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ELECTRON TRANSFER FROM HIGHLY STRAINED POLYCYCLIC MOLECULES

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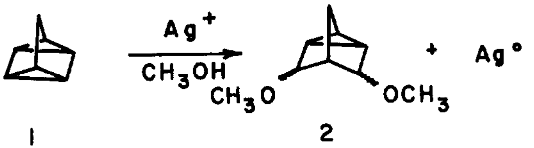
Abstract—The details of electron transfer from strained, saturated hydrocarbons in electrochemical oxidations on platinum have been studied. Among the systems investigated were tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane, tricyclo[4.1.0.0^{2,7}]heptane, pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane, pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane, pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane, bicyclo[2.1.0]pentane, and a variety of bicyclo[1.1.0]butane derivatives. The oxidation of 1,2,2-trimethylbicyclo[1.1.0]butane is discussed in detail.

Electron transfer from saturated hydrocarbons has been of interest to organic chemists for some time. Several studies of electrochemical oxidation exist. In general, anodic oxidation of saturated hydrocarbons requires voltages of 2.5-3.2 V vs saturated calomel reference electrodes (reported voltages vary widely with solvent and electrode systems).[1] Cyclopropane derivatives have been found to oxidize at somewhat lower potential than unstrained hydrocarbons.[2]

Our interest in electron-transfer reactions from strained, saturated hydrocarbons originated with our studies of transition-metal-promoted rearrangements of polycyclic systems.[3] In particular, our work[4] and that of Holgeveen and Volger[5] on the transition-metal-complex-promoted conversion of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**1**, quadricyclane) to bicyclo[2.2.1]hepta-2,5-diene has attracted considerable attention as the chemical basis for a solar energy storage cell.[6] Among the numerous studies which have been carried out on this transition-metal-promoted isomerization was an investigation of the silver-ion-induced reaction of **1** in methanol.[7] Koser and Faircloth found that **1** gave a mixture of products which contained the three possible stereoisomers of **2** and equivalent amounts of reduced silver.[8] These observations suggested to us that a relationship might exist between the transition-metal-complex-promoted rearrangement of strained polycyclic molecules and the ability of these same strained polycyclic molecules to undergo electron-transfer reactions. In order to establish whether highly strained polycyclic molecules were reactive electron sources, we embarked on a detailed study of the electrochemical oxidation of several different series of highly strained molecules.



1 2

Our initial studies involved **1** and related quadricyclic systems.[9] Much to our surprise and delight, we found that **1** had a half-wave oxidation potential versus a saturated calomel electrode (SCE)[10] of 0.91 V. *This was a full volt lower than any previously studied saturated hydrocarbon.* As shown in Table 1, the effect of incorporating heteroatoms into the quadricyclic skeleton, which were more electronegative than carbon, resulted in an increase in the half-wave oxidation potential. Similarly, the addition of electron-withdrawing substituents to **1** had the expected effect of also increasing the half-wave oxidation potential.

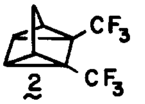
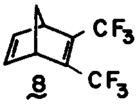
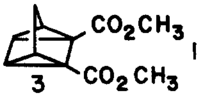
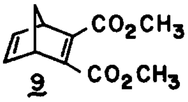
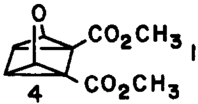
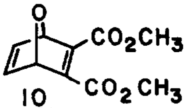
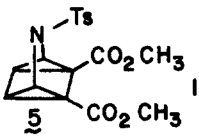
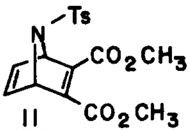
It is instructive to compare the quadricyclic compounds listed in Table 1 with their olefinic isomers. In each case the quadricyclane derivative was the more easily oxidized of the isomeric pair. On the basis of what is known about transition-metal-promoted rearrangements of quadricyclane derivatives to bicyclo[2.2.1]hepta-2,5-diene derivatives, it is also apparent that, *for each pair of isomeric compounds listed in Table* 1, the thermodynamically more stable isomer is the more difficult to oxidize. This should not lead one to believe that any type of straightforward relationship exists between ease of electron transfer and thermodynamic stability. Electron transfer undoubtedly occurs from the highest occupied molecular orbital (HOMO) of the strained ring system. Such orbital energies do not correlate, in general, with either thermodynamic stability or strain energy. A clear illustration of this point is provided by a comparison of the electron-releasing properties of the isomeric compounds **13** and **14**. Under conditions of silver-ion catalysis, **13** was readily converted to **14**,[11] establishing **14** as the thermodynamically more stable isomer. However, **14** was oxidized almost 0.2 V lower than **13**, indicating that **14** had the higher energy HOMO.

13 14

$E_{1/2}$ = 1.73 V $E_{1/2}$ = 1.54 V

In order to explore the range over which strained polycyclic hydrocarbons would transfer electrons to an anode and to obtain a better understanding of the HOMO energies of various highly strained systems, we

Table 1. Half-wave oxidation potentials for a series of quadricyclane type compounds and their diene isomers

COMPOUND	$E_{1/2}$ (V)	COMPOUND	$E_{1/2}$ (V)
 1	0.91	 7	1.56
 2	2.19	 8	2.51
 3	1.64	 9	2.06
 4	1.95	 10	2.26
 5	1.95, 2.36	 11	2.20, 2.37
 6	2.12	 12	1.95

compared the oxidative half-wave potintials (in acetonitrile) with the ionization potentials (gas phase) of the compounds shown in Table 2.[12] Figure 1 gives a plot of the half-wave oxidation potentials vs the adiabatic ionization potentials. The correlation coefficient of 0.988 indicated the presence of a clean relationship between the gas phase ionization potentials and the solution oxidation potentials. The relationship between these two sets of measurements was:

$$IP = 1.28\,E_{1/2} + 6.25.$$

The quality of the correlation clearly established that the electron transfer from the strained hydrocarbon to the anode was occurring from the HOMO in a straightforward fashion. This indicated to us that a variety of reactions which involved the HOMO of the highly strained ring system should show good correlations with the measured half-wave oxidation potentials (*vide post*).

The ease with which highly strained polycyclic molecules entered into electron-transfer reactions suggested that electrochemical oxidation might be able to be used in experimentally establishing the nature of the HOMO of individual strained ring skeletons. Of particular interest to us, both because of the existing theoretical studies[13,14] and because of our extensive studies of its transition-metal-promoted rearrangements,[3] was the bicyclo[1.1.0]butane system.

Theoretical calculations[13,14] indicated that the HOMO of **20** was associated with the C_1–C_3 bond. Typical of the problems which revolve around this point is the question of which bond of **20** is initially involved in its transition-metal-complex-promoted rearrangement. It is well established that **20** eventually is converted to the metal-

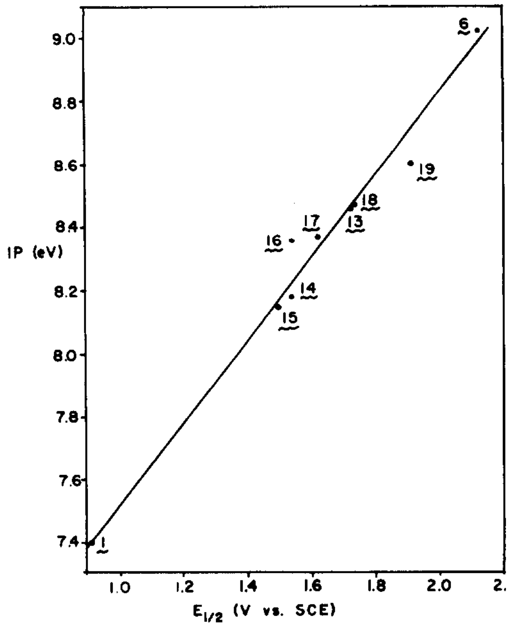
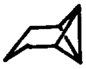


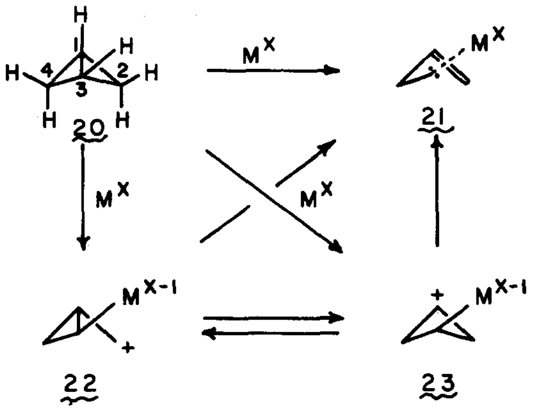
Fig. 1. Plot of ionization potentials (gas phase) versus anodic half-wave potentials (in acetonitrile) for the series of highly strained polycyclic molecules listed in Table 2.

Table 2. Measured oxidative half-wave potentials and ionization potentials of selected highly strained hydrocarbons

COMPOUND	$E_{1/2}$ (V vs. SCE)	ADIABATIC IP (eV)
 **1**	0.91	7.40
 **15**	1.50	8.15
 **14**	1.54	8.18
 **16**	1.54	8.36
 **17**	1.62	8.37
 **13**	1.73	8.46
 **18**	1.74	8.47
 **19**	1.91	8.60
 **6**	2.12	9.02

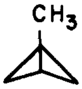
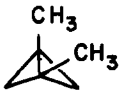
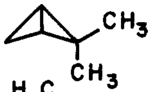
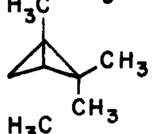
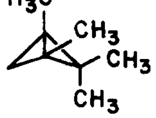
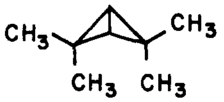
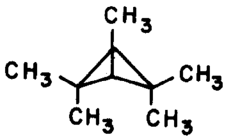
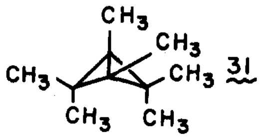
carbene complex, **21**.[3,15] Whether the formation of **21** from **20** is a concerted process, or whether a stepwise process involving **22** and/or **23** is involved, has been of considerable interest. Because of the well-established rapid interconversion of cyclopropylcarbinyl and cyclobutyl cations, trapping experiments have not provided any definitive evidence. However, the nature of the HOMO of **20** was central to this mechanistic consideration.

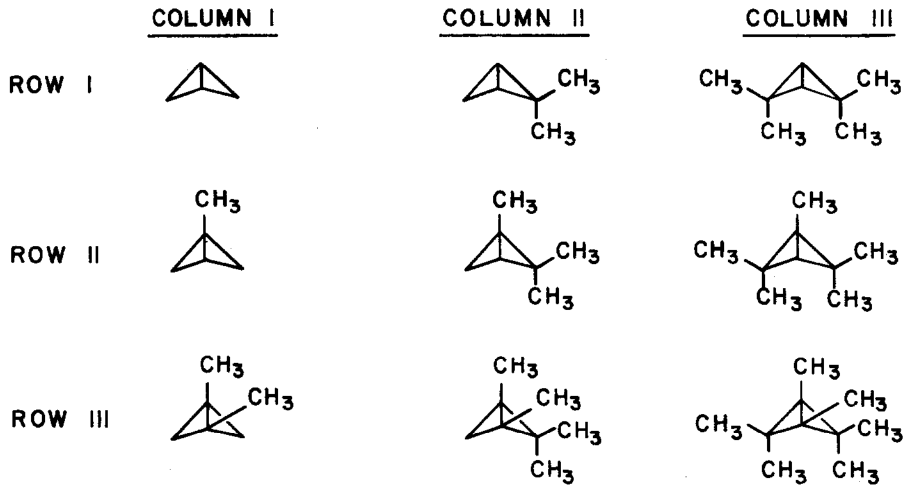
We reasoned that we could obtain experimental evidence for a HOMO to bond relationship through a systematic study of electron transfer from **20** and a series of Me-substituted derivatives of **20**. Table 3 lists the measured anodic half-wave potentials and the calculated gas phase ionization potentials.[13,16] Fig 2 shows a plot of the half-wave potentials versus the calculated ionization potentials. The calculated ionization potentials are derived from a theoretical treatment which also



associates the HOMO with the C_1-C_3 bond. Thus, the quality of the correlation between measured half-wave potentials and calculated ionization potentials supports an argument that the electrochemical oxidation involves electron transfer from an orbital which is primarily associated with the C_1–C_3 sigma bond. Added evidence for this suggestion is provided by the comparison of substituent effects on the bridge (2- and 4-positions) versus the bridgehead (1- and 3-positions). Comparison of the $E_{1/2}$ values of the compounds in column I to those of the compounds in column II showed that substitution of a Me group on the 2-position gave an average decrease in half-wave potential of 0.05 V per Me group. Comparison of column II with column III showed a similar average decrease of 0.05 V per Me group. In sharp contrast,

Table 3. Measured anodic half-wave potentials and calculated Ionization Potentials for Bicyclo[1.1.0]butane and its Methylated Derivatives[13]

COMPOUND	No.	$E_{1/2}$ (± 0.02V)	IP (eV)
	20	1.69	8.97
	24	1.47	8.66
	25	1.10	8.24
	26	1.56	8.77
	27	1.27	8.46
	28	1.03	8.12
	29	1.57	8.60
	30	1.20	8.31
	31	0.93	8.00



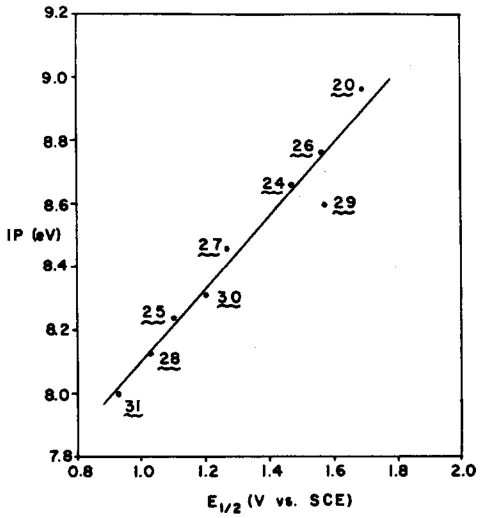
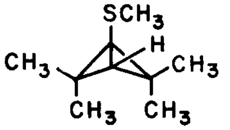
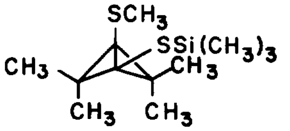


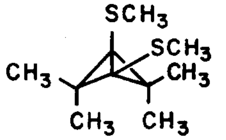
Fig. 2. Plot of measured half-wave oxidation potential versus calculated ionization potentials for the series of methyl-substituted bicyclo[1.1.0]butanes listed in Table 3. Correlation coefficient = 0.978; IP = 1.16 $E_{1/2}$ + 6.94.



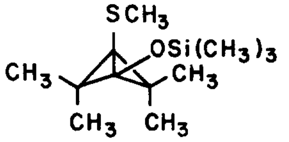
32 ($E_{1/2}$= 0.96V)



33 ($E_{1/2}$ = 0.71V)



34 ($E_{1/2}$= 0.57V)



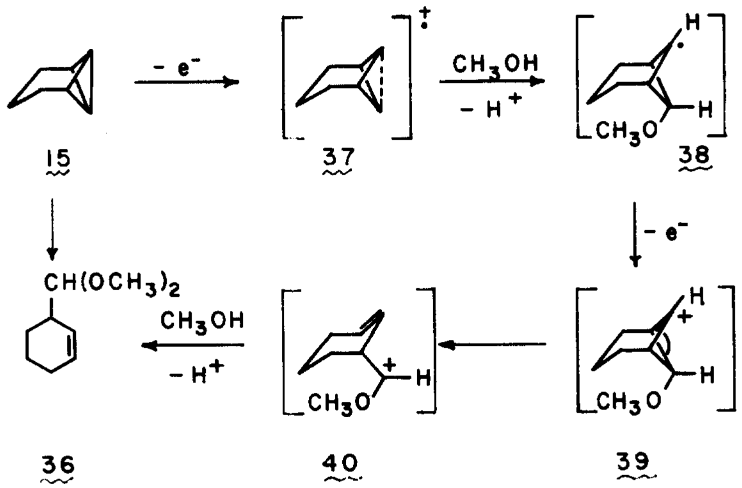
35 ($E_{1/2}$ = 0.44V)

comparison of row I with row II showed an average effect of a Me group at the 1-position of 0.29 V. Similar comparison of row II with row III showed that the effect of placing a Me at the second bridgehead position was identical to the effect of the first Me group, namely an average of 0.29 V per Me substituent. Since the substitution at the two bridgehead positions has approximately six times the effect of substitution at the 2- or 4-position, we believe that the electron transfer occurs from the bond connecting C_1 to C_3. Thus, the use of an electrochemical oxidation approach provided a strong confirmation of the theoretical predictions.

In a direct extension of the work described above on derivatives of bicyclo[1.1.0]butane, the effect of heteroatom substitution on C_1 and C_3 was investigated.[17] In this regard, compounds **32–35** were prepared and their anodic half-wave potentials were measured. The effect of a single bridgehead thiomethoxyl group (**32**) was approximately equal to the effect of two bridgehead Me groups (**31**). Comparison of **32** to **29** shows that the incorporation of the bridgehead thiomethoxyl function reduces the $E_{1/2}$ by approximately 0.6 V. Addition of a second thiomethoxyl as in **34** resulted in an additional 0.4 V increase in the ease of election transfer.

An obvious question relative to heteroatom substituted bicyclo[1.1.0]butane oxidation is whether the heteroatom or the hydrocarbon nucleus is undergoing oxidation. Dialkyl sulfides and silylated thiols undergo oxidation under our conditions at approximately 1.5 V.[17] Thus, it is evident that either the substitution of a heteroatom at the bridgehead of a bicyclo[1.1.0]butane significantly increases the HOMO of the hydrocarbon skeleton, or the attachment of the bicyclo[1.1.0]butyl group to a heteroatom makes the heteroatom more prone to electron transfer. The failure of **34** to yield sulfoxides or sulfones under conditions where sulfides are normally oxidized indicated that the bicyclo[1.1.0]butane was undergoing the oxidation, and that the sulfide groups of **32–35** were more resistant to oxidation than normal sulfides. This would be consistent with the known electron-withdrawing properties of the bicyclo[1.1.0]butyl group.[18]

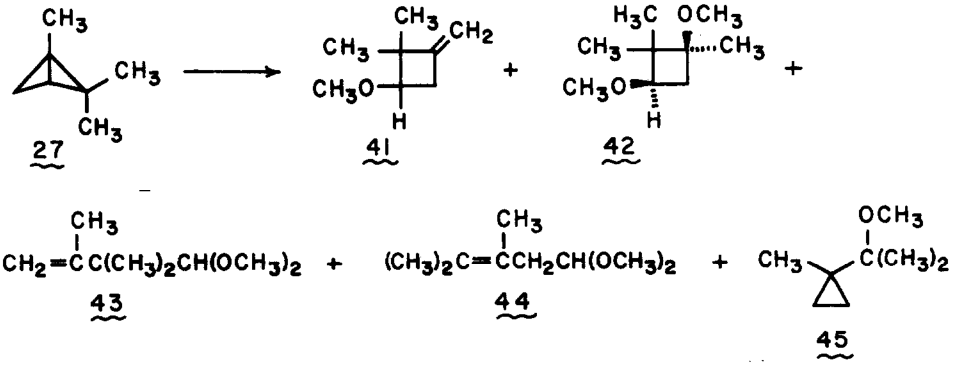
Product studies of electrochemical oxidations were extremely complex for reactions carried out in acetonitrile. As a result, those product studies which have been completed were carried out in methanol. Even in methanol, certain problems occurred. Trace amounts of acid generated through the oxidation of methanol led to rapid acid-catalyzed rearrangement of certain of the highly strained polycyclic hydrocarbons. In order to avoid this undesirable side reaction, pyridine was added. In 50:1 methanol-pyridine containing 0.1 M lithium perchlorate as electrolyte with platinum electrodes, **15** gave a half-wave potential of 1.63 V vs SCE (compared to 1.50 V in acetonitrile). Preparatively, **15**[19] gave a 65% yield of volatile products. Of this, 91% was the acetal, **36**. The remaining 9% consisted of a mixture of four components, one of which was 2-methoxybicyclo[4.1.0]heptane, the product of acid-catalyzed addition of methanol to **15**. The structure of **36** was established on the basis of spectral data[12] and through catalytic reduction to cyclohexanecarboxaldehyde dimethyl acetal, which was compared to an authentic sample.

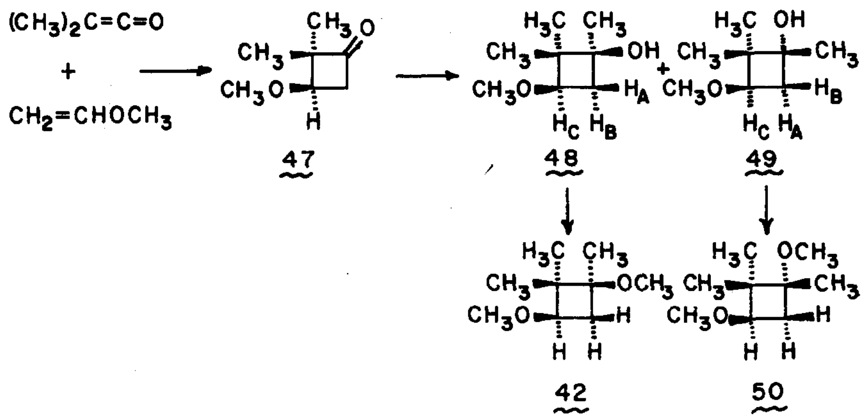


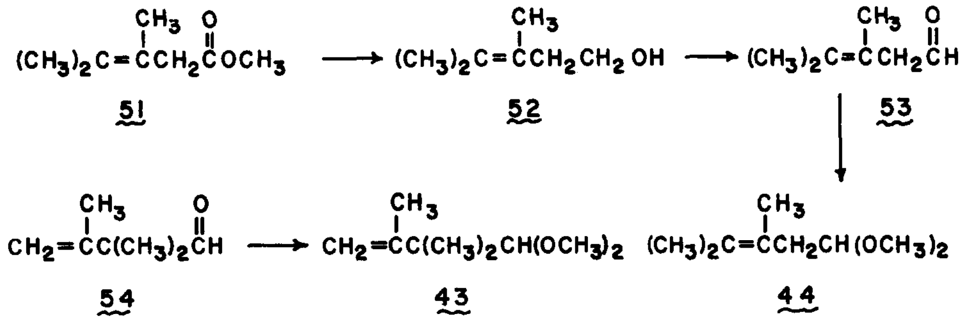
The formation of **36** required a two-electron process. Mechanistically, we view the overall process as one which involves electron transfer to generate initially the cation-radical **37**. Theoretical calculations [13] indicate that the cation-radical generated by removal of an electron from the C_1–C_3 sigma bond of bicyclo[1.1.0]butane would be structurally stable (although it would be expected to react readily with available nucleophiles). In view of the proposed structure of **37**, nucleophilic solvents would be expected to add from the "inside" of the bicyclo[1.1.0]butane envelope to give the radical, **38**. A second electron-transfer reaction should produce **39**, which would be expected to rearrange to the more stable cation **40**. Addition of a second equivalent of methanol would then produce the acetal, **36**.

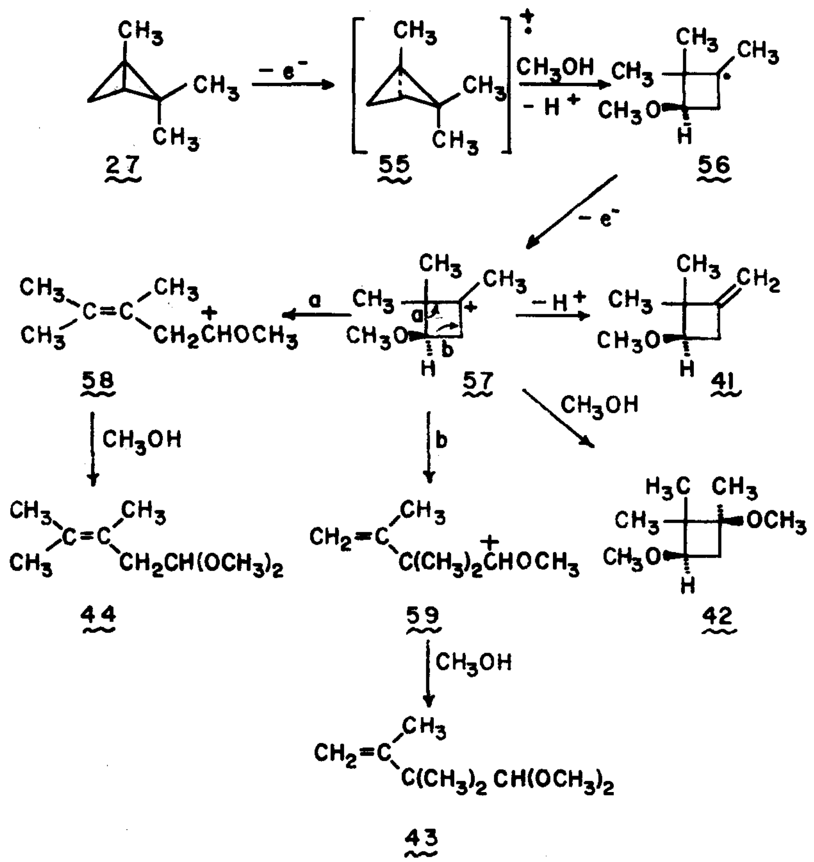
A second system which was studied in some detail was **27**.[20] This system was far more difficult to analyze than was **15** due to its extreme sensitivity to acid-catalyzed additions of methanol. In addition, it could be demonstrated that the primary oxidation products could be further oxidized to a complex mixture of secondary products. As a result, the products of two-electron oxidation were studied at low conversions. When **27** was oxidized at platinum electrodes in 50: 1 methanol-pyridine containing 0.1 M tetraethylammonium perchlorate as electrolyte, a mixture of **41**,[21] **42**, **43**, **44**, and the product of acid-catalyzed addition of methanol, **45**, was obtained. Examination of the reaction mixture after 0.10 Faraday/mol had been passed, showed **43** to be the major oxidation product, **41** to be a minor product and **42** and **44** to be very minor products. As the reaction proceeded, the relative amount of **43** decreased indicating that is was being converted into secondary products.[22] After the passage of 1 Faraday/mol of current (50% reaction) the ratio of **41**:**42**:**43**:**44**:**45** was 13:9:21:13:44.

The structure of **45** was established through comparison with an authentic sample.[3] Unfortunately, compounds **41**–**44** were unknown. The olefin, **41**, was identified through analysis of its ¹H- and ¹³C-NMR spectra (Experimental). The diether, **42**, was identified through comparison with an independently synthesized sample. Addition of dimethyl ketene to methyl vinyl ether according to the literature procedure gave the cyclobutanone, **47**.[23] Addition of methyl Grignard reagent to **47** gave a 1:2.2 mixture of the tertiary alcohols, **48** and **49**, respectively. The stereochemistry of **48** and **49** was assigned on the basis of both mechanistic speculation and spectral data. It was anticipated that the Grignard reagent would add preferentially from the side of the methoxyl group, due to partial complexation to




(CH3)2C=C=O
+
CH2=CHOCH3
47
48
49
42
50


51
52
53
54
43
44


27
− e⁻
55
CH3OH
− H⁺
56
− e⁻
a
b
57
− H⁺
41
58
CH3OH
44
59
42
43

this ether function. This would predict that the major isomer should have the OH and OMe groups *trans* to each other. In agreement with this assignment, the major isomer, **49**, had a ^{1}H-NMR spectrum in which H_A and H_B appeared as a single multiplet centered at δ 2.21. In contrast, the minor isomer, **48**, showed H_A[24] as a doublet of doublets at δ 2.22 (J=7 Hz and 12 Hz) and H_B[24] as a doublet of doublets at δ 1.86 (J = 7 Hz and 12 Hz). This difference in the chemical shifts of H_A and H_B of the minor isomer was consistent with the *cis* relationship of the OMe and OH groups. Methylation of the OH group of **48** and **49** with sodium hydride and methyl iodide gave **42** and **50**, respectively. The dimethoxylated cyclobutane derivative obtained from the minor isomer, **48**, was identical to the material obtained in the electrochemical oxidation of **27**. No trace of the epimeric compound, **50**, was detected in the electrochemical oxidation.

Compounds **43** and **44** were prepared in a straightforward manner as shown above. The methyl ester, **51**, was prepared according to the literature procedure.[25] Lithium aluminum hydride reduction of **51** gave **52**, which on oxidation with Collins reagent[26] gave the aldehyde, **53**. Conversion of **53** to its dimethyl acetal gave a compound which was identical in all respects to the oxidation product **44** than a similar fashion, conversion of the known[27] aldehyde, **54**, into its dimethyl acetal gave a product which was identical to the oxidation product **43**.

Mechanistically, these products can be readily explained as shown above. Removal of an electron from **27** should produce the cation-radical, **55**. Addition of methanol to **55** would produce the radical, **56**. Loss of a second electron would then produce **57** which, as a "classical" cyclobutyl cation, would have many possible reaction paths. Loss of a proton from **57** would give **41**, while collapse with solvent would yield **42**. Cleavage of bond α of **57** would produce the homoallylic cation **58**, which would be expected to collapse with solvent to give **44**. Cleavage of bond *b* of **57** should give the other reasonable homoallylic cation **59**, which on reaction with the nucleophilic solvent would give **43**.

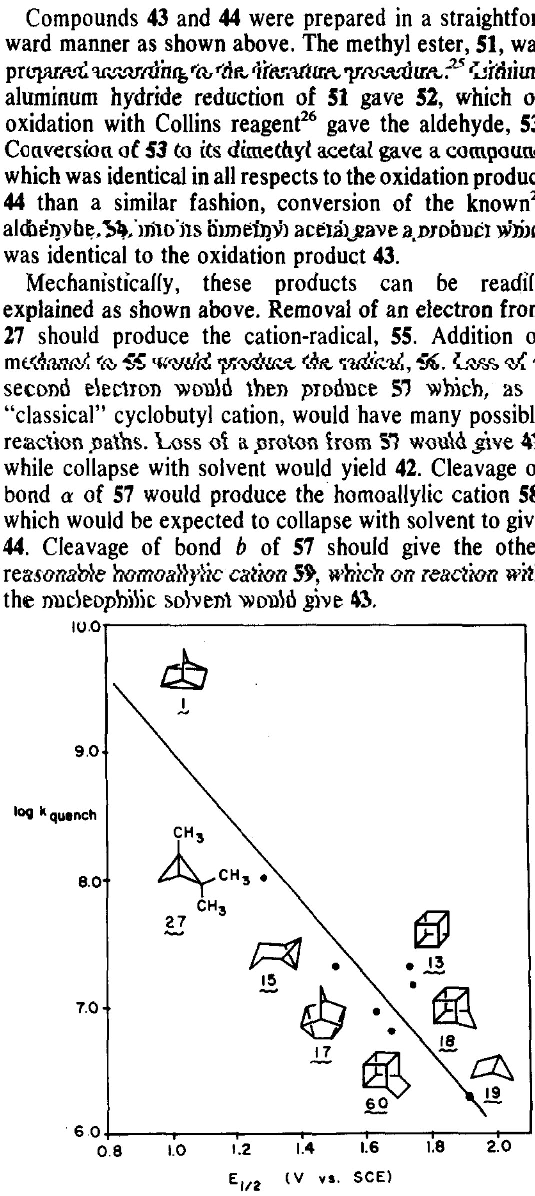


Fig. 3. Plot of log k_q for quenching of naphthalene fluorescence by highly strained hydrocarbons vs oxidation half-wave potentials for these same hydrocarbons. The solid line represents the least squares line represented by the equation $\log k_q = -2.92(E_{1/2}) + 11.95$. The correlation coefficient was 0.960.

As indicated above, the ease of oxidation of strained saturated hydrocarbons is a good measure of the relative energies of the HOMOs of these compounds. In principle, many reactions reflect the energies of the HOMO of one of the reactants. Thus, the measurements described above should correlate with a variety of reactions. In a preliminary study,[28] we have demonstrated that the ability of strained hydrocarbons to quench naphthalene fluorescence correlates reasonably well with the oxidative half-wave potentials of these hydrocarbons, and, as shown in Fig. 3, that this relationship covers a broad range of structural varients.

In summary, it appears that oxidative half-wave potentials of highly strained polycyclic hydrocarbons will be of use both in predicting new chemistry and in rationalizing old observations. The extreme ease with which certain of these hydrocarbons are oxidized, suggests that they may readily become involved in a variety of reactions which require electron transfer from HOMOs which are of unusually high energy.

EXPERIMENTAL

Anodic oxidation of 1,2,2[29]*trimethylbicyclo* [1.1.0] *butane* (27). In a 100-mL, flat-bottomed flask fitted with Pt electrodes and equipped for running under an inert atmosphere (N_2) was placed 50 mL of 0.1 M tetraethylammonium perchlorate in MeOH, 1.2 mL pyridine, and the mixture was magnetically stirred.[30] To this soln, 498 mg of **27** and 406 mg of n-heptane (as an internal standard) was added. The mixture was oxidized at constant current (50 mA) and the current use was monitored with a Vari-Tech VT 1176B Coulometer. Aliquots (1 mL) were removed after the passage of 0.1, 0.2, 0.4, 0.7, and 1.0 Faraday/mol of **27**. After 1 Faraday/mol had been passed, the oxidation was stopped and the mixture was poured into brine and extracted with pentane. The pentane soln was washed with brine and dried over $MgSO_4$. After filtration, the soln was analyzed by VPC against the aforementioned internal standard, n-heptane. Analysis showed that 49% of **27** had been consumed.[31] Five major products were detected. In order of elution these were **41**, **45**, **42**, **43**, and **44**, which were present in the ratio of 13:44:9:21:13, respectively. In addition, at least five very minor components were present. Since these minor components were not present after 10% reaction, they were considered to be secondary oxidation products and were neither isolated nor characterized. Analyses were carried out on a Carbowax 20 M column. For identification purposes, the major components were isolated by preparative vapor phase chromatography on Carbowax 20M and FFAP columns. Spectral data or other structural evidence for each of the components is given below.

2,2-*Dimethyl* - 3 - *methoxy* - 1 - *methylenecyclobutane* (41). The electrochemically generated component, **41**, was contaminated by a trace amount of **46**. The spectral components assigned to **46** (very weak signals) are given in brackets; ^{1}H-NMR ($CDCl_3$) δ 4.78 (q), 3.52 (t), 3.28 (s), 2.85-2.60 (br m), 1.63-1.52 (m), 1.51 (s), 1.12 (s), [5.70 (m), 3.13 (s), 1.09 (s)]; ^{13}C-NMR ($CDCl_3$) δ 152.56 (s), 103.44 (t), 80.00 (d), 57.09 (q), 49.30 (s), 36.34 (t), 26.16 (q), 20.82 (q), [125.00 (d), 85.07 (d), 23.36 (q), 20.22 (q)].

Acid-catalyzed reaction product, **45**. The acid-catalyzed reaction product was identified through comparison with an authentic sample of **45**.[3]

cis-1,3-*Dimethoxy*-1,2,2-*trimethylcyclobutane* (**42**). The diether, **42**, was identified through comparison with an authentic sample (*vide post*); ^{1}H-NMR ($CDCl_3$) δ 3.45 (1H, m), 3.25 (3H, s), 3.15 (3H, s), 2.50-2.15 (1H, m), 1.65 (1H, m), 1.19 (3H, s), 1.10 (3H, s), 1.00 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 79.81 (d), 77.75 (s), 56.95 (q), 50.51 (q), 35.38 (t), 20.53 (q), 18.58 (q), 18.20 (q).

2,2,3-*Trimethylbut*-3-*en*-1-*al dimethylacetal* (**43**). *The acetal*, **43**, was identified through analysis of its spectral data and through comparison with an independently synthesized authentic sample; ^{1}H-NMR ($CDCl_3$) δ 4.82 (2H, s), 4.05 (1H, s), 3.47

(6H, s), 1.79 (3H, s), 1.05 (6H, s); ^{13}C-NMR ($CDCl_3$) δ 110.76 (t), 58.50 (q), 44.69 (s), 22.36 (q), 22.04 (q).

3,4-*Dimethylpent*-3-*en*-1-*al dimethylacetal* (**44**). The acetal, **44**, was identified through analysis of its spectral data and through comparison with an authentic sample (*vide post*); ^{1}H-NMR ($CDCl_3$) δ 4.40 (1H, t), 3.22 (6H, s), 2.37 (2H, d), 1.69 (9H, br s); ^{13}C-NMR ($CDCl_3$) δ 126.87 (s), 123.16 (s), 104.62 (d), 53.28 (q), 38.10 (t), 20.73 (q), 20.52 (q), 19.16 (q).

2,2-*Dimethyl*-3-*methoxycyclobutanone* (**47**). This ketone was prepared from dimethyl ketene and methyl vinly ether according to the literature procedure.[23]

cis- and *trans*- 1,2,2-*Trimethyl*-3-*methoxycyclobutan*-1-*ol* (**48** *and* **49**). To a soln of 25 mmol MeMgI in 10 mL ether was added dropwise 1.00 g (7.8 mmol) of **47** over a 3-hr period at 25°. After stirring for 2 hr, the excess Grignard reagent was destroyed by dropwise addition of 4% HCl aq. The layers were separated and the ethereal soln was washed with satd $NaHCO_3$ aq, satd NaCl aq, and dried over $MgSO_4$. After filtration, the solvent was evaporated to give 0.97 g of a yellow oil which on vacuum transfer (bath tempe 60–65°, 15 mm) gave 0.42 g of a mixture of **48** and **49**. VPC analysis on Carbowax 20M indicated a **48**:**49** ratio of 1:2.2. Preparative VPC gave pure samples of each alcohol. Minor isomer, **48**: ^{1}H-NMR ($CDCl_3$) δ 3.65 (1H, t, J=7 Hz), 3.24 (3H, s), 2.22 (1H, d of d, J=7 Hz, 12 Hz), 1.86 (1H, d of d, J = 7 Hz, 12 Hz), 1.62 (1H, s), 1.22 (3H, s), 1.10 (3H, s), 0.99 (3H, s); IR 3320, 2900, 1470, 1370, 1210, 1100, 1015, 940 cm^{-1}. (Found: C, 66.80; H, 11.16. Calc. for $C_8H_{16}O_2$: C, 66.63; H, 11.18). Major isomer, **49**: ^{1}H-NMR ($CDCl_3$) δ 3.25 (3H, s), 3.20 (1H, t, J = 7 Hz), 2.21 (2H, m), 1.81 (1H, s), 1.20 (3H, s), 1.17 (6H, br s); IR 3300, 2850, 1570, 1470, 1225, 1200, 1110, 960 cm^{-1}. (Found: C, 66.40; H, 11.08. Calc. for $C_8H_{16}0_2$: C, 66.63: H, 11.18)

cis- *and trans*- 1,3-*Dimethoxy*-1,2,2-*trimethylcyclobutane* (**42** *and* **50**). To a soln of 240 mg of a 1:2.2 mixture of **48** and **49** and 420 mg MeI in 7 ml THF, was carefully added 85 mg NaH which had been washed five times with pentane and thoroughly dried. The mixture was stirred for 24 hr under N_2 and then concentrated under vacuum. Water was added carefully to the residue and the mixture was extracted with ether. The ethereal soln was washed with water and with satd NaCl aq, and dried over $MgSO_4$. After filtration, the solvent was evaporated under vacuum to give a yellow oil, which was vacuum transferred (bath temp 70–75°, 80 mm) to give 197 mg (73%) of a 1:2.4 mixture of **42** and **50**. The isomers were separated by preparative VPC on Carbowax 20M. Minor isomer, **42**: ^{1}H-NMR (CCl_4) δ 3.34 (1H, d of d, J=5 Hz, 7 Hz), 3.13 (3H, s), 3.05 (3H, s), 2.22 (1H, d of d, J=7 Hz), 12 Hz), 1.49 (1H, d of d, J = 5 Hz, 12 Hz), 1.11 (3H, s), 1.00 (3H, s), 0.92 (3H, s); IR 2900, 1460, 1370, 1210, 1090 cm^{-1}. (Found: C, 68.56; H, 11.45. Calc. for $C_9H_{18}O_2$: C, 68.31; H, 11.47). Major isomer, **50**: ^{1}H-NMR (CCl_4) δ 3.16 (3H, s), 3.06 (4H, superimposed s and t), 1.92 (2H, br m), 1.12 (3H, s), 1.05 (3H, s), 0.98 (3H, s); IR 2900, 1480, 1370, 1240, 1100, 1010 cm^{-1}. (Found: C, 68.63; H, 11.47. Calc. for $C_9H_{18}0_2$: C, 68.31; H, 11.47).

3,4-*Dimethylpent*-3-*en*-1-*ol* (**52**). To a suspension of 7.00 g LAH in 200 mL dry ether, was added dropwise 200 mL ether containing 10.31 g **51**.[25] The mixture was refluxed for 6 hr and the excess LAH was destroyed by the dropwise addition of EtOAc followed by satd Na_2SO_4 aq. The ethereal soln was separated, washed with brine, and dried over $MgSO_4$. After filtration, the solvent was evaporated and the residue was distilled to yield 8.11 g (98%, 95% purity) of **52**, b.p. 82–83° (20 mm). An analytical sample was prepared by preparative VPC: ^{1}H-NMR ($CDCl_3$) δ 3.63 (2H, t, J = 7 Hz), 2.32 (2H, t, J = 7 Hz), 1.66 (10H, br s); IR 3300, 2850, 1450, 1380, 1050 cm^{-1}. (Found: C, 73.46; H, 12.30. Calc for $C_7H_{14}O$: C, 73.63; H, 12.36).

3,4-*Dimethylpent*-3-*en*-1-*al* (**53**). To a soln of 9.41 g pyridine in 150 mL CH_2Cl_2 was added 6.00 g CrO_3 and the soln was stirred for 15 min.[26] To this stirred soln was added 1.14 g of **52** in 10 mL CH_2Cl_2 in one portion. A tarry black gum appeared. The mixture was stirred for 15 min and the soln was decanted from the solid residue. The residue was washed thoroughly with 200 mL ether and the combined organic phase was washed with three 100-mL portions of 5% NaOH aq, 100 mL 4% HCl aq, 100 mL 5% $NaHCO_3$ aq and 100 mL satd NaCl aq. The organic soln was dried over $MgSO_4$, filtered, and the solvent was evaporated to give a slightly yellow oil. This oil was distilled in a Kugel-rohr apparatus to give 0.74 g (66%, 98% purity) of **53**. An analytical sample was prepared by preparative VPC followed by molecular distillation (bath temp. 78–83°, 15 mm): ^{1}H-NMR (CCl_4) δ 9.48 (1H, t, J = 2.4 Hz), 3.03 (2H, d, J = 2.4 Hz), 1.68 (9H, br s); IR 2900, 1750, 1460, 1400, 1270 cm^{-1}. (Found: C, 74.81; H, 10.74. Calc. for $C_7H_{12}O$: C, 74.95; H, 10.78).

3,4-*Dimethypent*-3-*en*-1-*al dimethylacetal* (**44**). A soln of 0.46 g of **53**, 0.52 g trimethyl orthoformate, and 2 drops conc H_2SO_4 in 20 mL MeOH was allowed to stand for 1 hr at 25°. The mixture was poured into 70 mL 5% $NaHCO_3$ aq and extracted with ether. The ethereal extracts were washed with satd NaCl aq and dried over Mg SO_4. After filtration, the solvent was evaporated to yield an oil which on molecular distillation (bath temp. 60°, 50 mm) gave 0.44 g (68%, 93% pure) of **44**. An analytical sample was prepared by preparative VPC: ^{1}H-NMR (CCl_4) δ 4.28 (1H, t, J = 6 Hz), 3.20 (6H, s), 2.25 (2H, d, J=6 Hz), 1.64 (9H, br s); IR 2900. 1440, 1380, 1200, 1110, 1050, 975 cm^{-1}. (Found: C, 68.41; H, 11.45. Calc. for $C_9H_{18}O_2$: C, 68.31; H, 11.47).

2,2,3-*Trimethylbut*-3-*en*-1-*al* (**54**). This compound was prepared from 2,2,3-trimethylbut-3-en-1-ol[27] by the same procedure as described above for the preparation of **53**. The yield was 53% and the spectral data were identical to those reported in the literature for **54**.[27]

2,2,3-*Trimethylbut*-3-*en*-1-*al Dimethylacetal* (**43**). A soln of 0.49 g of **54**, 0.55 g trimethyl orthoformate, and 1 drop H_2SO_4 in 20 mL MeOH was allowed to stand for 2 weeks at 25°. The mixture was poured into 70 mL 5% $NaHCO_3$ aq and extracted thoroughly with ether. The ethereal extracts were washed with satd NaCl aq and dried over $MgSO_4$. After filtration, the solvent was evaporated to give a residue which was molecularly distilled (bath temp. 55–60°, 80 mm) to give 0.31 g (48%, 90% pure) of **43**. An analytical sample was prepared by preparative VPC: ^{1}H-NMR (CCl_4) δ 4.71 (2H, s), 3.92 (1H, s), 3.36 (6H, s), 1.73 (3H, br s), 0.98 (6H, s); IR 2900, 1640, 1450, 1380, 1100, 970, 900 cm^{-1}. (Found: C, 68.30; H, 11.37. Calc. for $C_9H_{18}0_2$: C, 68.31; H, 11.47).

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REFERENCES

[1] For unstrained a hydrocarbons, electrochemical oxidation results in cleavage of C–H bond. For selected examples see: M. Fleischmann, D. Pletcher, *Tetrahedron Letters* 6225 (1968); J. Bertram, M. Fleischmann, D. Pletcher, *Ibid.* 349 (1971); J Bertram, J. Coleman, M. Fleischmann, D. Pletcher, *J. Chem. Soc., Perkin Trans.* **2**, 374 (1973); D. B. Clark, M. Fleischmann, D. Pletcher, *Ibid.* 1578 (1973); V. R. Koch, L. L. Miller, *J. Am. Chem. Soc.* **95**, 8631 (1973); see also G. J. Edwards, S. R. Jones, J. M. Mellor, *J. Chem. Soc.*, Chem. Commun. 816 (1975); G. J. Edwards, S. R. Jones, J. M. Mellor, *J. Chem. Soc., Perkin Trans.* **2**, 505 (1977); T. M. Siegel, J. Y. Becker, and L. L. Miller, *J. Chem. Soc., Chem. Commun.* 341 (1974); F. Bobilliart, A. Thiebault, M. Herlem, *C. R. Acad. Sci.* 1485 (1974); S. Pitti, A. Thiebault, F. Bobilliart and M. Herlem, *Anal. Lett.* **8**, 241 (1975); S. Pitti, M. Herlem, J. Jordan, *Tetrahedron Letters* 3221 (1976);.

[2] For selected examples see: T. Shono, Y. Matsumura, *J. Org. Chem.* **35**; 4159 (1970); T. Shono, Y. Matsumura, Y. Nakagawa, *Ibid.* **36**, 1771 (1971); T. Shono, Y. Matsumura, *Bull. Chem. Soc. Jpn.* **48**, 2861 (1975); M. Klehr, H. J. Schafer, *Angew. Chem.* Int. Ed. Engl. **14**, 247 (1975).

[3] P. G. Gassman, F. J. Williams, *J. Am. Chem. Soc.* **92**, 7631 (1970); P. G. Gassman, G. R. Meyer, F. J. Williams, *Ibid.* **94**, 7741 (1972); P. G. Gassman and F. J. Williams, *Ibid.* **94**, 7733 (1972); P. G. Gassman and T. J. Atkins, *Ibid.* **94**, 7748 (1972); P. G. Gassman, T. J. Atkins and J. T. Lumb, *Ibid.* **94**, 7757 (1972).; P. G. Gassman, T. Sugawara and L. G. Tillotson, *J. Org. Chem.* **42**, 3785 (1977); and refs. therein.

[4] P. G. Gassman, D. H. Aue and D. S. Patton, *J. Am. Chem. Soc.* **90**, 7271 (1968).

[5] H. Hogeveen and H. C. Volger, *Ibid.* **89**, 2486 (1967). See also F. D. Mango and J. H. Schachtschneider, *Ibid.* **89**, 2484 (1967); S. J. Cristol and R. L. Snell, *Ibid.* **80**, 1950 (1958).

[6] It is interesting to note that a recent study of this well-known and extensively investigated transition-metal-complex-promoted release of strain energy was presented at the annual meeting of the Chemical Society of Japan on 1 April, 1981. In discussing this presentation in a major editorial, the *Japan Times* stated "We would speak in the same breath of the successful American space shuttle and the development by a group of Japanese scientists of a substance for cheap, efficient storage of solar energy"; *Japan Times* p 12. 19 April (1981).

[7] G. F. Koser and J. N. Faircloth, *J. Org. Chem.* **41**, 538 (1976).

[8] The oxidation of quadricyclane under electrochemical conditions was found to give the same type of products; A. J. Baggaley, R. Brettle and J. R. Sultan, *J. Chem. Soc., Perkin Trans.* 1 1055 (1975).

[9] P. G. Gassman, R. Yamaguchi and G. F. Koser, *J. Org. Chem.* **43**, 4393 (1978).

[10] Unless otherwise specified, all $E_{1/2}$ values were determined using single-sweep voltammetry (sweep rate 100 mV/s) on a Princeton Applied Research Model 174 polarographic analyzer equipped with platinum electrodes vs. a SCE. All measurements were made in high purity acetonitrile which contained either ~0.1 M lithium perchlorate or tetraethylammonium fluoroborate as supporting electrolyte. In certain systems which were especially acid sensitive, 0.5 mM pyridine was added as a base. All of the values cited assume that the measured electrode potentials are kinetically shifted (due to followup reactions) relative to the reversible potentials for each hydrocarbon.

[11] L. Cassar, P. E. Eaton and J. Halpern, *J. Am. Chem. Soc.* **92**, 6366 (1970).

[12] P. G. Gassman and R. Yamaguchi, *Ibid.* **101**, 1308 (1979).

[13] P. G. Gassman, M. J. Mullins, S. Richtsmeier and D. A. Dixon, *Ibid.* **101**, 5793 (1979).

[14] M. D. Newton and J. M. Schulman, *Ibid.* **94**, 767 (1972); M. D. Newton, *Modern Theoretical Chemistry: Applications of Electronic Structure Theory*. (Edited by H. F. Schaeffer) Vol. 3, p. 223. Plenum Press, New York (1977).

[15] P. G. Gassman and R. R. Reitz, *J. Organometal. Chem.* **52**, C51 (1973); P. G. Gassman and T. Nakai, *J. Am. Chem. Soc.* **94**, 2877 (1972); P. G. Gassman and T. Nakai, *Ibid.* **93**, 5897 (1971).

[16] Ionization potentials were calculated by the approximate molecular orbital method, partial retention of diatomic differential overlap (PRDDO): T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.* **58**, 1569 (1973); T. A. Halgren, D. A. Kleier, J. H. Hall Jr., L. D. Brown and W. N. Lipscomb, *J. Am. Chem. Soc.* **100**, 6595 (1978).

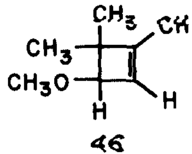
[17] P. G. Gassman and M. J. Mullins, *Tetrahedron Letters* 2219 (1980). See also P. G. Gassman and M. J. Mullins, *Ibid.* 4457 (1979).

[18] R. N. McDonald and R. R. Reitz, *J. Am. Chem. Soc.* **98**, 8144 (1976).

[19] W. R. Moore, H. R. Ward and R. F. Merritt, *Ibid.* **83**, 2019 (1961).

[20] W. R. Moore, K. G. Taylor, P. Muller, S. S. Hall and Z. L. F. Gaibel, *Tetrahedron Letters* 2365 (1970); L. Skattebol, *Ibid.* 2361 (1970).

[21] Small (trace) amounts of **46** contaminated **41**.



46

[22] The presence of at least five secondary products was established by VPC analysis after the passage of 1 Faraday/mol.

[23] J. C. Martin, *U.S. Patent* 3,312,741; *C.A.* **67**, P12118r (1967); R. H. Hasek, P. G. Gott and J. C. Martin, *J. Org. Chem.* **29**, 1239 (1964).

[24] The assignment of the signals to H_A and H_B is tentative. On the basis of literature precedent the assignments could be reversed [K. B. Wiberg; D. E. Barth and W. E. Pratt, *J. Am. Chem. Soc.* **99**, 4286 (1977); K. B. Wiberg and D. E. Barth, *Ibid.* **91**, 5124 (1969); see also K. Tori, Y. Takano and K. Kitahonoki, *Chem. Ber.* **97**, 2798 (1964)]. However, the addition of the lanthanide shift reagent (LSR), $Eu(FOD)_3$, resulted in the more downfield of these two protons experiencing the greater LSR induced downfield shift. It is interesting to note that in separate LSR experiments H_C of both **48** and **49** exhibited essentially the same slope. H_A and H_B of **49** also showed identical slopes in the presence of the LSR reagent.

[25] E. van Heyningen, *J. Am. Chem. Soc.* **77**, 4016 (1955); M. A. Schexnayder and P. S. Engel, *Ibid.* **97**, 4825 (1975).

[26] J. C. Collins, W. W. Hess and F. J. Frank, *Tetrahedron Letters* 3363 (1968).

[27] R. A. Schneider and J. Meinwald, *J. Am. Chem. Soc.* **89**, 2023 (1967).

[28] P. G. Gassman, K. D. Olson, L. Walter and R. Yamaguchi, *J. Am. Chem. Soc.* **103**, 4977 (1981).

[29] Boiling points and melting points are uncorrected. Elemental analyses were carried out by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

[30] For a detailed description of running conditions, electrode pretreatment, and other variables see Ref. 13.

[31] Of the material consumed (49%), 44% had been consumed in an acid-catalyzed process. Since the oxidation is a two-electron process and since one Faraday was passed, a current efficiency of 55% was indicated.