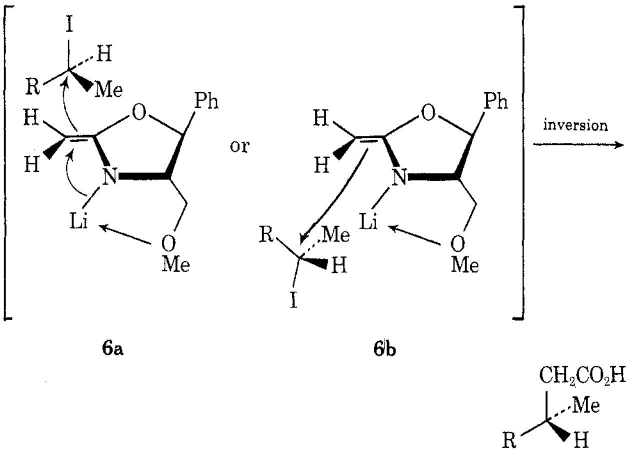
(Table I, ref *g*). To preclude any error in the reported maximum rotation of either the iodide **4** or the acid **5**, the alkylation of **1** was repeated using (+)-2-iodooctane[4] (70% optical purity, 1.8 equiv). The recovered iodide had $[\alpha]_{\mathrm{D}}$ +41° while the 3-methylnonanoic acid had $[\alpha]_{\mathrm{D}}$ +5.25°. Assuming 74% optical purity of the acid, this is corrected to be +7.1° for a maximum rotation. Thus, the acid derived from racemic 2-iodooctane and **1** had an optical purity of only 34% and suggested to us that the reported value was too low. This experiment tends to validate the technique reported here and should allow prediction of maximum rotation in these classes of compounds.

Reaction of **1** with a larger excess of racemic halide (6–8 equiv) gave recovered iodides (iodobutane and iodooctane in 6 and 9% optical purity, respectively) and increased optical purity of the corresponding acids (39–40%). Thus, the asymmetric yields of 3-methylalkanoic acids can be increased to even higher levels by employing these conditions.

Since the iodides **4** are recovered with the *R* enantiomer in excess, the transition state during alkylation must assume the orientation depicted in **6a** or **6b** which preferentially consumes the *S* enantiomer. This approach to the transition state appears to involve a minimum of nonbonded interactions. In contrast, the *R* enantiomer of the iodide generates considerably more interactions as the transition state is approached (**7a** or **7b**). The results of the alkylations are consistent with this view since iodide displacement on the more favorably disposed *S* enantiomer (whose Cahn–Ingold–Prelog sequencing is the same in both the halide and the acid) should proceed with inversion leading to the (*R*)-acids, **5**. The absolute configurations of the acids[5] **5** and the halides[5] **4** are known to be *R*.

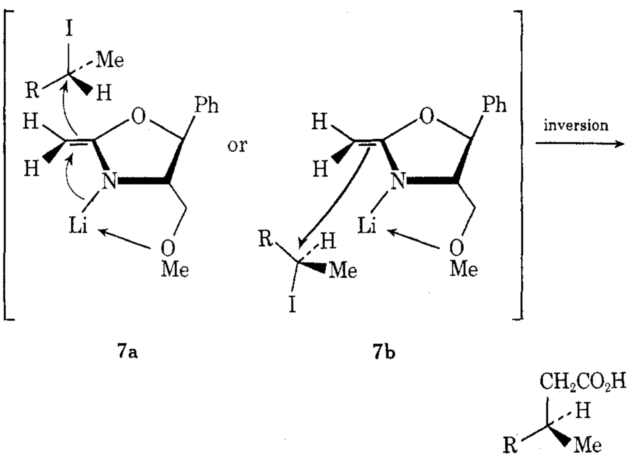
via S enantiomer



6a **6b**

(*R*)-**5**

via R enantiomer



7a **7b**

(*S*)-**5**

Although only three examples involving kinetic resolution of *sec*-alkyl iodides are reported here, this method indicates that it may now be possible, in addition to predicting maximum rotations, to correlate absolute configurations of halides (or their alcohol precursors) and 3-alkylalkanoic acids (or their derivatives, *e.g.*, alcohols, halides, ketones, etc.) by employing racemic starting materials, provided of course, that the absolute configuration of either the acid or halide is known. We continue to evaluate this useful new tool.

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(3) Prepared using acetonitrile imidate ether as described in ref 1, $[\alpha]^{25}_{\mathrm{D}}$ −113.8° (*c* 10.5, CHCl$_3$). The chiral methoxyamino alcohol was recovered after hydrolysis of **3** and recycled to the starting oxazoline **1**.

(4) Prepared according to Berlak (Table I, ref *c*) from commercial 2-octanol {$[\alpha]_{\mathrm{D}}$ −8.97° (neat)}. The (+)-iodooctane thus obtained had $[\alpha]_{\mathrm{D}}$ +44.07° (neat) which represents 70.4% optical purity (based on $[\alpha]_{\mathrm{D}}$ 62.6°).

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The Degenerate Rearrangement of the Benzo-6,7-bicyclo[3.2.2]nonatrienyl Anion. The Relative Stability of a Benzylic and an Allylic Anion[1]

Summary: The benzo-6,7-bicyclo[3.2.2]nonatrienyl anion undergoes a facile degenerate 7-carbon scrambling detected using ^{13}C nmr techniques; the rearrangement has been used to probe relative anion stabilities.

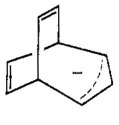
Sir: It was recently shown that the bicyclo[3.2.2]nonatrienyl anion I undergoes a degenerate rearrangement.[2] We now report that this facile rearrangement provides a convenient method for the determination of relative carbanion stabilities. When a substituent is introduced onto the bicyclo[3.2.2]nonatrienyl anion framework, a new equilibrium is established which reflects the substituent influence on carbanion stability. The benzo group is used here as a substituent to test the relative stabilities of a benzylic and an allylic anion. The literature data on this question are ambiguous.[3,4] The advantages of Stothers' method[5] for determining deuterium location by carbon-13 nmr spectroscopy are also illustrated.

Table I
Analysis of Deuterium Content of Benzo-6,7-bicyclo[3.2.2]nonatriene Derived from II-D

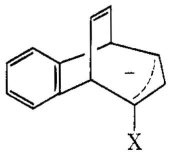
	Proton nmr integration[a]			Carbon nmr, intensity ratios[b]		
Position	Observed	Calcd for 5 C	Calcd for 7 C	Observed	Calcd for 5 C	Calcd for 7 C
1	0.91[c] ± 0.05	1.00	0.86	2.0 ± 1	1.5	2.0
2	0.87	0.80	0.86	2.8	3.0	2.0
3	0.79	0.80	0.86	[d]	1.0	2.0
4	1.60	1.80	1.86	1.6	3.0	2.0
5	0.91[c]	1.00	0.86	1.2	1.5	2.0
6				4.8 ± 3	∞	6.0
7				4.7 ± 3	∞	6.0
8	0.87	0.80	0.86	2.3	3.0	2.0
9	0.89	0.80	0.86	3.3	3.0	2.0

[a] Average of at least three quenches assuming that the benzo protons have intensity 4.00. [b] Ratio of "normal" peak to isotope shifted peak. [c] H-1 and H-5 overlap in the proton spectrum and these numbers are each half the observed sum. [d] Not determined owing to peak overlap.

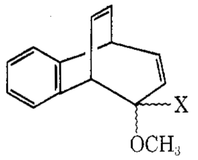
The benzo-6,7-bicyclo[3.2.2]nonatrienyl anion II and its monodeuterated derivative II-D were prepared from the methyl ethers III by sodium-potassium alloy cleavage using previously reported methods.[2b,6] The nmr spectrum of the anion defines the symmetrical allyl structure expected for II. It shows a narrow multiplet for the benzo protons (δ 7.01, width 4 Hz), a broad triplet (δ 5.42, 7 Hz, H-3) overlapping a complex symmetrical multiplet (δ 5.33, width 8 Hz, H-8, -9) and another complex pattern (δ 3.11, 7.5 Hz, H-1, -5, and δ 3.18, 7.5 Hz, H-2, -4) which simplified to an AB pattern on irradiation in the δ 5.4 region. No other anions were detected in the spectrum (<5%) which remained unchanged after 1 year at 25° in perdeuteriotetrahydrofuran. The chemical shift of the benzo protons show limited charge delocalization into the benzene ring. The remaining shifts agree closely with those of the bicyclo[3.2.2]nona-2,6-dienyl anion.[7]



I



II, X = H
II-D, X = D



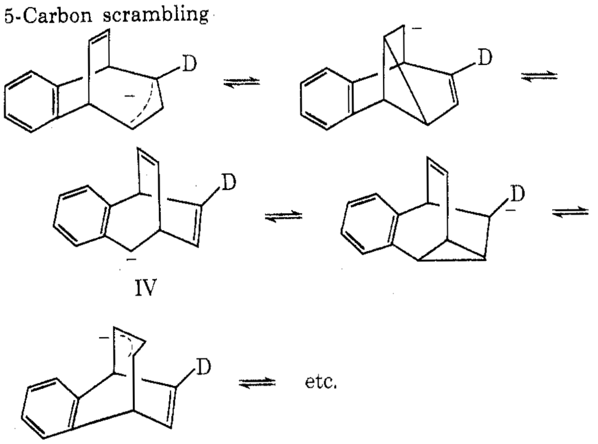
III, X = H
III-D, X = D

The 2-deuterio anion II-D was prepared in 30 min at 0°. The deuterium was still present at C-2 because H-3 appeared as a clean doublet. With a half-life of 1 hr at 32°, the spectrum changed. In particular, the H-3 doublet changed to an overlapping doublet and triplet. Thus the benzo anion II is rearranging in similar fashion and rate to the parent anion I. It is important to recognize that this scrambling proceeds *via* the benzylic ion IV as an intermediate. There is no evidence for IV in the anion nmr and a methanol quench of the anion gave an 85% isolated yield of benzo-6,7-bicyclonona[3.2.2]-2,6,8-triene (see also ref 6) with <1% of other volatile products detectable by gc.[8] We conclude that the benzylic anion IV is at least 2 kcal/mol less stable than its isomeric allylic ion II.

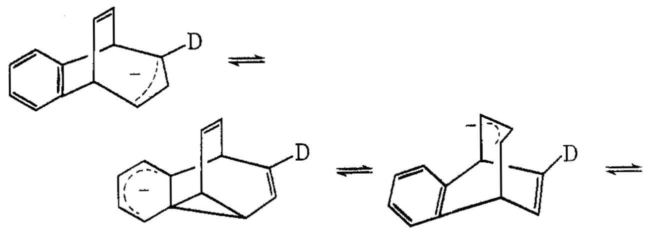
Experimental support for the rearrangement mechanism is extensive: Maercker's detailed work on the cyclopropylcarbinyl-homoallyl anion interconversion,[9] Staley's observation[10] of a barbaralane derivative from base exchange of a bicyclo[3.2.2]nonatrienyl system, and our observation that deuterium scrambling does not occur in the bicyclo[3.2.2]nona-2,6-dienyl anion.[7,11] For rearrangement to occur in the dienyl anion, ring opening to a bare secondary carbanion must compete with opening to an allylic ion.

A 5-carbon scrambling (see below) results from the application of the rearrangement to II. Deuterium cannot be incorporated into the benzylic positions, 1 and 5, because this would require breakage of the bonds to the benzene ring. For 7-carbon scrambling to occur (see below), a phenyl migration is required and such migrations are well established.[12]

5-Carbon scrambling



7-Carbon scrambling



Differentiation between a 5-carbon and 7-carbon scrambling required carbon-13 nmr analysis[5,13] of the benzobicyclo[3.2.2]nonatriene derived from quenching. Neither integration nor decoupling and multiplet analysis of the proton spectrum provided definitive data. Sensitivity limitations prevented an unambiguous conclusion from deuterium spectra. However, in the carbon spectrum, the use of the isotope shift induced at the adjacent carbons was straight-forward. The aliphatic carbons, C-1, C-4, and C-5, each appeared as two peaks in the deuterated hydrocarbon with an intensity ratio of ∼2:1. Also, C-6 and C-7 showed an isotope peak (approximate intensity ratio 5:1) but this observation was limited by the low sensitivity of these quaternary carbons. Thus, deuterium must be incorporated at C-1 and C-5 in accord with the 7-carbon scrambling process. Combined analysis of the carbon and proton results (Table I) shows essentially statistical scrambling of deuterium into all nonbenzo positions with a possible isotope effect slightly favoring deuterium at positions 3 and 4 at the expense of 1 and 5. These results clearly demonstrate the utility of carbon-13 nmr for the analysis of a deuterium label in highly scrambled systems.

While the experimental result that II is more stable than IV is clear-cut, its interpretation remains open to question. Do the relative stabilities of these homoaromatic[14] (if not bicycloaromatic[2,15]) ions reflect the stabilities of simple benzylic and allylic ions? In a zero-order approximation, the homoaromatic stabilization of an allylic or benzylic ion to generate a bishomocyclopentadienide or bishomoindenide ion, respectively, should be the same. In each case, the major homoaromatic stabilization arises from the antibonding MO of ethylene and the nonbonding MO of the ion. Equivalent stabilization is expected, because the nonbonding MO energies are equal. The third π bridge should have little effect on these conclusions because bicycloaromatic stabilization has little to add to homoaromatic stabilization.[7] Also, Brown[16] has shown that an ethylene bridge and a benzo bridge have similar stabilizing influence in homoaromatic interaction of anions. Thus, the stability difference between II and IV is best attributed to the difference between a benzylic and an allylic ion. However, throughout these orbital manipulations, one should not lose sight of the classical alternative that a bishomocyclopentadienide is more stable than a bishomoindenide ion as an attenuation of the known stabilities of the cyclopentadienide and indenide ions.[4]

We are continuing our investigation of substituent effects using the degenerate anion rearrangement.

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