Table I

	Reactant		
	1 or 2	**3**	**4**
	Temp, °C		
	165	168	169
	Catalyst : reactant wt ratio		
	7.0–8.6 : 1	5.4 : 1	7.5 : 1
	%		
Adamantane (**5**)	60		
1-Methyladamantane (**6**)		98	
2-Methyladamantane (**7**)		2	
1,3-Dimethyladamantane (**8**)			86
1-Ethyladamantane (**9**)[a]			7
1,X-Dimethyladamantane (**10**)[b]			7
Material recovery	98–100	98–100	98–100
Starting material	39	None	None
By-products	~1	None	None

[a] An authentic sample was synthesized from 2-(1-adamantyl)-acetic acid: K. Bott, *Angew. Chem., Int. Ed. Engl.*, **4**, 956 (1965); D. Grant, to be published. [b] This component was a mixture of 1,2-dimethyladamantane and *cis*- and *trans*-1,4-dimethyladamantane; *cf.* J. Vais, J. Burkhard, and S. Landa, *Z. Chem.*, **9**, 268 (1969); see also ref 3.

was obtained from either **1** or **2** or from mixtures of the two. Commencing with **1** there was initially a facile isomerization into **2** followed by adamantane formation. At the beginning of each run pure adamantane collected in the receiver, but as the reaction proceeded the catalyst suffered some deactivation; nevertheless, yields of up to 60% adamantane were realized with only *ca.* 1% by-product formation, so that the selectivity is almost as high as with the C_{11} and C_{12} cases. The problem of catalyst deactivation can be overcome by recycling the material, and the catalyst is easily reactivated by treatment first with a stream of oxygen at 500° and then by repeating the H_2–HCl–$SOCl_2$ procedure.

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D. E. Johnston, M. A. McKervey,* J. J. Rooney
Department of Chemistry, The Queen's University
Belfast, Northern Ireland
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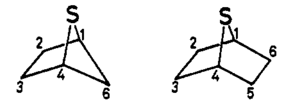
Carbon–Sulfur Bond Distances and Sulfur Valence Angles in 5-Thiabicyclo[2.1.1]hexane and 7-Thiabicyclo[2.2.1]heptane as Determined by Gas Electron Diffraction

Sir:

In a recent study of the acetolysis of 2-*endo*-chloro-7-thiabicyclo[2.2.1]heptane,[1] a change from an S_N1 mechanism to a mechanism of rate-determining solvent attack on the equilibrating sulfonium ion was observed. This drastic change in the rate-determining step may be closely related to the geometrical arrangement of the atoms in this molecule. A characteristic difference in the chemical shift observed for 5-thiabicyclo[2.1.1]hexane[2] may also depend on its structure. However, little is known about the structures of thiapolycyclics. Accordingly, we have made an electron-diffraction study of 5-thiabicyclo[2.1.1]hexane (I) and 7-thiabicyclo[2.2.1]heptane (II). Now we wish to report the



I II

significant differences observed in their C–S bond distances and C–S–C angles.

The samples, prepared by a method described elsewhere,[3] were vaporized[4] at 54 (I) and 104° (II) and diffraction photographs were taken[5] with 40-kV electrons at camera lengths of 11.3 and 24.9 cm. Molecular intensities ($10 \leq q \leq 110$) obtained by a standard process[6] were analyzed.[7]

The structural parameters listed in Table I were determined first from the radial distribution curves and then by a least-squares analysis,[6] with the following assumptions.[8] (1) Molecules I and II have C_s and C_{2v} symmetry, respectively. (2) The C_1–C_2 and C_2–C_3 distances are equal to each other and (for I) are shorter than the C_1–C_6 distance[9] by 0.034 Å. (3) All the C–H distances are equal. (4) All the C–C_1–H angles are equal. (5) All the H–C–H angles are equal. (6) The H–C_i–H plane (i = 2 and 6 for I and 2 for II) is perpendicular to the C–C_i–C plane, and the angles bisect each other. (7) The mean amplitudes of vibration (except for the bonded C–S amplitudes given in Table I) were estimated from those in norbornane[9] and used as constants. Uncertainties in the structural parameters originating from the above assumptions were estimated and included in the limits of error quoted in the table.

Table I. Geometrical Structures of I and II[a]

Parameter	I	II
r_g(C–S)[b]	$1.865_6 \pm 0.004$	1.837 ± 0.006
r_g(C–C)$_{av}$	$1.553_0 \pm 0.003$	1.549 ± 0.003
r_g(C_1–C_6)	$1.57_3 \; {}^{+0.01}_{-0.02}$	
r_g(C–H)$_{av}$	1.105 ± 0.008	1.108 ± 0.009
∠C_1–S–C_4, deg	69.7 ± 0.5	80.1 ± 0.8
θ[(C_1–S–C_4)–(C_1–C_2–C_3–C_4)],[c] deg	$115._2 \pm 3$	$122._4 \pm 1$
θ[(C_1–C_2–C_3–C_4)–(C_1–C_6–(C_5)–C_4)],[c] deg	$118._5 \pm 3$	$115._3 \pm 2$
l(C–S)[d]	0.061 ± 0.01	0.062 ± 0.01

[a] Uncertainties represent estimated limits of error. [b] Thermal-average bond distances in ångströms. [c] Dihedral angles. [d] Root-mean-square vibrational amplitudes.

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The C–S bond in I is found to be much longer than those in II, tetrahydrothiophene[10] (1.839 ± 0.002 Å), or dimethyl sulfide[11] (1.802 ± 0.002 Å); *i.e.*, I > II ≈ tetrahydrothiophene > dimethyl sulfide. The C–S–C angle in I is smaller than that in II by as much as 10° and contrasts with the corresponding angles in tetrahydrothiophene (93.4 ± 0.5°) and dimethyl sulfide (98.9 ± 0.2°); *i.e.*, I < II < tetrahydrothiophene < dimethyl sulfide. Analogous trends have been observed in the related hydrocarbons bicyclo[2.1.1]-hexane[12], norbornane,[9,13] cyclopentane,[14] and propane,[15] where the carbon valence angles corresponding to the above C–S–C angles are 85.4, 93.1 (or somewhat larger[13]), 102–106 (pseudorotation), and 112.4°, respectively.

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Tsutomu Fukuyama, Kozo Kuchitsu*
Department of Chemistry, Faculty of Science
The University of Tokyo, Bunkyo-ku, Tokyo, Japan

Yoshinao Tamaru, Zenichi Yoshida, Iwao Tabushi
Department of Synthetic Chemistry
Kyoto University, Kyoto, Japan

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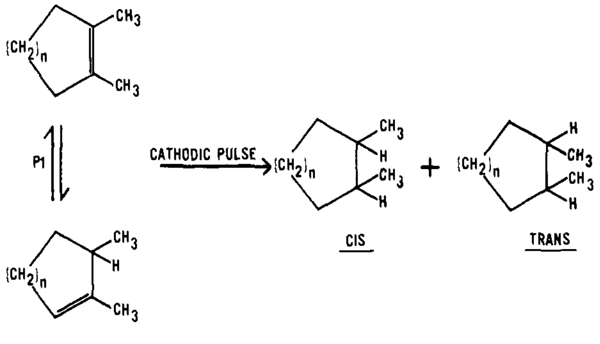
Molecular Rearrangement of a Cyclic Olefin at a Fuel Cell Electrode

Sir:

While investigating the adsorption and reactions of various cyclic olefins at fuel cell electrodes, a molecular rearrangement has been observed involving a one-carbon ring expansion of a dimethyl-substituted cyclopentene.

The products expected from cathodically pulsing an electrocatalyst upon which a 1,2-dimethylcycloolefin has been adsorbed are the corresponding *cis*- and *trans*-1,2-dimethylcycloalkanes.[1] These products have



been obtained under heterogeneous catalysis conditions for both dimethylcyclopentene[2,3] and dimethylcyclohexene,[3,4] and under conditions of electrocatalysis for dimethylcyclohexene.[5] Although both *cis*- and *trans*-1,2-dimethylcyclopentane are obtained on cathodically pulsing an electrocatalyst which has been in contact with 1,2-dimethylcyclopentene,[5] a competing reaction, highly dependent upon adsorption potential, has been observed.

The experimental apparatus has been described previously.[6] The working electrode was an LAA25 American Cyanamid type consisting of 25 mg/cm^2 of platinum black bonded with 25% Teflon on a tantalum screen and having a geometrical area of 20.2 cm^2. The electrolyte, 85% H_3PO_4, was maintained at 120° and contact to the reference electrode compartment was effected through a Luggin capillary. Water vapor losses from the electrolyte, due to the elevated working temperature, were replenished by passing humidified inert gas into the cell. The humidifier was kept at 69–70°, thus equalizing the water vapor pressure in both humidifier and cell. Potentials were measured against the dynamic hydrogen electrode[7] which was typically 40 mV cathodic to the normal hydrogen electrode in the same electrolyte. The working electrode potentials were controlled by a Wenking 66TS3 potentiostat monitored with a Keithley 610B electrometer, and galvanostatic pulses were obtained with a Kepco CK8-5M power supply.

A potential-step technique was used to prepare a reproducible catalyst surface.[8,9] The working electrode was initially held at 1.35 V under oxygen-free helium until the observed current had decreased to 10 mA to oxidize any adsorbed impurities. The potential was then decreased to 0.05 V for 20 min to reduce the oxide film. The electrode was then set at the adsorption potential and the hydrocarbon passed over the electrode in a helium carrier gas at a flow rate of 1.4×10^{-6} mol/min. Steady state was achieved in approximately 1 hr, after which reactant olefin was swept from the lines with helium. Cathodic pulsing of the electrode at a current of 1.0 A desorbed the hydrocarbons which were then trapped in chromatoquality *n*-octane.

Product separation and identification were accomplished with a 5750 Hewlett Packard gas chromatograph on a 20-ft Carbowax column at 81°, or with a Perkin-Elmer Model 154D vapor fractometer employing a 6-ft squalane column at various temperatures from 62 to 120°. The reactant olefin (K and K Laboratories) was determined to be 99% pure, with the major impurities being isomeric species. The absence of any six-membered-ring compounds, both saturated and unsaturated, in the reactant was verified by gas chromatography.

cis- and *trans*-1,2-dimethylcyclopentane were the principal products obtained upon cathodically desorbing hydrocarbons from a fuel cell electrode which had been maintained at 0.30 V during contact with 1,2-dimethylcyclopentene. 1,2-Dimethylcyclopentene isomerizes during adsorption to give an equilibrium mix-

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[1] On passing a 1,2-dimethylcycloolefin over the electrocatalyst, an equilibrium is established between the 1,2- and 2,3-dimethylcycloolefins. Thus the *cis*- and *trans*-dimethylcycloalkanes produced are the result of cathodically pulsing an electrode which has been in contact with an equilibrium mixture of isomeric olefins.

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