controlled by an anomeric effect[14] results from this oxidation, whereas oxidation with CrO_3 in pyridine gives a 2:1 mixture of **9** and its epimer at C(2). Displacement of the axial hydroxyl group to the equatorial amino group proved troublesome until we discovered that the Mitsunobu reaction[15] (PPh_3, diethyl azodicarboxylate, phthalimide) in *N*,*N*-dimethylformamide gave the desired product **10**, $[\alpha]^{22}_{\mathrm{D}}$ +26.4° ($CHCl_3$), mp 109 °C (dec), quantitatively. The stereochemistry at C(2) was established by its ^{1}H NMR spectrum which shows a proton of C(2) at δ 5.91 (d, J = 5 Hz), clearly indicative of an axial hydrogen. Replacement of the amino substituent and removal of the *tert*-butyldimethylsilyl group to **11**, $[\alpha]^{22}_{\mathrm{D}}$ −20.4° ($CHCl_3$), and oxidation to **12**, $[\alpha]^{22}_{\mathrm{D}}$ −56° ($CHCl_3$), were unexceptional.

Condensation of **12** with nitromethane was found to proceed smoothly to give **13** as a single stereoisomer, $[\alpha]^{22}_{\mathrm{D}}$ +26° ($CHCl_3$), quantitatively. The stereochemistry at C(5) is tentatively assigned as **13**. Acetylation of **13** followed by base-catalyzed elimination of the acetoxy group afforded **14**, $[\alpha]^{22}_{\mathrm{D}}$ +69° ($CHCl_3$), in a good yield. The structure of **14** was determined by its ^{1}H NMR spectrum which shows the methylene protons of the nitromethyl group at δ 4.78 and 5.16 (ABq, J = 15 Hz), a proton of C(4) at δ 4.71 (d, J = 6 Hz), and a proton of C(6) at δ 7.06 (S). Transformation of **14** to carboxylate **16**, $[\alpha]^{22}_{\mathrm{D}}$ −4.1° (MeOH), mp 194–198 °C (dec), was achieved via α,β-unsaturated aldehyde **15** produced by simply warming **14** in pyridine. Compound **16** was also successfully produced from **13** by the stepwise successive sequences without isolation.

A problem arose, however, as catalytic reduction[16] of **16** accompanied by elimination of the hydroxyl group at C(4) and hydride reduction[17] of the double bond proceeded unfavorably and without chemoselectivity. To circumvent this problem, **16** was stereoselectively hydrogenated to α,β-saturated hydroxymethyl compound **17** ($NaBH_4$, 1:10 CF_3CH_2OH/THF), $[\alpha]^{22}_{\mathrm{D}}$ +7.0° ($CHCl_3$). The ^{1}H NMR spectrum of **17** shows protons at δ 3.25 (t, J = 13 Hz, H-6 ax), 3.59 (dd, J = 5 and 13 Hz, H-6 eq), and 4.54 (dd, J = 3 and 8 Hz, H-4), clearly indicative of an axial hydrogen at C(5).

The remaining steps of the synthesis are rather straightforward. The carboxylic acid formed upon oxidation of **17** was converted by removal of protecting groups to crystalline **1**, $[\alpha]^{22}_{\mathrm{D}}$ +56° (H_2O) (lit.[7] 57.2° (H_2O)), mp 135–136 °C (dec) (lit.[7] 137 °C), in 10.3% overall yield from L-ribose. Its spectral properties (IR, ^{1}H NMR, ^{13}C NMR, mass spectrum) were superimposable with those of the natural specimen.

The enantiomer **3** was also synthesized from D-ribonolactam by the same method used in the synthesis of **1**. Compound **3** was identical in all respects with the synthetic and the natural **1** except for the sign of the specific rotation.

Thus, the absolute configuration of siastatin B has been elucidated as the (2*R*,3*R*,4*S*,5*S*)-isomer **1**.

The synthetic **1** shows the same inhibitory effects as the natural one against neuraminidases prepared from *Cl. perfringens*, *Streptomyces*, rat mammary gland, rat mammary liver, chorioallantoic membrane (IC_{50} = 3, 10, 110, 170 and 55 μg/0.5 mL, respectively), β-glucuronidase (IC_{50} = 4 μg/0.5 mL), and *N*-acetyl-β-D-glucosaminidase (IC_{50} = 18 μg/0.5 mL).[7] In contrast, compound **3** shows only weak activities against neuraminidases mentioned above (IC_{50}: more than 100 μg/0.5 mL), whereas **3** demonstrates activity against β-glucuronidase (IC_{50} = 25 μg/0.5 mL).

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Observation and Substituent Control of Medium-Dependent Hot-Molecule Reactions in Low-Temperature Matrices

Brian F. LeBlanc and Robert S. Sheridan*,[1]

Department of Chemistry, University of Nevada
Reno, Nevada 89557

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Although reaction from vibrationally excited products is common in the gas phase, hot-molecule chemistry in condensed phases is rare.[2] Vibrational energy transfer to the medium is generally faster than chemically activated reaction. There are, however, a handful of cases where hot-molecule reactions of ground-state products of thermal[3-5] or photochemical[6-8] processes in various media have been proposed to explain unexpected products. Reaction from upper vibrational levels in electronic excited states has also been suggested in several instances[9-11] to rationalize wavelength dependence in condensed phase photochemistry.

There is spectroscopic evidence that vibrational relaxation in inert-gas matrices may be slow relative to solution. For example, Bondybey[12] and Rentzepis[13] have observed relatively long-lived hot bands (ca. 300 ps) in the fluorescence spectra of various aromatics in rare-gas matrices at 4 K. The higher energy vibrational emissions are absent in hydrocarbon matrices[14] or when the substrates are methylated.[12b] The surprising lifetimes have been attributed to mismatch of the vibrations of the aromatics and the low-energy lattice modes of the matrices, leading to poor energy transfer.[12,13] IR induced conformational interconversions in matrices are also well known.[5] The possibility of slow vibrational relaxation of photoproducts raises concerns for the observation of highly reactive intermediates with matrix-isolation techniques. We now wish to report *chemical evidence*, based on media and substituent effects, for the formation of vibrationally hot *photoproducts* in low-temperature matrices and their subsequent ground-state reactions.

We have reported that irradiation of **1** in toluene-d_8 at 77 K gives primarily 7-norbornadienone (**2**), characterized by ^{1}H NMR at −78° C.[15,16] A minor product, tentatively assigned as **3**, was also observed. On warming to ca. −60 °C, **2** cleanly gave benzene (and CO), with $\Delta G^{\ddagger}$ = 15 kcal/mol. Side product **3** polymerized

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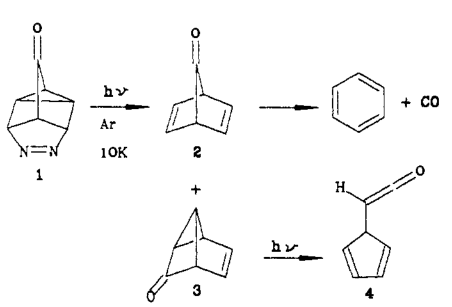


below room temperature.[15] Irradiation[17] of **1** in an argon matrix at 10 K (>340 nm) surprisingly produces mainly benzene and CO, with only minor amounts of **2** and another carbonyl compound tentatively assigned as **3** observed by IR.[15,18,19] The photoproducts are stable at these wavelengths. Subsequent irradiation at >300 nm rapidly converts **3** into a ketene-containing molecule (2130 cm^{-1}) that we suggest is **4**. Long-term irradiation with >220 nm light converts **2** into benzene and CO.

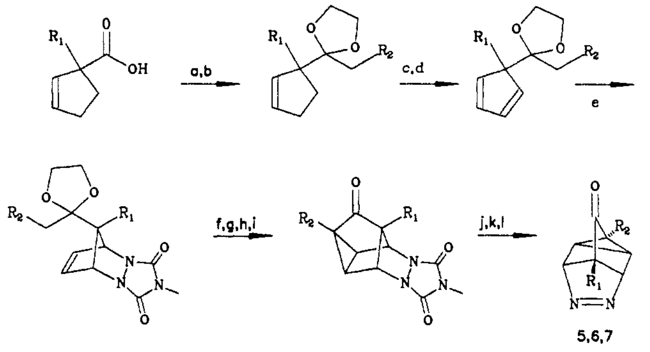
The photochemistry of **1** is strikingly matrix dependent. Irradiation (>340 nm) of **1** in an N_2 matrix at 10 K gives somewhat less benzene + CO and more **2**. In a matrix of 3-methylpentane (3-MP) under the same conditions, **1** gives considerably more **2**. The *relative* ratios of benzene: **2** in Ar, N_2, and 3-MP are 6.5, 2.9, and 1.0, respectively, based on the areas of select IR bands. Compound **3** is formed in only minor amounts in all matrices.

These results parallel spectroscopic indications of vibrational lifetimes in these media (vide supra) and suggest hot-molecule decarbonylation of initially formed **2**. To explore this possibility, we synthesized three alkyl-substituted derivatives of **1** by the route shown in Scheme I.[20]

All of the alkylated azo compounds photochemically produce the corresponding 7-norbornadienones, as judged by the similarities of the low-temperature ^1H NMR and IR spectra to the parent.[20] The alkyl groups only slightly influence the decarbonylation barriers, with $\Delta G^{\ddagger} = 15.2 \pm 0.15$ kcal/mol at −61 °C measured by ^1H NMR for the parent and all of the substituted norbornadienones. Alkyl substitution shuts off the amount of decarbonylation considerably in matrix photolyses of the precursors, however. One methyl (viz. **5**) substantially decreases the photochemical (>340 nm) conversion of azo to aromatic in argon or nitrogen matrices, in favor of methylnorbornadienone.[20] In 3-MP only traces of CO and toluene are observed. Two methyl groups (**6**), or one ethyl (**7**), nearly halt aromatic production even in Ar or N_2, and mainly the norbornadienones are observed. Comparably minor amounts of side products analogous to **3** and **4** were also observed in all cases. Although the photoreactions are difficult to quantify, comparison of integrated IR bands of the starting material and aromatic product in matrices and in calibrated solutions confirms these qualitative impressions. For example, in Ar matrices the approximate yield of aromatic is 56%, 24%, 14%, and 9% for **1**, **5**, **6**, and **7**, respectively. The last two numbers are especially uncertain due to the extremely small IR peaks observed and represent maximum values; only trace amounts of CO are observed from **6** and **7**.

We believe that these results indicate that matrix photolyses of the azo precursors generate highly vibrationally excited norbornadienones that decarbonylate in competition with cooling.[21]

Scheme I[a]



5, $R_1 = CH_3$, $R_2 = H$; **6**, $R_1 = R_2 = CH_3$; **7**, $R_1 = CH_2CH_3$, $R_2 = H$

[a] (a) $2R_2CH_2Li$; (b) $HOCH_2CH_2OH$, H^+; (c) NBS, AIBN; (d) 2,6-lutidine, Δ; (e) *N*-methyltriazolinedione; (f) H_3O^+; (g) NaH, $HCO_2CH_2CH_3$; (h) TsN_3; (i) $Rh_2(OAc)_4$; (j) KOH, *i*-prOH, Δ; (k) $CuBr_2$; (l) NH_4OH.

We estimate that **1** is ca. 38 kcal/mol higher in energy than **2** + N_2.[24] Adding the azo singlet energy (366 nm, 78 kcal/mol) indicates that **2** could be born with a maximum of 116 kcal/mol internal vibrational energy. Less initial energy is of course possible, depending on the mechanism of denitrogenation and the energy partitioning. If vibrational decay is slow, decomposition to benzene over the 15 kcal/mol barrier can compete. For example, RRKM calculations[27] indicate that the rate constants for decarbonylation of **2** are 6.9×10^9 and 3.1×10^{10} s^{-1} for internal energies of only 20 and 30 kcal/mol, respectively, in excess of the activation barrier. Bicyclic ketone **2** has few low-energy vibrations[28] that would be expected to couple well with the lattice modes of Ar (ca. 50 cm^{-1}). With additional internal vibrations, an N_2 matrix should couple somewhat better and 3-MP considerably better.[29] Low-energy torsional modes from alkyl substituents may promote better vibrational overlap with the medium. Moreover, increasing the number of vibrational modes in the product will decrease the rate of reaction of a vibrationally hot species.[30,31] The observed large difference in methyl- versus ethyl-substituted molecules is consistent with both effects.

These studies suggest noteworthy limitations for the photochemical generation of highly unstable molecules in rare-gas matrices. It is important to consider that the ca. 15 kcal/mol barrier for decarbonylation of these molecules is relatively large

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[17] For general matrix isolation conditions and a description of the apparatus, see: Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 844. Irradiations were performed either with a 300-W high-pressure Xe lamp with appropriate cut-off filters or with a PTI monochromator and 100 W high-pressure Hg lamp. FTIR spectra were recorded on a Perkin-Elmer 1800 spectrometer.

[18] Compound **3** exhibits ^1H NMR and IR absorptions consistent with the assigned tricyclic structure,[19] although we have not been able to isolate this minor product: IR (Ar matrix) 1759 s, 1258 w, 1181 w, 1096 w, 974 m cm^{-1}; for NMR see ref 15.

[19] Smith, A. B., III; Toder, B. H.; Richmond, R. E.; Branca, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 4001.

[20] All compounds were fully characterized spectroscopically. The aromatic products and CO were identified by comparison with authentic spectra. Spectral details for azo compounds **1**, **5**, **6**, and **7**, and the corresponding norbornadienones are given in the Supplementary Material.

[21] Although it is possible that adiabatically formed electronically excited products might give the observed decarbonylations (see for example ref 22), the dramatic effect of substitution so removed from the chromophores and the matrix effect would be unexpected. We also see no evidence for diazo formation in the IR spectra, as observed for related azo compounds by others.[23]

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[23] Adam, W.; Gillaspey, W. D.; Peters, K.; Rosenthal, R. J.; von Schnering, H. G. *J. Org. Chem.* **1985**, *50*, 580.

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[25] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

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[27] The Hase–Bunker program (Hase, W. L.; Bunker, D. L. *QCPE* **1973**, *11*, 234) was used for RRKM[30] calculations.

[28] Birney, D. M.; Wiberg, K. B.; Berson, J. A. *J. Am. Chem. Soc.* **1988**, in press. We thank Dr. Birney for providing a preprint of this work.

[29] Similar matrix effects have been observed in IR induced conformational interconversions at low temperatures.[5] Hot-molecule chemistry has also been proposed for reaction products of F_2 and olefins in low-temperature matrices although alternate mechanisms cannot be ruled out in these cases.[5]

[30] Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley: New York, 1972.

[31] The RRKM[27] calculated rate constants for decarbonylation of the methyl-, dimethyl-, and ethylnorbornadienones at 20 kcal/mol in excess of the energy barrier are 2.4×10^9, 1.2×10^9, and 7.3×10^8 s^{-1}, respectively.

compared to some of current interest.[7] These results may also be relevant to puzzling differences reported between Ar matrix and organic glass photochemistry, as in the case of phenyl azide.[32,33]

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Supplementary Material Available: Spectral data for azo compounds **1**, **5**, **6**, and **7** and the corresponding norbornadienones (2 pages). Ordering information is given on any current masthead page.

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[32] Leyva, E.; Platz, M. S.; Persey, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783.

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Counterattack Reagent Hexamethyldisilane in the Direct Conversion of Aldehydes, Ketones, and Allyl Alcohols to Allyltrimethylsilanes

Jih Ru Hwu[*,†]

The Department of Chemistry
Johns Hopkins University
Baltimore, Maryland 21218

Lung Ching Lin* and Ben Ruey Liaw

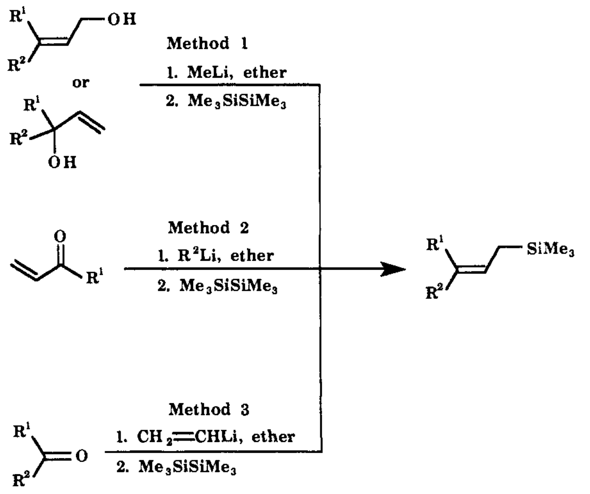
Department of Chemistry
National Taiwan University
Taipei, Taiwan, Republic of China

Received May 31, 1988

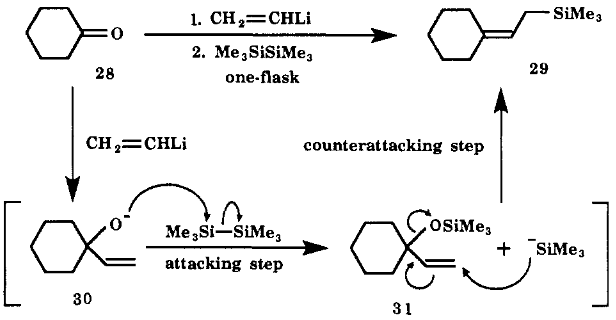
Counterattack reagent[1] Me$_3$SiSiMe$_3$ can efficiently silylate hydrazines under alkaline conditions.[2] We intended to use the counterattack method to prepare another important class of compounds—allyltrimethylsilanes. The allyltrimethylsilane moiety is versatile in organic synthesis.[3-8] This moiety possesses umpolung character and is regarded as a synthon for allyl cations and anions. Three new methods reported herein (see Scheme I) involve the use of Me$_3$SiSiMe$_3$ as a counterattack reagent; allyl alcohols, enals, enones, aldehydes, and ketones can be converted to allyltrimethylsilanes[9] in one flask.

We treated an ether solution of allyl alcohols (1.0 equiv) with MeLi (1.5 equiv) at 0 °C and then added Me$_3$SiSiMe$_3$ (1.5 equiv) and hexamethylphosphoramide (HMPA, ether/HMPA = 1:4). After ether was boiled off in situ under nitrogen, the reaction mixture was heated at 80 °C for 24 h. Aqueous workup followed by distillation provided the desired allylsilanes[10] (Table I and Scheme I, method 1). Under these conditions, geraniol (**1**) gave allylsilanes **2** and **3**[9a] in 72% yield; linalool (**4**) afforded the same products (**2** and **3**) in 75% yield as well as a small amount of silyl ether **5** (5%); (−)-myrtenol (**6**) provided allylsilane **7** (65%) and silyl ether **8** (15%). When benzyl alcohol (**9**) was used as the starting material, the corresponding trimethylsilane **10**[11] was obtained in only 30% yield. However we were able to convert a homobenzylic compound, phenylethyl alcohol (**12**), to (phenylethyl)silane **13** in 50% yield.

Scheme I



Scheme II



Method 2 in Scheme I illustrates a new method for the preparation of allyltrimethylsilanes[10] from enals and enones by use of alkyllithium and Me$_3$SiSiMe$_3$. We treated acrolein (**14**, 1.0 equiv) sequentially with *n*-BuLi (1.2 equiv) and Me$_3$SiSiMe$_3$ (1.2 equiv) to give allylsilanes **15** and **16**[12] in 48% yield (**15**/**16** = 5:1) as well as *sec*-silyl ether **17** in 10% yield. By use of the same procedure, methyl vinyl ketone (**18**) afforded allylsilanes **19**[9b] and **20** in 48% yield (**19**/**20** = 3:1).

We found that the reaction of saturated aldehydes or ketones with vinyllithium (1.3 equiv) and Me$_3$SiSiMe$_3$ (1.3 equiv) also produced allyltrimethylsilanes[10] (Table I and Scheme I, method 3). Thus 1-hexanal (**21**) gave allylsilanes **22** and **23** in 48% yield (**22**/**23** = 5:1); 2-heptanone (**25**) afforded allylsilanes **26** and **27** in 66% yield (**26**/**27** = 2:1); cyclohexanone (**28**) led to allylsilanes **29** in 75% yield.[13]

For the preparation of allyltrimethylsilanes by methods 1–3, the first step was to generate an allyl alkoxide: removal of the

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[†] Research fellow of the Alfred P. Sloan Foundation (1986–1990).

[1] For the definition, see: Hwu, J. R.; Gilbert, B. A. *Tetrahedron* **1989**, in press.

[2] Hwu, J. R.; Wang, N. *Tetrahedron* **1988**, *44*, 4181.

[3] Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200.

[4] Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlag, 1983; Chapter 11.

[5] Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1.

[6] Colvin, E. *Silicon in Organic Synthesis*; Butterworths: Boston, 1981; Chapter 9.

[7] Calas, R. *J. Organomet. Chem.* **1980**, *200*, 11.

[8] Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

[9] For recent reports on the preparation of allyltrimethylsilanes, see: (a) Biran, C.; Dunoguès, J.; Calas, R.; Gerval, J.; Tskhovrebachvili, T. *Synthesis* **1981**, 220. (b) Negishi, E.; Luo, F.-T.; Rand, C. L. *Tetrahedron Lett.* **1982**, *23*, 27. (c) Smith, J. G.; Quinn, N. R.; Viswanathan, M. *Synth. Commun.* **1983**, *13*, 1. (d) Smith, J. G.; Quinn, N. R.; Viswanathan, M. *Synth. Commun.* **1983**, *13*, 773. (e) Smith, J. G.; Drozda, S. E.; Petraglia, S. P.; Quinn, N. R.; Rice, E. M.; Taylor, B. S.; Viswanathan, M. *J. Org. Chem.* **1984**, *49*, 4112. (f) Shiragami, H.; Kawamoto, T.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 589. (g) Wang, K. K.; Dhumrongvaraporn, S. *Tetrahedron Lett.* **1987**, *28*, 1007. (h) Anderson, M. B.; Fuchs, P. L. *Synth. Commun.* **1987**, *17*, 621. (i) Narayanan, B. A.; Bunnelle, W. H. *Tetrahedron Lett.* **1987**, *28*, 6261.

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[11] Pons, P.; Biran, C.; Bordeau, M.; Dunogues, J.; Sibille, S.; Perichon, J. *J. Organomet. Chem.* **1987**, *321*, C27.

[12] Rajagopalan, S.; Zweifel, G. *Synthesis* **1984**, 113.

[13] For a previous transformation of **28** to **29**, see: (a) Seyferth, D.; Wursthorn, K. R.; Mammarella, R. E. *J. Org. Chem.* **1977**, *42*, 3104. (b) Fleming, I.; Paterson, I. *Synthesis* **1979**, 446.

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