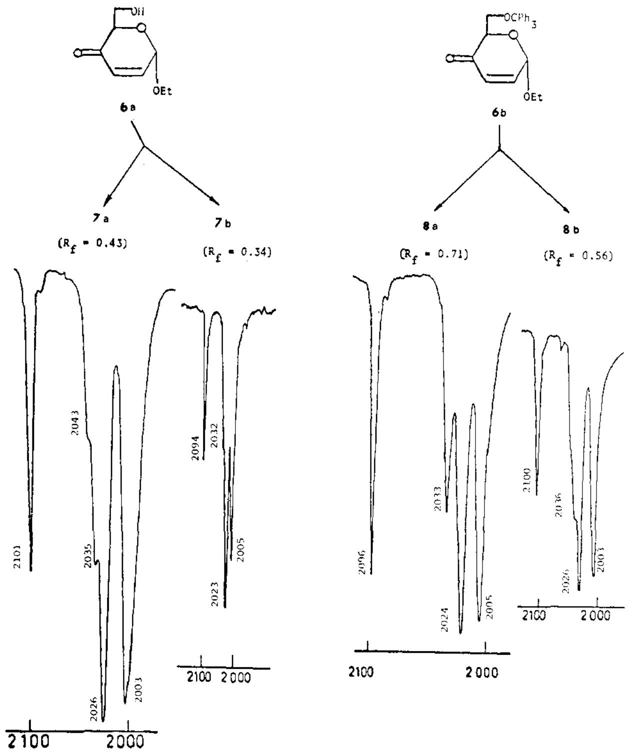
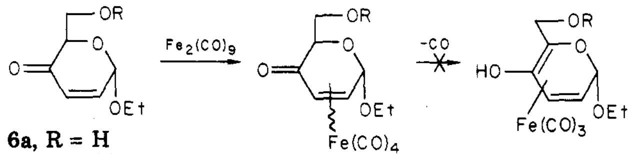


Figure 1. Infrared spectra of iron carbonyl complexes of **6a** and **6b**.

In addition to unreacted **6a**, three compounds were isolated having R_f values of 0.72, 0.45, and 0.34 on thin-layer chromatograms. Only the latter two charred on spraying with sulfuric acid. The first was therefore not carbohydrate and was characterized by IR and mass spectral data as triiron dodecacarbonyl.[14] The other two were identified as the diastereomeric pair **7a** and **7b** resulting from the two possible modes of addition of the iron carbonyl group to the double bond of **6a** (vide infra).



6a, R = H
b, R = CPh_3

7a,b, R = H
8a,b, R = CPh_3

3

The tritylated enone **6b** gave comparable results except that triiron dodecacarbonyl was not formed.[15] Apart from unreacted **6b**, two carbohydrate-containing products of R_f 0.71 and 0.56 were isolated by chromatography and identified (vide infra) as the diastereomers **8a** and **8b**.

The carbohydrate–iron carbonyl complexes **7a** and **7b** which were crystalline, and **8a** and **8b** which were not, proved to be exceedingly labile. They decomposed to metallic iron and the enone even when dissolved in highly purified solvents, and it was not possible to obtain satisfactory analytical data for any of these substances. However, their identity as iron carbonyl complexes was suggested by their ready oxidative cleavage with ferric nitrate in aqueous acetone, whereupon the parent enone was regenerated.[16]

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(7) R. E. Graf and C. P. Lillya, *J. Am. Chem. Soc.*, **94**, 8282 (1972).

(8) E. O. Greaves, C. R. Knox, and P. L. Pauson, *J. Chem. Soc., Chem. Commun.*, 1124 (1969).

(9) A. N. Nesmeyanov, K. N. Anisimov, and G. K. Magomedov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **715**, 959 (1970).

(10) R. Pettit, G. Emerson, and J. Mahler, *J. Chem. Educ.*, **40**, 175 (1963).

(11) A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. A*, 332 (1968).

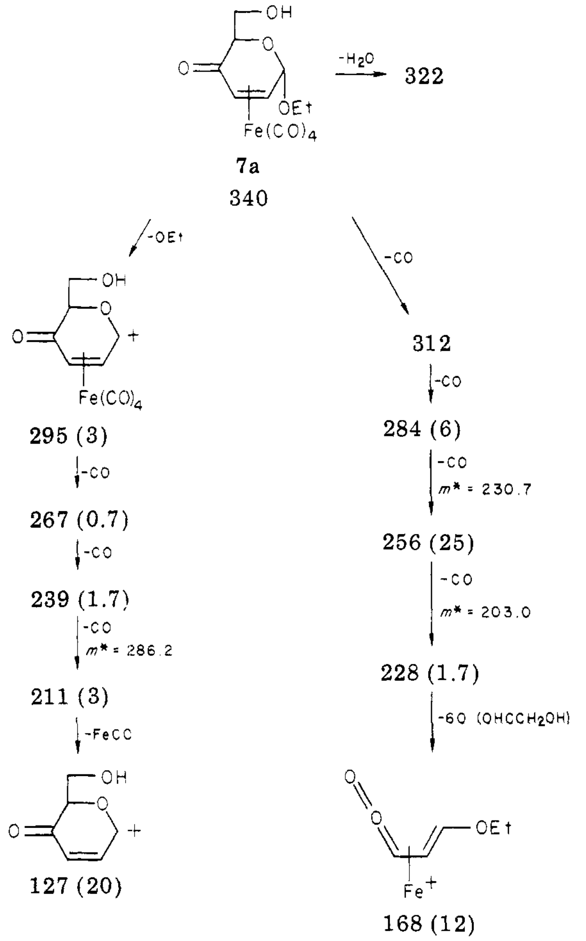
(12) C. H. Depuy, T. Jones, and R. L. Parton, *J. Am. Chem. Soc.*, **96**, 5062 (1974).

(13) R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, 1965, p 93.

(14) J. Lewis and B. F. Johnson, *Acc. Chem. Res.*, **1**, 245 (1968).

(15) The formation of $Fe_3(CO)_{12}$ with **6a** but not with **6b** is interesting. $Fe_2(CO)_9$ is known to disproportionate in base giving $Fe_3(CO)_{12}$. Presumably, an interaction between the free hydroxyl of **9a** and $Fe_2(CO)_9$ triggers the disproportionation.

Scheme II

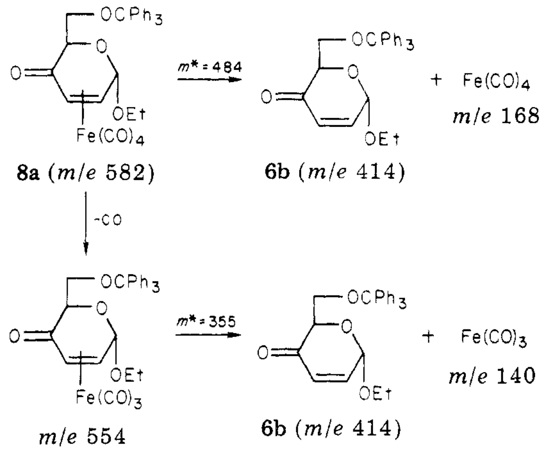


In order to determine the structure of the complexes, the carbonyl stretching region of the IR spectrum (~2000 cm^{-1}) was examined. For $Fe(CO)_3$ complexes with local C_{3v} symmetry two bands are predicted, but there is lower symmetry (e.g., C_s) where three bands may be observed. Thus two or three bands, but never more, have been observed.[10,17]

The pertinent data obtained from IR spectra (Figure 1) showed clearly that the complexes were not tricarbonyl and were probably tetracarbonyl. The latter sometimes show three[18] or more usually four[19,20] and occasionally five or six[18,19] bands. Furthermore, these absorptions are almost always above 2000 cm^{-1}. Comparison of the signals in Figure 1 suggested that **7a** and **8b** formed one structurally related pair, while **7b** and **8a** formed another. This fortuitous circumstance was helpful since the product of higher R_f from each enone, i.e., **7a** and **8a**, was obtained in greater purity and could therefore be subjected to more detailed investigations.

In the mass spectrum of **7a** (Scheme II), the base peak at *m/e* 84 was assignable to FeCO. The molecular ion appeared at *m/e* 340, and the successive loss[14] of four molecules of carbon monoxide was indicated by peaks at *m/e* 312, 284, 256, and 228. Metastable peaks associated with the formation of the last two ions were observed at *m/e* 230.7 and 203.0, respectively. The extrusion of glycolic aldehyde from the 228 ion is consistent with the results of Ferrier and co-workers.[21]

Scheme III

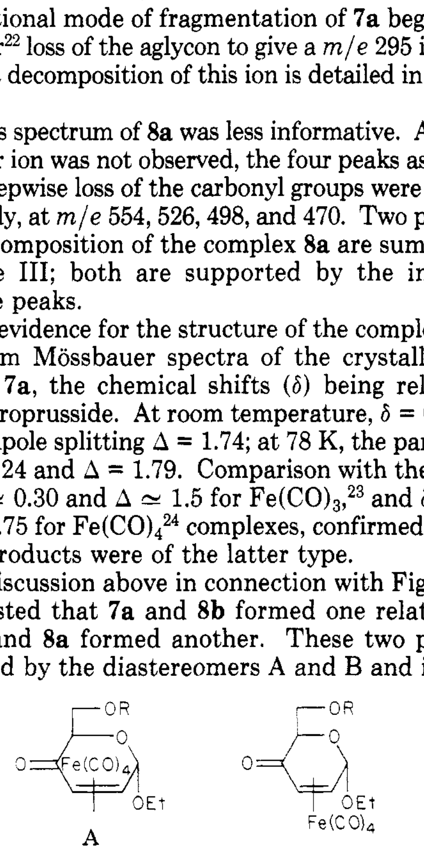


An additional mode of fragmentation of **7a** begins with the familiar[22] loss of the aglycon to give a *m/e* 295 ion. The subsequent decomposition of this ion is detailed in Scheme II.

The mass spectrum of **8a** was less informative. Although a molecular ion was not observed, the four peaks associated with the stepwise loss of the carbonyl groups were evident, albeit faintly, at *m/e* 554, 526, 498, and 470. Two pathways for the decomposition of the complex **8a** are summarized in Scheme III; both are supported by the indicated metastable peaks.

Further evidence for the structure of the complexes was sought from Mössbauer spectra of the crystalline diastereomer **7a**, the chemical shifts (δ) being relative to sodium nitroprusside. At room temperature, $\delta = 0.19$ and the quadrupole splitting $\Delta = 1.74$; at 78 K, the parameters were $\delta = 0.24$ and $\Delta = 1.79$. Comparison with the normal values, $\delta \simeq 0.30$ and $\Delta \simeq 1.5$ for $Fe(CO)_3$,[23] and $\delta \simeq 0.24$ and $\Delta \simeq 1.75$ for $Fe(CO)_4$[24] complexes, confirmed the fact that our products were of the latter type.

In the discussion above in connection with Figure 1, it was suggested that **7a** and **8b** formed one related pair, while **7b** and **8a** formed another. These two pairs are represented by the diastereomers A and B and it was of interest to see whether definitive assignments could be made. Unfortunately, this proved impossible because the complexes were too unstable, and even in dry, degassed solvents, they decomposed, depositing metallic iron. However, it was possible to observe that the olefinic protons had been shifted upfield by ~2 ppm from their positions in the enones **6a** and **6b**. This upfield shift is normally observed for $Fe(CO)^4$ complexes.[19,25]



A B

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[16] H. W. Whitlock and V. Y. Chauh, *Inorg. Chem.*, **4**, 424 (1965).

[17] R. T. Bailey, E. R. Lippincott, and D. Steele, *J. Am. Chem. Soc.*, **87**, 5346 (1965); G. Davidson, *Inorg. Chim. Acta*, **3**, 396 (1969); M. Cais and N. Maoz, *J. Organomet. Chem.*, **5**, 370 (1966); G. F. Emmerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964).

[18] R. L. Fields, G. L. Goodwin, and R. N. Hazeldine, *J. Organomet. Chem.*, **26**, C70 (1971).

[19] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdock, *Helv. Chim. Acta*, **46**, 288 (1963).

[20] D. C. Andrews and G. Davidson, *J. Organomet. Chem.*, **35**, 1961 (1972).

[21] R. J. Ferrier, N. Vethaviyasar, O. S. Chizhov, V. I. Kadentsev, and B. M. Zolotarev, *Carbohydr. Res.*, **13**, 269 (1970).

[22] N. K. Kochetkov and O. S. Chizhov, *Adv. Carbohydr. Chem.*, **21**, 39 (1966).

[23] E. Fluck in "Chemical Applications of Mössbauer Spectroscopy", V. I. Goldanski and R. Herber, Ed., Academic Press, New York, 1968, pp 268–313.

[24] R. L. Collins and R. Pettit, *J. Chem. Phys.*, **39**, 3433 (1963).

It was therefore apparent that the approach adopted by us would not yield the desired dienol complex **3**. Furthermore, the idea of enolising **7** or **8** as a possible approach to **3** was rejected because of the known instability of **6a** to bases,[26] as well as the extreme instability of **7** and **8** themselves.

Experimental Section

Thin-layer chromatography (TLC) was performed on glass plates coated with silica gel (HF-254, E. Merck) to a thickness of 0.3 mm using 1:1 ethyl acetate/petroleum ether (30–60 °C) (solvent A) or 1:4 ethyl acetate/petroleum ether (30–60 °C) (solvent B). The chromatograms were first viewed under ultraviolet light, then sprayed with concentrated sulfuric acid. Heating in an oven was required for complete visualization. For column chromatography, E. Merck silica gel (0.05–0.20 mm, 70–325 mesh A.S.T.M.) was used.

^{1}H NMR spectra were determined in the solvents indicated with tetramethylsilane as internal standard using either a Varian T-60 or a Varian HA 100 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 457, but for high resolution work, the Beckmann IR-9 or Perkin-Elmer 180 were used. Ultraviolet spectra were recorded on a Beckmann DBG instrument.

The Iron Carbonyl Adduct of Ethyl 2,3-Dideoxy-α-D-*erythro*-hex-2-enopyranosid-4-ulose (6a) and Its 6-*O*-Triphenylmethyl Derivative (6b). Ethyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosid-4-ulose (**6a**)[2a] (2.06 g; 12.0 mmol) was dissolved in purified degassed benzene (200 mL) and diiron nonacarbonyl[13] (8.7 g; 24 mmol) was added, an atmosphere of nitrogen being maintained throughout the operations. The flask was covered with aluminum foil, and the mixture was stirred under nitrogen for 16 h. At this time the thin-layer chromatograms developed in solvent A showed that some starting material still remained. However, preliminary experiments had indicated that the reaction could not be made to go to completion by adopting longer reaction times, or by using a larger excess of $Fe_2(CO)_9$.

The flask was transferred to a drybox where the mixture was filtered through a bed of Celite, which was washed previously with purified benzene. The filtrate was evaporated to dryness below 40 °C under reduced pressure, using a rotary evaporator equipped with a nitrogen inlet. The residue was examined by TLC (solvent A) and showed three spots with R_f 0.72, 0.45, and 0.34, in addition to residual **6a** (R_f 0.22). The first substance appeared green when viewed under UV and did not char with sulfuric acid. The middle two appeared yellow and charred.

Silica gel was dried in an oven and then degassed by use of a rotary evaporator and a high-vacuum pump. The silica was packed into a column, and hexane was allowed to percolate through with an atmosphere of nitrogen being maintained throughout. (The use of neutral alumina activity I or preparative layer chromatograms resulted in decomposition.) Hexane was used to elute the fraction of R_f 0.71 which was judged to be $Fe_3(CO)_{12}$: IR (hexane) 2051, 2028 cm^{-1} (terminal $C\equiv O$); IR ($CHCl_3$) 1866, 1832 cm^{-1} (bridging $C\equiv O$); lit.[27] (hexane) 2046, 2023 ($CHCl_3$) 1865, 1834 cm^{-1}. The MS showed m/e 504 (M^+) and corresponded exactly to the published spectrum.[14]

After removal of $Fe_3(CO)_{12}$, the eluant was changed to ether–hexane (1:1) by which the compound of R_f 0.45 (**7a**, 0.35 g)[28] was obtained fairly pure. However, the compound of R_f 0.34 (**7b**) was contaminated with unreacted **6a**. For **7a**: UV (hexane) λ_{max} 260, 217 nm; NMR (100 MHz, C_6D_6) δ 4.98 (1 H, H-1, s), 3.1–4.2 (6 H, H-2, H-3, H-6, H′-6, OCH_2, CH_3, m), 4.24 (1 H, H-5, m), 2.8 (1 H, OH, m), 1.24 (3 H, $OCH_2\mathbf{CH_3}$, t, J = 7 Hz); NMR (60 MHz, acetone-d_6) δ 5.42 (1 H, H-1 s), 3.5–4.2 (6 H, H-2, H-3, H-6, H-6′, $O\mathbf{CH_2}CH_3$, m), 4.27 (1 H, H-5 m), 2.9 (1 H, OH, m), 1.24 (3 H, t, $OCH_2\mathbf{CH_3}$ J = 7 Hz). H-1 was a sharp singlet in all solvents and was at 5.23 in CCl_4 and 5.65 in $CDCl_3$. For MS see Scheme II. For IR see Figure 1.

The tritylated enone **6b** was treated with $Fe_2(CO)_9$ in the same manner as described above for **6a** except that in this case equimolar amounts of the enone and $Fe_2(CO)_9$ were used and the reaction was stopped after 6 h. A similar isolation procedure was followed and the product showed two new substances on TLC, R_f 0.71 and 0.56 (solvent B), in addition to residual **6b** (R_f 0.45). $Fe_3(CO)_{12}$ was not formed in this case. Repeated chromatography on silica gel columns as described above using 1:9 ethyl acetate/hexane yielded the complexes **8a** and **8b** in reasonably high purity. The NMR spectra of both **8a** and **8b** were of little use due to severe line broadening, but IR data are given in Figure 1.

Oxidative Decomposition of 7a. After complex **7a** (51 mg, 0.15 mmol) was added to a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (0.297 g, 0.74 mmol) in 1:1 acetone–water (30 mL), the mixture was stirred under nitrogen at room temperature for 3 days. The solution was extracted with chloroform, and enone **6a** was identified by NMR and TLC.

Complex **8b** gave a similar result.

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Registry No. 6a, 25474-14-0; **6b**, 40555-08-6; **7a**, 70304-24-4; **7b**, 70354-64-2; **8a**, 70304-25-5; **8b**, 70354-65-3; $Fe_2(CO)_9$, 15321-51-4.

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[25] R. G. Kidd in "Characterization of Organometallic Complexes", Vol. 26, Part II, M. Tsutsui, Ed., Wiley, New York, 1971, p 323.

[26] B. Fraser-Reid, A. McLean, and E. W. Usherwood, *J. Am. Chem. Soc.*, **91**, 5392 (1969).

[27] K. Noack, *Helv. Chim. Acta*, **45**, 1847 (1962); G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, **2**, 1315 (1963); R. H. Herber, W. R. Kingston, and G. K. Wertheim, *ibid.*, **2**, 153 (1963).

[28] These figures do not represent the total amounts of the complexes formed.