of the materials and of the instrumentation.

Figure 1 shows typical plots of time against 9,10-dimethylanthracene fluorescence intensity at 410 nm excited at 260 nm in $CHCl_3$ solvent at 298 K. During the first several minutes the intensity varies (often wildly with excursions of the order of 75%), and then the variation in intensity becomes periodic. Oscillations have been observed for a duration of the order of 1 h. With time, the overall luminescence intensity gradually declines consistent with the measured irreversible consumption of the 9,10-dimethylanthracene. The period and the pattern of the oscillation and the induction time for the entrainment are not always the same. However, the aperiodic variations can always be induced immediately, and the prolonged periodic oscillations generally begins several minutes subsequent to the start of the experiment.

While we do not yet have a detailed interpretation of the results, we can state a number of additional facts that point toward a working hypothesis: (1) oscillations in fluorescence intensity are not observed for excitation wavelengths longer than ~300 nm in $CHCl_3$, and it appears that excitation of the chlorocarbon is necessary; (2) the oscillations in the emission are essentially independent of the monitoring wavelength (i.e., the entire fluorescence spectrum of the anthracene or 9,10-dimethylanthracene seems to oscillate with the same period and amplitude; (3) oscillations in a sample open to the air cease upon stirring and commence again when the solution is quiet, and when the solution is stirred we observe only a gradual, steady, decline in emission intensity; (4) a sample oscillating at a given amplitude at a given excitation intensity can be induced to oscillate at a larger amplitude by increasing the light intensity; (5) a sample stimulated to oscillate by 260-nm light will continue to oscillate if the excitation wavelength is then changed by a small amount, e.g., to 250 or to 275 nm, although the amplitude of the oscillation can change; (6) concentrations of the luminescent substances higher than those typically employed here seem to obscure the effect. All of these facts are admittedly qualitative in nature, but we feel that they at least lead us to the experiments necessary to understand and fully characterize these systems. We conclude that the excitation beam is both the stimulus for, and the probe of, variations in the anthracene or 9,10-dimethylanthracene concentration (approximately proportional to fluorescence intensity). One primary photochemical reaction is likely the generation of $CHCl_2$ radicals and Cl atoms which may attack ground-state anthracene.[4] Subsequent steps lead to final stable photoproduct(s) which are likely chlorination products.[4] The apparent need for an irradiation volume less than the total volume of the sample and the instant cessation of oscillations in fluorescence upon stirring a quiet solution both point to the importance of diffusion in and out of the irradiation zone. Oscillations have been observed in CCl_4 and CH_2Cl_2 solvents as well, and it is known that carbon-halogen bond cleavage is the general result of electronic excitation of alkyl halides.[5] We believe that a detailed analysis of the many features of the oscillations (amplitude, pattern, period) will provide important clues for a reaction mechanism.[6]

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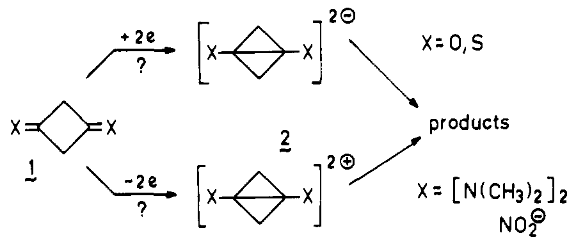
Bicyclo[1.1.0]butanes. A New Synthetic Route and Valence Isomerizations

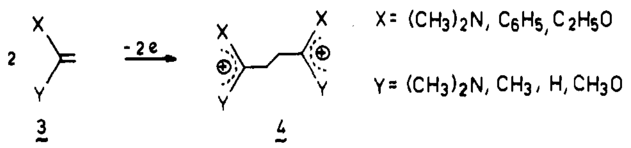
Sir:

In spite of their extremely high strain energy (67 kcal/mol[1]), bicyclobutanes are formed in reasonable yields by a variety of different reactions.[2] Ring closure of 1,3-disubstituted cyclobutanes by 1,3 elimination,[2,3] reduction,[4] or oxidation[5] are of special interest in comparison with our new approach. Conversion of 1,3-bismethylenecyclobutanes or their bisheteroanalogues **1** to the corresponding bicyclobutanes by removal or addition of two electrons has been unsuccessful to date.[6-8]



However, in some cases, the isolated products may have been formed via intermediate bicyclobutanes **2**.[6a] We now describe the first example of *reversible formation of bicyclobutanes* from a special type of **1** merely *by electron transfer*.

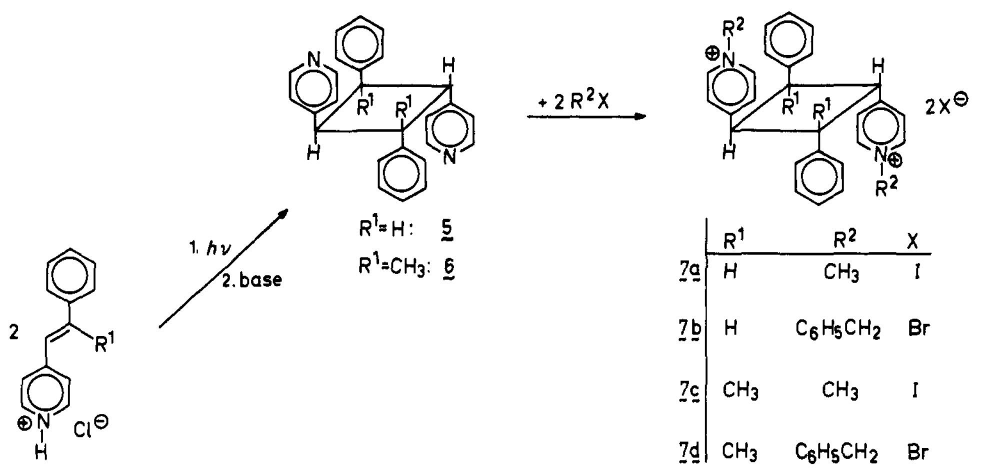
Formation of the bridging bond of bicyclo[1.1.0]butanes is based upon the well-documented reaction **3** → **4**,[9] except that



in our systems the resonance stabilization of the end groups of **4** is enhanced by the presence of an aromatic nucleus.

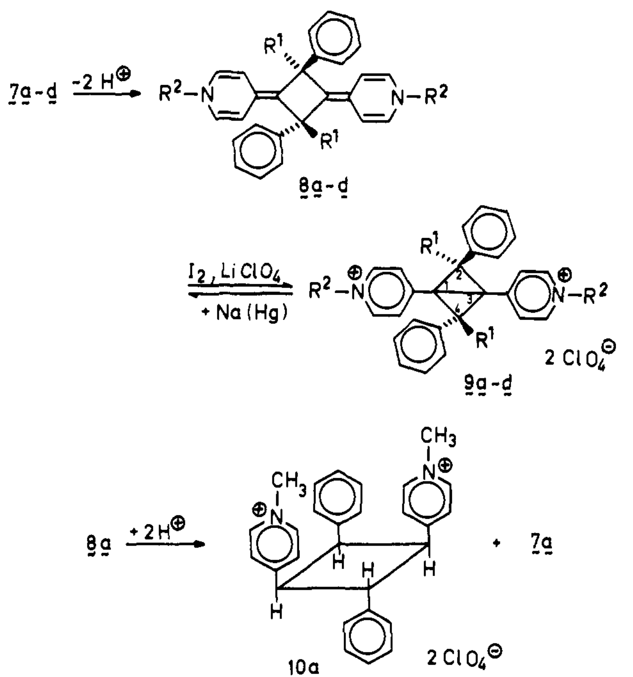
Cyclobutanes **5** and **6** were obtained by photodimerization of the corresponding styrylpyridines in dilute hydrochloric acid,[10,11] followed by treatment with base. In contrast to literature reports,[11] **5** and **6** may also be synthesized in high yields (**5**, 90%; **6**, 70%) by irradiation of the styrylpyridine hydro-

Scheme I



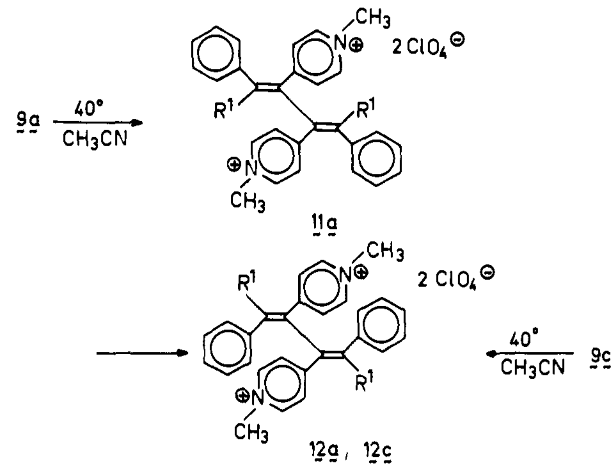
	R^1	R^2	X
7a	H	CH_3	I
7b	H	$C_6H_5CH_2$	Br
7c	CH_3	CH_3	I
7d	CH_3	$C_6H_5CH_2$	Br

chlorides in the solid state. The proposed structure and configuration of **5**[10,11] was confirmed by its ^{1}H NMR spectrum at 360 MHz.[12] Alkylation of **5** and **6** by methyl iodide or benzyl bromide yields smoothly the quaternary salts **7a-d**[13] (Scheme I). **7a** is also produced by photodimerization of 4-styrylpyridine methiodide in water[14] or in the solid state (80 and 89% yields), respectively.



8a[13] (79%, yellow crystals, mp 198-201 °C dec) is formed on addition of sodium hydroxide to a degassed aqueous solution of **7a**. Similarly, deprotonation of **7c** by sodium methoxy ethanolate and of **7b** and **7c** by sodium ethanolate at 0 °C yields **8b-d**:[13] **8b**, 65%, mp 202 °C dec; **8c**, 94%, mp 234-235 °C dec; **8d**, 83%, mp 216-218 °C dec. **8a** and **8b** rapidly turn green in air. Reprotonation of **8a** with aqueous acid produces a mixture of the stereoisomers **7a** and **10a**, from which **10a** can be isolated as its perchlorate (62%).

Solutions of **8a-d** in ethanolic lithium perchlorate react rapidly with iodine and the bicyclobutane derivatives **9a-d**[13] precipitate in high yields (NMR in Me_2SO-d_6): **9a**, 78%, mp 162-163 °C, δ (ppm) 8.82 (d, J = 6 Hz, 4 H), 7.92 (d, J = 6 Hz, 4 H), 7.38 (s, 5 H), 7.30-6.70 (m, 5 H), 5.63 (s, 1 H), 4.22 (s, 6 H), 3.53 (s, 1 H); **9c**, 58%, mp 167-170 °C, δ 8.95 (d, J = 6 Hz, 4 H), 7.98 (d, J = 6 Hz), 7.98-6.66 (m, 10 H), 4.48 (s, 6 H), 1.28 (s, 6 H; in pyridine δ 1.31, 1.24); **9b**, 65%, mp 243-245 °C; **9d**, 45%, mp 156 °C. Except for the signals of the N substituents, NMR spectra of **9b** and **9d** correspond to those of **9a** and **9c**. **9a-d** are the first examples of bicyclobutanes with aromatic substituents at each ring carbon atom.



The bridging bond in **9** is easily cleaved by reduction (e.g., with sodium amalgam in acetonitrile), regenerating the original 1,3-bismethylenecyclobutanes: **9a** → **8a** (80%), **9b** → **8b** (75%). These preparative results agree fully with the electrochemical redox behavior.[15] Reductive cleavage of **9c** and **9d** suffers from side reactions, although voltammetry and UV spectroscopy support reactions **9c,d** → **8c,d**.

Known bicyclobutanes isomerize thermally to butadienes at temperatures above 120 °C.[2] **9a-d** are less stable, being transformed to 1,4-diphenyl-2,3-di(4-pyridinium)butadienes **11** not only upon melting but also during recrystallization from water. The configuration of the products is consistent with an orbital symmetry controlled reaction.[16] From **9a** the *Z,Z* isomer **11a** (R^1 = H) is produced ($t_{1/2}$ = 45 min in CH_3CN, 40 °C), 90%, mp 280 °C, identified by the NMR absorption (Me_2SO-d_6, singlet at δ 6.62 ppm) of the olefinic protons. As shown by NMR, **11a** isomerizes slowly in Me_2SO-d_6 through an intermediate *E,Z* isomer to form the *E,E* isomer **12a** (R^1 = H), 75%, mp 205-207 °C dec, olefinic proton absorption (singlet at δ 8.15 ppm). This isomerization is thought to be base-catalyzed, because it is suppressed in Me_2SO-d_6/CF_3CO_2H (80/20). **9c** isomerizes much more slowly ($t_{1/2}$ = 19.5 h in CH_3CN, 40 °C) and the *E,E* isomer **12c** (R^1 = CH_3)[17] is observed as the only product. The remarkably mild conditions for the rearrangments **9** → **11** are probably due to the four aromatic substituents. From related examples of valence isomerizations,[17,18] phenyl substituents are known to lower activation energies considerably.

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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

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

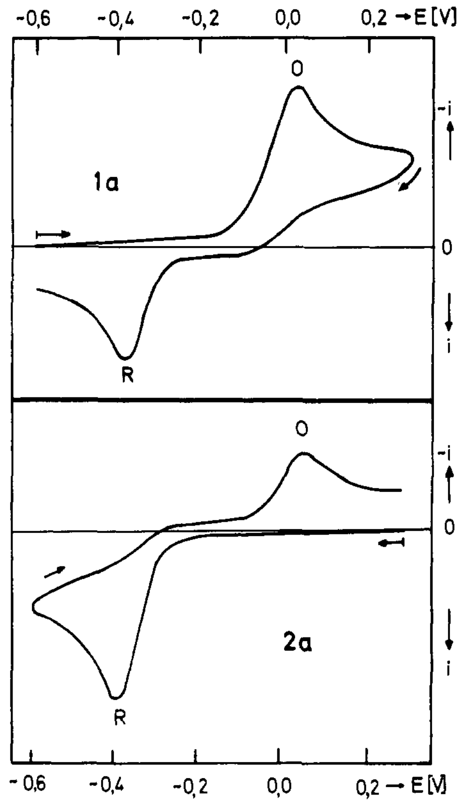
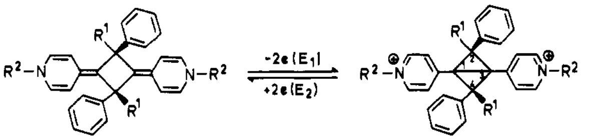


Figure 1. Cyclic voltammograms of **1a** and **2a** (200 mV/s; DMF/TBA • BF_4; Pt vs. Ag/AgCl/AN[13]).

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.



1 **2**

	a	b	c	d
R^1	H	H	CH_3	CH_3
R^2	CH_3	$C_6H_5CH_2$	CH_3	$C_6H_5CH_2$

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