with a Néel temperature near 140 K. As the Ti–Ti distance is decreased and the bulk magnetic properties change abruptly from paramagnetic to antiferromagnetic, the interaction of Ni with the support changes; Ni/Ti_7O_{13} chemisorbs almost twice as much H_2 as Ni/Ti_6O_{11}. This is an interesting example of how bulk electronic properties can effect surface chemistry.

In summary, we have shown that the chemisorption of H_2 at 295 K on Ni dispersed on Ti_nO_{2n-1} decreases as n decreases. Furthermore, the change in H_2 chemisorption is not a smooth function of n but a large drop is observed between Ti_7O_{13} and Ti_6O_{11} where large changes in bulk properties occur. These findings are consistent with the model that Ni reacts with TiO_x to form a metastable Ni–Ti–O composite. We conclude that the energy of activation to form this composite is smaller for more reduced titanium oxides.

Atom-Transfer Cyclization. A Novel Isomerization of Hex-5-ynyl Iodides to (Iodomethylene)cyclopentanes

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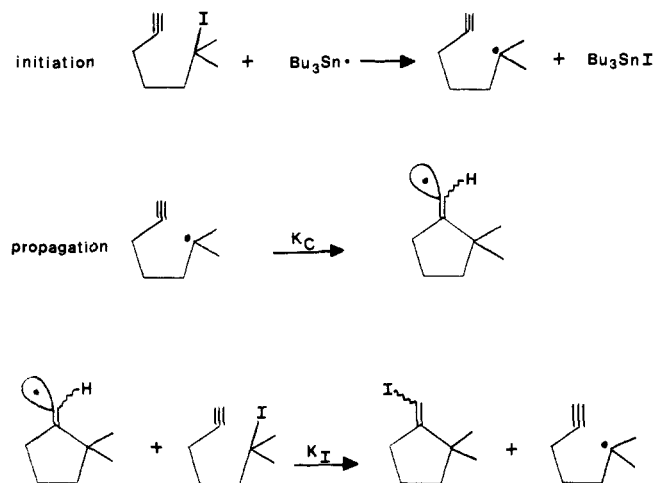*Pittsburgh, Pennsylvania 15260*

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Synthetic sequences based on free radical carbon–carbon bond-forming reactions are generally terminated by a hydrogen atom transfer.[2,3] Clearly, the ability to terminate a sequence of radical reactions with other elements is most desirable.[4] We now report a novel isomerization of hexynyl iodides to iodomethylene cyclopentanes. This reaction occurs via a free radical chain mechanism with near-diffusion-controlled iodine atom transfer from an alkyl iodide to a vinyl radical as the key chain-propagating step. We propose the name "atom-transfer cyclization" for this type of reaction which, in effect, terminates a single or tandem radical cyclization with a synthetically versatile iodine atom.[5,6]

Treatment of 2-iodo-2-methyl-6-heptyne (**1**) with a catalytic amount of tri-*n*-butyltin hydride (10 mol %) and AIBN (5 mol

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(2) Review: Hart, D. J. *Science (Washington, D.C.)* **1984**, *223*, 883.

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(5) (a) Review: Danen, W. C. In *Methods in Free Radical Chemistry*; Huyser, E. S., Ed.; Marcel Dekker: New York, 1974; Vol. 5, pp 1–100. (b) Hiatt, R.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 25. (c) Castelhano, A. L.; Griller, D. *Ibid.* **1982**, *104*, 3655. (d) Brace, N. O. *J. Org. Chem.* **1966**, *31*, 2879.

(6) Related intermolecular addition of *stabilized* radicals to olefins followed by halogen atom transfer have been reported: Kharasch, M. S.; Skell, P. S.; Fisher, P. *J. Am. Chem. Soc.* **1948**, *70*, 1055. Nakano, T.; Kayama, M.; Matsumoto, H.; Naigai, Y. *Chem. Lett.* **1981**, 415. Giese, B.; Hurler, H.; Leising, M., submitted for publication in *Chem. Ber.* Halogen atom transfer also likely intervenes in a recently reported lactone synthesis: Kraus, G. A.; Landgrebe, K. *Tetrahedron Lett.* **1984**, *25*, 3939. Formally related cyclizations of unsaturated *N*-chloroamines have also been observed. While many such reactions are metal-promoted, some may occur through a mechanism similar to that proposed in Scheme I. See: Stella, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 337. For other halogen atom transfer reactions, see ref 5.

Scheme I

%) in refluxing benzene for 1–2 h induced a smooth isomerization to 2,2-dimethyl-1-(iodomethylene)cyclopentane (**2**). The ratio of **2E**/**2Z** was 15/1 and the combined yield of **2** was 84% as indicated by ^1H NMR integration experiments against an internal standard. A trace amount (2–5%) of the reduced product, 2,2-dimethyl-1-methylenecyclopentane (**3**), was also formed whenever tri-*n*-butyltin hydride was used to initiate this isomerization (eq 1).

$$\tag{1}$$
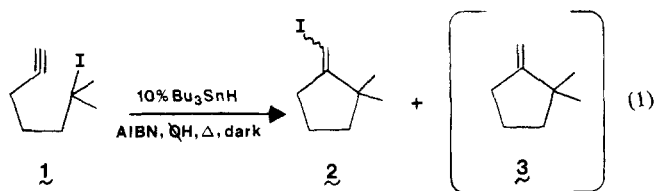
The proposed mechanism for this novel atom-transfer cyclization reaction is outlined in Scheme I. Abstraction of an iodine atom by tri-*n*-butyltin radical initiates the chain. Standard 5-hexynyl radical cyclization[3] is then followed by a rapid iodine atom transfer from a molecule of the starting alkyl iodide to the intermediate vinyl radical. This is the key chain-transfer step. Rapid iodine atom transfer between alkyl radicals and alkyl iodides as illustrated in eq 2 is a well-known process.[5] While a wealth of thermodynamic

$$R\cdot + R'-I \rightleftharpoons RI + R'\cdot \tag{2}$$
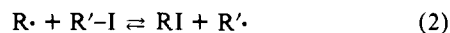
and kinetic data is available from such transformations,[5b,c] the reversible nature of this reaction may be undesirable from a synthetic perspective since the product iodides are recycled to the radical pool.[5d]

The intermediacy of the vinyl radical is then central to the above atom-transfer cyclization. It seems likely that the mechanism outlined in Scheme I is under kinetic control. Rapid iodine atom transfer from the alkyl iodide to the vinyl radical is effectively irreversible and the kinetically formed vinyl iodide is *not* recycled to the radical pool due to the increased strength of the vinyl iodide bond relative to an alkyl iodide counterpart.[6,7]

An estimate of the rate constant (k_I) for iodine atom transfer is readily obtained by a simple competition experiment for the vinyl radical. Treatment of **1** with one full equivalent of tri-*n*-butyltin hydride provides mixtures of **2** and **3** with the ratio varying according to reaction time. At low conversion (<20%), vinyl iodide **2** is the major product (3/1), demonstrating that iodine atom transfer from **1** is more rapid than H atom transfer from Bu_3SnH. In fact, k_I approaches the diffusion-controlled limit! An estimate of $k_I \geq 10^9$ mol^{-1} s^{-1} at 80 °C is obtained by using the recent kinetic data of Beckwith and Ingold as a reference for the competitive H atom transfer.[8] Not surprisingly, this rate constant

(7) Evidence that alkyl radicals will not abstract iodine from the related phenyl iodides is available. See: Cooper, R. A.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* **1972**, *94*, 545. Also, ref 5a,c.

Table I. Isomerization of Hexynyl Iodides

hexynyl iodide	vinyl iodide	E/Z	conditions[a]	yield[b]

		15/1	A	84%
$R_1 = R_2 = CH_3$		15/1	B	c
		15/1	C	95%
$R_1 = CH_3, R_2 = H$		3.3/1	A	67%
		3.3/1	C	87%
$R_1 = R_2 = H$		–	A	67%
		–	B	70%
		–	C	77%

N = 1, R = CH_3		24/1	A	22%[d,e]
N = 2, R = CH_3		19/1	A	40%[d,e]
N = 1, R = H		1.3/1	A	42%[d,e]
N = 2, R = H		5/1	A	40%[d,e]

		6/1	B	74%[d]

[a] A: 10% Bu₃SnH, 5% AIBN (added in two separate portions at 1-h intervals), C_6D_6, reflux, 2 h. B: 10% Me₃SnSnMe₃, PhH, reflux, 10 h. C: 10% Bu₃SnSnBu₃ hr 275-W sunlamp, PhH, 70–75 °C, 30 min. [b] Yields refer to ¹H NMR or GC yield against an internal standard unless otherwise indicated. [c] Rapid decomposition of starting material was observed. [d] Isolated yield after flash column chromatography. [e] Yield is reduced due to difficulties in obtaining pure iodide.
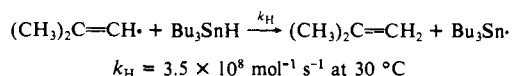
is several orders of magnitude greater than the rate constants for the alkyl radical/alkyl iodide transfer illustrated in eq 2.[5,9]

A variety of other hexynyl iodides were isomerized to the corresponding (iodomethylene)cyclopentanes and the results are collected in Table I. To avoid the presence of even a small amount of H atom donor (Bu₃SnH), other initiation conditions were also investigated. While dark initiation with hexabutylditin/AIBN was successful in several cases, more rapid conversion was observed by irradiating a solution of the alkynyl iodide (~0.3 M, PhH) and 10% Bu₃Sn–SnBu₃ with a 275-W GE sunlamp.[4c] Sufficient heat was produced to raise the reaction temperature to 70–75 °C. Vinyl iodides were not formed in the absence of organotin additives and heating of **1** with or without AIBN in the light or dark led only to unidentified decomposition products.

Note that primary, secondary, and tertiary alkyl iodides all serve as useful substrates for the atom-transfer cyclization. In addition, modest to good selectivities are observed for formation of the (E)-vinyl iodide. This is readily rationalized by assuming that the rapidly inverting vinyl radical[10] abstracts an iodine atom from the less hindered side. Finally, the last entry demonstrates that tandem radical cyclizations may also be terminated by iodine atom transfer.[11]

In conclusion, this alkyl iodide → cyclic vinyl iodide isomerization provides a powerful method for termination of a radical cyclization sequence by an iodine atom transfer. The synthetic utility of this atom-transfer cyclization is enhanced by the versatility of the resultant vinyl iodide which is the synthetic equivalent for both a vinyl anion and a vinyl cation and may also be used to regenerate a vinyl radical in a subsequent step. We

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$$(CH_3)_2C=CH\cdot + Bu_3SnH \xrightarrow{k_H} (CH_3)_2C=CH_2 + Bu_3Sn\cdot$$

$$k_H = 3.5 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 30 °C$$

(9) Evidence that related phenyl radicals will rapidly abstract iodine from alkyl iodides is available, see ref 5a,c.
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are presently investigating the generality of this particular atom-transfer cyclization and the possibility for the extension of the basic principles outlined above to the design and development of related radical chain reactions.

Radical Isomerization during Grignard Reagent Formation. A Quantitative Treatment

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Alkyl group isomerizations during Grignard reagent formation from magnesium metal and alkyl halides in diethyl ether occur through intermediate alkyl radicals (eq 1–3).[1–9] Mechanistic

$$RX + Mg \rightarrow R\cdot \tag{1}$$

$$R\cdot \xrightarrow{k} \hat{R}\cdot \tag{2}$$

$$R\cdot \rightarrow RMgX \tag{3a}$$

$$\hat{R}\cdot \rightarrow \hat{R}MgX \tag{3b}$$

details that are not specified here are uncertain. One question concerns the mobility of the intermediate alkyl radicals: Are they adsorbed on the magnesium surface,[1,9] or do they diffuse freely in solution?[5,8d]

Kinetic considerations bear on this point. For isomerizations of many alkyl radicals, values of rate constants k are known.[10]

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