sequentially, when a full equivalent of activating agent is added. In addition, while silyl ethers are stable to Tf_2O/base activation of anomeric sulfoxides, they are good glycosyl acceptors when catalytic triflic acid is the activating agent; however, they react more slowly than unprotected alcohols because they must be unmasked to couple. The ability to manipulate the reactivity of both the glycosyl donors and the glycosyl acceptors suggested the novel strategy of synthesizing a complicated trisaccharide in one step.

We chose the ciclamycin 0 trisaccharide as a target for two reasons. First, we are interested in the mode of action of ciclamycin 0 (Figure 1) and it is difficult to obtain from natural sources.[6] Second, and more germane to the point here, Danishefsky has published an impressive stepwise synthesis of this trisaccharide using the best available methods for 2-deoxy oligosaccharide synthesis. The Danishefsky synthesis therefore sets a high standard to evaluate the efficacy of our one-step approach.[7,8]

The ciclamycin 0 trisaccharide was synthesized stereospecifically from the readily available monosaccharides **1**, **2**, and **3** as shown in Scheme I.[9-12] The major product, isolated in 25% yield after flash chromatography on silica gel (20% ethyl acetate/petroleum ether), was the desired trisaccharide **5**. No other trisaccharides were produced, and the only other significant coupled product of the reaction was disaccharide **4** (Scheme I, 15% yield), the precursor to the trisaccharide. The yield of trisaccharide **5** in the reaction is limited *not* by any undesired cross-coupling[13] but by the instability of the glycosyl donors, particularly keto sulfoxide **1** which decomposes readily at room temperature even in the absence of activating agent.

The products of the reaction indicate that glycosylation takes place in a sequential manner as hoped, with *p*-methoxyphenyl sulfoxide **2** activating faster than phenyl sulfoxide **1** and C-4 alcohol **3** reacting faster than C-4 silyl ether **2**. Consistent with this, if the reaction is quenched at −100 °C, *only* the silyl ether of disaccharide **4** can be isolated (60%). We have thus manipulated the reactivity of both the glycosyl donors and the glycosyl acceptors to control the order in which glycosylation takes place.

By way of comparison, the Danishefsky synthesis of the ciclamycin trisaccharide, which makes elegant use of glycal chemistry,[14] requires 14 steps starting from the 3 glycal precursors and produces the trisaccharide in an overall yield of 9%.[7] Several steps are needed simply to modulate the reactivity of the donor/acceptor pairs (glycals) to achieve coupling specificity. Although the glycal method remains a very effective method for the construction of 2-deoxy oligosaccharides, the sulfoxide method has allowed us to achieve coupling specificity and construct the ciclamycin trisaccharide stereospecifically in a single step. This has resulted in a dramatic savings in time and labor (less than 3 h from monosaccharides to purified trisaccharide).

Finally, it should be noted that the trisaccharide (**5**) produced in the one-step reaction has an anomeric phenyl sulfide on the A ring. Anomeric phenyl sulfides are stable ("disarmed") to the conditions that activate anomeric phenyl sulfoxides for glycosylation, but they can be readily oxidized under mild conditions.[5,15] Thus, the sulfoxide glycosylation reaction also lends itself well to an iterative strategy for oligosaccharide synthesis.[5,14c,d,15,16] The ciclamycin trisaccharide **5** was oxidized to the corresponding sulfoxide in 80% yield (1.2 equiv of *m*-CPBA, CH_2Cl_2, −78 to −50 °C, 2 h) and is ready for coupling to the ciclamycin chromophore.

Acknowledgment. This work was supported by the National Institutes of Health.

Supplementary Material Available: MS (FAB) and ^1H and ^{13}C NMR spectra for compound **5** and ^1H NMR spectra for compounds **1**-**4** (16 pages). Ordering information is given on any current masthead page.

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(10) **2** and **3** are prepared from L-fucose with overall yields of 47% and 52%, respectively. (a) Giese, B.; Groninger, K. S.; Witzel, T.; Korth, H.-G.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 233. (b) Reference 9c. (c) Ogawa, T.; Matsui, M. *Carbohydr. Res.* **1978**, *62*, C-1.

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(13) Less than 5% of the disaccharide from the cross-coupling of phenyl sulfoxide **1** and free alcohol **3** was detected even though **1** is present in excess; no disaccharide from the cross-coupling of **1** and **2** was detected.

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Regio- and Stereoselective Formation and Isomerization of 1,3-Cyclohexadienes Catalyzed by Titanium Aryloxide Compounds†

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One of the conceptually simplest strategies for the synthesis of the 1,3-cyclohexadiene nucleus involves the selective (2 + 2 + 2) cycloaddition of 2 equiv of an alkyne with an olefin.[1] The overall formation of three new carbon-carbon bonds during this reaction offers the potential for controlling both the regio- and the stereochemistry of the products.[2] This communication reports our observations concerning the ability of titanium aryloxide compounds to catalyze this reaction as well as some mechanistic

† Dedicated to Professor Bob Squires on the occasion of his 40th birthday.

(1) (a) Shore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(2) (a) Sternberg, E. D.; Vollhardt, K. P. C. *J. Org. Chem.* **1984**, *49*, 1564. (b) Sternberg, E. D.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 4839. (c) Wakatsuki, G.; Yamazaki, H. *J. Organomet. Chem.* **1977**, *139*, 169. (d) Gadek, T. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 802. (e) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, *51/52*, 4549.

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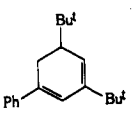
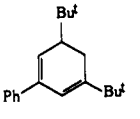
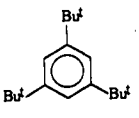
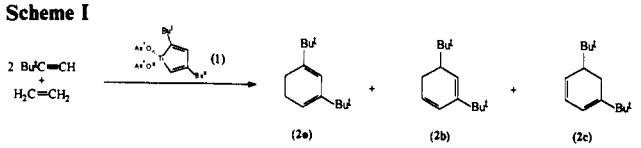
Table I[a]

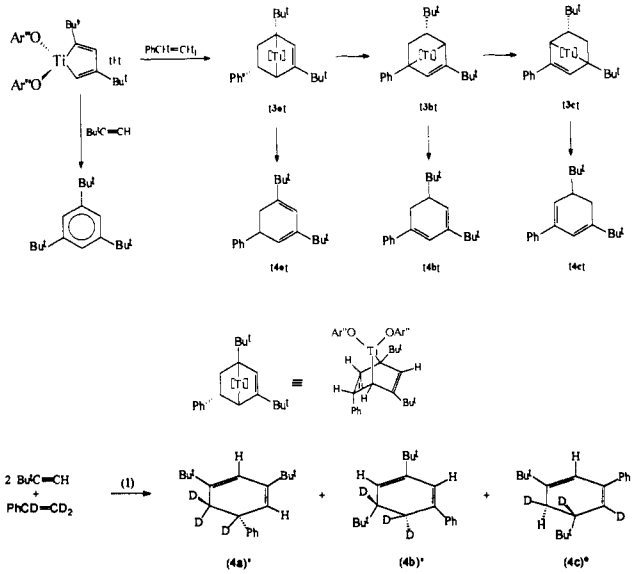
substrates			products/%		
[Bu^{t}C≡CH]/ M	[PhCH=CH$_2$]/ M	t/ °C	 (4b)	 (4c)	
2.90	0.73	90	13	47	40
2.90	1.45	25	47	34	19
2.90	1.45	90	16	65	19
2.90	2.90	25	62	30	8
2.90	2.90	90	31	59	10
2.90	4.35	25	74	20	6
1.45	1.45	25	48	45	7
1.45	1.45[b]	25	75	20	5

[a] [1] = 0.072 M for all experiments; solvent is C_6D_6; products analyzed by ^{1}H NMR. [b] Reaction utilized styrene-d_8, $C_6D_5CD{=}CD_2$.

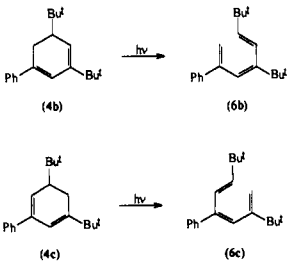
Scheme I



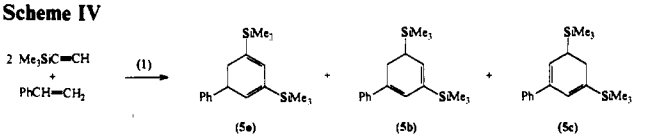
Scheme II



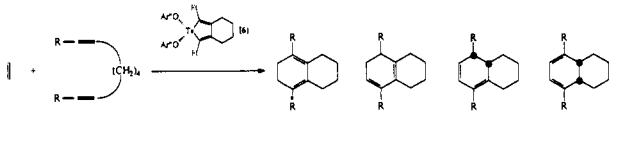
Scheme III



Scheme IV



Scheme V



R	T(°C)		%		
Et	25	-	45	45	10
Et	80	-	40	40	20
SiMe$_3$	25	-	35	35	30
SiMe$_3$	80	-	15	15	70

insight into factors that determine the nature of the final products.

The titanacyclopentadiene complex [(Ar″O)$_2$Ti(C$_4$H$_2$Bu$^t_2$)] (**1**) (Ar″O = 2,6-diphenylphenoxide)[3] will slowly catalyze the formation of 1,3,5-tri-*tert*-butylbenzene from Bu^{t}C≡CH at 25 °C in hydrocarbon solvents. However, addition of ethylene (1 atm) to a benzene solution containing **1** and excess Bu^{t}C≡CH causes rapid formation of di-*tert*-butylcyclohexa-1,3-dienes with only minor amounts of cyclotrimerization (Scheme I).[4] Although the three possible isomeric products shown were observed by GC/MS analysis, the major component of the reaction mixture was identified (NMR) as the regioisomer **2b**.

The formation of isomers is also observed in the reaction of PhCH=CH$_2$ with Bu^{t}C≡CH catalyzed by **1** (Scheme II, Table I).[5] The results obtained can be accommodated into the reaction sequence shown in Scheme II. Rate-determining (competitive) attack of either Bu^{t}C≡CH or PhCH=CH$_2$ on **1** eventually leads to either 1,3,5-tri-*tert*-butylbenzene or a substituted 1,3-cyclohexadiene. A proposed (undetected) intermediate in the latter reaction is a cyclohexadiene (titananorbornene) complex[6] with the phenyl substituent located exo (vide infra). Isomerization of this initial intermediate **3a** via a metal-mediated 1,5-hydrogen shift[7,8] leads to **3b**. Two competing reaction pathways for **3b** are

(3) Compound **1** was obtained by Na/Hg reduction of [(Ar″O)$_2$TiCl$_2$] in the presence of 3,3-dimethyl-1-butyne. See: Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211. ^{1}H NMR (C_6D_6, 30 °C): δ 6.8–7.5 (aromatics); 7.72, 7.25 (d, 1 H each, Ti(C$_4$Bu$^t_2$H$_2$), $^4J_{H\text{-}H}$ = 4.4 Hz); 1.00, 0.34 (s, 9 H each, C(CH_3)$_3$). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 240.6 (TiC^{t}Bu); 160.3 (TiO*C*); 28.1, 29.1 (C*Me*$_3$); 37.9, 40.1 (*C*Me$_3$).

(4) Spectroscopic data on the cyclohexadiene compounds are contained in the supplementary material. The mixtures of cyclohexadiene products were isolated from the reaction by thin-layer chromatography. The catalytic coupling of 3-hexyne and ethylene has been mentioned previously, see: Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 15.

(5) Reactions (Table I) were performed in 5-mm NMR tubes using C_6D_6 as solvent and analyzed by ^{1}H NMR. In each experiment the total reaction volume was 0.6 mL. During the course of the reactions, complex **1** was still observed in the reaction mixture by ^{1}H NMR spectroscopy.

(6) (a) Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1981. The η^4-binding of cyclohexadiene rings to early, d-block metal aryloxide fragments with a d^2 electron configuration has been shown to lead to metallanorbornene structures, see: (b) Steffey, B. D.; Chesnut, R. W.; Kerschner, J. L.; Pellechia, P. J.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1989**, *111*, 378. (c) Visciglio, V.; Rothwell, I. P., results to be published.

(7) (a) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1980**, *102*, 3490. (b) Karel, K. J.; Brookhart, M.; Aumann, R. *J. Am. Chem. Soc.* **1981**, *103*, 2695.

displacement of product **4b** by either $PhCH{=}CH_2$ or $Bu^tC{\equiv}CH$ or further isomerization via a second 1,5-hydrogen shift to produce **3c**.[9] The product distribution obtained using styrene-d_8, C_6D_5-$CD{=}CD_2$, shows that a primary kinetic isotope effect is present for the isomerization step (Table I, Scheme II), thus leading to a modification of the ratio of **4b*** to **4c*** but no decrease in overall 1,3-cyclohexadiene formation compared to cyclotrimerization.[10] Careful analysis of the ^1H and ^{13}C NMR spectra of the products **4b*** and **4c*** obtained using styrene-d_8 shows that the sequential 1,5-hydrogen shifts occur in a highly stereoselective, mutually cis fashion consistent with the pathway proposed (Scheme III).[11-13] The lack of isomerization of either **4b** or **4c** upon thermolysis (90 °C, 12 h) or upon exposure to a mixture of **1**, $Bu^tC{\equiv}CH$ and $PhCH{=}CH_2$ shows that the observed product distributions are kinetic in origin.

The catalytic cycloaddition of $Me_3SiC{\equiv}CH$ and $PhCH{=}CH$ in the presence of **1** yields slightly different results (Scheme IV). In this case, although the initial isomeric mixtures obtained are dependent upon the reaction conditions, the isomerization of **5a** to **5b** occurs over time within the reaction mixture. This indicates that recoordination of the generated trimethylsilyl-substituted 1,3-cyclohexadienes can occur, allowing further metal-mediated isomerization.

The scope of this reactivity has been further investigated by utilizing the diyne substrates $[RC{\equiv}C(CH_2)_4C{\equiv}CR]$ (R = Et, $SiMe_3$). Reduction of $[(Ar''O)_2TiCl_2]$ in the presence of 3,9-dodecadiyne leads to titanacyclopentadiene **6** (Scheme V).[14] Compound **6** catalyzes the reaction of 3,9-dodecadiyne with ethylene to produce a mixture of three corresponding hexalins (Scheme V).[15,16] In the case of the bis(trimethylsilyl) substrate, (2 + 2 + 2) cycloaddition with ethylene in the presence of **6** was also found to lead to a mixture of three products (Scheme V). The stereochemistries of **7c**, **7d**, **8c**, and **8d** were confirmed by their ^1H and ^{13}C NMR spectra. This cis stereochemistry is consistent with the stereoselective isomerization shown for **3** (Scheme II). Extended reaction times at 90 °C were found to lead to formation of the corresponding disubstituted tetralin.[15]

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Supplementary Material Available: Spectroscopic data for 1,3-cyclohexadiene products (16 pages). Ordering information is given on any current masthead page.

(8) The isomerization should proceed via cyclohexadienyl hydride intermediates. See: Fischer, M. B.; James, E. J.; McNeese, T. J.; Nyburg, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941.

(9) The results in Table I indicate that release of the final product 1,3-cyclohexadiene can occur by displacement with either olefin or acetylene. The ratio of **4b** to **4c** increases as the concentration of either styrene (Table I, entries 2, 4, and 6) or *tert*-butylacetylene (Table I, entries 2 and 7) increases. Use of $PhCD{=}CD_2$ also increases the ratio of **4b*** to **4c***, entries 7 and 8. However, it is possible that a dissociative pathway is also present, involving an intermediate fragment $[(Ar''O)_2Ti]$ which may be stabilized by intramolecular π-bonding to the aryl substituents of the 2,6-diphenylphenoxide ligands. See: (a) Kerschner, J. L.; Torres, E. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 1424. (b) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 1431.

(10) Analysis of **4b*** and **4c*** by GC/MS shows no loss of deuterium content by exchange with the other species.

(11) For a discussion of the NMR of 1,3-cyclohexadienes, see: *The Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*; Rabideau, P. W., Ed.; VCH Publishers, Inc.: New York, NY, 1989; Chapter 3.

(12) The ^1H NMR spectra of **4b** and **4c** are consistent with a ground-state structure containing a pseudoequatorial *tert*-butyl substituent. The aliphatic ring proton in **4c*** (Scheme II) is pseudoaxial on the basis of ^1H NMR spectra, i.e., mutually cis to the *tert*-butyl group. See: (a) Lightner, D. A.; Bouman, T. D.; Gawroński, J. K.; Gawroński, K.; Chappuis, J. L.; Crist, B. V.; Hansen, A. E. *J. Am. Chem. Soc.* **1981**, *103*, 5314. (b) Copley, S. D.; Knowles, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5008.

(13) The ground-state stereochemistries of **4b** and **4c** have been confirmed by photochemical ring opening to produce the corresponding linear triene (Scheme III). For leading references to the photochemistry of 1,3-cyclohexadienes and related molecules, see: Woning, J.; Lijten, F. A. T.; Laarhoven, W. H. *J. Org. Chem.* **1991**, *56*, 2427.

(14) Anal. Calcd for $TiC_{48}H_{44}O_2$: C, 82.27; H, 6.33. Found: C, 82.24; H, 7.19%. ^1H NMR (C_6D_6, 30 °C): δ 6.8-7.5 (aromatics); 2.04 (m), 1.41 (m, CH_2CH_2); 1.53 (q, CH_2CH_3); 0.44 (t, CH_2CH_3). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 229.9 (TiCEt); 159.6 (TiOC); 132.4 (β-C); 27.9, 24.1, 21.9 (CH_2); 13.0 (CH_2CH_3).

(15) (a) Jacobson, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 2579. (b) Dauben, W. G.; Hart, D. J.; Ipakschi, J.; Kozikowski, A. P. *Tetrahedron Lett.* **1973**, *44*, 4425.

(16) (a) Matuszewski, B.; Burgstahler, A. W.; Givens, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 6874. (b) Dauben, W. G.; Kellogg, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 4456.

α-C-H and α'-C-C Bond Cleavage in an Iridacyclohexadiene. Interchange of α-Hydrogen and α'-Phenyl Substituents without Accompanying Skeletal Rearrangement

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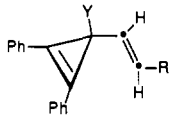
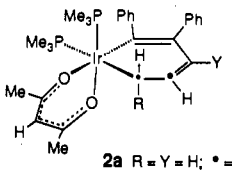
While metallacyclohexadienes have been invoked as key intermediates in the Dötz reaction,[2] few isolated examples exist, and their reaction chemistry is poorly defined. The first isolable examples were obtained from the ring-opening reactions of 3-vinyl-1-cyclopropenes with low-valent transition-metal complexes.[3] Subsequently, iridacyclohexadiene species, obtained by a different route,[4] were shown to undergo a facile deprotonation at the α-carbon to afford the first examples of iridabenzene complexes.[5] Here we report the unprecedented rearrangement of a 1,2-disubstituted iridacyclohexadiene to its 1,4-disubstituted isomer, which is shown by isotope labeling experiments to proceed by a quantitative interchange of H and Ph substituents between the α- and α'-carbon atoms of the metallacyclic ring rather than by a skeletal reorganization.

Room temperature reaction of the 16-electron Ir(I) complex $[Ir(acac)(PMe_3)_2]$ (acac = acetylacetonate) with 1,2-diphenyl-3-vinyl-1-cyclopropene (**1a**) affords the iridacyclohexadiene complex (**2a**).[6] On heating **2a** in benzene solution (95 °C, 33 h), a smooth isomerization occurs to give the corresponding trans isomer **3a** without any isomerization of the metallacycle. However,



1a R = Y = H; • = ^{12}C
1b R = Y = H; • = ^{13}C
1c R = D; Y = H; • = ^{12}C
1d R = H; Y = D; • = ^{12}C



2a R = Y = H; • = ^{12}C
2b R = Y = H; • = ^{13}C
2c R = D; Y = H; • = ^{12}C
2d R = H; Y = D; • = ^{12}C

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(6) Full details of the synthesis and spectroscopic characterization of all compounds reported herein and the crystallographic characterization of **4a** are provided as supplementary material.

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