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(12) The remarkable compound $Mn(CO)_3[(C_6H_5)_2PCH_2P(C_6H_5)_2C(H)S_2]$[13] has one phosphorus atom of the DPM chelate bonded to the carbon atom of the $C(H)S_2$ group. The resulting tetravalent carbon atom has a structural arrangement, C–S = 1.83 Å and S–C–S = 105°, very similar to that of the H_2CS_2 ligand in our complex.[5,6]
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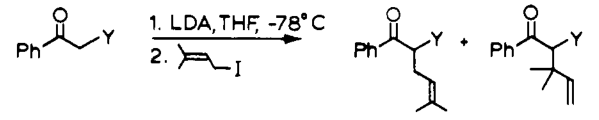
Selenium Stabilized Carbanions.[1] Ylide Formation during Alkylation of Selenium and Sulfur Substituted Enolates

Sir:

We report here unambiguous evidence that seleno- and thio-substituted ketone enolates can undergo significant or even predominant alkylation at the heteroatom. The key observations are shown in Scheme I. Treatment of the enolate of α-(phenylseleno)acetophenone[2] with prenyl iodide or bromide led to the unexpected material **3a** (formally corresponding to an S_N2' attack on the allyl halide), in addition to the normal alkylation product **2a**. Varying the reaction conditions gave different amounts of the two products, **3a** being formed in all cases. It was convenient to analyze the deselenated or desulfenylated products **2b** and **3b** obtained by treatment with benzene- or methanethiol and triethylamine in ethanol.[3]

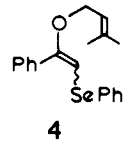
Scheme I



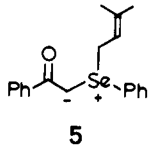
1a Y = SePh
b Y = H
c Y = SPh

1a, THF, 0°C	47:53 (60%)
1a, THF, HMPA, -78° to 25°	61:39 (66%)
1c, THF, 0°C	69:31 (67%)
1b, THF, 0°C	>99:<1 (43%)

Two reasonable pathways for the formation of **3a** can be envisaged: (1) O-alkylation to give **4**, followed by [3,3] sigmatropic rearrangement, or (2) alkylation at selenium to give the ylide **5** followed by [2,3] sigmatropic rearrangement. Direct S_N2' displacement is not considered likely with prenyl halides, nor is any observed during alkylation of acetophenone enolate (Scheme I).



4



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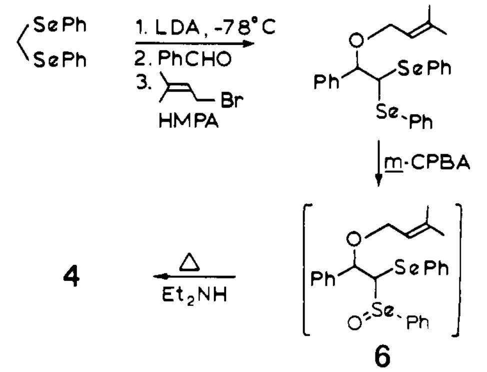
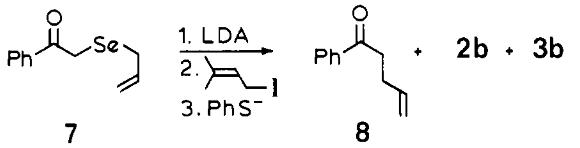
Authentic **4** was prepared by the method outlined in Scheme II. It is essential to perform the syn elimination of the selenoxide **6** in the presence of diethylamine to trap PhSeOH which otherwise reacts with the enol ether.[4] Compound **4** rearranges to **3a** slowly at 85 °C ($k_1 = 3.6 \times 10^{-5}$ s^{-1} in THF-d_8); it can therefore be ruled out as a precursor of **3a** during the alkylation of **1a** since **3a** is formed when the reaction is carried out below room temperature.

Scheme II

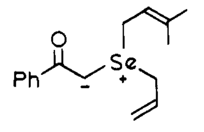


6

Support for the ylide mechanism was provided by the product mixture from alkylation of α-allylselenoacetophenone (**7**).[5] The *C*-allyl product (**8**) must be formed by [2,3] sigmatropic rearrangement of an intermediate (**9**) capable of allyl migration.[6] When the selenium is highly hindered (as in the mesitylene system **10**), 63% of **2** and only trace amounts (~1%) of abnormal product (**3**) are formed on alkylation with prenyl iodide. An ylide intermediate analogous to **9** was also generated by a different route. Treatment of diprenyl selenide with phenacyl trifluoromethanesulfonate[7] gave an intermediate selenonium salt which was observed spectroscopically. Deprotonation with DBU led to rapid conversion to **3** (Y = Se-prenyl). The ylide was not detected by NMR observation at 25 °C. After deselenation with $PhSH/NEt_3/EtOH$ a 61% yield of **3b** was isolated. The absence of **2b** strongly suggests that Stevens rearrangement does not compete with [2,3] sigmatropic rearrangement of the intermediate ylide.



35:58:6 (69%)



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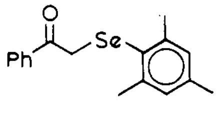

10

Reaction at the heteroatom is not limited to seleno-substituted enolates, nor to unusual alkylating agents such as prenyl iodide. α-(Phenylthio)acetophenone (**1c**) gives 31% abnormal product **3c** with prenyl iodide. Alkylation of the enolate from **7** with methyl iodide (0 °C, THF) gives, after deselenation, a 41:59 ratio of **8** and propiophenone.

Alkylation at sulfur has been suggested to account for unusual reactivity in reactions involving cycloalkylation of a lithium reagent derived from a methylthiocarboxylic acid[8] and methylation of a methylthiovinylcopper derivative.[9] Our results would indicate that anomalous alkylations are more common than had been previously suspected. Moreover, it is likely that low yields sometimes reported for alkylation of thio substituted enolates are a consequence of the formation of stable ylides. These are lost as water-soluble sulfonium salts upon protonation and workup.[10]

Our survey of a number of thio- and seleno-substituted lithium reagents has revealed few other cases of anomalous

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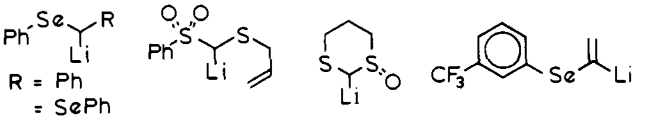
alkylation with prenyl iodide. The dianion prepared from phenylselenoacetic acid gives 10% alkylation at selenium, whereas the enolate of ethyl phenylselenoacetate gives only 2%. The other anions shown below, however, give no detectable amounts of abnormal products.



Acknowledgment. We thank the National Science Foundation for support of this work.

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(2) Deprotonation of **1a** with lithium diisopropylamide (LDA) is accompanied by 5–8% deselenation, giving the enolate of acetophenone. This side reaction becomes much more pronounced with α-phenylselenopropiophenone.

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(5) Compound 7 was prepared by heating a mixture of phenacyl bromide and diallyl selenide.

(6) Control experiments showed that the enolate of 7 itself did not undergo rearrangement under the reaction conditions. α-Allylthio-substituted ester enolates have been shown to rearrange (Baldwin, J. E.; Tzodikov, N. R. *J. Org. Chem.* **1977**, *42*, 1878).

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Electrochemical Oxidation of Strained Hydrocarbons

Sir:

Although the electrochemical oxidation of C–H bonds is well established,[1] and the similar oxidation of olefins and aromatic hydrocarbons has been extensively explored,[2] relatively little is known about the electrochemical oxidation of saturated C–C bonds.[1] Relatively simple substituted cyclopropanes have been studied[3] and both the chemical[4] and electrochemical oxidations[5] of quadricyclane (**1**) have been reported. In counterpoint, it should be noted that bicyclo[1.1.0]butane derivatives have been prepared under oxidative conditions.[6] In view of the extensive interest in the chemistry of highly strained hydrocarbons, it is surprising that little is known about the behavior of this category of compounds under oxidative conditions.[7] We now wish to report our preliminary findings on the electrochemical oxidation of strained hydrocarbons.

In order to obtain a quantitative relationship for the oxidizability of strained polycyclic molecules, we first turned our attention to the determination of the half-wave potentials for compounds **1**–**11**[8] vs. a saturated calomel electrode (SCE). Table I lists the values obtained by single-sweep voltammetry (sweep rate 100 mV/s) on a Princeton Applied Research Model 174 polarographic analyzer equipped with platinum electrodes. All measurements were made in high-purity acetonitrile containing 0.1 M lithium perchlorate as the supporting electrolyte. Substrate concentration was ca. 10^{-3} M As can be seen from Table I, the observed half-wave potentials range from 0.91 to 2.12 V. These values can be compared to those of simple alkylated cyclopropanes, which have half-wave potentials vs. SCE of 2.05 to >2.5 V.[3]

Table I. Oxidation Potentials and Ionization Potentials of Typical Strained Polyclic Hydrocarbons

compd	$E_{1/2}$ vs. SCE, V[a]	adiabatic IP, eV
tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**1**)	0.91	7.40[b]
1,2,2-trimethylbicyclo[1.1.0]butane (**2**)	1.23	
tricyclo[4.1.0.0^{2,7}]heptane (**3**)	1.50	8.15[b]
pentacyclo[4.2.0.0^{2,4}.0^{3,8}.0^{5,7}]octane (**4**)	1.54	8.18[c]
pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane (**5**)	1.54	8.36[d]
pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**6**)	1.62	8.37[d]
pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (**7**)	1.67	
pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (**8**)	1.73	8.46[c]
pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**9**)	1.74	8.47[c]
bicyclo[2.1.0]pentane (**10**)	1.91	8.60[b]
tricyclo[2.2.1.0^{2,6}]heptane (**11**)	2.12	9.02[e]

[a] All half-wave potentials are the average of several runs. All runs agreed within ±0.02 V. [b] Reference 10. [c] This study. [d] Reference 11. [e] Reference 12.

In principle, it would seem likely that the oxidation of these hydrocarbons involved the transfer (removal) of electrons from the highest occupied molecular orbitals (HOMO) of the strained polycyclic molecules. Substantiation of this concept would permit the use of oxidation potentials of strained polycyclic hydrocarbons in a predictive sense relative to a wide variety of reactions of these systems. Fortunately, it was relatively easy to confirm the relationship between the half-wave oxidation potential and the HOMO of the strained hydrocarbons. Adiabatic ionization potentials, as measured by photoelectron spectroscopy, are considered to be a good measure of the energy of the HOMO of a wide variety of organic compounds.[9] Included in Table I are the values of the adiabatic ionization potentials for 9 of the 11 compounds studied.[10-15] Figure 1 provides a plot of the adiabatic ionization potentials vs. the corresponding half-wave oxidation potentials. Excellent correlation was obtained ($r = 0.988$). Using a least-squares determination, it was found that the relationship between ionization potential and half-wave oxidation potential was IP = 1.28$E_{1/2}$ + 6.25. The excellent correlation observed provides firm support for the relationship of the half-wave oxidation potential to the HOMO of the strained polycyclic hydrocarbon. It should be noted that ample precedent exists for relating oxidation potentials to ionization potentials. Since Hoijtink first reported the correlation between polarographic oxidation potentials of aromatic compounds and their ionization potentials,[16] several examples of such correlations have appeared.[17] Thus, there would appear to be little doubt but that reactions involving the HOMO of the strained polycyclic hydrocarbons should correlate with the observed half-wave potential.[18]

Product studies for the oxidative processes described above presented some difficulties. Trace amounts of acid generated during the electrochemical oxidation led to rapid acid-catalyzed rearrangements of the strained-ring systems. In order to circumvent this problem and to generate easily characteri-

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