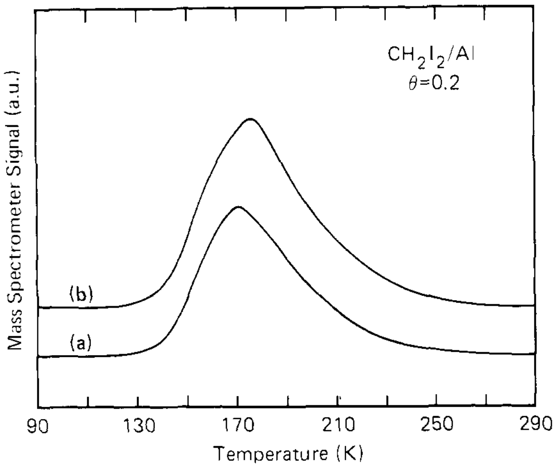

Figure 1. Thermal desorption spectra of CH_2 (a) and C_2H_4 (b) for CH_2I_2 adsorbed on Al at 90 K: $\theta = 0.2$ and heating rate about 30 K/s.

We have investigated the adsorption and decomposition behavior of CH_2I_2 on a clean Al surface at low temperatures. A polycrystalline Al disk (12-mm diameter) was cleaned by Ar^+ bombardment and annealed at 700 K. The sample was cooled down to about 90 K by LN_2 before being exposed to CH_2I_2. The surface cleanliness as well as the CH_2I_2 coverage (θ) was determined by X-ray photoemission spectroscopy (XPS). Here $\theta = 1$ means one monolayer of coverage of about 4×10^{14} molecules/cm^2. After the dosage of CH_2I_2, the sample was warmed up by a rf induction heating method.[4] The desorbed species were detected by a quadrupole mass spectrometer.

Figure 1 shows the thermal desorption spectra (TDS) of CH_2^+ (14 amu) and $C_2H_4^+$ (28 amu) at $\theta = 0.2$. The signals increased with the surface coverage. A trace of 42 amu species, probably due to C_3H_6, was also detected at ca. 170 K. In contrast, no desorption signals of I^+, CH_2I^+, and $CH_2I_2^+$ or species that can be attributed to C_2H_6 or CH_4 were observed at $\theta \leq 1$. When the coverage was increased to $\theta = 1.5$, CH_2I^+ desorption was detected at 210 K. This may be due to a different CH_2I_2 dissociation channel at a coverage slightly higher than a monolayer. At $\theta \geq 4$, the desorption of $CH_2I_2^+$ parent molecules was clearly observed at 260 K. The results suggest that at $\theta \leq 1$, CH_2I_2 dissociates on the Al surface with the increase of substrate temperature from 90 to 170 K. Apparently, CH_2 radicals are formed around 150–170 K and subsequently desorb as CH_2 and C_2H_4 species. The integrated intensity ratio of $CH_2^+/C_2H_4^+$ signals was 0.8 at $\theta = 0.2$, whereas the ratio of $CH_2^+/C_2H_4^+$ for pure C_2H_4 cracking in our mass spectrometer was 0.08. Thus, the major part of observed CH_2^+ signal should be attributed to methylene desorbed from the surface and not from the cracking of C_2H_4 in the mass spectrometer. A small but clear difference in the peak positions of TDS between CH_2^+ and $C_2H_4^+$ (Figure 1) also supports this conclusion. To our knowledge, this is the first direct observation of methylene desorption from a solid surface.

The XPS spectra of I(3d$_{5/2}$) and C(1s) were taken before and after the thermal desorption. The result at $\theta = 1$ is shown in Figure 2. For I(3d$_{5/2}$), the peak position shifted from 621.3 to 619.6 eV when the sample was heated from 90 to 300 K. The former corresponds to the iodine of associatively adsorbed CH_2I_2 and the latter to I^- species.[5] A small part of adsorbed CH_2I_2 may dissociate even at 90 K, because the peak is skew slightly toward the lower binding energy. The signal intensity after the thermal desorption was almost the same as before the treatment. This means that I^- remains on the surface after the molecular decomposition. When the sample was heated to 700 K, I(3d$_{5/2}$) signal disappeared, probably due to the desorption of AlI_3 (boiling point = 645 K). For C(1s), the peak shifted from 286.2 eV, corresponding to the carbon in CH_2I_2, to ca. 283.5 eV after the thermal desorption up to 300 K. The intensity decreased to ca. 40% of the original value (see Figure 2). Thus, about 60% of adsorbed CH_2I_2 desorbed as methylene and ethylene by heating to room temperature. Judging from the C(1s) binding energy, the remaining carbon seems to exist as an adsorbed surface carbon[2] or as a carbide.

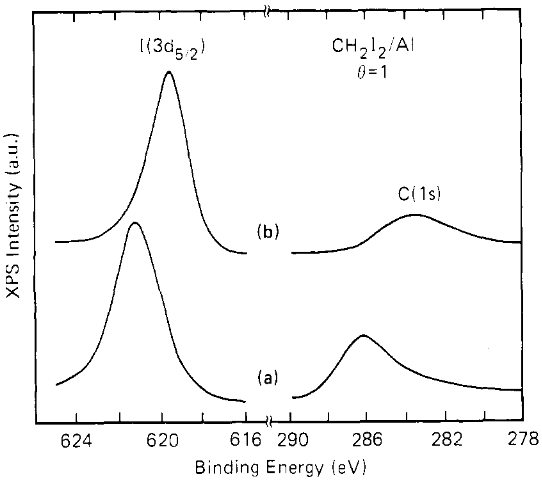

Figure 2. I(3d$_{5/2}$) and C(1s) XPS spectra of a monolayer of CH_2I_2 adsorbed on Al at 90 K (a) and after heating to 300 K (b).

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(4) For details, see: Chuang, T. J.; Seki, H.; Hussla, I. *Surf. Sci.* **1985**, *158*, 525–552, and references therein.

(5) See: *Handbook of X-ray Photoelectron Spectroscopy*; Muilenberg, G. E., Ed.; Perkin-Elmer Corp.: Eden Prairie, MN, 1979; pp 124–125.

Intramolecular Radical Additions to the Azo Group. Fast and Indiscriminate 5-Exo and 6-Endo Cyclizations

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The utility of free radical cyclizations for the synthesis of ring systems has been demonstrated with many recent examples.[1] Most of the studies involved a carbon-centered radical, an olefinic or acetylenic multiple bond, and a product with one or more newly formed carbocyclic rings. Although radicals having a heteroatom at the radical site or between the radical site and the unsaturated group also cyclize, there are few examples of radical cyclizations that afford a heterocyclic ring by closure onto the heteroatom of

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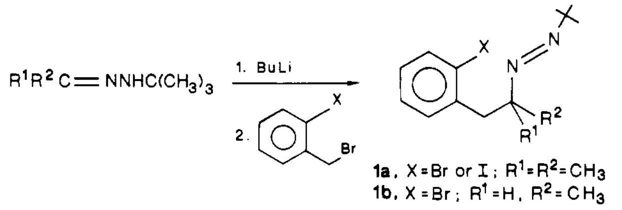
Scheme I



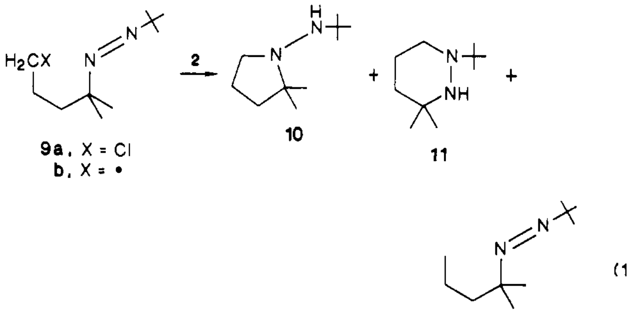
1a, X = Br or I; $R^1 = R^2 = CH_3$
1b, X = Br; $R^1 = H$, $R^2 = CH_3$

carbonyl, thiocarbonyl,[2] imino, or azo groups. The only examples of radical ring closure by addition to sp^2-nitrogen appear to be two involving the azido group[2] and one involving the azo group.[3] Neither unimolecular nor bimolecular rate constants for radical additions to sp^2-nitrogen are known except for rate constants for spin trapping by nitroso compounds.[4] In the absence of information concerning the kinetics and regiochemistry of radical cyclizations onto azo nitrogen and in view of the increasing popularity of free radical methodology in synthesis, we chose to evaluate the potential of radical ring closure for the synthesis of *N*-heterocycles from azo compounds. We report fast 5-exo and 6-endo radical cyclizations to azo nitrogen.

Treatment of **1**, prepared according to Scheme I, with tri-*n*-butyltin hydride (**2**) at 82 °C in benzene containing AIBN afforded **6**, **7**, and **8** (Scheme II) in the relative yields given in Table I. Total yields of isolated products were 90% or greater.

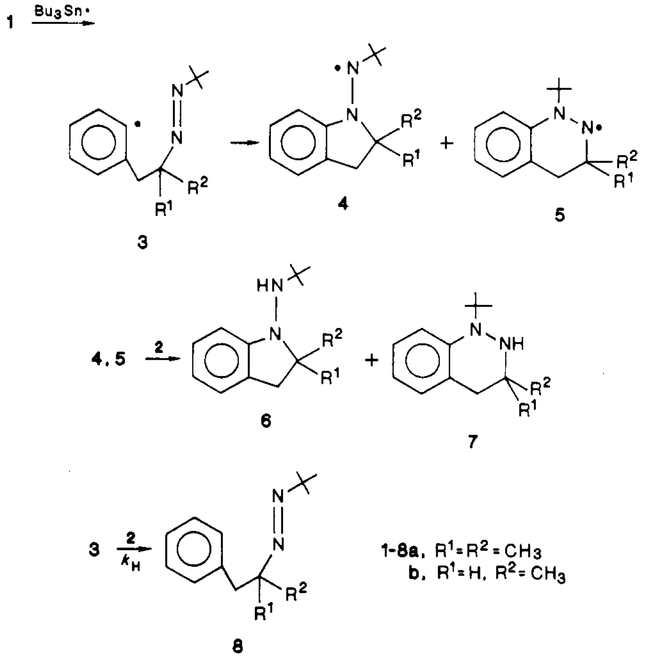
Heterocycles **6** and **7** were identified from their UV, ^{1}H NMR, ^{13}C NMR, and mass spectra. Catalytic hydrogenation of **6a** afforded *tert*-butylamine. The acyclic products **8** were synthesized independently from benzyl bromide by the method in Scheme I.

Diazene **9**, prepared from 1-chloro-3-iodopropane by the method in Scheme I, gave **10**, **11**, and **12** in the ratios 4:1:1.2 upon treatment with **2** (0.55 M) and AIBN in benzene at 80 °C, eq 1. Structures **10** and **11** were assigned on the basis of ^{1}H NMR and ^{13}C NMR spectra. Compound **12** was synthesized independently from 1-iodopropane.



(1)

Scheme II



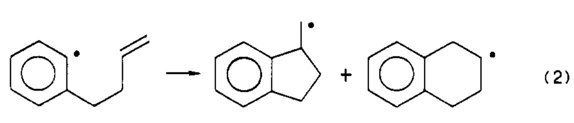
1-8a, $R^1 = R^2 = CH_3$
b, $R^1 = H$, $R^2 = CH_3$

Table I. Relative Yields and Derived Rate Constants (82 °C)

radical	[SnH][a]	rel yields,[b] % **8**	**6**	**7**	ratios of rate csts (M)[c] k_5/k_H	k_6/k_H
3a	0.20	4.9	38.1	57.0	1.55	2.33
	0.73	14.2	35.9	49.9	1.84	2.56
	0.99	17.4	28.3	54.3	1.61	3.09
	1.27	23.4	31.3	45.3	1.70	2.46
	1.50	26.4	30.2	43.4	1.72	2.47
3b	0.52	33.5	18.9	47.5	0.29	0.74
	1.27	38.2	20.1	41.7	0.67	1.38
	1.57	48.8	16.4	34.9	0.53	1.12

[a] Effective concentration of Bu_3SnH, in 12.8–13.4-fold excess. The numbers are average concentrations, based on assumed 1:1 stoichiometry. Correction for the thermal expansion of benzene from room temperature to 82 °C is included. [b] Of products corresponding to the starting material, for example, **8a** from **1a** and **8b** from **1b**. The sum of isolated yields was 90% or greater in all cases. Relative yields (GC) are corrected for small differences in detector responses. [c] Close comparison of these ratios for the different radicals is probably not warranted because k_H (here modelled with $k_H{}^{Ph}$) must itself be dependent on radical structure because of the steric requirements of both $HSnBu_3$ and the ortho substituents in **3a** and **3b**.

Ratios of rate constants, k_5/k_H and k_6/k_H (Table I) from closure of **3** to **4** (5-exo closure) and **5** (6-endo closure) were calculated from the product composition and the concentration of **2**. Substitution into average values of k_5/k_H and k_6/k_H, of the literature[5] value of k_H for attack of the phenyl radical on **2**, k_H^{Ph} (82 °C) = 9.0×10^8 M^{-1} s^{-1}, gives $k_5^{3a} = 1.5 \times 10^9$ s^{-1}, $k_6^{3a} = 2.3 \times 10^9$ s^{-1}, $k_5^{3b} = 4.5 \times 10^8$ s^{-1}, and $k_6^{3b} = 9.7 \times 10^8$ s^{-1}. Although the validity of the above value of k_H^{Ph} has been questioned,[6] recent results,[7] obtained by the nitroxide-trapping technique,[8] indicate that it cannot be grossly in error. In spite of some uncertainty about the absolute values of the above cyclization rate constants, it is clear that they are comparable to that for cyclization of **13** in the 5-exo sense (eq 2, $k_5^{13} = 9.4 \times 10^8$ s^{-1})[9] and significantly larger than k_6^{13} ($< 1.8 \times 10^7$ s^{-1}) at 82 °C. The rate constants for **13** are also based on the above value for k_H^{Ph}.[9] There are no data yet for the effects of methyl (or *gem*-dimethyl) and *tert*-butyl substituents (as in **3**) on rate constants for cyclization of aryl radicals similar to **13**. In alkenyl radicals, *gem*-dimethyl substitution increases k_5 by ca. one order of magnitude.[1p] The *tert*-butyl group in **3** is expected, by analogy to alkenyl radicals,[1p] to reduce k_6. The observed ratios, $k_5^{3a}/k_6^{3a} = 0.65$ and $k_5^{3b}/k_6^{3b} = 0.45$ compared to ca. 100 for **13**, are therefore striking results.



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(2)

The geometry of azo compounds (N═N bond length 1.22 Å, N═N—C angle 114–115°)[10] compared to that of alkenes (C═C,

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1.34 Å, C=C—C ca. 120°) may be largely responsible for the facile 6-endo cyclizations of **3**. Double bond shortening and angle tightening in **3** probably improve the interorbital alignment between the semioccupied orbital of the radical site and the π^*-orbital of the double bond in the transition structure[1p,11] for 6-endo closure, compared to that alignment in **13**. The fact that $(k_5/k_6)^{3a} > (k_5/k_6)^{3b}$ suggests that the *gem*-dimethyl effect (see above) may be operating to increase k_5^{3a}. Finally, the resonance stabilization of the cyclic hydrazyls ($R_2\ddot{N}\dot{N}R \leftrightarrow R_2\overset{+}{N}\text{-}\bar{N}R$) probably means that the cyclizations that form them have transition states that are more reactantlike than those for corresponding cyclizations to C=C bonds and are therefore less selective and less sensitive to steric factors.

In summary, both aryl and alkyl radicals cyclize rapidly to the N=N functional group and the k_5/k_6 ratios in three cases lie between 0.45 and 5. High yields of heterocycles were obtained by working with concentrations of **2** much lower than those in Table I.

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Raman Spectroscopy of the High T_c Superconductor $YBa_2Cu_3O_7$ and the Semiconductor $YBa_2Cu_3O_6$

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The recent discoveries of superconducting materials with extraordinarily high-transition temperatures immediately raise the question of whether an electron–phonon mechanism as in the Bardeen–Cooper–Schrieffer (BCS) theory is operative or if some entirely new mechanism must be invoked.[1] The common structural features of these materials are extended Cu–O chains and sheets.[2–6] Since the standard BCS theory predicts that T_c is proportional to the Debye temperature, it has been suggested that the comparatively high frequencies of Cu–O breathing modes could be responsible for these very high-transition temperatures.[7–9] While this mechanism may be adequate to account for the T_c below 50 K in the lanthanum–copper oxide systems, it is difficult to see how it could apply to the 90 K materials, the yttrium–barium–copper oxides. There is also very recent evidence that there is no isotope effect in the latter system, in disagreement with the requirements of the standard theory.[10] Motivated by the generally accepted empirical correlation between the existence of phonon anomalies, lattice instabilities, and high T_c's in other materials,[11] we have begun to investigate the role of lattice phonons in high T_c superconductors. We report here the Raman spectra of the superconducting $YBa_2Cu_3O_7$ phase and the semiconducting $YBa_2Cu_3O_6$ phase.

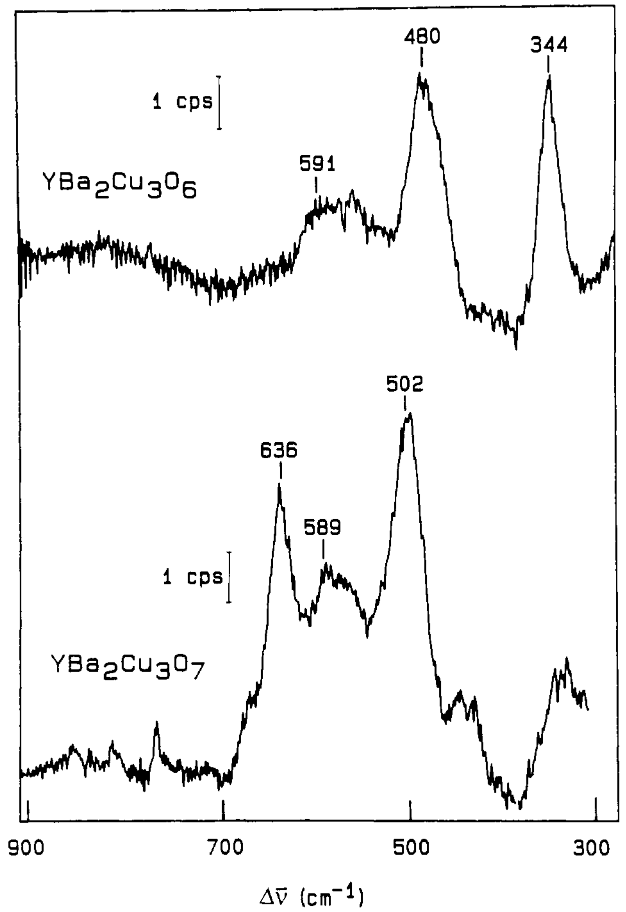

Figure 1. Raman spectra of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$: laser line 514.5 nm and laser power 20 mW for O_7 and 10 mW for O_6 measured at sample surfaces.

The samples were prepared from starting materials Y_2O_3, CuO, and $BaCO_3$ of nominal purities 99.99%, 99.9%, and 99.8%, respectively. These compounds were mixed in a stoichiometric ratio of 0.165:0.335:0.50 (Y/Ba/Cu mole fractions as the oxides) and heated for 20 h at 950 °C in a platinum or zirconium crucible in air.[4] A single-phase material $YBa_2Cu_3O_{7-x}$ (based on powder X-ray diffraction analysis) was then obtained and was pressed into a disk and sintered at 950 °C. Two fragments of the sintered disk were further treated: one, by annealing at 350 °C in O_2 for 20 h to make $YBa_2Cu_3O_7$; and another, by heating in flowing Ar at 620 °C for 20 h to make $YBa_2Cu_3O_6$. The oxygen content analysis gave 6.96 and 6.11, respectively, for the two materials. Both the orthorhombic, superconducting and the tetragonal,

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[†] Department of Chemistry.

[‡] Department of Chemical Engineering.

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