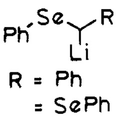
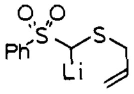
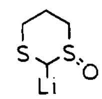
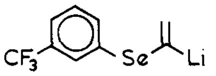
alkylation with prenyl iodide. The dianion prepared from phenylselenoacetic acid gives 10% alkylation at selenium, whereas the enolate of ethyl phenylselenoacetate gives only 2%. The other anions shown below, however, give no detectable amounts of abnormal products.









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

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(1) For previous papers in this series, see the following. Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.* **1975,** *97,* 3250; **1977,** *99,* 263. Reich, H. J. *J. Org. Chem.* **1975,** *40,* 2570. Reich, H. J.; Chow, F. *J. Chem. Soc., Chem. Commun.* **1975,** 790. Reich, H. J.; Shah, S. K. *J. Org. Chem.* **1977,** *42,* 1773.

(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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(11) Alfred P. Sloan Fellow, 1975–1979.

Hans J. Reich,*[11] Martin L. Cohen
Department of Chemistry, University of Wisconsin—Madison
Madison, Wisconsin 53706

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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} MAs 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 = $1.28E_{1/2} + 6.25$. 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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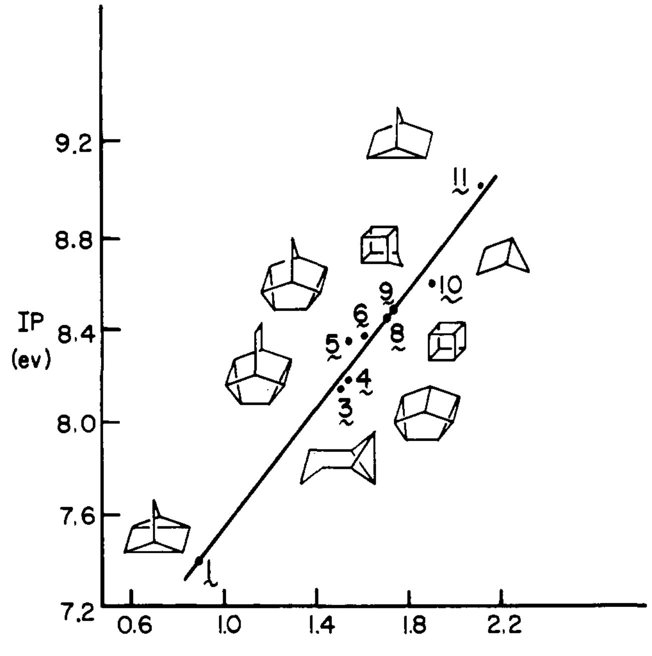
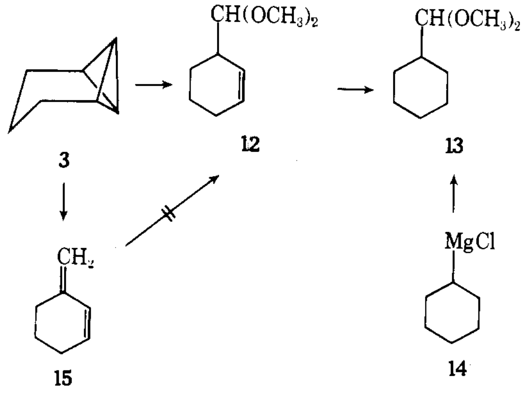


Figure 1. Plot of adiabatic ionization potentials versus half-wave potentials for A series of highly strained polycyclic hydrocarbons. The values cited for electrode potentials assume that the measured electrode potentials are kinetically shifted (due to followup reactions) relative to the *reversible* potentials for each hydrocarbon.

zable oxidation products, preparative oxidations were carried out in methanol, using platinum electrodes and tetraethylammonium perchlorate as supporting electrolyte. Pyridine was added to maintain a nonacidic solution.[19] Only **3** has been studied in detail at this time. In 50:1 methanol-pyridine using platinum electrodes and 0.1 M lithium perchlorate as electrolyte, **3** gave a half-wave potential of 1.63 V vs. SCE. This should be compared to 1.50 V in acetonitrile. On a preparative scale, **3** gave a 65% yield of volatile products. Of this, 91% was the acetal **12**, which is the product of two-electron oxidation.[20]



The remaining 9% consisted of four components, one of which was identified as the product of acid-catalyzed addition of methanol (2-methoxynorcarane, 0.2%). The structure of **12** was assigned on the basis of extensive spectral data and on the basis of its catalytic reduction to **13**, which was independently synthesized through the reaction of **14** with trimethyl orthoformate.

It is known that certain transition metal complexes (including platinum oxide) promote the conversion of **3** into **15**. Thus, it might be suggested that **3** was converted into **15** on the electrode surface and that **15** was then oxidized to give **12**. This possibility was ruled out by control experiments which showed that oxidation of **15** under the reaction conditions gave four major products, none of which was **12**.

In summary, the oxidation potentials of strained polycyclic hydrocarbons indicate that these compounds are readily oxidized. The ease of oxidation, which is a reflection of the level of the HOMO of each structure, should prove to be a measure of a variety of different chemical reactivities. It is interesting to note that the HOMO of these systems is associated with a C–C bond in contrast to unstrained hydrocarbons, where it appears to be associated with a C–H bond. We are continuing to investigate the applications of these findings and to extend our studies of the nature of the oxidation products of compounds **1–11** and related strained hydrocarbons.

Acknowledgment. We are indebted to the National Science Foundation and to the General Electric Foundation for grants which supported this investigation.

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(15) We wish to thank Mr. J. B. Leane of Perkin-Elmer, Ltd., Beaconfield, Bucks, England, for obtaining PS-18 spectra of compounds **4**, **8**, and **9** for us.

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(19) A methanol/pyridine ratio of 50:1 (v/v) was used. In the absence of pyridine, it was shown that **3** was completely consumed after the passage of less than 0.3 F/mol. Only products resulting from the acid-catalyzed addition of methanol to **3** were observed. The relatively small change in half-wave potential observed in the two different solvents might be interpreted to mean that the solvation of the strained hydrocarbons does not change significantly in going from acetonitrile to methanol.

(20) Satisfactory elemental analyses and spectral data were obtained for all new compounds.

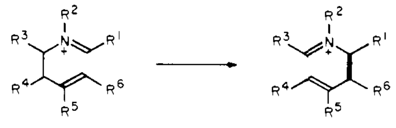
Paul G. Gassman,* Ryohei Yamaguchi
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received September 11, 1978

Carbon–Carbon Bond Formation via Directed 2-Azonia-[3,3]-Sigmatropic Rearrangements. A New Pyrrolidine Synthesis

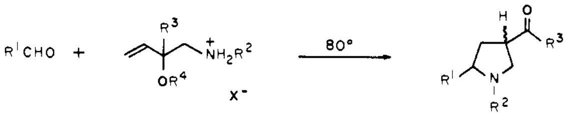
Sir:

The development of versatile methods for forming carbon–carbon bonds under mild conditions is a central objective of synthetic organic chemistry. The 2-azonia-[3,3]-sigmatropic rearrangement[1,2] (eq 1, the C–C bond produced is emboldened) appears to us to be a particularly attractive vehicle for the elaboration of methodology of this type. This reversible[4] carbon-carbon bond-forming reorganization occurs under remarkably mild conditions (typically 100–200 °C below the corresponding Cope rearrangement),[3-6] and a variety of simple methods are available for preparing the starting iminium ion **1**.[7] To be synthetically useful the 2-azonia-[3,3]-sigmatropic rearrangement must be irreversible in the desired direction, and to date essentially all applications have been in benzoheterocyclic systems[5,8] where the rearrangement is driven by aryl conjugation of the product iminium ion (R^3 = aryl). In this communication we outline our preliminary efforts to develop general methods for directing this rearrangement. In particular we report an intramolecular trapping procedure which for the first time allows the less stable iminium ion isomer to be captured in high yield.[9]



1 2 (1)

The strategy is to incorporate a nucleophilic substituent in such a fashion that it is latent in the starting sigmatropic isomer, but upon rearrangement is unleashed and irreversibly captures the desired product iminium ion (eq 1, R^4 = heteroatom functionality). Within this context we have found that the reaction of aldehydes and salts of 2-alkoxy-3-butenamines affords substituted 3-acylpyrrolidines in a single step, and in excellent yield, eq 2. In a typical experiment a mixture of



(2)

3, $R^2 = C_3H_7$, $R^3 = R^4 = Me$, $X = BF_4$

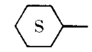
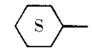
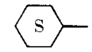
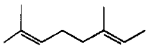
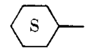
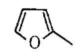
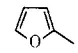
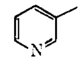
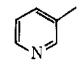
8, $R^2 = C_3H_7$, $R^3 = H$, $R^4 = Me$, $X = BF_4$

4, $R^1 = Ph$, $R^2 = C_3H_7$, $R^3 = Me$

9, $R^1 = C_6H_{13}$, $R^2 = C_3H_7$, $R^3 = H$

10, $R^1 = Ph$, $R^2 = C_3H_7$, $R^3 = H$

Table I. Preparation of 3-Acetylpyrrolidines According to Eq 2 (R^3 = Me)

entry	R^1	R^2	OR^4	reaction conditions[a] procedure[b]	reaction conditions[a] time, h	isolated yield,[c] %
1	C_6H_5	n-C_3H_7	OMe	A	5	87
2	C_6H_5	n-C_3H_7	OMe	B	24	85
3		n-C_3H_7	OMe	A	24	95
4		n-C_3H_7	OMe	B	24	84
5		n-C_3H_7	OMe	B[d]	24	90
6	n-C_6H_{13}	n-C_3H_7	OMe	A	24	97
7		n-C_3H_7	OMe	A	24	90
8	n-C_6H_{13}		OMe	A	24	95
9	C_6H_5	$C_6H_5CH_2$	OMe	B	24	54
10	C_6H_5	$C_6H_5CH_2$	OMe	B	72	89
11	C_6H_5	$C_6H_5CH_2$	OH	B	24	94
12		$C_6H_5CH_2$	OMe	B	24	57
13		$C_6H_5CH_2$	OH	B	24	95
14		$C_6H_5CH_2$	OH	B	24	91
15		CH_3	OH	B	24	84

[a] A benzene solution of the amine salt (0.6 M) and the aldehyde (1.1 equiv) were heated at reflux for the indicated time. Twenty-four hours was taken as a convenient standard time and many of the reactions were done much sooner. [b] A, the crystalline amine tetrafluoroborate salt was used; B, the free amine plus 0.9 equiv of d-10-camphorsulfonic acid was used. [c] All pyrrolidines were a mixture of acetyl epimers.[11] [d] 0.1 equiv of d-10-camphorsulfonic acid was employed.

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