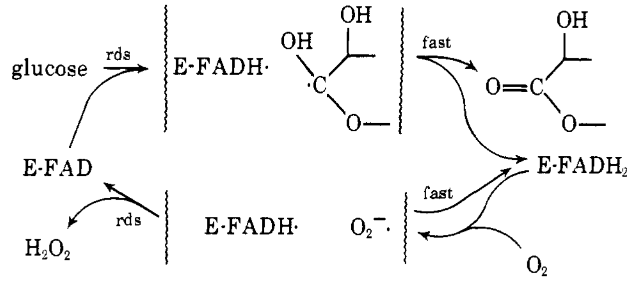
mal substrates of the enzymes.[8,16,17] If a radical pair formed from enzyme bound flavin and substrate were an intermediate then there should be no expectation that enzyme radical would react with substrate.

The results of this study establish one electron transfer mechanisms for reduction of glucose oxidase by furoin and its reoxidation by nitroxide (model substrates for glucose and O_2, respectively). On the basis of these results, the partial mechanism of Scheme I does not appear to be unreasonable for the glucose reduction of glucose oxidase and O_2 oxidation of reduced glucose oxidase.

Scheme I



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(13) Glucose oxidase was dissolved in phosphate buffer (0.01 M, pH 8, μ = 1 with KCl); 100 μL each of 0.1 M glucose and 0.1 M nitroxide solution were added. The pink enzyme radical so obtained was purified by Sephadex Chromatography (G25, medium).
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Preparation, Dipole Moment, and Quadrupole Coupling Constants of 2*H*-Azirine

Sir:

Derivatives of 2H-azirine have been prepared by pyrolysis[1] and photolysis[1,2] of substituted vinyl azides, but the unsubstituted compound was not previously known. We have prepared 2*H*-azirine by flash vacuum pyrolysis and have characterized it by its pure rotational spectrum.

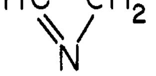

Table I. Microwave Spectrum of 2*H*-Azirine[a]

Transition	Obsd frequency (MHz)	Calcd frequency (MHz)
$1_{01} \leftarrow 0_{00}$	37 288.52	37 288.53
$1_{10} \leftarrow 1_{01}$	20 550.63	20 550.62
$2_{11} \leftarrow 2_{12}$	21 476.73	21 476.73
$2_{11} \leftarrow 2_{02}$	29 902.88	29 903.49
$3_{13} \leftarrow 2_{20}$	36 067.20	36 068.55
$4_{22} \leftarrow 4_{23}$	25 045.93	25 048.87
$6_{33} \leftarrow 6_{34}$	25 326.90	25 335.75
$8_{44} \leftarrow 8_{45}$	23 586.67	23 603.95
$10_{55} \leftarrow 10_{56}$	20 756.66	20 783.78

[a] These frequencies have been corrected for quadrupole splittings.

Table II. Rotational Constants (MHz) and Moments of Inertia (amu Å^2) of 2*H*-Azirine

	Exptl	STO-3G
A	35615.43	35005
B	22223.72	22678
C	15064.81	15152
I_a	14.18989	14.437
I_b	22.74052	22.285
I_c	33.54699	33.354
$I_c - I_a - I_b$	−3.38342	−3.368

Vinyl azide, prepared by the method of Wiley and Moffat,[3] was passed through a 10 cm length of 12 mm heated quartz tubing. The products were immediately pumped through the absorption cell of a Stark-modulated microwave spectrometer. The pressure was estimated to be between 10 and 100 mT and the Stark cell temperature was at either room temperature or the temperature of dry ice. The intensity of the rotational spectrum of vinyl azide was seen to decrease as the quartz tube was heated above 200 °C and new absorption lines appeared. At 400 °C the vinyl azide lines had virtually disappeared and the new lines were of maximum strength.

The frequencies of the new lines were compared to those previously observed and tabulated in the National Bureau of Standards Microwave Spectral Tables.[4] A series of lines due to acetonitrile was assigned, but other strong lines could not be assigned to any known compound.

On the basis of resolved Stark effects, the transitions in Table I were assigned to a species with rotational constants and moments of inertia listed in Table II. This table also lists the rotational constants calculated for 2*H*-azirine based on the optimized structure calculated by Lathan et al.[5] using ab initio methods with the STO-3G basis set.

All of the assigned lines were found to be multiplets when observed under the best resolution available. The splittings were measured and attributed to the effect of a single nitrogen nucleus in the molecule with quadrupole coupling constants χ_{aa} = 1.04 MHz, χ_{bb} = −3.43 MHz, and χ_{cc} = 2.39 MHz.

Measurement of the Stark effects of four of the transitions gave the following values of the principal axes components of the dipole moment (in D): $\mu_a = 0.54 \pm 0.02$ and $\mu_b = 2.07 \pm 0.04$. The total dipole moment is thus 2.14 ± 0.05 D. Ab initio calculations[5] using the 6-31G basis set with the STO-3G optimized geeometry gave a dipole moment value of 2.56 D.

Some rotational transitions of the compound with ^{15}N and ^{13}C isotopes in natural abundance have been assigned and found to be consistent with the STO-3G calculated structure. Complete assignments including the weaker a-type rotational transitions will probably require enriched samples.

In the rigid rotor approximation, a molecule, with all atoms in the A-B plane, has a value of $I_c - I_a - I_b = 0$. For molecules with light atoms out of plane, the value of $I_c - I_a - I_b$ indicates the amount of mass out of plane. The assumed 2*H*-azirine structure has two hydrogen atoms out of plane as do the closely related molecules cyclopropene and diazirine. $I_c - I_a - I_b$ for 2*H*-azirine is −3.383 amu Å^2 whereas for the latter two molecules, −3.333 and −3.478 amu Å^2 were obtained.[6,7]

All of the above evidence obtained from the microwave spectrum is consistent with the proposed cyclic structure of 2*H*-azirine. The stability of the compound is somewhat greater than initially expected as it can be trapped at liquid nitrogen temperature and revaporized. Decomposition to acetonitrile apparently occurs in benzene and cyclohexane solution thus far preventing observation of its NMR spectrum.

Photolysis of vinyl azide in the same apparatus with the addition of a 450-W Hanovia 379A36 mercury lamp resulted in a very small yield of 2*H*-azirine along with acetonitrile, propionitrile, and ammonia.

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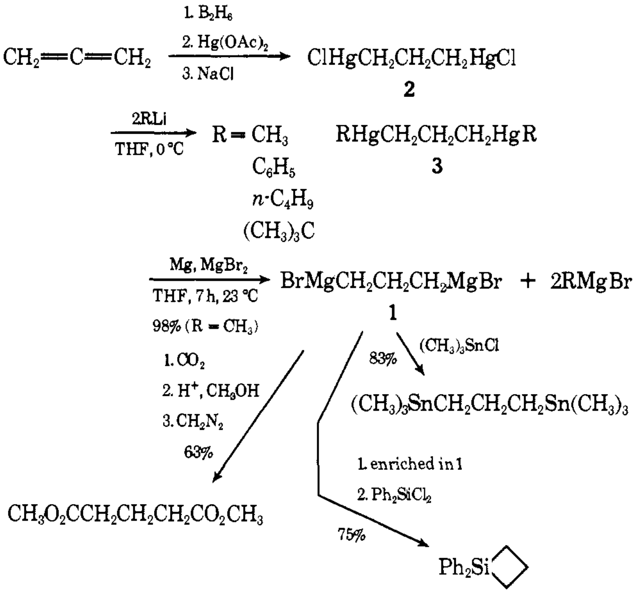
Propane-1,3-di(magnesium halide)[1]

Sir:

Metallocyclic compounds are intermediates in a number of interesting metal-catalyzed reactions.[2] A useful method for preparing authentic metallocycles having rings of five or more members for mechanistic studies is the reaction of a metal halide with an alkane-α,ω-dimagnesium or -dilithium reagent. It has not been possible to prepare four-membered metallocycles—metallocyclobutanes—by this procedure, since the requisite dimagnesium or dilithium reagents have not been available: reaction of 1,3-dihalopropanes with magnesium or lithium yields primarily cyclopropane, and does not generate propane-1,3-dimetal compounds.[3,4] We report here a preparation of propane-1,3-di(magnesium halide) (**1**), and illustrate its usefulness in the preparation of metallocyclobutanes by syntheses of 1,1-dimethyl- and 1,1-diphenylsilacyclobutane (Scheme I).

Hydroboration-mercuration[5] of allene gave propane-1,3-di(mercury(II) chloride) (**2**). Attempts to convert **2** directly to **1** by transmetalation[6] with magnesium, or to propane-1,3-dilithium by reaction with lithium, produced only an unreactive, insoluble mixture of polymeric dialkylmercury compounds. To prevent the formation of these compounds on exposure of the propane-1,3-dimercury(II) moiety to magnesium, **2** was first treated with 2 equiv of an organolithium reagent, RLi, and converted to *soluble* dialkylmercury reagents (**3**).[7,8] Treatment of **3** with magnesium powder in THF containing magnesium bromide (prepared in situ by reaction of magnesium with 1,2-dibromoethane) yielded a mixture of **1** and monofunctional organomagnesium reagents, RMgX.

Scheme I. Preparation, Isolated Yields, and Reactions of Propane-1,3-di(magnesium halide) (1) and Related Compounds



The composition of these mixtures of organomagnesium reagents was assayed by addition of an excess of trimethyltin chloride, and GLC examination of the resulting organotin compounds. In a typical reaction sequence carried through using methyllithium to convert **2** to **3** (R = CH$_3$), the organotin compounds detected were (GLC yields, %, based on **2**): $(CH_3)_3SnCH_2CH_2CH_2Sn(CH_3)_3$ (98), $(CH_3)_4Sn$ (100), $CH_3CH_2CH_2Sn(CH_3)_3$ (2), $CH_2{=}CHCH_2Sn(CH_3)_3$ (<1). Control experiments established that the conditions used in these assays converted *n*-decylmagnesium bromide to *n*-decyltrimethyltin quantitatively. The presence of **1** was confirmed by isolation of dimethyl glutarate in 63% yield following carbonation and esterification, and by preparation of 1,1-dimethylsilylcyclobutane in 66% yield (GLC), and 1,1-diphenylsilylcyclobutane in 75% yield (isolated) following reaction with the appropriate diorganosilicon dihalides (Scheme I).[9]

The unsymmetrical dialkylmercury compounds (**3**) could be isolated. For preparative reactions, however, isolation was not necessary: when a suspension of 1.0 equiv of **2** and 30 equiv (a large excess) of magnesium powder in THF was treated in sequence with 2.0 equiv of an organolithium reagent and 2.0 equiv of 1,2-dibromoethane, and the resulting mixture allowed to stir for 7 h at room temperature, **1** was generated in yields that depended on the structure of the organolithium reagent used (yield of **1**, %, based on **2**): CH_3Li (98), C_6H_5Li (95), *n*-C_4H_9Li (80), $(CH_3)_3CLi$ (60). For most preparative work, **3** (R = CH$_3$) was the most convenient material with which to work. The preparation of **1** by this procedure is necessarily accompanied by the formation of 2 equiv of monofunctional Grignard reagent (RMgX). For further reactions with monofunctional substrates, use of this mixture presented little difficulty, since the products were easily separated. For metallocyclobutane formation, however, it was desirable to use a solution of **1** which contained less RMgX. Two techniques produced solutions which were enriched in **1**. In the first, addition of diethyl ether to the reaction mixture in THF resulted in the separation into two phases, with **1** concentrated in the lower. Removal of the upper layer, solution of the lower layer