

Communications to the Editor

Formation of the Totally Degenerate Bicyclo[3.2.2]nonatrienyl Radical by Electron Transfer

Sir:

Nucleophilic substitutions of *p*-nitrobenzylic and aromatic derivatives have been amply demonstrated to proceed by one-electron transfer entailing a radical-chain mechanism.¹ We sought to ascertain whether nucleophilic substitution of compounds which possess low-lying, easily accessible LUMOs and moreover for which the HOMO of the radical would be bonding would involve electron transfer. Possible candidates would be derivatives of systems which can form aromatic, bishomoaromatic, or bicycloaromatic anions. To test this prediction, nucleophilic substitution of bicyclo[3.2.2]nonatrienyl derivatives was examined since our investigations of the bicyclo[3.2.2]nonatrienyl radical (I) revealed a degenerate rearrangement that would be indicative of the intermediacy of I.



I	X = •	II	X = •
III	X = OSO ₃ ⁻	V	X = EtS
IV	X = EtS	VII	X = N ₃
VI	X = N ₃	VIII	X = OSO ₃ ⁻

We found that addition of neat tributyltin hydride at 4 °C to 9-deuterio-9-bromobarbaralane² (prepared from 9-barbaralol-9-*d* by treatment with CBr₄ and tributylphosphine at 20 °C) generated a 98:2 mixture of bicyclononatriene and barbaralane in ~85% yield. ¹H NMR (180 MHz) revealed the deuterium to be distributed over all nine carbons of the bicyclononatriene.^{3,4} Thus (1) the bicyclononatrienyl radical (I) and barbaralyl radical (II) interconvert rapidly to completely scramble the label prior to hydrogen atom abstraction from the tin hydride; and (2) under kinetic control, bicyclononatrienyl products are formed.

These results, in conjunction with previous studies establishing that solvolysis of bicyclononatrienyl *p*-nitro- and dinitrobenzoates generated only barbaralyl products,⁵ permit one to distinguish among the various mechanistic pathways available for nucleophilic substitutions of bicyclononatrienyl derivatives. Thus, if the reaction entails a cationic intermediate, then barbaralyl products will result. Bicyclononatrienyl products will be formed by either an S_N2 reaction or electron transfer. Deuterium labeling can distinguish between these two possibilities since a radical intermediate will totally scramble the label by equilibrating all nine carbons.

To avoid an S_N1 reaction, bicyclononatrienol⁶ was converted to the nonlabile bicyclo[3.2.2]nonatrienyl sulfate (III) by SO₃/pyridine.⁷ When sulfate III was treated with 3 equiv of a 1:1 mixture of potassium ethylthiolate (EtSK) and ethyl mercaptan in THF at 20 °C for 7 days, 2-bicyclononatrienyl ethyl sulfide (IV)⁸ was formed in 75% yield. No bicyclono-

natriene was formed despite the presence of ethyl mercaptan. If the temperature was raised to 70 °C, a 12:5 mixture of sulfide IV and 9-barbaralyl ethyl sulfide (V)⁹ was obtained.¹⁰ If a catalytic amount of potassium was added, sulfide IV was formed in 80% yield in <30 min at 20 °C. The unusual nature of this transformation was revealed when III-*d*, specifically deuterated at C₂, was treated with EtSK/EtSH in the absence of potassium at 20 °C. By ¹H NMR the resultant monodeuterated sulfide IV-*d* contained equal amounts of deuterium at each of the nine bicyclononatrienyl carbons.^{3,4}

When III was treated with a suspension of NaN₃ in either THF, DMF, or pyridine at 20 °C, an ~2:1 mixture of the bicyclononatrienyl azide (VI)¹¹ and barbaralyl azide (VII)¹² was obtained. The conversion of III to VI and VII in DMF at 20 °C was 33% after 10 days.¹³ If the temperature was increased to 70 °C, the ratio of VI to VII decreased to 1:7. The partitioning of sulfate III between VI and VII was not altered by varying the concentration of sulfate III from 5 × 10⁻² to 5 × 10⁻¹ M in a saturated suspension of NaN₃ in DMF nor by absence of light nor by the presence of 14 mol % of *p*-dinitrobenzene. When III-2-*d* was treated with NaN₃ in DMF, the deuterium distribution of the two azide products was different.^{3,4} A 270-MHz ¹H NMR spectrum revealed equal amounts of the deuterium at each of the nine carbons of bicyclononatrienyl azide VI-*d*. However, a 180-MHz ¹H NMR spectrum revealed that the barbaralyl azide VII-*d* contained 70% of the deuterium at C₆ and C₈, 20% at C₁ and C₅, and 10% at C₂ and C₄; i.e., the majority of the label was anti to the azide.¹⁴

The labeling pattern found for azide VII-*d* suggests that solvolysis of sulfate III-2-*d* occurs with participation of the double bond to generate the barbaralyl cation as a tight ion pair which is captured by azide ion prior to total scrambling of the deuterium over C₁, C₂, C₄, C₅, C₆, and C₈ by degenerate divinylcyclopropylcarbinylium cation rearrangements. The asymmetric deuterium distribution of azide VII-*d* is reminiscent of that reported by Winstein for the barbaralyl *p*-nitrobenzoate-*d* formed by internal return during the solvolysis of bicyclononatrienyl *p*-nitrobenzoate-2-*d*, in which the preponderance of deuterium was at C₂ and C₄.^{5a} The differing stereochemical relationship between deuterium and the C₉ substituent reflects whether product formation arises by internal return as opposed to capture by an external nucleophile.

Formation of bicyclononatrienyl azide VI or sulfide IV by a similar cationic pathway is not in agreement with the prior observations that solvolysis of bicyclononatrienyl *p*-nitrobenzoate generates only barbaralyl products. Our observation that sulfate III reacted with KOAc/18-crown-6 ether or KOH/H₂O in the THF to give only barbaralyl acetate and barbaralol, respectively, excluded the possibility that the substitution of a nonpolar solvent THF for aqueous acetone could change the product distribution. Furthermore, both the temperature dependence on product composition and the different label distribution of azides VI-*d* and VII-*d* require the existence of two competing pathways. Prior deuterium scrambling in either sulfate III-2-*d* or in a common cationic intermediate could not produce these labeling results. Only the intermediacy of the totally degenerate bicyclononatrienyl radical will account for the formation of bicyclononatrienyl products and the label distribution thereof.¹⁵

A priori, the same degenerate radical I could be formed by electron transfer during nucleophilic substitution of the cor-

responding barbaralyl sulfate VIII. When sulfate VIII-9-d was treated with EtSK/EtSH in THF at 20 °C for 3 days, a 1:1 mixture of sulfide IV-d and 9-deuteriobarbaralyl ethyl sulfide (V-9-d) was obtained in low yield. If the solution was refluxed, the ratio changed to 1:6 favoring V. The sulfate VIII reacted very sluggishly in DMF at 70 °C with NaN₃ to give a 3:22 mixture of azides VI and VII. Since solvolysis of 9-deuteriobarbaralyl tosylate was reported to give only barbaralyl products,¹⁷ the formation of bicyclonatrienyl sulfide IV-d and azide VI-d underscores the existence of a previously undetected reaction pathway. Since the same labeling pattern was observed in sulfide IV-d, formed from sulfates III-2-d and VIII-9-d, both sulfates probably reacted via the same intermediate.

We propose that the bicyclonatrienyl products obtained from either sulfate III or VIII are the result of nucleophilic capture of the totally degenerate bicyclonatrienyl radical I.¹⁸ To date, we have found that only polarizable, easily oxidized nucleophiles react with sulfates III and VIII to generate radical I. As the ionization potential of the nucleophile increases, a cationic pathway becomes increasingly competitive with electron transfer. The products observed are in accord with this analysis. EtSK reacts only by electron transfer, whereas the higher ionization potential of NaN₃ results in both pathways being competitive. Substitution of an even less easily oxidized nucleophile such as KOAc/18-crown-6 ether or KOH leads to exclusive formation of barbaralyl products.

The nature of the chemical bonding of the bicyclonatrienyl radical is intriguing since the radical may be delocalized in the same sense as was suggested for the bicycloaromatic bicyclonatrienyl anion.²¹ To date, such nonclassical radicals are unknown.^{22,23} Experiments are currently underway to elucidate this matter as well as to determine the generality of the reaction pathway for other appropriate systems.

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References and Notes

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- The choice of the nucleophilic group was quite limited since the propensity of the bicyclonatrienyl derivatives to isomerize to the barbaralyl counterpart precluded the preparation of more reactive derivatives. When bicyclonatrienyl *p*-nitrobenzoate or dinitrobenzoate was substituted for sulfate III, the addition of KSET, NaN₃, or KOAc/18-crown-6 ether generated a blue-colored solution (presumed to be a charge-transfer or Meisenheimer complex) which, upon workup, gave only starting material.
- ¹H NMR (CCl₄) δ 1.28 (t, 3 H, *J* = 8 Hz), 2.63 (q, 2 H, *J* = 8 Hz), 3.25 (m, 3 H), 4.93 (d of m, 1 H, *J* = 5 Hz), 6.15 (m, 3 H), 6.6 ("t", 2 H, *J* = 7 Hz); mass spectrum *m/e* 178, 149, 117, 115 (base).
- ¹H NMR (CCl₄) δ 1.20 (t, 3 H, *J* = 8 Hz), 2.5 (m, 5 H), 4.0 (m, 4 H), 5.6 (m, 2 H); mass spectrum of V-9-d *m/e* 179, 150, 118, 116 (base).
- Controls revealed that sulfides IV and V do not interconvert at 70 °C. Likewise azides VI and VII are also stable under the reaction conditions.
- ¹H NMR (270 MHz) (CDCl₃) δ 3.32 (m, 1 H), 3.50 (m, 1 H), 3.73 (m, 1 H), 5.02 (m, 1 H), 6.27 (m, 3 H), 6.79 (m, 2 H); mass spectrum *m/e* 131 (p - N₂), 130 (base); IR 4.8 μ.
- ¹H NMR (180 MHz) (CDCl₃) δ 2.64 (m, 2 H), 3.31 (m, 1 H), 4.08 (m, 4 H), 5.57 ("t", 1 H, *J* = 7 Hz), 5.84 ("t", 1 H, *J* = 7 Hz); IR 4.8 μ.
- The apparent low yields reflected the low conversion of sulfate III since, after workup, addition of KOH to the aqueous layer hydrolyzed the residual III to give barbaralol with an overall material balance of 80%.
- At 180 MHz, the multiplet of VII-d at δ 4.08 split into two multiplets centered at 3.97 and 4.19, corresponding to H₆ and H₈ (anti to the azide) and H₂ and H₄ (syn to the azide). The proton assignment assumes that the C₂ and C₄ hydrogens which are syn to the azide will be more deshielded than the C₆

- and C₈ hydrogens. A similar shielding effect has been reported for the 9-barbaralyl *p*-nitrobenzoate-d.^{5a}
- An identical scrambling of labels has been observed for the 2-deuteriobicyclonatrienyl anion;¹⁸ however, the anion is not a viable intermediate for this reaction. The half-life for the deuterium scrambling of the anion is too long, i.e., 10 min at 28 °C in THF. Moreover, no bicyclonatriene arising from protonation by the ethyl mercaptan was observed.
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 - At the present, one cannot state whether electron transfer occurs prior to or subsequent to cleavage of the carbon oxygen bond of sulfates III and VIII. During the reaction of III with EtSK, the catalysis observed from potassium argues for a S_{RN}1 pathway (radical chain). The failure to obtain any C₉H₁₀ hydrocarbon despite the presence of EtSH suggests a radical-cage mechanism. The insensitivity of the azide product distribution to reaction conditions is inconsistent with a radical-chain pathway. Electron transfer from azide ion would be somewhat surprising since azide ion, unlike thiolate anions, do not engage in S_{RN}1 reactions without prior photostimulation or entrainment.^{19,20} Preliminary electrochemical data involving irreversible processes indicate that electron transfer from EtSK to sulfate III may be endothermic by ~0.1 V, whereas the same process involving the azide ion is endothermic by ~1.0–1.5 V.
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On the Role of Trimethylsilylmethylsilylene in the Gas-Phase Reactions of Tetramethyldisilene

Sir:

In view of the crescendo of activity in the area of silene (compounds containing a silicon-carbon (p-p) π double bond) chemistry¹ in the past 6 years, the apparent lack of interest in disilenes (compounds with silicon-silicon double bonds) is somewhat surprising. To date the reported reactions of transient tetramethyldisilene (**1**) are restricted to Diels-Alder addition to dienes,^{2,4} cycloaddition to an acetylene,³ addition to benzaldehyde,⁴ and an intriguing rearrangement to 1,3-disilacyclobutanes in the gas phase.^{2,3,5} This rearrangement, discovered in the pioneering work of Peddle,² was proposed to proceed by the mechanism shown in Scheme I.

The key feature of this mechanism is the 1,2 migration of hydrogen from carbon to a silyl radical, which must occur twice to generate the observed major products **3** and **4**. We have never been particularly enamored of this mechanism since it would suggest an inherent instability for any organosilyl

Scheme I

