centered radicals of this type.[24]

The intrinsic barriers for the analogous carbon-centered systems are also of considerable interest. Hiatt and Benson[25] have estimated activation energies for gas-phase halogen atom transfer of alkyl systems of ~10 (Cl), ~6 (Br), and 2–4 (I) kcal mol^{-1}. With X = I, the "self-exchange" process is sufficiently rapid in alcohol solvents to lead to epimerization of the norbornyl iodide starting material.[26] Studies of alkyl radical/alkyl halide transfer in benzene suggest transfer rates at zero driving force of ca. 10^2 (X = Cl), 10^3 (X = Br), and 10^5 (X = I) $M^{-1}\ s^{-1}$ at 50 °C.[27] Since the Mo–Cl (72.4 ± 0.9 kcal/mol[19]) and CCl_3–Cl (68.9 ± 0.7 kcal/mol[28]) bond energies are very similar, our data (Table I) implicate a greater intrinsic barrier for the Cl transfer to the Mo radical from CCl_4 than for the entirely metal-centered process.

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Note Added in Proof. In the broader context of multiequivalent atom transfer reactions, the extraordinarily facile transfer of nitride between Mn(V) and Mn(II) porphyrin centers, a three-electron transfer coupled to atom transfer, should be noted. (Woo, L. K.; Goll, J. G.; Czapla, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478–8484 and references cited therein.)

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Intramolecular 1,4-Addition of α-Heteroatom-Substituted Radicals to β,β-Disubstituted Enones. Applications to Tandem Cyclizations

Seongkon Kim and P. L. Fuchs*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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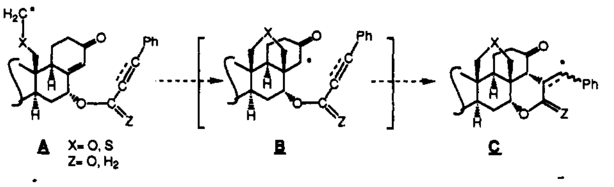
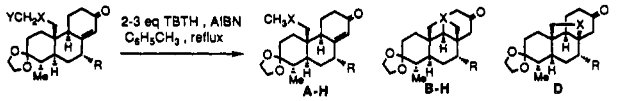
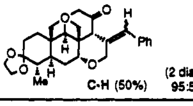
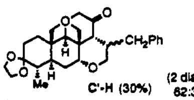
In conjunction with a synthetic problem in our laboratory, we elected to investigate a tandem cyclization (**A** → **B** → **C**) which is initiated by the intramolecular 1,4-addition reaction of α-heteroatom-substituted radical to a β,β-disubstituted enone (**A** → **B**).



While the annulation chemistry of many types of carbon-centered radicals is now a standard synthetic protocol,[1] less attention has been paid to the synthetic applications of α-heteroatom-substituted radicals.[2] While this paper was under revision, Rawal reported the cyclization (principally 5-*exo*-trig) of a number of simple α-alkoxy radicals.[3]

Table I



Precursor				# of eq. TBTH	Addn.Time (hrs)	Product Yields[*]		
Cmpd	X=	Y=	R=			A-H	B-H	D
4a	O	SePh	H	3.0	24	8	68	0
4b	O	SPh	H	2.4	14	5	0; recov 4b, 58	10
5	S	SePh	H	2.0-2.3	12-20	15	45	10
7	O	SePh	OH	2.5	14	tr	45	0
9a	O	SePh	OAc	2.5	12	0	70	0
9b	O	SePh	$O_2CC{\equiv}CPh$	2.5	12	no products identified		
9c	O	SePh	$OCH_2C{\equiv}CPh$	2.4	11	0	0	15
							 C-H (50%)	(2 diast. 95:5)
9d	O	SePh	$OCH_2CH{=}CHPh$ (E)	2.3	14	0	15%	tr.
							 C'-H (30%)	(2 diast. 62:38)

[*] In some instances the yield and product ratio was assigned after hydrolysis of the ketal moiety to facilitate separation.

Synthesis of the appropriate substrates began with the readily available[4] tricyclics **1** and **2**. Treatment of neopentyl alcohol **1** with α-halo sulfide, α-halo selenide, and diiodomethane did not provide the desired α-alkoxy derivatives **3a–c**. However, alkylation with α-iodomethyl tributylstannane[5] under these conditions produced **3d** in 70% yield. Conversion of α-alkoxy stannane **3d** to α-alkoxy organolithium **3e** by treatment with *n*-BuLi in THF[6] at −78 °C did not proceed in the absence of additives such as HMPA or TMEDA, even using 2 equiv of *n*-BuLi. When only

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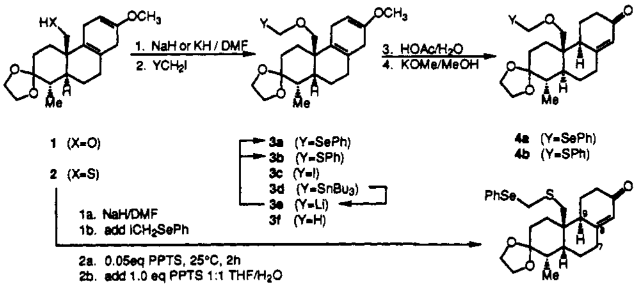
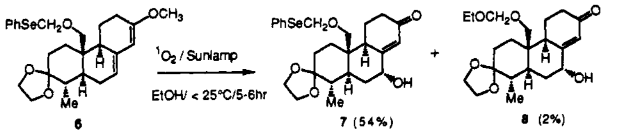
1 equiv of *n*-BuLi in the presence of additives was used in either the sulfenylation or selenylation reactions, a mixture of starting material **3d** (40%), desired product **3a** (29%), and proton-quenched product **3f** (12%) resulted. Fortunately α-alkoxy stannane **3d** was cleanly selenylated[3] (91% yield of **3a**/**3f** in a 96:4 ratio) or sulfenylated (75% yield of **3b**/**3f** in a 92:8 ratio) provided that 2.1 equiv of *n*-BuLi[6] and 4.0 equiv of TMEDA were used to form the α-alkoxy anion. α-Alkoxy derivatives **3a**,**b** were treated with aqueous acetic acid (to generate the β,γ-unsaturated ketones) followed by reaction with potassium methoxide in methanol to provide conjugated enones **4a**,**b** in 46% and 60% overall yield, respectively.

Conversion of mercaptan **2** to compound **5** was accomplished by alkylation with α-iodomethyl phenylselenide.[7] While aqueous acetic acid hydrolysis quantitatively provided the $\Delta^{8,9}$ β,γ-unsaturated ketone, potassium methoxide-mediated conjugation only provided **5** in 15% yield. A preferable method involves PPTs[8]-catalyzed isomerization of **2** to a dienyl ether mixture followed by addition of water to generate **5** (55%) which is easily separated from a 2:1 mixture of the $\Delta^{8,9}$ and $\Delta^{7,8}$ β,γ-unsaturated ketones (23%).



With these precursors in hand, attention was next directed to the introduction of the C-7 oxygen functionality required for the tandem cyclization. Under strictly anhydrous conditions, isomerization[4,9] of **3a** to the thermodynamically more stable conjugated dienyl ether **6** using PPTs occurred in 67% yield. Treatment of the oxidatively-labile dienyl ether **6** with various oxidants such as mCPBA,[10] oxone,[9] or Pd[II][11] gave a mixture which contained only traces of the desired product **7**. However, when oxidation was carried out with molecular oxygen in a Rayonet reactor (300 nm, Pyrex flask) or using a sun lamp[12] in the absence of sensitizer, γ-hydroxy enone **7** was formed along with a small amount of acetal **8**. Standard reactions[13] effected conversion of **7** to substrates **9a**–**d**.



Cyclization experiments were conducted as summarized in Table I. These involved slow addition of a 0.1 M solution of tributyl tin hydride in toluene containing 10 mol % AIBN to a 0.01 M solution of the substrate in toluene at reflux.[14] As expected, α-alkoxy selenide **4a** proved to be far superior to α-alkoxy sulfide **4b**. By way of contrast, α-thioselenide **5** afforded a mixture which was enriched in the product resulting from hydride quenching of the α-thio radical[15] intermediate. Cyclizations of γ-alkoxy enones **7** and **9a** were successful, but attempts to extend the protocol to a tandem cyclization with propargylic ester **9b** produced an exceptionally complex mixture.

We were pleased to find that propargylic *ether* **9c** underwent clean conversion to the bisannulated product[16] **C–H** in 50% isolated yield along with a small amount of bridged tetrahydrofuran **D** which likely arises via cyclization of neopentyl alcohol produced by acid-catalyzed fragmentation of the α-selenyl ether moiety (see table). Similar reaction with *trans*-cinnamyl ether terminator **9d** was less efficient. In this instance, the tetrahydropyranyl-cyclized α-ketoradical intermediate is partitioned between tandem cyclization to **C–H** and simple reduction to **B–H**.

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Electronic Structure and Optical Absorption of Poly(biisothianaphthene–methine) and Poly(isonaphthothiophene–thiophene): Two Low-Band-Gap Polymers

J. Kürti*

Institute for Solid State Physics
University of Vienna
Strudlhofg. 4, A-1090 Vienna, Austria
Department of Atomic Physics, R. Eötvös University
Puskin 5-7, H-1088 Budapest, Hungary

P. R. Surján*

Laboratory for Theoretical Chemistry
R. Eötvös University, Budapest
H-1518 Budapest, 112, P.O.B. 32, Hungary

M. Kertesz*

Department of Chemistry, Georgetown University
Washington, D.C. 20057

Received July 18, 1991

Recent interest in the search for low-band-gap polymers has been stimulated by the significant intrinsic conductivity and good nonlinear optical properties due to the small gap.[1] Among conjugated polymers, poly(isothianaphthene) (PITN) was known so far to have the smallest energy gap ($E_g \approx 1.0$ eV) found both experimentally[2] and theoretically.[3] For a related system, polythiophene (PT), it was suggested that the energy gap can be lowered significantly[4] by inserting additional CH units between the monomers (poly(bithiophene–methine), PBTM): the gap of PT is 2.1 eV experimentally[5] and 1.8 eV theoretically,[3] while the theoretical estimation for PBTM is 1.2 eV.[6,7] These systems are

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