7 is positive ($\Delta H° = 13.2$ and $\Delta G° = 7.6$ kcal for the pure liquids), which makes this process light energy storing.

The mechanism derived from the laser photolysis studies is corroborated by results obtained from continuous illuminations of alcoholic benzophenone solutions. These were carried out with light of a XBO 450-W xenon lamp which was passed through water and a Corning CS 7-51 interference filter. The latter transmits in the 320–380-nm region allowing for selective excitation in the n-π* absorption band. The irradiation vessel contained ~24 mL of solution and was equipped with a septum through which gas samples could be taken for chromatographic analysis. A Gow-Mac thermal conductivity detector with a limit of 0.1 μmol was used for hydrogen analysis. The ferrioxalate actinometry gave a value of 1×10^{18} quanta/min for the light flux.

In Figure 2 spectrophotometric data obtained prior and after irradiation of samples with and without catalyst are compared. In the case of the Pt-free solution a photolysis time of 30 min suffices to remove >70% of the benzophenone absorption at 260 nm. In striking contrast to this result, one finds practically no depletion of $Ph_2C{=}O$ under illumination if the Pt catalyst is present in solution. (The turnover number for benzophenone is ~2 after this irradiation time.) Instead, hydrogen is evolved, which is readily shown by the gas chromatographic analysis. From this, we infer that the catalyst can intervene efficiently to prevent the ketyl radical dismutation or recombination making feasible water reduction via eq 6. The quantum yield for H_2 production in this system was found to be 0.9 ± 0.1, showing that the water reduction occurs stoichiometrically.

In conclusion, we find that, in the presence of Pt catalyst, benzophenone sensitizes the dehydrogenation of 2-propanol to acetone. Although a similar catalytic system has been reported previously,[8] it was necessary in the latter case to add an electron relay, such as V^{3+} or Eu^{3+} which produced H_2 after scavenging the ketyl radicals. The importance of the findings presented here lies in the fact that the finely dispersed colloidal Pt particles can operate on the radical reaction itself to produce hydrogen selectively.

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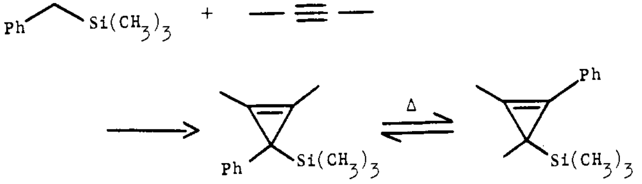
Trimethylsilyl Shifts in Cyclopropenes[1]

Sir:

Although the sigmatropic shift has been known as an important class of "no mechanism" reaction for 15 years,[2] and migrations in small rings found to be commonplace,[3] there exists but one report of such a reaction in a cyclopropene.[4,5] Moreover, in this lone example intramolecularity has not demonstrated. Although such shifts have been specifically considered in simple systems, they have not been found. 3,3-Dialkylcyclopropenes undergo thermal ring opening to vinylcarbenes without prior sigmatropic shift.[6] 3-Aryl-1,2,3-triphenylcyclopropenes rearrange apparently without formation of the 2-arylindenes which would signal a shift of phenyl in the original cyclopropene.[7] We describe here the relatively rapid rearrangement of the trimethylsilyl group in cyclopropenes.

Phenyltrimethylsilylcarbene[8] was allowed to add to 2-butyne to produce cyclopropene **1**.[9] Pyrolysis of **1** in benzene-d_6 in sealed ampules at 117–148 °C, as monitored by nuclear magnetic resonance and gas chromatography, revealed a clean equilibration with a new cyclopropene, **2**.[9] Measurements at four temperatures for at least 2 half-lives over a 30 °C range gave the following activation parameters for the forward and reverse reactions: forward (**1** → **2**), $E_a = 31.22 \pm 0.52$ kcal/mol, log $A = 12.06 \pm 0.10$; reverse (**2** → **1**), $E_a = 32.80 \pm 0.52$ kcal/mol, log $A = 12.16 \pm 0.25$. The activation energy for this new rearrangement thus falls squarely in between that for 1,3 trimethylsilyl shifts in simple allyl systems ($\Delta H^{\ddagger}$ = 41–46 kcal/mol)[3] and the 1,5 trimethylsilyl shift in 5-trimethylsilylcyclopentadiene ($\Delta H^{\ddagger}$ = 13.0 kcal/mol).[10]



1 **2**

For this new reaction to be considered a true sigmatropic shift of the trimethylsilyl group, it must obviously be shown that it is indeed the trimethylsilyl group that migrates and that the reaction is intramolecular. The first point is less simple than it seems. Although there is no evidence for phenyl shifts in cyclopropenes,[7] there does not appear to have been a concerted search for the reaction, and the phenyl ring is known to be a good migrating group.[3]

The distinction between **2** and the product of a phenyl shift, **3**, was made using ^{13}C and ^{29}Si NMR. In going from compound **1** to **2**, one expects a relatively large upfield shift at C_a as phenyl is replaced by methyl,[11a] and an upfield shift for C-1 of the benzene ring (C_b) in moving from the 3 position to the 1 position on the cyclopropene.[11b] This is in fact exactly what is observed: C_a shifts from 23.3 to 14.5 ppm and C_b from 150.0 to 130.6 ppm.

We predict just the opposite effects for the hypothetical compound **3**. Here we would expect small downfield shifts for both C_a and C_b. Thus both the methylene and substituted aromatic carbons in benzyltrimethylsilane[12a] appear at higher field than the corresponding positions in ethylbenzene.[12b]

Confirmation of the assignment of structure **2** was obtained by ^{29}Si NMR. The ^{29}Si resonances and **1** and **2** appeared at 1.18 and 1.84 ppm downfield from $(Me)_4Si$, respectively. Attachment of the trimethylsilyl group to a vinyl carbon as in **3** should result in a substantial upfield shift of the silicon resonance relative to **1**.[13] For instance, the ^{29}Si signal in trimethylvinylsilane appears at −6.8 ppm, 8.4 ppm upfield from that of ethyltrimethylsilane.[13]

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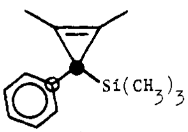

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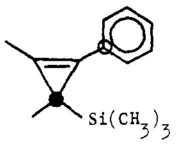
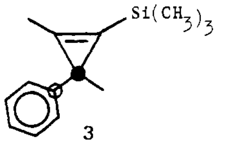


2

	1	2
● C_a (ppm)	23.3	14.5
○ C_b (ppm)	150.0	130.6
^{29}Si (ppm)	1.18	1.84



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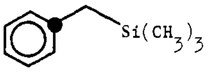
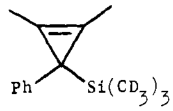


● (ppm)	140.16	144.1
$\underline{C}H_2$ (ppm)	26.94	29.2

The intramolecular nature of the reaction was demonstrated by a classical "crossover" experiment. Copyrolysis of 94.3% deuterated **4** and cyclopropene **5** for 10 half-lives, followed by gas chromatographic separation of the $C_{14}H_{20}Si$ and $C_{18}H_{28}Si$ components, showed no loss of deuterium in **4** or its isomer, $C_{14}D_9H_{11}Si$. There was no deuterium incorporation observed in **5** or its isomerization product.



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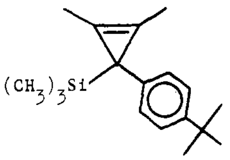

5

Furthermore, changing the solvent for pyrolysis of **1** from benzene-d_6 to benzene-d_6-nitrobenzene-d_5 (2:1) did not change the rate significantly. We conclude, therefore, that the process is intramolecular and proceeds without ionic intermediates.

It remains to determine the sterochemistry of the migration as well as the effect of other metals on the rate and to probe the application of this reaction to more complicated systems.

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Reactions of Superoxide in Aprotic Solvents. A Superoxo Complex of Copper(II) *rac*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane

Sir:

Understanding the nature of the interaction between copper and dioxygen (or species derived from it such as superoxide or peroxide) has been a continuing and often frustrating challenge to chemists[1] and biochemists[2] for many years. The few stable characterized copper dioxygen complexes are binuclear μ-peroxo species of the type $[Cu^{II}-O_2^{2-}-Cu^{II}]$ which are formed by reaction of Cu(I) with O_2.[3-5] Although 1:1 copper–dioxygen complexes have been proposed as intermediates in Cu(I) autoxidation reactions[1] and in reactions of Cu(II) with superoxide in aqueous media,[6] no 1:1 complexes have ever been directly detected by spectroscopic or other techniques. Presumably the 1:1 complex $[CuO_2]^+$ reacts rapidly with either Cu(I) or protons and therefore is not observed when these species are present.[1] We have taken a different experimental approach to the problem of synthesizing 1:1 complexes of dioxygen and copper. We react complexes of Cu(II) with superoxide in aprotic media to generate such species in the absence of Cu(I) or available protons. We have found that the choice of Cu(II) complex is critical because most previously studied Cu(II) complexes are reduced by superoxide to produce Cu(I) and dioxygen.[7-9] The complex we chose to study, therefore, was the perchlorate salt of the N_4 macrocyclic complex Cu(tet b)$^{2+}$ [10] which has a relatively low reduction potential[11,12] and an affinity for an additional anionic ligand.[13-15] Such factors are in part responsible for the recent successful synthesis of a stable Cu(tet b)$^{2+}$–thiolate complex.[15] We report here the characterization of a solution species best formulated as an ESR-silent pentacoordinate superoxide complex of Cu^{II} tet b synthesized by reaction of superoxide with Cu(tet b)$^{2+}$ in Me_2SO.

Addition of 18-crown-6 solubilized KO_2 (0.1 M)[7,8] to solutions of Cu(tet b)$(ClO_4)_2$[16] (1-5 mM) in Me_2SO caused the purple solutions to turn immediately to a dark forest green. The resulting solution was stable for several days in the absence of excess superoxide. The long-wavelength absorption band at 672 nm[17] (see Table I) that appeared upon reaction of Cu(tet b)$^{2+}$ with O_2^- is characteristic of $Cu^{II}N_4X^+$ chromophores where N_4 = tet b or 4,11-diene[10] and X^- = RS^-,[15] Cl^-,[14] or CN^- [13] (see Table I) and has been assigned as a ligand field transition of these low symmetry five-coordinate Cu(II) complexes. Similar spectra were obtained from reaction of Cu(tet b)$^{2+}$ with solutions of $(NEt_4)F$ or $(NBu_4)OH$ in Me_2SO or CH_3CN (see Table I) and are presumed to result from the corresponding X^- = F^- and OH^- species. The similarity of the visible spectra of the products formed by reaction with O_2^-, F^-, and OH^- implies that they are all structurally similar five-coordinate complexes. When an excess of O_2^- (>2 equiv), OH^- (>1.5 equiv), or F^- (>5 equiv) was added to the Cu(tet b)$^{2+}$ solution, the green color slowly turned to brown, the visible spectra had no distinct maxima, and, in the case of OH^-, the ESR signal due to Cu(II) disappeared. The strong basicity of O_2^-, F^-, and OH^- in Me_2SO solutions[8,18] suggests

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