The Case for π-Assisted Ionization in the Solvolysis of 9-Bicyclo[4.2.1]nona-2,4,7-trienyl Esters[1]

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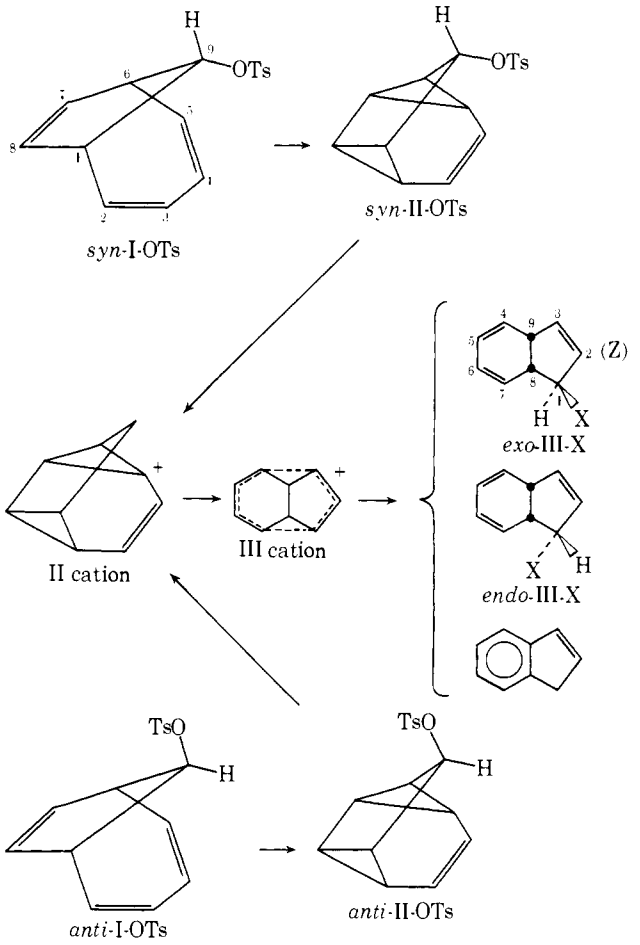
Abstract: Rate constants are reported for the 9-bicyclo[4.2.1]nona-2,4,7-trienyl tosylate epimers (I-OTs) and their more saturated isomers. The observed sensitivity of the k's to variations in solvent, leaving group, and substituent groups suggests that the I-OTs epimers ionize via distinct pathways involving π participation. Both I-OTs epimers produce the same product mixture consisting of rearranged products only. Product studies using deuterium label reveal that the rearrangement step is highly specific. These results are discussed in view of the recently proposed solvolysis mechanisms for these esters.

A recent communication by Kirmse[2] dismissed the possibility of π participation in the solvolysis of *syn*-I-OTs and *anti*-I-OTs. Instead a mechanism involving rate-determining formation of tetracyclic alkyl esters via an intramolecular Diels-Alder reaction was proposed. The authors felt this mechanism best accommodated the identical solvolysis rates for the epimers at 50.1° in aqueous methanol, the same product mixture from both epimers, and the low-solvent sensitivity of *syn*-I-OTs. This explanation is inconsistent with our previous interpretation,[3] and we now wish to present our results in this area which will hopefully help resolve this situation.

Scheme I



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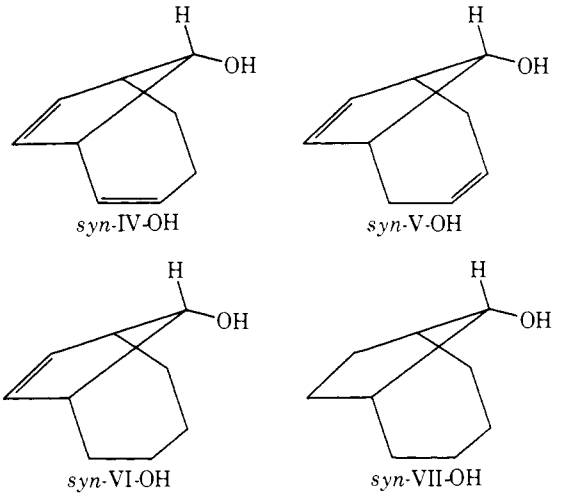
Results

The preparations of the various *syn*-bicyclo[4.2.1]nonyl alcohols used for this study are already published.[3,4] The preparation of *anti*-I-OH was recently accomplished in several laboratories by epimerization of *syn*-I-OH with aluminum isopropoxide.[2,5] Thus, *anti*-VII-OH is available by hydrogenation of *anti*-I-OH. The most characteristic spectral observation found for distinguishing between each pair of epimers was the signal for the α hydrogen in the NMR spectra. For the syn epimers, the signal is a triplet, while the signal for the anti epimers is a singlet. The corresponding alkyl toluenesulfonate esters (ROTs) were prepared as previously described.[3]



The rates of acetolysis of the various alkyl toluenesulfonate esters were followed by titrating the produced toluenesulfonic acid. Good first-order kinetics were observed in every case except with *anti*-VII-OTs which showed a significant upward drift within a run. The integrated rate constants drift up ca. 70% at one half-life. It may well be that *anti*-VII-OTs solvolyzes with rearrangement to *exo*-2-hexahydroindenyl tosylate, which is expected to be approximately twice as reactive.[6] The k's are summarized in Table I.

In the syn epimeric series, all the alkyl esters have comparable reactivities except for the fully unsaturated *syn*-I-OTs.[7] As previously reported, while *syn*-VI-OTs and *syn*-VII-OTs have more comparable reactivities, their reactions are mechanistically different, where the ionization of the former involves π participation and that of the latter proceeds primarily without assistance. It is reasonable, then, that *syn*-IV-OTs and *syn*-V-OTs also solvolyze with π participation and the reduced k's, compared with those of *syn*-

Table I. Summary of Rate Constants for the Various 9-Bicyclo[4.2.1]nonyl Tosylates

ROTs	Solvent	Temp, °C	10^6k, s^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
syn-I-OTs	AcOH	50.0	63.7[a]	23.0	−6.7
	AcOH	75.0	901[a]		
	AcOH	125.0	68 000[a]		
	EtOH	50.0	33.8 ± 0.1		
	75% MeOH	50.0	141[b]		
anti-I-OTs	AcOH	50.0	35.0 ± 1.1	24.7	−2.6
	AcOH	75.0	600 ± 20		
	EtOH	50.0	14.9 ± 0.3		
	75% MeOH	50.0	138[b]		
syn-IV-OTs	AcOH	125.0	6.70 ± 0.20	29.1	−9.8
	AcOH	148.8	56.4 ± 1.0		
syn-V-OTs	AcOH	125.0	2.60 ± 0.12	27.1	−16.7
	AcOH	148.8	19.0 ± 0.6		
anti-V-OTs	AcOH	75.0	3.81 ± 0.05	29.4	0.76
	AcOH	100.0	70.4 ± 1.1		
syn-VI-OTs	AcOH	125.0	7.5[a]		
syn-VII-OTs	AcOH	75.0	0.016[c]		
	AcOH	125.0	3.35[a]	28.5	−12.7
anti-VII-OTs	AcOH	75.0	110 ± 2	26.6	−0.3
	AcOH	100.0	1670 ± 40		

[a] Reference 7. [b] Extrapolated value using data in ref 2. [c] Extrapolated value data in ref 7.

Table II. Summary of Products Generated in the Solvolysis of 9-Bicyclo[4.2.1]nona-2,4,7-trienyl Esters

		Product distribution, %			
		(2-Z)-III-X			2-Z-Indene
9-Z	Conditions	X	Exo	Endo	
	syn-I-OTs				
D	NaOAc, HOAc, 50°[a]	OAc	99		1
H	4 M $NaBH_4$, 67% diglyme, 50°	H	98		2
		OH			
H	4 M $NaBD_4$, 67% diglyme (D_2O)	D	89	<1	2
		OH[b]	9		
D	Lutidine, MeOH, reflux[c]	OMe	83.7	8.4	7.9
Ph and *p*-An	NaOAc, 60% acetone, 125°[d]	OH	80	10	10
	2,6-Lutidine, MeOH, 50°	OMe	93	7[e]	0.5
	anti-I-OTs				
D	NaOAc, HOAc 50°	OAc	99		1
H	Lutidine, MeOH, reflux[c]	OMe	84	8.8	7.2

[a] Reference 7. [b] The carbinol product most likely arises from an inferior quality of $NaBD_4$ used in this experiment. [c] Reference 2. [d] ROPNB esters, ref 3. [e] Tentatively assigned.

VI-OTs, reflect the inductive effect of the extra double bond.

In the anti epimeric series, again the trienyl *anti*-I-OTs solvolyzes faster than the more saturated analogues. However, here the range in reactivities within the series is much smaller where *anti*-I-OTs is only ca. 10 times more reactive than *anti*-VII-OTs which in turn is ca. 15 times more reactive than *anti*-V-OTs. In this case, *anti*-V-OTs and *anti*-VII-OTs most likely react via the same mechanism involving σ participation, and the lower reactivity of *anti*-V-OTs again results from the inductive effect of the double bonds.

The reactions of the I-OTs epimers proceed by a mechanism distinct from that of the other compounds in the series. As seen in Table I, the epimers have comparable reactivities, different solvent sensitivities, and fortuitously the same reactivity in 75% methanol at 50°. In acetic acid and ethanol, the syn epimer is more reactive.

In contrast, the saturated epimers, VII-OTs, show a large difference in reactivity where the anti epimer is 2×10^4 times more reactive. Clearly this difference results from the enhanced reactivity of *anti*-VII-OTs arising from the more favorable geometry for σ participation. As a result the I-OTs/VII-OTs rate ratio is substantially reduced in the anti epimeric series.

We have previously reported[7] the acetolysis products of *syn*-I-OTs. We find the same acetolysis products from *anti*-I-OTs, 99% *exo-cis*-dihydroindenyl acetate (*exo*-III-OAc) and 1% indene. Again, no *endo*-III-OAc was observed where our procedure permits the detection of 0.15% ROAc. Deuterium label was placed at C_9 by epimerization of *syn*-I-OH with aluminum tris(isopropoxide-d_7). Analysis was performed on the recovered ROTs and the ROAc product after 50% reaction in the acetolysis of *anti*-I-OTs. NMR analysis of the recovered ROTs-*d* showed it to be >95% *anti*-I-OTs with <1% proton at C_9. Thus the ionizations of *anti*-I-OTs and *syn*-I-OTs are not accompanied by epimerization or rearrangement processes. In the ROAc product, the label was found exclusively at C_2, as was the case with *syn*-I-OTs.

Even in more nucleophilic conditions, such as 67% aqueous diglyme containing 4 M $NaBH_4$ where intermediate cation lifetimes are reduced significantly, the product from *syn*-I-OTs is again cis-fused dihydroindene plus a trace of indene. When $NaBD_4$ is used, the NMR spectrum of the recovered product shows multiplets for the aliphatic hydrogens at δ 3.47, 3.03, and 2.22. The corresponding portion of the spectrum for the protio analogue shows multiplets at δ 3.48, 3.02, 2.66, 2.22, and the results clearly show the absence of one hydrogen (>99 ± 1%). The signal at δ 3.03 is assigned to the endo methylene hydrogen on the basis of its 4-Hz coupling to H_8. A coupling of 9 Hz is observed between H_8 and the exo-methylene hydrogen at δ 2.66.

The formation of *endo*-III-OH product is observed in the solvolysis of 9-arylbicyclo[4.2.1]nona-2,4,7-trienyl esters. $J_{1,8}$ is 7 Hz in *endo*-II-X vs. 3.8 Hz in *exo*-III-X. Solvolysis products in a variety of conditions are summarized in Table II.

In the acetolysis of *anti*-VII-OTs, three acetate products are produced. The major product (54%) is *exo*-2-hexahydroindanyl acetate. The other two products (30 and 16%) remain unidentified, but the *syn*- and *anti*-VII-OAc structures can be ruled out on the basis of GLC retention times.

In anhydrous methanol containing 2,6-lutidine, *syn*-I-OTs produces 94% *exo*-III-OMe, 6% of another ROMe product, plus <0.5% indene. The amount of the second product produced was found to vary depending on the nature of the buffer used where the highest amount, 10%, was found with $NaHCO_3$. Furthermore, *exo*-III-OMe was found to be sensitive to base in methanol and to GLC conditions at higher temperatures. The NMR spectra of the above produced mixture show a new peak at δ 4.47 (broad doublet, J = 7 Hz), appropriate for the exo-1 hydrogen of *endo*-III-OMe. However, the 6% ROMe product was not isolated or identified. Also not settled is whether or not it is a primary product.

Discussion

One important point that should be discussed first is that with regard to the mode of ionization of the I-OTs epimers. Do the compounds ionize with π participation[7] or do the reactions begin with an internal Diels–Alder isomerization followed by the ionization step.[2] The latter case was proposed because the epimers have near-equal solvolytic reactivities in 75% methanol at 50° and produce the same product mixture.

Table III. Summary of k's for Various ROTs Esters at 50°

ROTs	10^6k, s^{-1} EtOH	AcOH	75% MeOH	a value
p-Methoxyneophyl[a]	42.3	119	610 ± 70[b]	
anti-7-Norbornenyl[c]	236 ± 10	370[d]	1990 ± 200	0.92 (0.83)[f]
syn-I	33.8	63.7	141[e]	0.40
anti-I	14.9	35.0	138[e]	0.88

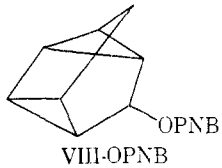
[a] Reference 8. [b] Interpolated value. [c] 25.0°. [d] Reference 10. [e] Extrapolated value using data in ref 2. [f] Value corrected for temperature.

Table IV. Summary of k's for Various ROTs Esters in AcOH

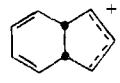
ROTs	Temp, °C	k, s^{-1}	k(monoene)/k(satd)
anti-7-Norbornenyl	25	3.7×10^{-4} *a*	
7-Norbornyl	25	6.2×10^{-14} *b*	6×10^9
anti-8-Bicyclo[3.2.1]-octa-6-enyl	50	2.34×10^{-5} *c*	7×10^4
8-Bicyclo[3.2.1]octyl	50	3.2×10^{-10} *d*	
syn-VI	125	7.5×10^{-6} *d*	
syn-VII	125	0.7×10^{-6} *e*	11

[a] Reference 10. [b] Reference 7. [c] Extrapolated value using data in ref 16. [d] Value corrected for temperature and k_s contribution using data in ref 17. [e] Corrected for k_s contribution, ref 7.

As seen in Table I, not only do the epimers have different k's but the k's show different sensitivities to solvent variation. The k's for the I-OTs epimers are collected in Table III along with those for other ROTs esters in order to make the analysis more clear. In determining the appropriateness of the solvent sensitivity, comparisons should be made between compounds that ionize with similar mechanisms. In this case, the k's for the I-OTs epimers can more appropriately be compared with those of *p*-methoxyneophyl tosylate,[8] which ionizes with anchimeric assistance rather than with *tert*-butyl chloride which ionizes to produce an open cation.[9] As can be seen in Table III, the k's for *syn*-I-OTs and *anti*-I-OTs show different solvent sensitivities, where *anti*-I-OTs (a = 0.9) is as sensitive as *p*-methoxyneophyl-OTs and *anti*-7-norbornenyl-OTs (a = 0.8) which ionizes with π participation to produce the homoaromatic bishomocyclopropenyl cation. On the other hand, *syn*-I-OTs is significantly less sensitive (a = 0.4), possibly resulting from interactions between the incipient tosylate anion and the butadiene moiety.[5] While a wider range in solvents is always desirable for solvent studies, the limitation in the present case results from our desire to include *anti*-7-norbornenyl-OTs in the comparison. The high reactivity of this compound makes it difficult to include more highly ionizing solvents.



VIII-OPNB



IX cation

Establishing that the solvolytic k's for the I-OTs epimers are appropriately sensitive to solvent changes and that those of each epimer show a different sensitivity supports the proposal that the mechanisms involve π participation where the rearrangement lags behind the C–O bond cleavage. It would be difficult to explain this difference in solvent behavior for the two I-OTs epimers if the reactions involved a rate-determining intramolecular Diels–Alder reaction of the un-ionized esters.

Other evidence which may help distinguish between the two mechanisms proposed is the sensitivity of the reaction to changes in the leaving group. Thus in 80% acetone at 125°, *syn*-I-OTs is ca. 20 000 times more reactive then *syn*-I-OPNB. Furthermore *syn*-I-OPNB is ca. 5000 times less reactive than VIII-OPNB,[11] which in turn is already uniquely unreactive compared to other less strained biscyclopropylcarbinyl esters.[12] Certainly this difference in reactivity cannot be attributed to a shift of the rate-determining step in the reaction from the internal Diels–Alder reaction to the C–O ionization step (Scheme I), since *syn*-II-OPNB is expected to have a larger solvolytic k than what is observed for *syn*-I-OPNB. On the other hand, the results are consistent with a reaction proceeding with π participation where the ROTs/ROPNB reactivity ratio is expected to be large; e.g., for *anti*-7-norbornenyl esters the ratio is ca. 10^7.[10,13]

Finally, aryl substitution at C_9 of *syn*-I-OPNB produces significant rate increases, much too large for a reaction involving a rate-determining Diels–Alder reaction of the un-ionized esters.[14]

In summary, the kinetic results involving variations in solvent, leaving group, and substituents at C_9 are consistent with a reaction mechanism where the rate-determining step is an ionization step ocurring with π participation and where the rearrangement process lags behind this step. The magnitude of the solvent and structural effects on the reaction rates observed here would not be exhibited by Diels–Alder reactions.[15]

The solvolytic behavior of *syn*- and *anti*-I-OTs is consistent with the two distinct ionization processes suggested in Scheme II which must fortuitously proceed with comparable ease and merge at some unknown point. The scheme shows the distinct transition states, some stage along the reaction pathway where the anion is sufficiently dissociated for the two reactions to merge, and III cation, possibly the only intermediate in the reaction. This scheme is consistent with all the results observed in protic solvents with the exception of the deamination of I-N_2^+ where capture of I cation by solvent competes with rearrangement to III cation.[2]

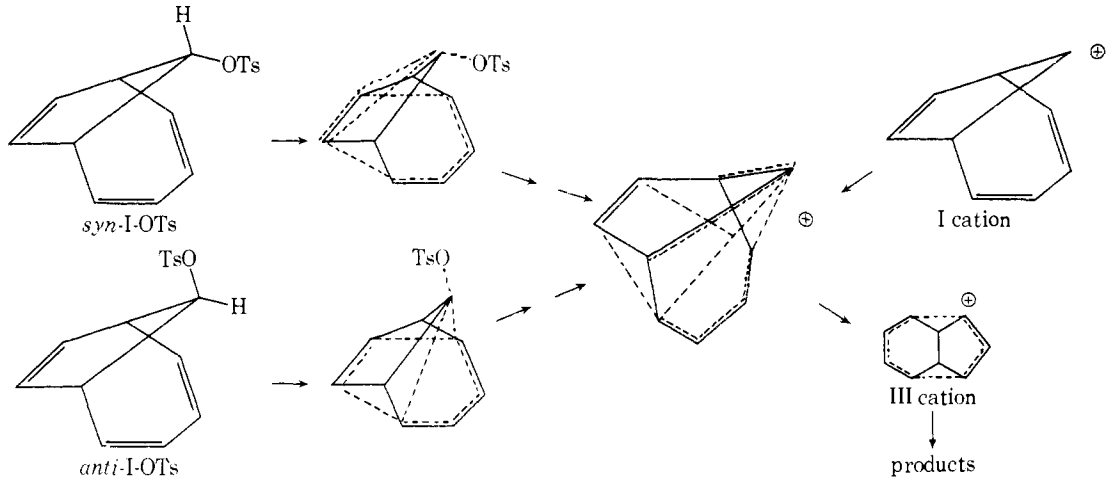
The solvolysis of *syn*-VI-OH also proceeds with π participation to generate a bishomocyclopropenyl cation which yields *syn*-VI-OAc product only. However, because of the open geometry of the five-membered ring, the rate enhancement due to anchimeric assistance is modest. Thus, k(*syn*-VI-OTs)/k(*syn*-VII-OTs) is 11.[7] The dependence of the assisted-ionization process on geometry is better appreciated by inspection of the results summarized in Table IV. As can be seen, as the puckering of the five-membered ring increases in this series of bicyclo[n.2.1]alkenyl tosylates, not only do the actual rate constants increase, but more significantly the differences in reactivity between the monoene and the corresponding saturated esters increase.

The presence of the second double bond in *syn*-IV-OTs and *syn*-V-OTs does not affect the reactivity of these compounds over that of the monoene, *syn*-VI-OTs, except for normal inductive effects. Even in the anti series, the presence of the two double bonds in V-OTs reduces its reactivity compared to the fully saturated analogue. Certainly no rate enhancements are observed due to bicycloconjugation.[18]

The results from product analyses suggest that the solvolysis reactions of both trienyl I-OTs epimers proceed with a very efficient rearrangement to generate a bishomotropylium cation. The rearrangement process proceeds in a very specific and highly symmetrical way to make C_9 of I-OTs C_2 of III.

Capture of the cation is also specific where the principal acetolysis product formed is the *exo*-2-*cis*-dihydroindenyl

Scheme II



derivative (99%) plus a trace of indene. The reaction of *syn*-I-OTs was repeated in 67% diglyme using sodium borodeuteride in order to test further the stereoselectivity of chemical capture. These solvolytic conditions were selected because they have produced isomeric product mixtures in those cases where in acetic acid solvent only one product is produced.[19] However, even in these more nucleophilic aqueous conditions only one product is produced, *exo*-III-D, with the nucleophile attaching specifically exo.

On the other hand, methanolysis of *syn*-I-OTs was found to produce 6% of a second ROMe product as reported by Kirmse.[2] It was not characterized but is appropriate for *endo*-III-OMe. This result bears directly on the concern regarding the nature of III cation. The formation of endo product certainly implies capture of an open allylic cation like IX cation.[20] However, the origin of the 6% ROMe product is questionable. Furthermore, the fact that only a negligible amount of elimination product is formed is inconsistent with capture of an open cation.

Thus, our results are consistent with the formation of the ring-closed bishomotropylium cation, III cation, in the reaction which in turn is captured with high specificity to yield exo product only. Our results do not suggest the presence of an open allylic cation, IX cation,[20] which will produce exo and endo products plus elimination products except when there is a stabilizing group at C_2 of III.[3]

The final point for discussion is how does the rearrangement occur and at what point do the two I-OTs epimers merge into the same reaction pathway? Clearly, both epimers generate the rearranged bishomotropylium cation, and our results show that neither I-OTs epimer undergoes epimerization during the solvolysis reaction. Therefore, each reaction begins distinctly, and the merging point in the reaction occurs possibly before the formation of III cation. It seems reasonable that the two pathways become the same by the time the initially formed epimeric R^+OTs^- ion pairs are dissociated.

The results from calculations on I cation reveal that the dissociated cation can gain considerable stabilization, ca. 18 kcal (in the absence of solvent), by undergoing some geometrical distortions which may be in line with the rearrangement process.[5] The distortion involves tipping the one-carbon bridge away from the two-carbon bridge by 10° (7 kcal) and tipping the four carbon bridge towards the two carbon bridge by 30° (11 kcal). The added stabilization at this geometry is accompanied by considerable delocalizations of $\sigma_{1,2}$ and $\sigma_{5,6}$ and an increase in the interactions between $C_2(C_5)$ and $C_8(C_7)$, and between $C_1(C_6)$ and C_9. In this geometry the charge is delocalized among C_9, $C_1(C_6)$, and $C_2(C_5)$.

Since the calculations show that the cation gains stability when the interactions are increased between C_9 and the butadiene moiety, it seems that the geometry of *anti*-I-OTs is stereoelectronically more favorable for this interaction early in the ionization process and for the consequent rearrangement process. The *syn*-I-OTs, on the other hand, ionizes with back-side participation by the monoene and with possible interaction between the oxygen atom of the incipient tosylate anion and the butadiene moiety.[5] It is this interaction with the oxygen atom which may facilitate bridge-flipping of C_9 from the monoene to the diene, providing the entry into the rearrangement process. Without this interaction, bridge-flipping may be difficult as evidenced with the 7-norbornadienyl cation.[21]

It is still not clear whether epimeric precursor can ionize and generate distinct bicycloconjugated ions which can be chemically captured in competition with any possible electronic rearrangement. While the present system seems appropriate for testing this possibility, the presence of distinct bicycloconjugated ions in these reactions is difficult to determine because of the facile rearrangement processes which make it difficult even to determine when the two pathways merge.

Experimental Section

***syn*-9-Bicyclo[4.2.1]nona-2,7-dienyl Toluenesulfonate (*syn*-IV-OTs).** The carbinol, *syn*-IV-OH, prepared as previously described[4] was esterified as were the other carbinols with toluenesulfonyl chloride in pyridine in the usual manner. Recrystallization of *syn*-IV-OTs from ether–pentane gave white needles, mp 63.5–64.5°: δ_{Me_4Si} (CCl_4) 7.2 and 7.8 (q, 4 H, aromatic), 5.0–6.0 (m, 4 H, olefinic), 4.75 (t (J = 7.0), 1 H, α-H), 2.7–3.2 (m, 2 H, bh), 2.46 (s, 3 H, methyl), and 2.0 (m, 4 H, methylene).

***syn*-9-Bicyclo[4.2.1]nona-3,7-dienyl Toluenesulfonate (*syn*-IV-OTs).** The carbinol, *syn*-V-OH, prepared as previously described[4] was esterified as above. Recrystallization of *syn*-V-OTs from ether–pentane gave white crystals, mp 99.5–100.5°: δ_{Me_4Si} (CCl_4) 7.2 and 7.8 (q, 4 H, aromatic), 5.62 (d, 2 H, vinyl), 5.22 (m, 2 H, vinyl), 4.98 (t, 1 H, α-H), 2.72 (m, 2 H, bh), 2.43 (s, 3 H, methyl), and 2.20 (m, 4 H, methylene).

***anti*-9-Bicyclo[4.2.1]nona-2,4,7-trienyl Toluenesulfonate (*anti*-I-OTs).** The carbinol, *anti*-I-OH, prepared as previously described[5] was esterified as above. Recrystallization of *anti*-I-OTs from 4:1 hexane–chloroform gave white crystals, mp 78.5–79.0°: δ_{Me_4Si} (CCl_4) 7.67 and 7.26 (q, 4 H, aromatic), 5.78 (m, 4 H, butadiene), 5.17 (d (J = 1 Hz), 2 H, monoene), 4.53 (s, 1 H, α-H), 3.08 (d (J = 7 Hz), 2 H, bh), and 2.41 (s, 3 H, methyl).

***anti*-9-Deuteriobicyclo[4.2.1]nona-2,4,7-trien-9-ol (*anti*-9-*d*-I-OH).** Aluminum perdeuterioisopropoxide was prepared from perdeuterioisopropyl alcohol (99.0% D) and aluminum[22] and used without further purification. To ca. 4.5 g of the freshly prepared aluminum isopropoxide was added 10 ml of xylenes containing 1.5

g of bicyclo[4.2.1]nona-2,4,7-trien-9-one. The solution was refluxed for 63 h and work up as previously described. The purified carbinol had mp 82.5–84.0°: δ_{Me_4Si} (CS_2) 5.81 (m, 2 H, H_2 and H_5), 5.67 (m, 2 H, H_3 and H_4), 5.12 (d (J = 1.5 Hz), 2 H, monoene), 2.79 (dd (J = 7.5 and 1 Hz), 2 H, bh), 2.28 (s, 1 H, OH).

No signal was detected at δ 3.77 (<1%). The alkyl toluenesulfonate ester of *anti*-9-*d*-I-OH was recrystallized from 4:1 hexane–chloroform as white crystals, mp 79.2–79.8°: δ_{Me_4Si} (CS_2) 7.22 and 7.56 (q, 4 H, aromatic), 5.82 (m, 4 H, butadiene), 5.12 (2 H, monoene), 3.00 (d, 2 H, bh), and 2.39 (s, 3 H, methyl). No signal was detected at δ 4.53 (<1%).

***anti*-9-Bicyclo[4.2.1]nona-3,7-dienyl Toluenesulfonate (*anti*-IV-OTs).** The carbinol was available to us from another study. The ester, *anti*-V-OTs, was prepared as above and recrystallized from pentane as white needles, mp 113–114°: δ_{Me_4Si} (CCl_4) 7.2 and 8.0 (q, 4 H, aromatic), 5.62 (s, 2 H, olefinic), 5.26 (m, 2 H, bh), 2.53 (s, 3 H, methyl), and 2.25 (m, 4 H, methylene).

***anti*-9-Bicyclo[4.2.1]nonyl Alcohol (*anti*-VII-OH).** Hydrogenation of 167 mg of *anti*-I-OH in 1 ml of ethanol containing 20 mg of PtO_2 during ca. 16 h produced *anti*-VII-OH in quantitative yield. The carbinol was recrystallized from pentane, mp 172–174°: δ_{Me_4Si} (CCl_4) 3.97 (s, 1 H, α-H), 2.30 (m, 5 H), and 1.51 (m, 10 H).

***anti*-9-Bicyclo[4.2.1]nonyl Toluenesulfonate (*anti*-VII-OTs).** The carbinol, *anti*-VII-OH, was esterified as above. Recrystallization of *anti*-VII-OTs from 5:1 pentane–ether yielded white crystals, mp 127–128°: δ_{Me_4Si} (CS_2) 7.33 (q, 4 H, aromatic), 4.58 (s, 1 H, δ H), 2.45 (s, 3 H, methyl), 2.38 (m, 2 H, bh), and 1.45 (m, 12 H, methylenes).

Kinetic measurements were performed as previously described.[3]

Product analysis was performed on *anti*-I-OTs as previously described.[3] As is the case with *syn*-I-OTs, analysis by GLC (10% Carbowax, 100°) of the acetolysis products from *anti*-I-OTs failed to reveal any other ROAc product (<0.15%) besides *exo*-III-OAc. These conditions are sufficient to separate *syn*- and *anti*-I-OAc by 35 min.

A solution of *syn*-I-OTs (290 mg) and 2,6-lutidine (0.17 ml) in 20 ml anhydrous methanol was heated to 50° for 30 h in a sealed tube. The solution was extracted with ether, washed with sodium bicarbonate and water, and dried over magnesium sulfate. GLC analysis on 10% Carbowax 20M, 120°, revealed three products. The product mixture contained 94% *exo*-III-OMe readily identified by NMR, plus 6% of another ROMe product appropriate for *endo*-III-OMe, along with 0.5% indene.

References and Notes

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On the Mechanism of the Sensitized Photooxygenation of Pyrroles[1]

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Abstract: In the dye-sensitized photooxygenation of alkylpyrroles, 1,4 addition of singlet oxygen leads to the formation of unstable *endo*-peroxides whose existence was provided by low-temperature NMR. The *endo*-peroxides have been shown to undergo rapid ground-state reactions leading, inter alia, to 5-hydroxy-Δ^3-pyrrolinones by two mechanisms: internal rearrangement and reaction with water. The extent of the latter mechanism was investigated by the incorporation of [^{18}O]water with the conclusion that, except in water solvent, the former mechanism predominates. The more stable *endo*-peroxide of *N*-phenylpyrrole liberates singlet oxygen upon warming.

Introduction

Although dye-sensitized photooxygenations of pyrroles[1] and furans[2,3] have been widely studied, there are few details describing the mechanism of their initial reaction with singlet oxygen ($^1O_2$) or the subsequent reaction of the $^1O_2$ adducts. It has been assumed that the major final products arise from nonphotochemical reactions of an *endo*-peroxide intermediate, which itself is derived from 1,4 cycloaddition of $^1O_2$ to the recipient pyrrole[4,5] or furan.[6] A direct observation of a pyrrole *endo*-peroxide has not been reported, although Foote and Kane[7] have observed the formation of furan *endo*-peroxides by NMR and have studied their photochemistry and ground-state reactions. The ground-state chemistry of *endo*-peroxides derived from furans has been examined in aprotic and alcoholic solvents[2,3,6,7] but not water. The incorporation of solvent is clearly implicated in some cases, e.g., methanolysis, but the ambiguity associated with hydrolysis[4,8] did not arise. Since the first reported photooxidations of pyrrole[4,9,10] involved aqueous solvent, and because of the importance of pyrrole compounds, e.g., hemopyrrole,[11] porphobilinogen,[12] and bilirubin,[13,14] in