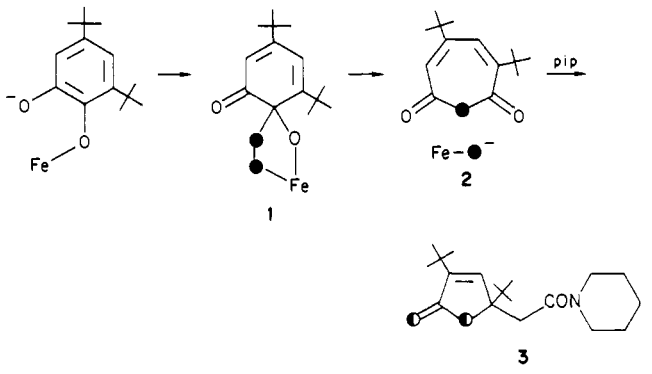
$[Fe(EHPG)]^-$ (2.16 Å),[16] and $[Fe_2(tacn)_2(OAc)_2O]^{2+}$ (2.18 Å).[17] The Fe–N bond in $[Fe(EDTA)H_2O]^-$[18] is similarly constrained and exhibits a bond length of 2.33 Å. The weaker Fe–N bond results in the stronger Fe–O bond trans to it, giving rise to an unsymmetrically chelated catecholate. This may enhance the formation of the monodentate form derived from breaking the longer Fe–O bond. We propose that this monodentate form is the species that reacts with O_2 and that the reaction proceeds by the mechanism shown below.



Studies on the reaction of $(pipH)_2[Fe(NTA)DBC]$ with $^{18}O_2$ in DMF provide further mechanistic insight. The product from the reaction, **3**,[19] obtained in 80% yield, shows the clean incorporation of one ^{18}O (98%) label. The CI-MS data on the product show the M + 1 ion at m/z 324 and the M + 1 − CH_4 ion at m/z 308, while the EI-MS data show a base peak at m/z 126 corresponding to the acetamide side chain, showing that the label is localized on the furanone ring. This is consistent with the formation of an intermediate anhydride, **2**, which is subsequently cleaved by piperidine. Attack of the anhydride at the C-6 carbonyl is expected on steric grounds.

This clean incorporation of a single ^{18}O label contrasts the results from other model cleavage reactions where substantial label scrambling occurs; the cleavage product in the latter cases exhibits varying amounts of label, ranging from molecules with no label incorporated to molecules with as many as four labels incorporated.[20] Such scrambling is thought to result from intermolecular side reactions involving the peroxy adduct **1**; these side reactions probably lower the effective yield of cleavage product as well. The absence of such scrambling in the Fe–NTA system and the high reaction yield suggest an additional role for the iron in the mechanism of oxidative cleavage. We propose that the ferric center coordinates the peroxy adduct and channels its decomposition toward the anhydride by stabilizing the oxide anion which would result from the Criegee rearrangement. This study thus suggests that the ferric center in the dioxygenases not only participates in the activation of substrate but also facilitates the latter stages of the reaction. In the enzyme active site, the oxide anion formed as a result of the rearrangement remains in the active site and acts as the nucleophile that opens the anhydride, thereby giving rise to dioxygenated product.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for $(dabcoH)_2[Fe(NTA)DBC]\cdot DMF$ (5 pages). Ordering information is given on any current masthead page.

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(20) Label scrambling has been observed in $^{18}O_2$ experiments using systems discussed in ref 2, 4, 5, and 6. White, L. S.; Que, L., Jr., manuscript in preparation.

New Stereocontrolled Approach to 3-Deoxy-D-*manno*-2-octulosonic Acid Containing Disaccharides

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3-Deoxy-D-*manno*-2-octulosonic acid (KDO) occurs as a ketosidic component in all lipopolysaccharides (LPS) and several acidic exopolysaccharides (K antigens) located at the cell surface of Gram-negative bacteria.[1] On the basis of ^{13}C and ^1H NMR results, it is believed that KDO displays in bacteria both the β- and α^2-D anomeric configurations. It is interesting to mention that sialic acid presents only one anomeric configuration[3] (α-D anomer).

The synthesis of KDO-containing oligosaccharides has only been approached so far by conventional glycosylation procedures[4] involving either methyl 3-deoxy-4,5,7,8-tetra-*O*-acetyl-α-D-*manno*-octulopyranosonate chloride or bromide. We would like to present a new and stereocontrolled approach to this synthetic challenge.

2,3-Di-*O*-benzyl-D-mannose[5] (**1**) was converted (EtSH, HCl, 24h, O °C) into **2** (85%) mp 78–79 °C (ether–hexane) then ((i) Ac_2O, pyridine, 12 h, room temperature; (ii) red HgO, $BF_3\cdot Et_2O$, aqueous THF, 40 min, room temperature) into the aldehyde **3** (93%), which represents the general precursor of the KDO unit.

Condensation of the aldehyde **3** with the phosphonate **4**[7] (THF, NaH, 1 h, 0 °C) afforded the *E* and *Z*[8] enol ethers **5** and **11** (85%, *E*/*Z* ratio 3:2), easily separated by silica gel chromatography. Deacetylation (MeONa–MeOH) gave the *E* and *Z* enol ethers **6** (95%) and **12** (95%). When the *E* isomer **6** was submitted to Hg(II)-induced cyclization [(i) $Hg(OCOCF_3)_2$, THF, 2 h, 0 °C; (ii) aqueous KCl, 12 h, 0 °C], the chloromercurio derivative **7**, mp 114–115 °C (ethanol), was obtained *as the only detectable isomer* in about 85%. The remarkable stereospecificity of the mercuriocyclization may be rationalized as previously postulated by us[7] in the case of sialic acid. The regiospecificity of the cyclization is also noteworthy. Demercuration of **7** (Ph_3SnH, AcONa, toluene, 3 h, room temperature) gave **8** (90%), which after catalytic hydrogenolysis (Pd/C) was converted into the anomerically pure β-linked disaccharide **9**[9,10] (90%) and finally

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(5) 2,3-Di-*O*-benzyl-D-mannose was prepared in six steps from commercially available methyl α-D-mannopyranoside ((a) isopropylmethyl ether, DMF, *p*-TsOH;[6] (b) BnBr, NaH, DMF; (c) AcOH 60%; (d) Ac_2O, pyridine; (e) Ac_2O, H_2SO_4; (f) MeONa, MeOH).
(6) Copeland, C.; Stick, R. V. *Aust. J. Chem.* **1978**, *31*, 1371–1374.
(7) Paquet, F.; Sinaÿ, P. *Tetrahedron Lett.* **1984**, 3071–3074. This phosphonate was used as a diastereoisomeric mixture.
(8) The *Z* geometry is deduced from the chemical shift of the vinylic proton of **11** ($CDCl_3$, 90 MHz) δ 6.26 (d, 1 H, J = 9 Hz). See: Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868–2877.

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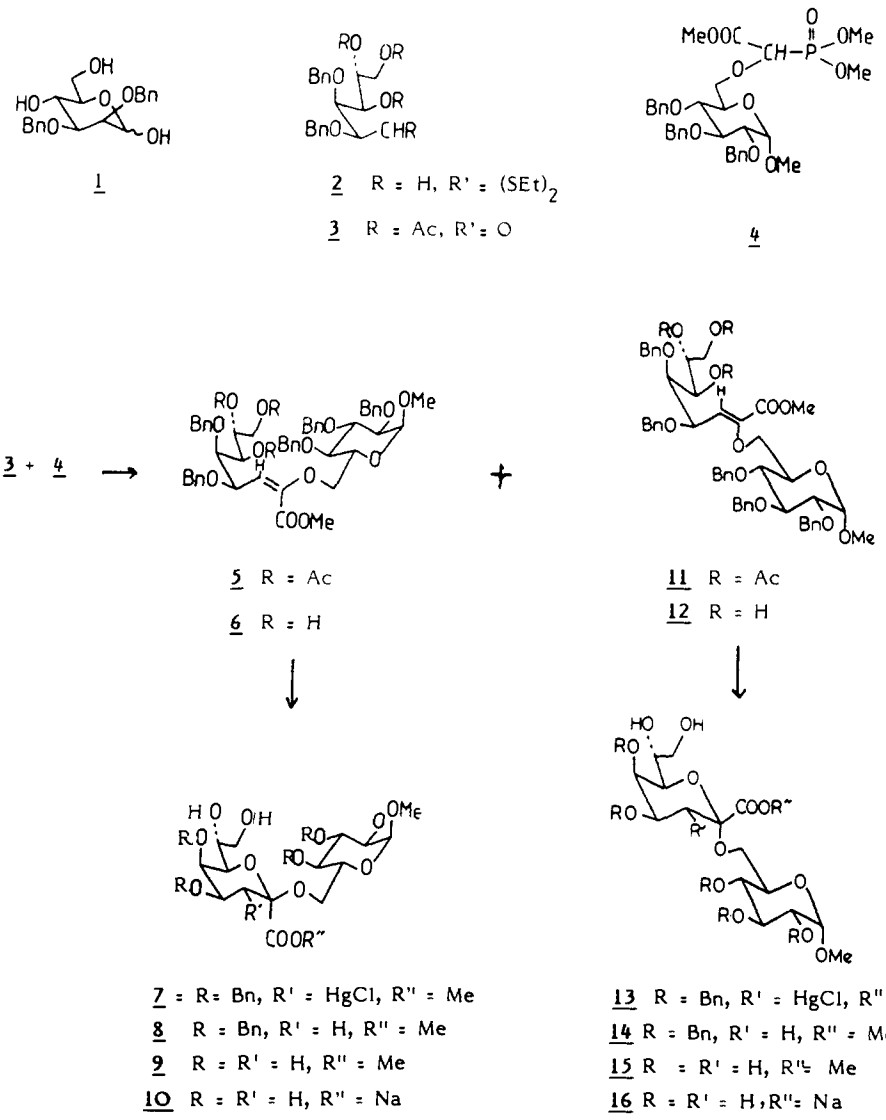
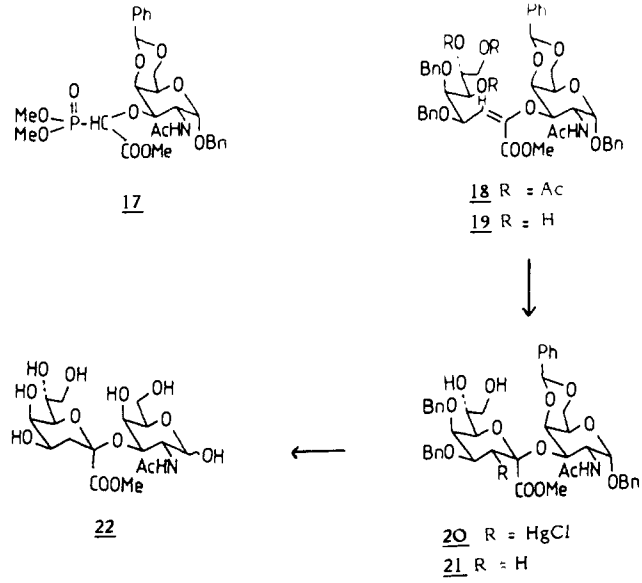
Scheme I



saponified (NaOH) to provide the sodium salt **10**[11] (72%). Cyclization of the *Z* isomer **12** likewise provided *exclusively* the chloromercurio derivative **13** (85%), which was transformed into the α-linked disaccharide derivatives **14** (90%), **15** (90%), and **16** (72%), as previously described.

This oxymercuration–demercuration strategy provides an entirely novel approach to the challenging problem of the stereocontrolled synthesis of KDO α- and β-glycosides and should find wide applicability in the field of natural products.

In a typical example, insertion reaction[12] of methyl diazo(dimethylphosphono)acetate[13] ($Rh_2(OAc)_4$, benzene, 2 h, reflux) into benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside[14] gave the phosphonate **17** as a diastereoisomeric mixture (75%). Condensation of **17** with the aldehyde **2** (THF,



(9) The difference in chemical shifts between H'-3(a) and H'-3(e) in **9** (0.44 ppm), compared to that in the α-anomer **15** (0.22 ppm), discriminates between β- and α-linked KDO including the esterified form. See: Dabrowski, U.; Friebolin, H.; Brossmer, R.; Supp, M. *Tetrahedron Lett.* **1979**, 4637–4640. See also ref 1.

(10) After acetylation of **9** (Ac_2O, pyridine), the chemical shift of H'-4 (δ 4.95) compared to that of the corresponding acetylated α-anomer (δ 5.34) is again in agreement with the structure. See: Unger, F. M.; Stix, O.; Schultz, G. *Carbohydr. Res.* **1980**, *80*, 191–195.

(11) The ^{13}C chemical shifts of C'-2 (δ 102.11) and C'-6 (δ 74.57) in **10**, compared to the corresponding values in **16**, C'-2 (δ 100.93) and C'-6 (δ 72.57), confirm the assigned β-anomery. See: Neszmelyi, A.; Jann, K.; Messner, P.; Unger, F. M. *J. Chem. Soc., Chem. Commun.* **1982**, *1017*–1019.

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(13) Regitz, M.; Anschlitz, W.; Liedhegener, A. *Chem. Ber.* **1968**, *101*, 3734–3743.

NaH, 1 h, 0 °C) gave *exclusively* the *E* isomer **18** (80%), which, after quantitative deacetylation into **19**, was stereo- and regiospecifically mercuriocyclized into the chloromercurio compound **20** (80%). Demercuration (86%) and catalytic hydrogenolysis gave the pure β-linked disaccharide **22** (82%), which is the repeating disaccharide unit[15] of the K antigen of *Neisseria meningitidis* 29e. Application of this strategy to the synthesis of various KDO-containing oligosaccharides is under way in our laboratory.

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Supplementary Material Available: Spectral information, elemental analyses, and physical constants for new compounds (4 pages). Ordering information is given on any current masthead page.

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Intramolecular Cyclotrimerization of Macrocyclic and Acyclic Triynes with Group 6 Metal Carbonyls. The Formation of Fulvene and Benzene[1]

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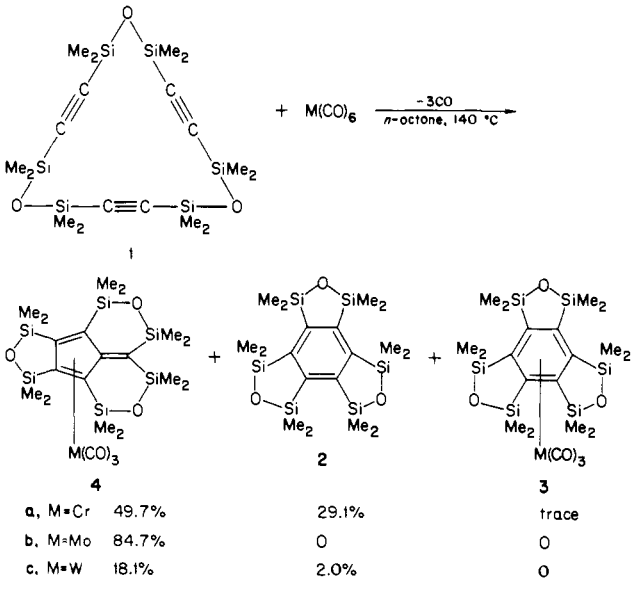
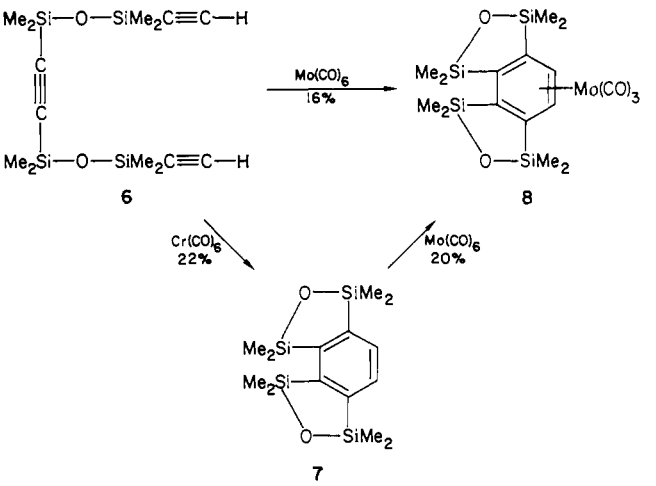
The transition-metal-catalyzed trimerization of alkynes has attracted organic chemists for a long time and several mechanisms and intermediates have been proposed for respective metals, triacetylene complexes (M = Cr, Ni),[2] metallacyclopentadienes (M = Co, Ir),[3] and halogenohexatrienyl metal complexes (M = Pd).[4] Herein we report a novel intramolecular trimerization of macrocyclic and acyclic triynes.



Dodecamethyl-4,9,14-trioxa-3,5,8,10,13,15-hexasilacyclopentadeca-1,6,11-triyne (**1**) undergoes thermal intramolecular cyclotrimerization to the corresponding benzene derivative **2** in low yield,[5] but when **1** was heated in the presence of group 6 transition-metal carbonyls [$M(CO)_6$, M = Cr, Mo, and W], both black to black-violet crystalline complexes **4** and an intramolecular cycloadduct, **2**, were obtained in addition to a trace amount of the corresponding (arene)metal tricarbonyl complexes **3**.



The formation of **2** was indeed catalyzed by the metal complexes, because, in the absence of metal complexes, **1** did not isomerize under such mild conditions. The arene complex **3b** was obtained in good yield by the independent reaction of **2** with $Mo(CO)_6$. However, neither **3a** (M = Cr) nor **3c** (M = W) was obtained by the reaction of **2** with the corresponding metal carbonyls under the same conditions. Interestingly, the main products of the reaction accompanied by the intramolecular trimerization of acetylenes are not benzene complexes but fulvene complexes. Although several fulvene complexes have been prepared by direct complexation of the preformed hydrocarbon with group 6 metal carbonyls, this is the first synthesis of fulvene complexes from acetylenes.[6]

The molecular structure of **4b**, determined by the X-ray diffraction analysis (final *R* value = 0.0656) of the single crystal at room temperature, is given in Figure 1.[7] The Mo complex

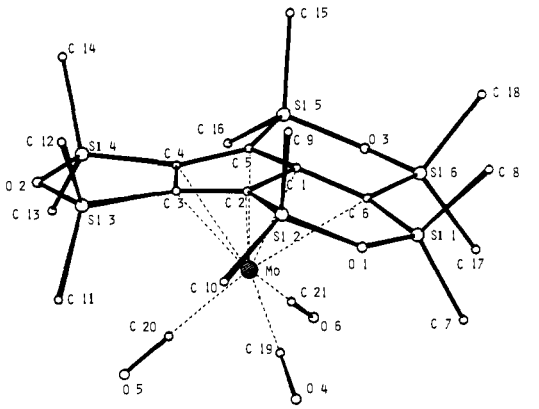


Figure 1. Perspective view of **4b** together with numbering of atoms.

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