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Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Cations Generated by Deamination and Solvolysis

Sir:

The bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation has evoked interest because of its potential homoaromaticity[1] and bicycloaromaticity.[2] The solvolysis of *syn*-bicyclo-[4.2.1]nona-2,4,7-trien-9-yl *p*-toluenesulfonate (**1**) afforded *exo*-dihydroindenyl acetate (**5**)[3] and/or indene,[4,5] depending on the reaction conditions. **1**-*9-d* produced **5** and **7** with effectively all of the deuterium at C-2.[3,5] This result eliminates the possibility of a simple 1,2 shift of carbons 1 or 6 to the C-9 cationic center. Interaction of the monoene and diene units of the cation, visualized by structures **2** and **3** of the intermediate, has been suggested to account for the observed path of rearrangement.

5, X = OAc
6, X = OCH₃

The process leading from **1** to **3** involves an appreciable change of the reactant geometry ("nonvertical" ionization). In reactions of this type the results of tosylate solvolysis and deamination may differ substantially. Solvolysis, with its transition state "late" on the reaction coordinate, favors relocation of atomic nuclei such as to achieve a minimum energy path. Deamination, on the other hand, starting from the highly energetic diazonium ion, passes its transition state "early" and without significant distortion of nuclear positions ("vertical" ionization).[6] Consequently, deamination may produce cations of undistorted geometry which are bypassed in solvolysis (leading directly to more stable bridged species). *We report here that the bicyclo-[4.2.1]nona-2,4,7-trien-9-yl cation generated by deamination can be trapped by nucleophiles and rearranges by simple 1,2 shifts.*

Photolysis of bicyclo[4.2.1]nona-2,4,7-trien-9-one tosylhydrazone (**8**)[4] in CH₃OH–CH₃ONa afforded *syn*-9-methoxybicyclo[4.2.1]nona-2,4,7-triene (**11**) and **6** as the major products. Minor products were *endo*-dihydroindenyl methyl ether (**12**), indenyl methyl ether (**13**), and indene (Table I). Photolysis of tosylhydrazone sodium salts generates diazo compounds[8] which are protonated by protic sol-

Table I. Product Distribution Obtained from Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Derivatives

Reaction	Yield (%)	6	7	11	12	13
8, CH₃OH, 0.66 N NaOCH₃ hv,[b] 25°	96	40.9	6.3	46.4	3.4	1.0[a]
syn-**1**, CH₃OH, lutidine (1.4 equiv), 25°, 10 days	98	91.1	1.0		6.8	1.1
syn-**1**, CH₃OH, lutidine (1.4 equiv), 1.5 hr reflux	92	83.7	7.9		8.4	
anti-**1**, CH₃OH, lutidine (1.4 equiv), 1.5 hr reflux	93	84.0	7.2		8.8	

[a] 2% of unidentified material. [b] A 70-W medium-pressure mercury arc, Pyrex vessel.

Table II. Rates of Methanolysis of *syn*-**1** and *anti*-**1**[11]

Temp, °C	10⁴*k*, sec⁻¹	Temp, °C	10⁴*k*, sec⁻¹
50.80	1.49	51.90	1.85
52.40	1.79	54.40	2.38
54.65	2.40	57.90	3.83
55.90	2.78	60.30	4.57
57.90	3.30		
58.95	3.58		
59.85	4.13		

[a] $\Delta H^* = 22.9 \pm 0.9$ kcal, $\Delta S^* (55°) = -5.5 \pm 2.8$ eu. [b] $\Delta H^* = 23.4 \pm 0.9$ kcal, $\Delta S^* (55°) = -3.8 \pm 2.9$ eu.

vents to give diazonium ions and products derived therefrom.[9] Both syn and anti diazonium ions may be involved in the present reaction. Photolysis of **8** in CH₃OD–CH₃ONa introduced deuterium at C-9. The nmr spectrum of **6**-*d* which was isolated from the CH₃OD photolysis revealed distribution of deuterium over the bridgehead positions; the intensity of each of the bridgehead hydrogens was reduced to half and the large vicinal coupling ($J = 12.5$ Hz) observed with **6** was absent in **6**-*d*. Obviously, the *cis*-dihydroindenyl cation produced from **9** arises by a shift of carbons 2,5 from carbons 1,6 to carbon 9. **11**-*d* was also isolated and shown to carry all of the label at C-9 (no signal of H-9 was observed in the nmr spectrum).

12   13

The dramatic differences between the deamination of **9** and the previously studied solvolysis of *syn*-**1** might be due to different reaction conditions rather than to different leaving groups. Therefore, we have solvolyzed **1** in methanol. Our results (Table I) differ from those obtained by Diaz, *et al.*,[3] in acetic acid only by the detection of some *endo*-dihydroindenyl ether (**12**). Significantly, the solvoly-

sis of **1-9-d** in methanol afforded **6-2-d**, identified by its nmr spectrum which matched closely the reported spectrum of **5-2-d**.[3]

We have also prepared *anti*-bicyclo[4.2.1]nona-2,4,7-trien-9-yl *p*-toluenesulfonate (*anti*-**1**).[10] The product distribution obtained by solvolysis of *anti*-**1** in methanol was virtually identical with that from *syn*-**1** (Table I). Moreover, the rates of solvolysis of *syn*-**1** and *anti*-**1** in 75% aqueous methanol agreed within experimental error[11] (Table II).

Our results suggest that the solvolysis of *syn*-**1** is not assisted by double bond participation, as implied in **2**. Rate-determining formation of tetracyclic tosylates (**14**) by intramolecular Diels–Alder reaction would account for the similar solvolytic rates for the **1** epimers and for the small solvent effect.[12] The discussion of alternative explanations will be deferred to a full paper. The cationic intermediate of the deamination reaction, quite distinct in its behavior, may be represented by **10**, or a slightly delocalized version to explain the exclusive formation of *syn*-**11**.

syn-1 ⟶

syn-14 ⟶ 3 ← anti-14 ← anti-1

4
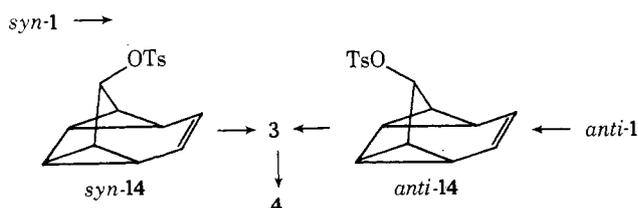
We should like to contrast the bicyclo[4.2.1]nona-2,4,6-trien-9-yl cation with its isomer, the barbaralyl cation (**16**), as a typical case of vertical stabilization.[13] The rigid barbaralyl skeleton does not permit substantial molecular distortion, and such distortion is not required to achieve optimal stabilization of positive charge at C-9. Schleyer, *et al.*,[14] studying the solvolysis of barbaralyl-9-d tosylate (**15**, X = OTs), uncovered a degenerate rearrangement of the barbaralyl cation which distributes deuterium over the positions 3, 7, and 9. EHT calculations support a triply degenerate intermediate (**17**) as the cationic species of lowest energy.[15] In less nucleophilic solvents, and on repeated formation of the barbaralyl cation, complete scrambling of D is observed in a process of slightly higher activation energy.[14]

15 → 16 and/or 17
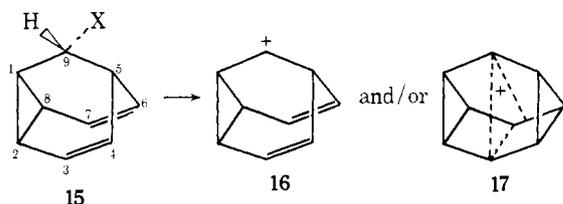
Photolysis of barbaralone tosylhydrazone sodium salt in CH₃OD afforded barbaralyl methyl ether (**15**, X = OCH₃) with 80% of the deuterium at C-9 and 20% distributed over positions 3 and 7, according to ¹H and ²H nmr. When the reaction was carried out in D₂O–CH₃OD (1:1),[16] the barbaralol (**15**, X = OH) contained 55% D at C-9, 34% at C-3 and C-7, and 10% at other positions. Our results, combined with those of Schleyer, *et al.*,[14] strongly indicate that the amount of rearrangement depends solely on the nucleophilicity of the solvent and not on the nature of the leaving group. Solvolysis and deamination produce virtually the same barbaralyl cation.

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(10) *syn-* and *anti*-Bicyclo[4.2.1]nona-2,4,7-trien-9-ol were equilibrated by aluminium isopropoxide–isopropyl alcohol–acetone at 150° and separated by glpc. The anti alcohol and its tosylate are characterized by their nmr spectra which show singlets for 9-H.[4] A syn:anti ratio of 78:22 was approached on prolonged heating.
(11) Solvolyses were carried out in 75% aqueous methanol in the presence of a tenfold excess of NaHCO₃, the evolution of CO₂ being recorded. These conditions closely approach those of the preparative runs. The product distribution by glpc agreed with Table I, except for the presence of small amounts of alcohols. The accuracy of this semimicro technique is inferior to titration methods.
(12) A referee has pointed out that a change of solvent from acetic acid (ref 3) to 75% aqueous methanol changes the solvolytic rate of *syn*-**1** by less than a factor of 3. Winstein Y values for these solvents suggest that there should be an approximately 100-fold rate difference for rate-determining ionization.
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Rate Constants for the Formation of Oxiranes from β-Peroxyalkyl Radicals. The *gem*-Dialkyl Effect in Homolytic Ring Closure

Sir:

β-Peroxyalkyl radicals are involved in the decomposition of peroxides,[1] in the autoxidation of alkenes,[2] and in the cool flame combustion of alkanes[3] and, by intramolecular homolytic substitution (SHi) at the oxygen in the 3-position, are thought to be responsible for the formation of oxiranes.

$$\cdot\text{CCOOR} \longrightarrow -\text{C}-\text{C}- \;+\; \cdot\text{OR} \qquad (1)$$
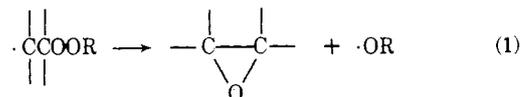
Hitherto, no method has been available for studying these cyclization reactions in isolation, and estimates of their rates, even for peroxyalkyl radicals of similar structure, have varied over a wide range.[2-5]

We have now prepared the β-peroxyalkyl radicals Me₃COOCMe₂ĊH₂, Me₃COOCHMeĊH₂, and Me₃COOCH₂ĊH₂ by causing the corresponding β-bromoperoxides[6] to react with trialkyltin radicals; the peroxyalkyl radicals have been identified by esr spectroscopy, and their rates of ring closure have been determined.

In benzene solution at 25°, the β-bromoperoxides (Ia–c) react with hexamethylditin in the presence of di-*tert*-butyl hyponitrite as initiator, to give the corresponding oxiranes (IIa–c) in excellent yield (nmr). The reaction proceeds by abstraction of bromine by the trimethyltin radical, to give the appropriate β-peroxyalkyl radical (III; eq 3),[7] and these