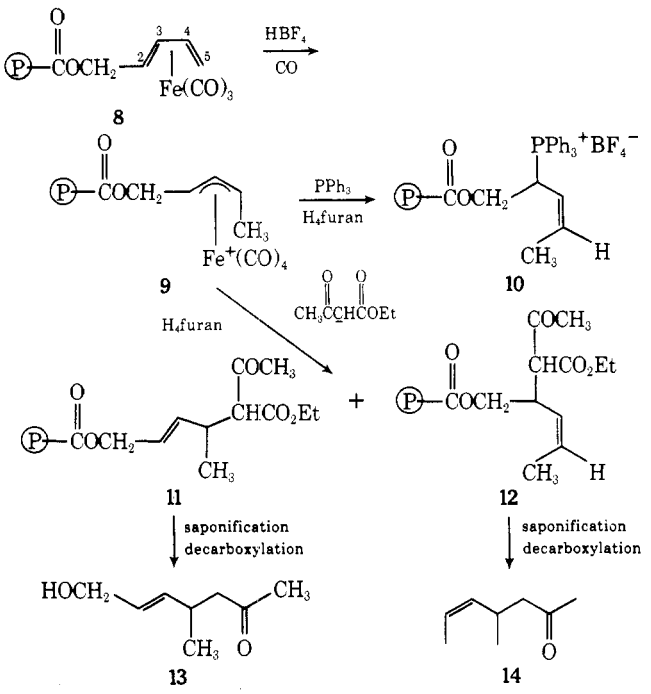
Scheme II



lar reactions in polymeric π-allyliron tetracarbonyl cations. Copolymers of η^4-(2,4-pentadienyl acrylate)tricarbonyliron and styrene[1] (*i.e.*, **8**) (Scheme II), upon treatment with HBF_4 and CO, gave polysalt **9**, which arises from predominant protonation at C-5. Polysalt **9** could be isolated.[7] Suspension of **9** in H_4furan and addition of the nucleophile resulted in an instantaneous reaction. For example, the addition of excess PPh_3 to **9** gave **10** in which the iron had been completely replaced from the purified poly(phosphonium salt).[8] With the anion of ethyl acetoacetate, nucleophilic attack occurred at both termini of the allylic system resulting in units of both **11** and **12** within the polymer. Saponification and decarboxylation resulted in the isolation of **13** and **14** in a ratio of 7:1 in 53% overall yield.[5,9] Isolation of **13** and **14** confirms that protonation of **8** occurs predominately at C-5,[10] and that nucleophile attack is favored at the allylic site most removed from the polymer backbone.

No evidence was obtained for the presence of intermediate olefin–iron tetracarbonyl complexes after treatment with triphenylphosphine or pyridine. Such complexes, resulting from disubstituted allyl cations, such as **4** or **9**, are very unstable relative to the corresponding complexes derived from the unsubstituted π-allyliron tetracarbonyl cation.[11]

Using this technique it should be possible to convert the η^4-(diene)tricarbonyliron moiety into a variety of pendant functional groups. Since the reactivity ratios are known for the copolymerization of **1** with several organic monomers,[1,12] it is possible to specifically tailor the amount of **1** in copolymers, thereby specifically controlling the number of functional groups to be later introduced *via* the π-allyl cation route.

Acknowledgments. This work was supported in part by the National Science Foundation, Grant No.-GH-37566, and by the University of Alabama Research Grants Committee, Project 672.

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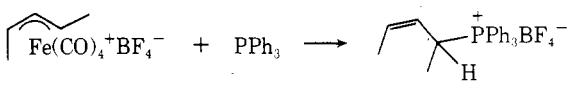
(2) (a) G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 4591 (1962); (b) G. F. Emerson, Ph.D. Thesis, University of Texas, 1964; *Diss. Abstr.*, **25**, 4955 (1965); (c) for a review, see R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964).
(3) Monomeric π-allyliron tetracarbonyl cations have been prepared and characterized previously; see D. H. Gibson and R. L. Vonnahme, *J. Amer. Chem. Soc.*, **94**, 5090 (1972). Stereospecifically deuterium-labeled allyliron cations are readily produced using deuterated acids; see T. H. Whitesides and R. W. Arhart, *ibid.*, **93**, 5296 (1971).
(4) This is inferred based on the products (**7a** and **7b**) which are isolated upon reacting **4** with the anion of ethyl acetoacetate followed by saponification and decarboxylation. Cation **4b** could only lead to *cis*-4-(hydroxymethyl)-5-octen-2-one or *trans*-4-ethyl-5-hepten-7-ol-2-one but not to **7a** or **7b**.
(5) Satisfactory ir, nmr, and mass spectra as well as elemental analyses were obtained for each compound. The cleavage products are readily separated from the polymer backbone by precipitation of the polymer into excess hexane.
(6) T. H. Whitesides, R. W. Arhart, and R. W. Slaven, *J. Amer. Chem. Soc.*, **95**, 5792 (1973).
(7) The polymeric salts were precipitated upon adding diethyl ether to the acidic solutions. The starting polymers contained from 3 to 23 mol % of the organometallic monomer.
(8) That a mixture of **10** and Ⓟ-$CO_2CH_2CH{=}CHCH(CH_3)(PPh_3^-)BF_4^-$ was formed has not been ruled out. Compound **10** is presumed to predominate based only on Whitesides[4] observation that the *syn,anti*-(1,3-dimethylallyl)iron tetracarbonyl cation gave rise to a 74% yield of the cis allylphosphonium salt shown.



However, in that case steric effects of the polymer backbone were not present.
(9) Yields were based on the number of η^4-(diene)tricarbonyl units initially present in the polymer and were determined by vpc. Products **13** and **14** were isolated and purified both by liquid chromatography and by preparative vpc.
(10) Predominant protonation at C-2 followed by nucleophilic attack of $CH_3COCHCOOEt$, saponification and decarboxylation would result in the formation of either 3-(2-hydroxyethyl)-5-hexen-2-one or *cis*-5-octen-8-ol-2-one.
(11) For example, Whitesides[4] reported the isolation and characterization of allylpyridiniumiron tetracarbonyl tetrafluoroborate.
(12) Defining **1** as M_1, $r_1 = 0.26$, $r_2 = 1.81$ when styrene is M_2. By adding from 1 to 4% divinylbenzene to copolymerizations of **1** and styrene (where the **1**:styrene ratio is 1:6), a crosslinked swellable resin is obtained which can be used for the solid phase synthesis of **7** and **8**. This is analogous to solid support peptide synthesis.[13,14]
(13) (a) R. B. Merrifield, *J. Amer. Chem. Soc.*, **85**, 2149 (1963); (b) J. M. Stewart and J. D. Young, "Solid Phase Peptide Synthesis," W. H. Freeman, San Francisco, Calif., 1969.
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A Chemical Synthesis of Benzylated Methyl α-Isomalto Oligosaccharides

We are engaged in a systematic study of the stepwise synthesis of oligosaccharides. Our work, at present, involves the use of reactive glycosyl leaving groups and a variety of hydroxyl blocking groups in order to achieve rapid completely stereoselective syntheses of glycosides in high yield.[1-6] Recently we have reported that reaction of 2,3,4-tri-*O*-benzyl-6-*O*-(*N*-phenylcarbamoyl)-1-*O*-tosyl-D-glucopyranose (I) with alcohols in diethyl ether gives high yields of pure α-D-glucosides.[6] We now wish to report the stepwise synthesis of methyl octadeca-*O*-benzyl-α-isomaltohexaoside.

Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (II; 1 equiv) was allowed to react with I (1.2 equiv) in diethyl ether for 16 hr as previously reported.[5] The product was extracted with dichloromethane, washed with water, and evaporated to a syrup. The syrup was crystallized from di-

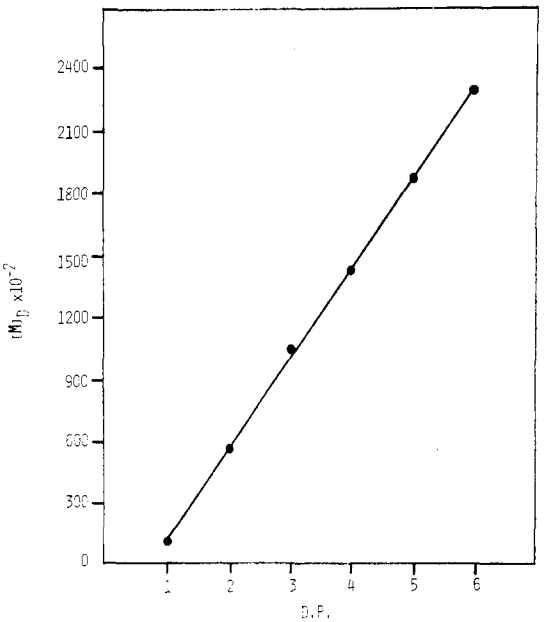

Figure 1. The relation between DP and molecular rotation $[M]_D$.

ethyl ether–petroleum ether to give methyl 2,2′,3,3′,4,4′-hexo-*O*-benzyl-6′-*O*-(*N*-phenylcarbamoyl)-α-isomaltoside in an 85% yield. The *N*-phenylcarbamate group was removed by sodium ethoxide in ethanol at reflux temperature. The product, methyl 2,2′,3,3′,4,4′-hexa-*O*-benzyl-α-isomaltoside, was crystallized from diethyl ether–petroleum ether in a 90% yield.

The disaccharide was then coupled with I under the same conditions as above. The resulting total trisaccharide fraction was isolated from the reaction mixture by short-column chromatography on silicic acid in an 85% yield. The *N*-phenylcarbamate blocking group was removed by sodium ethoxide in ethanol to give methyl nona-*O*-benzyl-α-isomaltotrioside.

The higher oligosaccharides were synthesized by the same reaction sequence of coupling with I followed by removal of the *N*-phenylcarbamate group. In each case the product was isolated from monomeric impurities by column chromatography as a noncrystallizable syrup. The yields for the coupling reaction were in all cases around 85% and the yields of the decarbanilation reactions were about the same. Losses appeared to be manipulative. Methyl octadeca-*O*-benzyl-α-isomaltohexaoside was obtained in 0.400-g quantity.

The oligosaccharides were free of the lower oligomer and homogeneous on examination by thin-layer chromatography and had the correct elemental analysis. The degree of polymerization of each oligosaccharide was confirmed from the ratio of the N–H proton to the aromatic or benzyl and ring proton absorption in the proton nmr spectrum. The oligosaccharides also showed a linear relationship between molecular rotation and the degree of polymerization of the oligomer as shown in Figure 1 for the decarbanilated oligosaccharides.

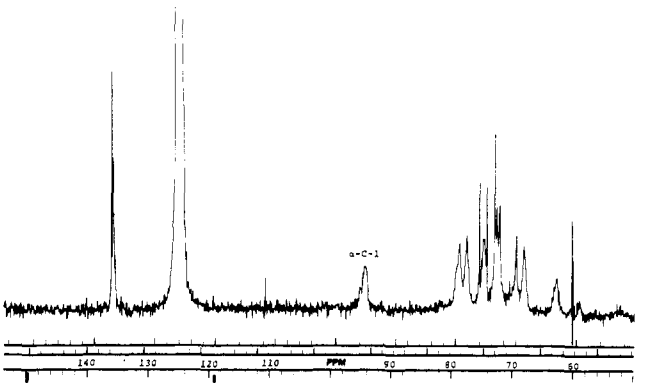

Figure 2. ^{13}C nmr spectrum of methyl octadeca-*O*-benzyl-α-isomaltohexaoside.

The α-linked structure of each of the oligosaccharides was indicated by its high specific rotation, ($[\alpha]^{25}D$ +87.3° (*c* 1, $CHCl_3$) for the decarbanilated hexamer), and by its ^{13}C nmr spectrum. Each spectrum shows peaks at 97–98.5 ppm from Me_4Si corresponding to the C-1 carbon of an α-linked glucopyranoside. Moreover, even in the ^{13}C nmr spectrum of methyl octadeca-*O*-benzyl-α-isomaltohexaoside, in which cumulative anomeric impurities should be most evident, no resonance is observed at 105.5 ppm from Me_4Si. This position is indicative of analogous β linkages, for example, methyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside. From this evidence we conclude that the reaction is virtually completely stereoselective and that the linkages are all α (Figure 2).

Recently Koto *et al.*[7] have reported the synthesis of 11 mg of isomaltooctaose using a modified Koenigs–Knorr method, in which disaccharide derivatives are coupled to form tetrasaccharides and tetrasaccharides to form the octasaccharide. Their method has some interesting features, but the reactions are excessively slow—48 hr for tetrasaccharide synthesis and 1 week for the octasaccharide coupling. The final coupling was also achieved in only 11% yield (to the free oligosaccharide) and anomeric impurities are indicated. We suggest that a careful selection of reactants and conditions in homogeneous systems is thus required for continuing improvements in oligosaccharide synthesis.

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