on the hydrocarbon fragment a set of atomic motions that carries it to a part of the potential energy hypersurface where the arrangement of atoms is closer to the structure of **4x** than **4n**. For the triplet state, which requires a spin change before product formation can occur, such dynamic events may be of little consequence, but for the singlet biradical, which could presumably collapse to products very rapidly, the dynamics might provide an explanation for the experimentally observed preference for formation of **4x** over **4n**. This picture is supported by the previous trajectory calculations.[4]

The pictorial representation of the reaction dynamics can be translated into a semiquantitative prediction of the product ratio.[6] The Cartesian atomic displacements corresponding to the reaction coordinate represent the elements of a $3N$-dimensional vector (where N is the number of atoms). We hypothesize that the product ratio can be estimated by comparing components of the mass-weighted reaction coordinate vector along directions leading to post-transition-state minima on the potential energy hypersurface (in the case of **2** these minima would correspond to the two products, **4x** and **4n**, and to cyclopentane-1,3-diyl-*cis*-4,5-d_2 (**3**), which is presumed to lead in turn to **4x** and **4n** with equal probability). This is accomplished by taking dot products with normalized transformation vectors that describe conversion of the transition state into the structures at the subsequent potential energy minima.[7] A first approximation to the requisite transformation vectors comes from mass-weighting a vector derived by taking the difference in x, y, and z coordinates of corresponding atoms in the transition structure and in each of the structures **3**, **4x**, and **4n**.[7] The need to conserve total translational and rotational momentum defines the orientation in space of each of the post-transition-state structures. The problem with transformation vectors defined in this way is that they correspond to linear synchronous transit (LST) reaction paths, which are generally unrealistic representations of the true paths. Thus, in order to accommodate curvature in the reaction paths, a short step down each LST path was used as a starting point for a subsequent geometry optimization.[8] Unit vectors in the directions of these reoptimized points were then used in the dot-product calculations. The results from the AM1 CI calculations are as follows: for azo compound **1**, the calculated k_i/k_r ratio[6] is 4.3 and the observed value is 4.9 ± 0.9; for 2,3-diazabicyclo[2.1.1]hex-2-ene-*exo*-5-d,[9] the calculated value is 1.9 and the observed value is 1.2.[10]

We have also measured an isotope effect on the product ratio for 2,3-diazabicyclo[2.2.1]hept-2-ene by comparing k_i/k_r for **1** and for 2,3-diazabicyclo[2.2.1]hept-2-ene-*endo,endo*-1,4,5,6,7,8-d_6. The calculated isotope effect, defined as $k_i(d_2)k_r(d_6)/k_i(d_6)k_r(d_2)$, is 1.099, and the measured value[11] is 1.10 ± 0.04 (95% confidence interval for four measurements).

It appears that the model presented here can give reasonable results even from relatively low-level (and hence inexpensive) molecular orbital calculations, perhaps because it makes its predictions on geometric rather than energetic grounds.

New Trialkylsilyl Enol Ether Chemistry. Direct β-Azido Functionalization of Triisopropylsilyl Enol Ethers

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The direct conversion of a saturated ketone into a β-functionalized derivative can only be achieved through the intermediacy of an α,β-unsaturated ketone, followed by conjugate addition of a nucleophile (Scheme I). Here we report the unprecedented single-step transformation of a triisopropylsilyl enol ether into a β-azido triisopropylsilyl enol ether.

Treatment of a suspension of iodosobenzene in dichloromethane with trimethylsilyl azide (2.0 equiv) at −78 °C followed by warming to −45 °C gives what is presumed to be the bis-azido adduct **2**.[1] If this solution is warmed to 0 °C, it cleanly decomposes to iodobenzene, nitrogen, and hexamethyldisiloxane [(Me₃Si)₂O] (Scheme II).

Addition of the triisopropylsilyl enol ether **3** to a dichloromethane solution of **1/2** at −45 °C gave two products, **4** and **23** (90%, 1:1). Reduction of the mixture of **4** and **23** with LiAlH₄/ether at 0 °C and workup with *p*-toluenesulfonyl chloride gave the known sulfonamides **24** and **25**.[2] To further conclusively confirm the structure of **4** the 2-naphthylsulfonamide derivative **26** gave crystals that were suitable for single-crystal X-ray crystallography.[3] If the reaction of **1/2** with **3** is carried out in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (BMP) at −45 °C, the β-adduct **4** becomes the major product (ca. 4:1). However, addition of trimethylsilyl azide to a suspension of iodosobenzene and the triisopropylsilyl enol ether **3**, at −18 °C to −15 °C (no pyridine), rapidly (15 min) gave the β-azido triisopropylsilyl enol

(6) Since the bicyclo[2.1.0]pentane label isomers interconvert under the reaction conditions, it is actually more precise to use a ratio of phenomenological rate constants for inversion and retention (k_i/k_r) than to use the product ratio as an experimental measure to be compared with the calculations.

(7) Since it is the direction of these transformation vectors rather than their length that is of importance, they are normalized prior to mass weighting.

(8) The LST vector is defined by taking differences in Cartesian coordinates for corresponding atoms in the transition state and the post-transition-state minimum. A scalar multiple (<1) then defines the length of the step down this path. The structure resulting from a short step (scalar multiple typically 0.3) is subjected to geometry reoptimization with a single constraint (in the present cases, distance between the nominal radical carbon atoms), using the optimization routine of the molecular orbital program being employed.

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(10) In the computational model as applied to **1**, approximately 83% of **4x** and 26% of **4n** are formed without passing through the cyclopentane-1,3-diyl intermediate. For 2,3-diazabicyclo[2.1.1]hex-2-ene-*exo*-5-*d*, the corresponding percentages are 80% and 60%.

(11) In presentation of this work at the ACS meeting in New York (August 1991), the measured value was erroneously reported by one of us (B.K.C.) to be 1.88. This error was due to misassignment of a nuclear magnetic resonance.

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(2) Magnus, P.; Lacour, J.; Bauta, W.; Mugrage, B.; Lynch, V. *J. Chem. Soc., Chem. Commun.* 1991, 1362. Treatment of the triisopropylsilyl enol ether **3** with (TsN)₂Se gave **25** (<5%) and **24** (37%). Magnus, P.; Mugrage, B. *J. Am. Chem. Soc.* 1990, *112*, 462. Magnus, P.; Coldham, I. *J. Am. Chem. Soc.* 1991, *113*, 672. Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* 1972, *94*, 7154. Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. O. *J. Am. Chem. Soc.* 1976, *98*, 269. Sharpless, K. B.; Singer, S. P. *J. Org. Chem.* 1976, *41*, 2504; 1978, *43*, 1448.

(3) While the chemical correlation of **4** with **24** is good evidence for the correct structure assignment, the structure of **24** is only based on ¹H and ¹³C NMR spectroscopy. Given the unusual nature of this transformation, we felt that it was prudent to unambiguously confirm the structural assignment by X-ray crystallography on the derivative **26**.
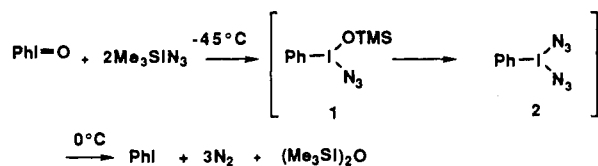
Table I

| entry	substrate	product	conditions (% yield)
1	**3**	**4**	**3** (10 mmol)/PhIO (1.2 equiv) Me₃SiN₃ (2.4 equiv) (>95% crude, 83% purified)
2	**5**	**6**	**5** (1.5 mmol)/PhIO (1.2 equiv) Me₃SiN₃ (2.4 equiv) (>95% crude, 92% purified)
3	**7**	**8**	as for **5** (>95% crude)
4	**9**	**10**	**9** (1.5 mmol)/PhIO (1.6 equiv) Me₃SiN₃ (3.2 equiv) (>95% crude)
5	**11**	**12**	as for **9** (>95% crude, 76% purified)
6	**13**	**14**	as for **5** (>90% crude)
7	**15**	**16**	as for **5** (>95% crude, 89% purified)
8	**17**	**18**	as for **5** (>95% crude, 73% purified)
9	**19**	**20**	as for **5** (>95% crude, 95% purified, 4:1 *E/Z*)
10	**21**	**22**	as for **5** (*Z* 42%, *E* 30%, 2,3-diazide 28%, purified)

Scheme I
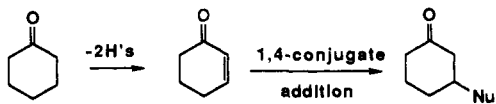
Scheme II

ether **4** (>95%, crude), with only traces of the α-adduct **23** (Scheme III).

Table I lists a number of triisopropylsilyl enol ethers and the conditions required for their conversion into the β-azido adducts.[4,5]

(4) β-Azido ketals have been made from α,β-unsaturated ketones/ Me₃SiN₃/SnCl₄/ethylene glycol. Gil, G. *Tetrahedron Lett.* **1984**, *25*, 3805. Cyclohexenone reacts with IN₃ to give, among other products, 2-iodo-3-azidocyclohexenone. McIntosh, J. M. *Can. J. Chem.* **1971**, *49*, 3045.
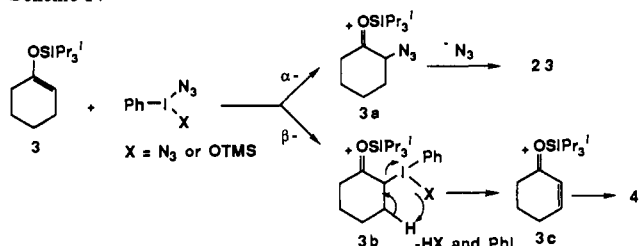
(5) 1-Methoxycyclohexene and dihydropyran react with PhIO/Me₃SiN₃ to give i (95%) and ii (80%), respectively.

Scheme III

24(R = Ts)
26(R = SO₂Np-2)
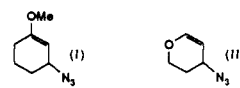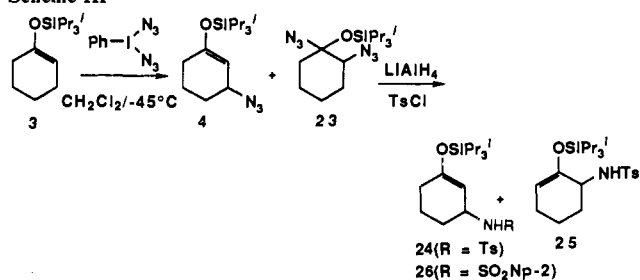
Scheme IV

In all cases, the reaction is complete within a few minutes at −15 °C, and the β-azido product is formed in very high yield. The only other products are iodobenzene and hexamethyldisiloxane, which are removed under vacuum. For entries 3 and 4, the β-azido compounds **8** and **10** are a 1:1 mixture of diastereomers. Particularly noteworthy is the conversion of **13** into the anomeric azide **14** (entry 6). The major azide **16** (6:1 epimers), entry 7, is assigned an axial configuration from the ¹H NMR coupling of the equatorial proton ($J_{a/e} = J_{e/e} = 6.5$ Hz).

Representative Experimental Procedure. To a suspension of iodosobenzene (2.64 g, 12 mmol) and 1-[(triisopropylsilyl)oxy]-cyclohexene (3) (2.55 g, 10 mmol) in dichloromethane (100 mL) stirred under nitrogen and cooled to between −16 and −19 °C was added trimethylsilyl azide (3.19 mL, 24 mmol). After 15 min at −16 °C, the suspension became a clear solution and was allowed to warm to 25 °C. The solvent was removed in vacuo, and the resulting yellow oil was placed for 24 h under high vacuum. Flash chromatography of the oil using silica gel (230–400 mesh, 20 g) and hexane as eluent gave **4** (2.47 g, 84%) as a colorless oil after removal of the solvent.

A plausible mechanistic speculation is outlined in Scheme IV. The α-pathway is the conventional and expected reaction sequence. The β-pathway involves nucleophilic attack of **4** on the iodine atom in either **1** and/or **2** to give the oxonium ion **3b**. Elimination of HX (syn?) and PhI results in the α,β-unsaturated oxonium ion **3c**, which can add azide to give **4**. We have not detected any products resulting from 1,2-addition to **3c**, although in some cases trace amounts of α,β-unsaturated ketone is present in the crude product mixture, possibly formed by desilylation of **3c**.[6]

The scope and mechanism of this unusual new reaction is being studied, as are the potential uses of β-azido triisopropylsilyl enol ethers in synthesis.

Supplementary Material Available: Details of the X-ray structure determination of **26**, tables of fractional coordinates, isotropic thermal parameters, anisotropic thermal parameters, bond lengths and angles, and torsion angles, and spectral details for compounds **3–24**, **26**, and i/ii (32 pages). Ordering information is given on any current masthead page.

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(6) It is possible that **3c** is trapped by azide to give a 1,2-adduct (kinetic), which subsequently undergoes allylic rearrangement to the 1,4-adduct **4**. Gagneux, A.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1960**, *82*, 5956. VanderWerf, C. A.; Heasley, V. L. *J. Org. Chem.* **1966**, *31*, 3534.

Nanoscale Platinum(0) Clusters in Glassy Carbon: Synthesis, Characterization, and Uncommon Catalytic Activity

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The preparation of nanoscale metal clusters is important because of their potential for high catalytic activity.[1] In addition, the synthesis of atomic to macrosized metal clusters is interesting from a fundamental viewpoint.[2] Successful methods for the preparation of metal clusters include metal ion reduction to give small crystallites on various surfaces[3] or colloidal dispersions,[4] metal ion reduction into polymer films coated on electrode surfaces,[5] decomposition of organometallic compounds,[6] evaporation of metals,[7] and sol–gel processes.[8] We expected that the incorporation of metals on the molecular level in a carbon precursor, followed by thermolysis, would result in a conductive, dimensionally stable carbon matrix containing metal particles of controlled composition, size, and catalytic activity. We report here the synthesis of nanoscale platinum(0) clusters in glassy carbon, the characterization of these materials, and their catalytic activity with respect to H⁺ and dioxygen reduction.

We chose to incorporate platinum in a glassy carbon precursor by the reaction of poly(phenylenediacetylene) (**1**)[9] with (ethyl-

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