(1970), and references therein; (b) P. H. Kasai and D.McLeod, Jr., *ibid.*, **94**, 720 (1972).
(29) H. Nakatsuji, *J. Am. Chem. Soc.*, **96**, 24, 30 (1974).
(30) Langhoff and Davidson[8c] note that their extensive calculation of methylene shows bent bonds, but they do not discuss the implications of the Hellman–Feynman theorem. The theorem is not satisfied by their results, and it would be interesting if including polarization functions on the hydrogens would improve the agreement.
(31) R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **95**, 7180 (1973).

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A Novel Synthesis of 1,2-*cis*-Disaccharides[1]

Sir:

Much effort is currently devoted to the efficient and stereocontrolled preparation of 1,2-*cis*-disaccharides.[2] The availability of a general procedure is of paramount importance as it opens the way to many biologically and clinically active substances like antibiotics and antigens. As the scope for improvement of existing methods appears to be limited, novel reactions are desirable. The discovery in our laboratory that secondary amides react smoothly with halogeno sugars in the presence of a silver salt to give a new class of imidates paved the way to a novel method of selective activation of the anomeric center of carbohydrates, which appears full of promise in the field of glycosidic synthesis as amply demonstrated herein through the practical approach to eleven disaccharides.

A benzene solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride[3] (1 equiv) was stirred for 12 h at room temperature in the presence of *N*-methylacetamide (1 equiv), silver oxide (3 equiv), diisopropylethylamine, and powdered 4-Å molecular sieves to give 1-*O*-(*N*-methyl)acetimidyl-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranose (**1**, 88%) as a syrup, $[\alpha]^{20}_D$ + 28.6° (*c* 1.51, $CHCl_3$).[5] The stereospecificity of this attack may be attributed to a push–pull mechanism at the surface of the insoluble silver oxide. This reaction is general and a variety of benzylated imidates have been prepared.[6] They all react with alcohols in various solvents and in the presence of *p*-toluenesulfonic acid to give a good yield of α-glucosides.[7] A study of this glucosylation reaction using various imidates has shown that **1** is the best suited for this purpose.

In a typical procedure, methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[8] (**2**) was chosen as a crucial model for glucosylation at the redoubtable[9] 4-hydroxyl group of a hexopyranoside derivative ($^4C_1$ chair form). A solution of aglycon **2** (0.5 mmol) in dry benzene (20 mL) was treated at room temperature with the imidate **1** (0.75 mmol) and *p*-toluenesulfonic acid (0.5 mmol) under rigorously anhydrous conditions. The solution was stirred for 6 days and neutralized with triethylamine. After workup and purification (silica gel column), methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside was isolated as a clear syrup (**3**, 85%), $[\alpha]^{20}_D$ +48° (*c* 1.05, $CHCl_3$). After catalytic hydrogenolysis (Pd/C), methyl α-maltoside was obtained as a foam (85%, $[\alpha]^{20}_D$ +172.5°.[10]

Similar glucosylation of methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside[8] (20 h) followed by column chromatography gave the disaccharide derivative **4** as a colorless foam (81%); likewise, the isomaltoside **5** was obtained (80%), mp 101.5 °C $[\alpha]^{20}_D$ +59.3° (*c* 1.78, $CHCl_3$).[11]

The 2-hydroxyl group of D-galactopyranosides has been glucosylated in poor yield (25%) using either 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride[2b] or 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide[12] under halide ion catalyzed conditions.[2c] When benzyl 3,4,6-tri-*O*-benzyl-β-D-galactopyranoside[13] was glucosylated with **1**, the disaccharide derivative **6** was obtained (90%) as a pure foam, $[\alpha]^{20}_D$ +23° (*c* 1, $CHCl_3$). A further example of effective α-glucosylation was provided by the reaction of **1** with 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**7**), where the protected disaccharide **8** was obtained in crystalline form (70%), mp 90–91 °C, $[\alpha]^{20}_D$ +46° (*c* 2, $CHCl_3$). A small amount of crystalline β anomer (3%) was isolated, mp 118–119 °C, $[\alpha]^{20}_D$ +1° (*c* 1, $CHCl_3$).

This imidate procedure was then applied to stereospecific α-L-fucosylations, as α-L-fucose containing oligosaccharides are of widespread occurence in living systems. Under the agency of the Vilsmeier reagent,[4] 2,3,4-tri-*O*-benzyl-α-L-fucopyranose[14] (**11**) was conveniently transformed into crystalline 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl chloride (**12**, 92%), mp 72–73 °C, $[\alpha]^{20}_D$ −169° (*c* 1, CH_2Cl_2), which was in turn converted into 1-*O*-(*N*-methyl)acetimidyl-2,3,4-tri-*O*-benzyl-β-L-fucopyranose (**13**, 90%), mp 89–90 °C, $[\alpha]^{20}_D$ −67° (*c* 1, C_6H_6). The imidate **13** has been most successfully used for the preparation of various protected di- and trisaccharides, as shown in Table I. Owing to its crystallinity, its

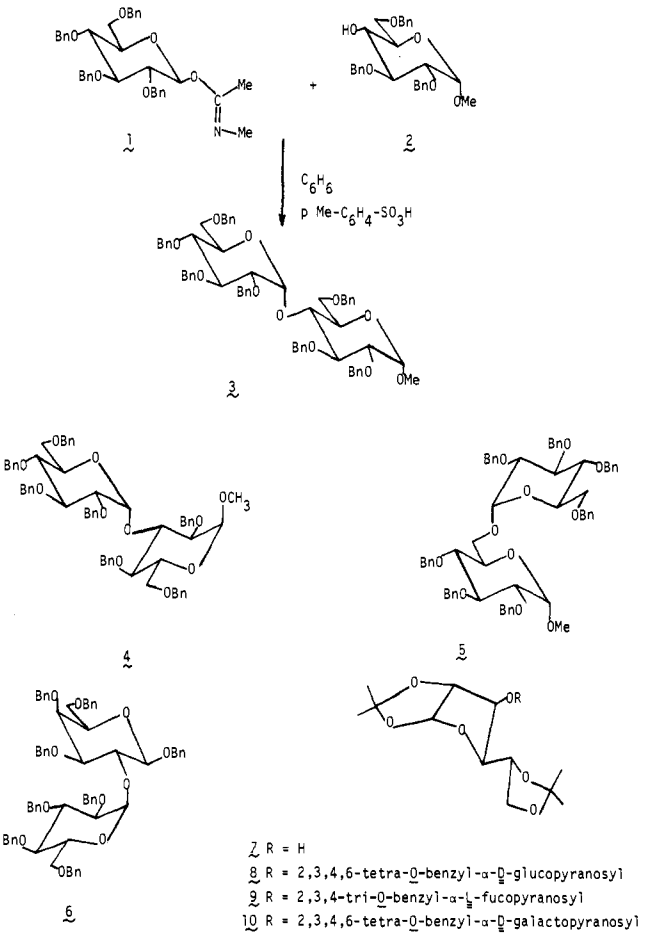
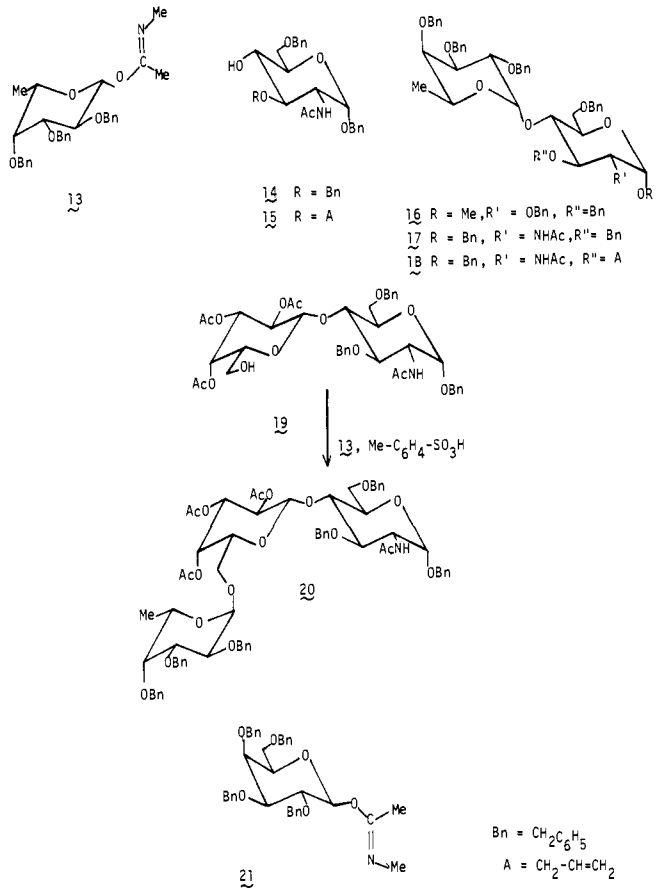


Table I. α-L-Fucosylation of Various Alcohols Using the Imidate Derivative **13**

Alcohol	Protected disaccharide (or trisaccharide)	Yield,[a] %	Mp °C	$[\alpha]^{20}_D$,[b] degree
2	**16**	74		−65.5
7	**9**	92	116–117	−118
14	**17**	84	129–130	+3
15	**18**	93	87–88	+2
19	**20**	86		+19

[a] No evidence for the formation of β anomer was obtained in any of the experiments. [b] In chloroform, *c* 1.



stability and its ease of preparation from hemiacetal **11**, the imidate **13** appears as an efficient α-L-fucosylating agent. Further use for the syntheses of blood group substances is now under way in our laboratory.

Finally, 1-*O*-(*N*-methyl)acetimidyl-2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranose (**21**) was used to prepare the protected disaccharide **10** (74%) as a glass, $[\alpha]^{20}_D$ +33° (*c* 1.1, $CHCl_3$).[15]

The examples reported herein prove that this novel approach is of wide applicability for the preparation of a wide variety of di- and oligosaccharides.

References and Notes

(1) Research supported by Centre National de la Recherche Scientifique, Institut National de la Santé et de la Recherche Médicale and Délégation Générale à la Recherche Scientifique et Technique (ASCO, Grant No. 74 7 0973 and 75 1 1364).

(2) (a) G. Wulff and G. Röhle, *Angew. Chem., Int. Ed. Engl.*, **86**, 173 (1974); (b) P. A. Gent and R. Gigg, *J. Chem. Soc., Perkin Trans. 1*, 1446 (1974); (c) R. U. Lemieux, K. B. Hendricks, R. V. Stick, and K. James, *J. Am. Chem. Soc.*, **97**, 4056 (1975); (d) K. Igarashi, J. Irisawa, and T. Honma, *Carbohydr. Res.*, **39**, 341 (1975); (e) D. E. Iley and B. Fraser-Reid, *J. Am. Chem. Soc.*, **97**, 2563 (1975).

(3) This chloride was conveniently prepared in one step (85%) from commercially available 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (Pfanstiehl, Waukegan, U.S.A.), under the agency of dimethylchloroformiminium chloride (prepared from dimethylformamide and phosphorus pentachloride according to ref 4).

(4) H. H. Bosshard, R. Mory, M. Schmid, and Hch. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

(5) All new compounds gave correct microanalyses and exhibited IR and NMR spectral characteristics that were in accord with their structures.

(6) See J. R. Pougny and P. Sinaÿ, *Tetrahedron Lett.*, 4073 (1976), for the syntheses of some aromatic imidates.

(7) Except in acetonitrile where a majority of β-glucoside was obtained, presumably through a nitrilium intermediate.[6] Benzene was finally selected as a standard solvent, but the nature of the solvent was not optimized in each specific case.

(8) J. M. Kuster and I. Dyong, *Justus Liebigs Ann. Chem.*, **12**, 2179 (1975).

(9) When methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside was partnered with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide according to Lemieux et al.,[2c] no disaccharide was formed. In general many difficulties have been experienced with the glycosylation of the 4-hydroxyl group of glucopyranoside derivatives and it is only recently that a practical synthesis (44%) of a maltose derivative has been described.[2d]

(10) A value of +174° (*c* 0.9, water) was reported for pure methyl α-maltoside: W. E. Dick, Jr., D. Weisleder, and J. E. Hodge, *Carbohydr. Res.*, **18**, 115 (1971).

(11) In this case, ~15% of the β anomer was present in the reaction mixture, as shown by GLC. The pure β anomer was isolated in small amount after column chromatography, mp 133–133.5 °C, $[\alpha]^{20}_D$ +17.1° (*c* 0.42, $CHCl_3$).

(12) P. J. Garegg, I. J. Goldstein, and T. Iversen, *Acta Chem. Scand. B*, **30**, 876 (1976).

(13) J. C. Jacquinet and P. Sinaÿ, *Tetrahedron*, **32**, 1693 (1976).

(14) M. Dejter-Juszynski and H. M. Flowers, *Carbohydr. Res.*, **18**, 219 (1971).

(15) In the case of the three amorphous disaccharides **3**, **4**, and **10**, no β anomer was detectable using ^1H NMR spectroscopy.

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Stepwise Reduction of the Carbon–Nitrogen Triple Bond of Acetonitrile on the Face of a Triiron Nonacarbonyl Cluster

Sir:

The use of transition metal clusters as homogeneous catalysts[1] and stoichiometric reagents[2] is currently of great interest.[3] Metal atom clusters permit a greater variety of interactions with substrates than is possible in mononuclear complexes. Some examples can be cited for the cluster chemistry of iron,[4a,b] but an even richer field has been found for ruthenium and osmium.[4b,c,5] This greater diversity of interactions is also believed to be responsible for the ability of clusters to carry out reactions which mononuclear species generally can not, such as the reduction of triple bonds.[3b] We report here the preparation of a unique series of complexes (Scheme I) which clearly delineate a sequence for the reduction of the carbon–nitrogen triple bond of an organic nitrile on the face of an $Fe_3(CO)_9$ cluster.

In an attempt to extend our studies of hydridocarbonyl cluster chemistry[6] to that of the more common metals we treated $W(CO)_5I^-$ with $Fe_2(CO)_8^{2-}$ in refluxing acetonitrile. The resulting anion mixture (later shown to contain **2**)[7a] was acidified and the neutral product thus obtained was analyzed by mass spectrometry. Surprisingly, it contained no tungsten, but it did contain the elements of a molecule of acetonitrile. Spectroscopic data[7b] indicated structure **3** which has been confirmed by an x-ray determination.[8] The tungsten byproduct was determined to be $W(CO)_3(CH_3CN)_3$. We have subsequently found that anion **2** is also formed by the base disproportionation reaction[9] of $Fe(CO)_5$ in moist acetonitrile, presumably via $HFe_3(CO)_{11}^-$ (**1**) (vide infra). Some $HFe(CO)_4^-$ as well as iron metal also forms. The $HFe(CO)_4^-$ decomposes when sodium iodide is included in the reaction mixture, thereby facilitating workup.[10] The only apparent reference to acetonitrile-induced base disproportionation of $Fe(CO)_5$ is a patent claiming $Fe(CO)_5$ as a catalyst precursor for the hydrogenation of nitriles to amines (500–5000 psi H_2, 100–300 °C).[11] The existence of metal carbonyl infrared spectral changes was noted (but not documented) in that work during preparation of the catalyst from $Fe(CO)_5$ in refluxing acetonitrile.

The neutral product $HFe_3(CO)_9(CH_3C{=}NH)$ (**3**) is slowly air oxidized in solution to give $Fe_3(CO)_9(CH_3C{\equiv}N)$ (**6a**)[12] in 20% yield. (The remaining iron can be approximately accounted for as $Fe(CO)_5$ and iron oxide.) Significantly, **6a** could not be prepared directly from either $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ and acetonitrile. It (**6a**) can, however, be hydrogenated back