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Conjugation in Bicyclo[1.1.0]butanes. LUMO Properties of the Bridging Bond

Sir:

The nature of the central bond is the focal point of bicyclo[1.1.0]butane chemistry.[1,2] Very recent NMR studies[3] have shown the bridgehead carbons overlap with nearly pure p orbitals in good agreement with a calculated sp^{18} hybridization. Furthermore low energy LUMOs in cyano- and carbomethoxy-substituted bicyclobutanes are said to be responsible for the photolytic cleavage of the bridging bond followed by hydrogen abstraction from the solvent instead of an electrocyclic transformation to butadienes.[4] In addition, it has been found that widening of the dihedral angle in bicyclobutanes raises the energy of the HOMO, largely localized in the central bond.[5] We now provide quantitative data concerning the effect of π substituents and geometry on the LUMO energies in bicyclobutanes.

In the newly synthesized bicyclobutanes **2a–d**, the bridgehead carbons are connected to pyridinium rings and positions 2 and 4 to substituents of different size. We have characterized this specific system by voltammetry, UV spectroscopy, and photochemical isomerizations.

Electrochemical oxidation transforms the 1,3-bismethylenecyclobutane **1a**[6] into **2a** which in turn is reduced back to **1a**. Owing to the difference in structure and geometry of **1a** and **2a** both the electron transfers

$$\mathbf{1a} \xrightarrow{-2e} \mathbf{2a} \quad \text{and} \quad \mathbf{2a} \xrightarrow{+2e} \mathbf{1a}$$

are irreversible. However, the complete redox cycle is a *reversible* one. Evidence for this curious behavior is provided by cyclic voltammograms (CV) of **1a** and **2a** (Figure 1), in which the nearly identical peak potentials can be identified as those of **1a** (oxidation) and **2a** (reduction),[7] despite the irreversible oxidation (O) and reduction (R) waves. The observation of such high reduction potentials (≈−0.4 V)[8] for **2** is striking in view of the finding that lithium/amine[9] is required for reduction of normal bicyclobutanes.[10] This result indicates a large decrease in the energy of the LUMO of **2a** into which the two electrons are added.

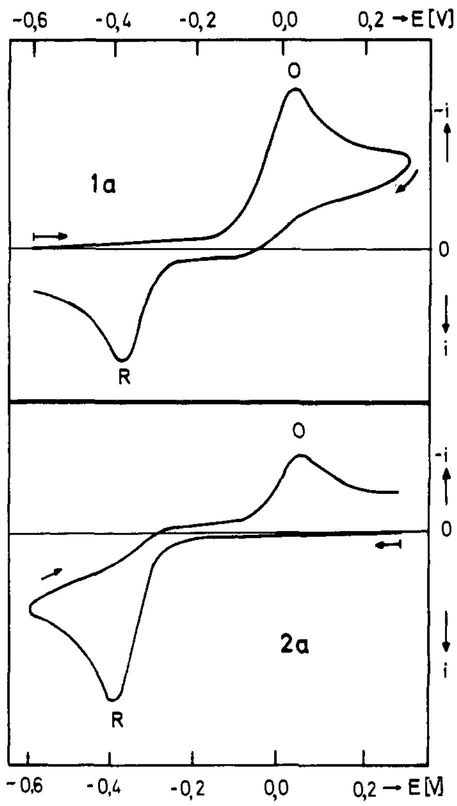
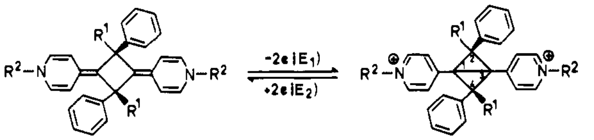


Figure 1. Cyclic voltammograms of **1a** and **2a** (200 mV/s; DMF/TBA · BF$_4$; Pt vs. Ag/AgCl/AN[13]).



1 2

	a	b	c	d
R¹	H	H	CH$_3$	CH$_3$
R²	CH$_3$	C$_6$H$_5$CH$_2$	CH$_3$	C$_6$H$_5$CH$_2$

While the mechanism of the related cathodic formation of bicyclobutanes from 1,3-dihalocyclobutanes is still controversial,[11] both oxidation **1** → **2** and reduction **2** → **1** occur through an ECE[12] process. This conclusion can be derived from

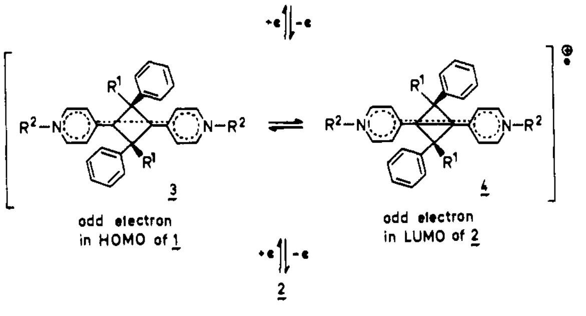


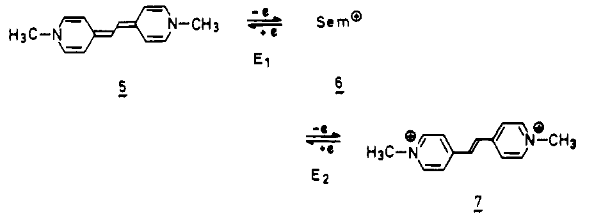
Table I. Oxidation $(E_1)^a$ and Reduction $(E_2)^a$ Potentials[b] and UV Maxima[c]

Compd	λ_{max}, nm (ϵ)	E_1, V	E_2, V
2a	322 (14 800), 274 (16 200)		−0.355 irrev $(-0.46)^d$
2b	331 (16 800), 278 (20 100)		−0.32 irrev
2c	298 (11 400), 268 (14 200)		−0.375 irrev
2d	291 (1690), 274 (16 100), 268 (15 500)		−0.38 irrev
1a	346 (34 400), 333 (37 400)	+0.05 irrev	
1c	343 (34 000), 330 (37 400)	$+0.17^d$ irrev	
8c	324 (15 100), 311 (18 700)	+0.36 rev	
9a	257 (11 900), 220 (45 600)		-1.38^d irrev
7[c]	332 (28 200), 318 (41 700), 307 (35 500)		−0.39 rev
5[c]	438 (60 500), 414 (48 000), 397 (34 000)	−0.56 rev	

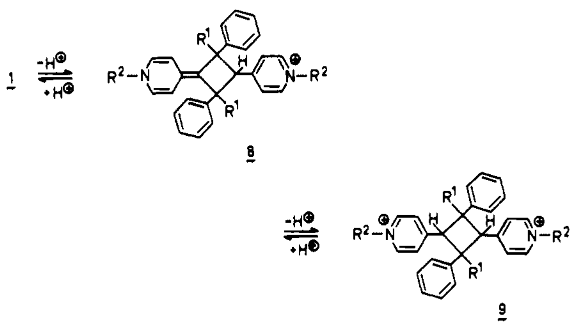
[a] CV (200 mV/s); E_1, E_2 determined at 85% of i_p. [b] DMF/TBA·BF_4/Pt vs. Ag/AgCl/AN.[13] [c] in AN.[13] [d] 20 V/s.

CV data[12] for solutions in AN, DMF, and DCM.[13] At the observed potentials, only one electron is initially transferred. Presumably abstraction of e from the HOMO of **1** affords the radical cation **3**, whereas addition of e to the LUMO of **2** yields the radical cation **4**. The "chemical" step of the overall process consists of a valence tautomerism **3** ⇌ **4**, which immediately is followed by the transfer of the second electron at same potential.[14]

The redox system **1**/**2** can be linked to a general structure of two-step redox systems,[15] if its special conjugation is changed into normal π conjugation. Thus replacement of the methylene bridges in **1** and **2** by a σ bond leads to **5** and **7**. The potential E_2 (**6**/**7**) is surprisingly close to that of **1**/**2** (Table 1). However, the thermodynamic stability of radical ion **6**[16] ($K_{SEM(5/7)} = 7 \times 10^2$) is higher than that of **3**/**4** by a factor of ~10^{14} ($K_{SEM(1a/2a)} \approx 10^{-11}$). Here disproportion reactions, e.g., **3** + **4** → **1** + **2**, dominate (E_2 being cathodic of E_1). The known through-space and through-bond interactions in 1,3-bismethylenecyclobutanes[17] are also found in **1**. This can be seen from the bathochromic shift of 19 nm (**1c**) compared to **8c** where those interactions are prevented by monoprotonation of **1c**. The difference of 0.23 eV is mainly due to a *higher lying HOMO in* **1c** as can be estimated from the difference (0.19 eV) of the oxidation potentials of **1c** and **8c** (Table I). The same conclusion can be drawn from comparison of **1c** with **5**. The longer wavelength absorption of **5** by 95 nm (0.78 eV) corresponds to a more positive oxidation potential of **5** by 0.73 eV.



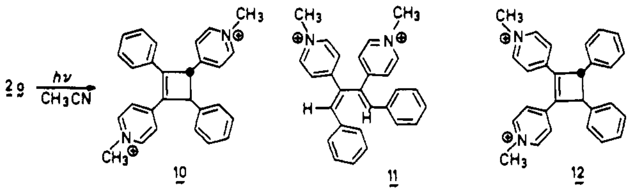
In bicyclobutanes **2a–d** strong conjugation causes absorption maxima which are very similar to those of **7**, the main difference being in ϵ only. Full protonation of **1** leads to **9** which is a model for **2** with the 1,3 interactions excluded. The excitation energy of **2a** is lowered by as much as 0.8 eV compared to **9a**. Correspondingly, the reduction potential of **2a** is much more positive than that of **9**. The difference of 0.92 eV indicates that conjugation between the bicyclobutane moiety and the pyridinium groups[18] is responsible for the *low lying LUMO in* **2a**. The strong interaction of the pyridinium groups in **2** is connected to their low lying LUMOs as indicated by similar UV effects of the electron-attracting cyano[1] and carbomethoxy groups[19] compared to the weak interaction of phenyl substituents.[20-22]



The difference between the potentials of **8c** and **9a** (models for **1a** and **2a** without 1,3 interactions) of 1.56–1.74 eV corresponds to as much as 37–40 kcal/mol. However, in the case of **1c**/**2a**, this energy difference is markedly reduced to 0.63 eV (≈15 kcal/mol). This singly-occupied frontier orbitals of the radical ions **3** and **4** are evidently so similar in energy that making and breaking of the bridging bond is reversible.

Widening of the dihedral angle of the bicyclobutane ring by substitution of R^1 = H by R^1 = CH_3 (**2a** → **2c** and **2b** → **2d**) causes significant effects. Strong hypsochromic shifts of 24 nm (0.4 eV) and 40 nm (0.6 eV), respectively, are observed, whereas the reduction potentials remain nearly unaffected (ΔE 0.02 and 0.06 eV). Consequently the HOMO of the whole system (**2c** and **2d**) has been lowered. This in turn indicates reduced interaction between the pyridinium and the bicyclobutane moieties. Since the HOMO of the former is lower,[23] it follows that widening of the dihedral angle raises the HOMO of the bicyclobutane moiety. In 1,3-diphenyl-substituted bicyclobutanes[19-21] the *higher* lying phenyl HOMO[23] causes bathochromic shifts when the ring is flattened. This conclusion is supported by very recent theoretical,[5] spectroscopic,[24,25] and kinetic[5] results on bicyclobutane geometry. Inspection of molecular models excludes special steric effects on the pyridinium residues in **2c** and **2d**. In addition, hyperconjugation from the 2,4 positions can be neglected because of the small orbital coefficients.[24]

The photoreactivity of **2** is also strongly influenced by the low lying LUMO of the bridging bond. Irradiation of **2a** (Hanovia TQ 150, Pyrex, AN,[13] 4 h, 15 °C) yields nearly 100% of the thermolabile cyclobutene **10**: NMR (Me_2SO-d_6) δ (ppm) 8.83 (d, J = 6 Hz, 4 H), 7.97 (d, J = 6 Hz, 4 H), 7.96–7.35 (m, 5 H), 7.13 (s, 5 H), 4.94 (s, 2 H), 4.31 (s, 6 H). In AN[13] the two ring protons show an AB pattern at δ 4.96 and 4.98 ppm, J = 6 Hz (= trans coupling). The isomeric structures **11** and **12**, which are expected from electrocyclic rearrangements, can definitely be excluded.[25] Consequently, the low energy LUMO of **2a** facilitates photolytic cleavage of the central bond and a subsequent 1,2-hydrogen shift finally produces **10**.



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(7) Voltammetry and UV spectroscopy of **1c** and **1d** points to the same reaction cycle. However, preparative results[6] were not conclusive.

(8) DMF/tetrabutylammonium tetrafluoroborat (TBA·BF_4)/Pt vs. Ag/AgCl/AN.

(9) This reagent reduces even benzene, which is reduced at −3.3 V; cf. F. Gerson, H. Ohya-Nishiguchi, and C. Wydler, *Angew. Chem.*, **88**, 617 (1976); *Angew. Chem., Int. Ed. Engl.*, **15**, 552 (1976).

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(13) AN = acetonitrile; DMF = dimethylformamide; DCM = dichloromethane; TBA·BF_4 = tetrabutylammonium fluoroborate.

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(25) Detailed discussion see M. Horner, Dissertation, University of Würzburg, 1977.

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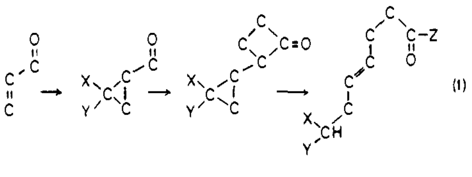
New Synthetic Reactions. Double Chain Extension

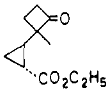
Sir:

We wish to report that carbon can function as a nucleofugal atom in the Grob fragmentation and consequently can allow chain extension of an α,β-unsaturated carbonyl system at both the carbonyl group and the β carbon as outlined in eq 1. Nucleophilically triggered ring opening of doubly activated cyclopropanes has generated a number of useful reagents and novel synthetic strategy.[1-4] The driving force provided by cleavage of cyclobutanone rings in secoalkylation,[5,6] when combined with the cyclopropanation of olefins, offers a unique opportunity to extend both termini of an α,β-unsaturated system where the two ends are differentially functionalized and the double bond is introduced stereo- and regioselectively between the carbonyl carbon and the α carbon of the starting enone.



(1)

In a fragmentation such as illustrated in eq 1, ~55 kcal/mol of strain energy is released. To ascertain how much of a driving force this provided, we attempted to cleave cyclobutanone (**1**) unsuccessfully by refluxing in methanolic sodium methoxide for 3.5 days. For comparison, epoxycyclobutanone (**2**) fragments in 10 min at room temperature.[7] On the other hand, the presence of a second substituent on the cyclopropane ring does lead to success.



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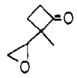
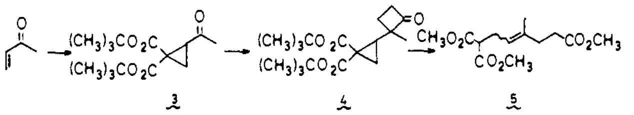
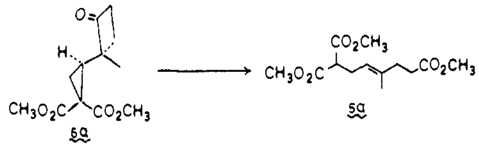


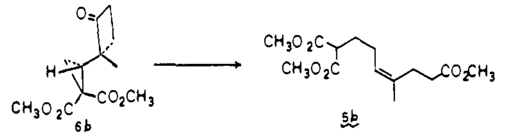
2

Addition of di-*tert*-butyl bromomalonate[8,9] to methyl vinyl ketone (KOC_4H_9-*t*, *t*-C_4H_9OH, 15 °C) gave the crystalline cyclopropane **3**, mp 51–53 °C.[10] Cyclobutanation to **4**[9] used diphenylsulfonium cyclopropylide (precursor salt, KOC_4H_9-*t*, Me_2SO, room temperature) followed by lithium fluoroborate) (PhH, room temperature, 82%).[11] The mixture of diastereomers of **4** was directly subjected to sodium methoxide in refluxing methanol which cleanly produced the *E* and *Z* isomers of fragmented product **5**[9] in 74% yield in which transesterification accompanied fragmentation.



To determine the stereospecificity of the reaction, **4** was converted to its methyl esters (CF_3CO_2H, 0 °C, then CH_2N_2, ether) **6a**[9,12] and **6b**[9,12] which were separated by VPC.[13] Subjection of each pure isomer to the fragmentation reaction led to the correspondingly isomerically pure olefins **5a**[9,12] and **5b**[9,12] in 80 and 84% yields, respectively. The stereochemistry of the olefins follows from the higher field position of the protons and carbon of the vinyl methyl group in the *E* isomer **5a** (^1H NMR δ 1.64, ^{13}C NMR δ 15.9) compared to the *Z* isomer **5b** (^1H NMR δ 1.68, ^{13}C NMR δ 22.9).





Having established the stereospecificity of the fragmentation, we endeavored to find a simple system in which cyclobutanone formation was highly stereocontrolled. Indeed, a single cyclobutanone was obtained from 2-methacrolein by first cyclopropanating ($BrCH(CO_2C_4H_9\text{-}t)_2$,$(CH_3)_2NC(=NH)N(CH_3)_2$, DMF, room temperature) to **7**,[9,14] mp 99–101.5 °C and then cyclobutanating with diphenylsulfonium cyclopropylide (precursor salt, KOH, Me_2SO, room temperature, then $LiBF_4$, PhH, room temperature) to **8**.[9,12] Both ^1H and ^{13}C NMR[12] and chromatography establish the stereo-