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 (14) The predominance of rearrangement of **7** to **10** cannot be rationalized in terms of a more favorable allyl migration outpacing an A-ring cyclization having an intrinsic rate comparable to that of a hexa-1,5-diene 1,2-oxide, as indicated by the fact that the analogous product (**13**) from **2** is the major one, despite the absence of any allylic phenomenon.
 (15) In that (anchimerically unassisted) solvolysis of pent-4-enyl sulfonate does not give rise to the relatively high energy cyclopentyl cation,^{16,17} it might be assumed that the low yield, and therefore low cyclization rate, of **1** is due to an equally high ΔH^\ddagger for formation of an analogous cationic species. Although this factor may contribute, it should be pointed out that the starting material **1** features epoxy oxygen as the triggering group, a comparatively high energy unit which should result in a distinctly lower ΔH^\ddagger than that of the pent-4-enyl sulfonate solvolysis. Similarly, this effect may overshadow any energy differences due to varying steric contributions of substituents in the formation of cyclopentyl and cyclohexyl cationic types in the cyclization of **1** and squalene oxide (or related systems), respectively.
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 (20) Binding without subsequent cyclization, and the absence of binding, presumably differentiable through appropriate competitive inhibition experiments with **1**, **2**, and squalene oxide, can both be thought of as possible consequences of the same special character and specificity of the enzyme postulated above, based upon the presence in the natural substrate of epoxide and π -bond moieties a prescribed distance apart.

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 Received April 27, 1977

Inelastic Electron Tunneling Spectroscopy of a Chemically Modified Surface

Sir:

Chemical modification of metal oxide surfaces for electrochemical purposes has attracted a considerable amount of attention since the first report by Murray.¹⁻⁵ The modifications can be performed in a controlled manner using commercially available silane derivatives and the technique provides a novel approach for studying and controlling surface reactions. Fundamental to this objective, however, is the need to understand clearly the bonding and structural aspects of the bonded molecules. Thus, it becomes attractive to take advantage of the very sensitive inelastic tunneling spectroscopy (IETS), which will give vibrational structure information of organic monolayers on metal oxide surfaces. The silylation approach of covalently bonding organic moieties to a metal oxide surface provides an alternative to the vapor and liquid phase surface doping techniques⁶ generally used in IETS studies. We now present some preliminary results of such a study.

The metal/insulator/metal sandwiches of 1-mm² cross section were prepared on clean 10 × 15 mm glass slides. First an aluminum strip 1 mm wide was vacuum evaporated using the appropriate shadow mask and immediately oxidized by admitting pure oxygen into the vacuum system. The plate was next immersed in an anhydrous benzene solution containing the molecule of interest, for example triethoxyvinylsilane (1% v/v) and allowed to stand for 5 min. The excess reagent was removed by rinsing the plate with six portions of fresh benzene. The entire silylation process was carried out under an anhydrous nitrogen atmosphere since the presence of trace amounts of moisture will generate thick polymeric films. A 1-mm-wide strip of lead was subsequently evaporated for the counter

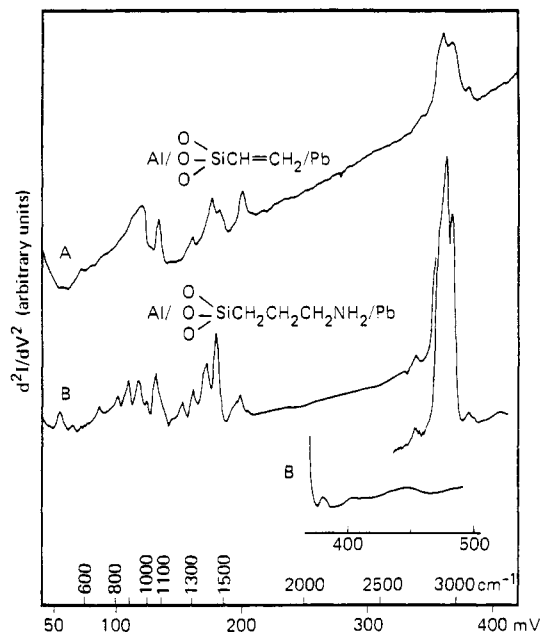


Figure 1. Tunneling spectra at 4.2 K of covalently bonded vinylsilyl (A) and 3-aminopropylsilyl (B) derivatives.

electrode. The junction resistances were in the range of 50–5000 Ω/mm^2 . The junction was next mounted for cooling to 4.2 K as previously described.⁶

As can be seen in Figure 1, good tunneling spectra (d^2I/dV^2 vs. V) are obtained of the organic material when it is introduced into the sandwich junction by a chemical reaction as an alternative to the normal⁶ doping procedures. The IETS spectrum for the vinylsilyl derivative (A) is relatively simple and compares well with the IR spectrum for trichlorovinylsilane.⁷ While not shown in Figure 1, plot A reveals only a very small broad peak in the region near 3600 cm^{-1} suggesting the extensive removal of surface OH groups.⁶ Of particular interest is the presence of bands at 1070, 2853, and 2944 cm^{-1} which indicates the presence of $-\text{OCH}_2\text{CH}_3$ groups on the surface. When the aluminum surface is silylated with excess triethoxyvinylsilane and not rinsed, then these bands become much stronger plus other weaker bands appear as expected. The simplest conclusion is that some ethoxy groups survive the silylation reaction and remain intact as $\text{Si}-\text{O}-\text{CH}_2\text{CH}_3$. This result shows that during the reaction of the triethoxysilyl derivative with the surface some $\text{Si}-\text{OCH}_2\text{CH}_3$ groups remain and may be available for reaction with Lewis bases. The region 800–1100 cm^{-1} is not well resolved which is unfortunate since it could provide some insight into the $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{O}-\text{Al}$ bonding structure.⁸

The spectrum for the 3-aminopropylsilyl derivative (B) shows somewhat better resolution than the IR spectrum for the starting material, 3-aminopropyltriethoxysilane.⁷ The major difference is the position and the weakness of the N–H stretching bands at 3320 and 3250 cm^{-1} which are displaced to lower frequencies by $\sim 80 \text{ cm}^{-1}$. While this shift is appropriate for the presence of intermolecular hydrogen bonding,⁸ it is dangerous to draw definite conclusions on the molecular structure of the 3-aminopropylsilyl insulator layer without understanding clearly the influence of the deposited lead contact.

Silylation of the aluminum oxide surface using 3-(2-aminoethylamino)propyltrimethoxysilane also produced a good sandwich junction and the resulting IETS spectra is similar to that of the 3-aminopropylsilyl derivative. A general observation is that the resistivity of the junction increases with increasing molecular size of the covalently bonded molecule suggesting that this factor may be a limitation for studying

large molecules of this type by IETS. Our current effort focuses on studying chemical derivatives of these type of surface-bonded structures.

Acknowledgments. The authors wish to thank M. Ochoa and A. Poenisch for their technical support.

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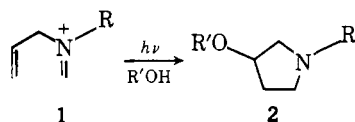
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Received May 9, 1977

Photochemistry of *N*-Allyliminium Salts. A Novel Photocyclization Reaction Leading to Pyrrolidines

Sir:

The photochemistry of unsaturated hydrocarbons containing nonconjugated π chromophores linked through saturated carbon chains remains as one of the more interesting areas of organic chemistry. The number of unique molecular transformations observed have served as the basis for elucidation of the mechanistic details of excited-state reactions and for the synthetic utility of organic photochemistry. The di- π -methane rearrangement,¹ which transforms compounds containing the 1,4-pentadiene grouping to vinylcyclopropanes, and intramolecular [2 + 2] cycloaddition reactions of 1,5-hexadienes and higher homologues² stand as exceptionally general examples of this point. Our interest in this area of photochemistry led recently to an exploration of the excited-state chemistry of compounds containing the *N*-allyliminium salt functionality (**1**) in which one of the two nonconjugated π moieties is part of the imine (C=N) group. We wish to report the preliminary results of this investigation which demonstrate that these systems undergo a novel cyclization process to produce pyrrolidines, a reaction of potential synthetic and mechanistic interest.



Initial investigations were conducted using the 5-phenyl-2-isobutenyl-1-pyrrolinium salts, **10** and **11**, prepared by sequences starting with the known³ 2,4,4-trimethyl-1-pyrroline 1-oxide (**3**). Isobutenylmagnesium bromide⁴ was added to **3** (THF, reflux) to produce the hydroxylamine **4** (70%, mp 42–44 °C)⁵ which was converted to the nitron **8** (HgO, CHCl₃, 98%). Addition of phenylmagnesium bromide to **8** (Et₂O, reflux) gave the 5-phenyl-1-hydroxypyrrolidine **5**^{6a} which was subsequently reduced (LiAlH₄, AlCl₃, Et₂O, 96%) to pyrrolidine **6** and chlorinated (NCS, Et₂O, 100%) furnishing the *N*-chloramine **7** as a mixture of diastereomers.^{6b} Dehydrochlorination was performed using methanolic KOH and provided the 5-phenyl-2-isobutenyl-1-pyrroline (**9**, 72% after silica gel chromatography). The tetramethyl-1-pyrrolinium perchlorate (**10** (mp 126–127 °C) was derived from **9** by reaction with methyl iodide (EtOH, reflux) followed by per-

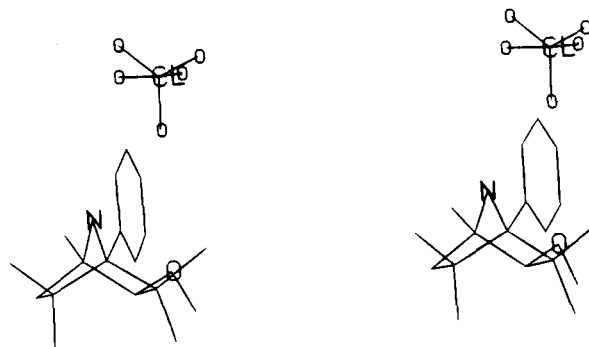
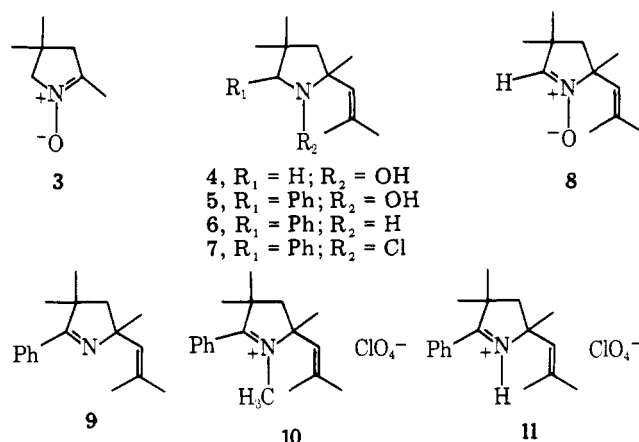


Figure 1. Unretouched photograph of stereodisplay of atomic coordinates and connectivity of the ammonium perchlorate derivative of **12**, taken on a Vector General Graphic System, programmed by S. M. Swanson and C. Morimoto. All unlabeled atoms are carbons. The perchlorate ion is shown as it appears with inversion disorder.

chlorate anion exchange (Dowex 1-X8, 38%). Generation of the protonated 1-pyrrolinium salt **11** was performed prior to irradiation by addition of 70% aqueous HClO₄.⁷



Irradiation of a solution of **11** (4.3 mM, from **9** and 2 equiv of HClO₄) in methanol using Corex-filtered light^{8a} led to consumption of the starting material and simultaneous production of a major photoproduct **12** which was isolated in pure form (44%)^{8b} by neutralization (saturated NaHCO₃) and concentration of the photolysate followed by silica gel TLC (50% Et₂O-hexane). Identification of **12** as 1,3,3,5,5-pentamethyl-2-*exo*-methoxy-4-phenyl-7-azabicyclo[2.2.1]heptane was made on the basis of spectroscopic data and by single-crystal x-ray diffraction⁹ of its ammonium perchlorate derivative (mp 288–290 °C, from CHCl₃) (Figure 1).¹⁰ Photolysis of **11** (4.3 mM) in 25% aqueous acetonitrile was shown to follow a similar course; workup of the crude photolysate in the manner described above followed by preparative GLC (OV-101, 170 °C) gave the *exo*-azabicycloheptanol **13** (58%, mp 96–98 °C). Structural and stereochemical assignments to

