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CATIONIC REARRANGEMENT OF THE BICYCLO[4.2.1]NONA-2,4,7-TRIEN-9-YL SYSTEM. AN EXAMPLE INVOLVING VIRTUALLY NON-IONIC RATE-DETERMINING STEP.

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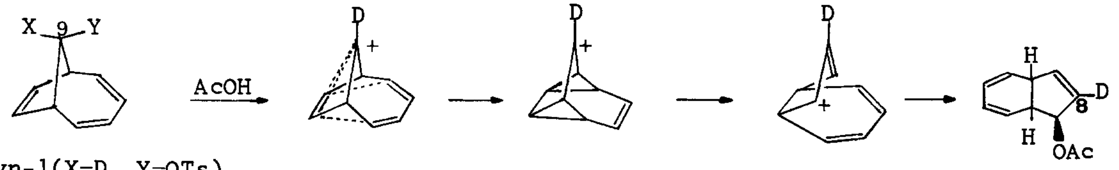
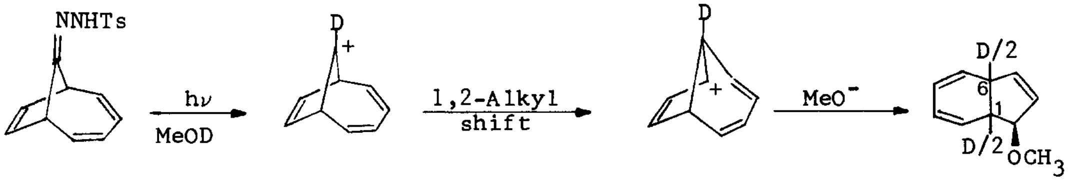
The apparent controversy as to the mechanism of the cationic rearrangement of the bicyclo[4.2.1]nona-2,4,7-trien-9-yl system into the bicyclo[4.3.0]nona-2,4,7-trien-9-yl one has been the subject of special interest[1,2] in connection with its predicted π-electron stabilization.[3] Two modes of the rearrangement have hitherto been reported.[1,2] The solvolysis of the tosylate (1) in acetic acid afforded exo-9-acetoxy-8-d derivative (2) and the mechanism involving the bicycloconjugated cation 4, which undergoes the intramolecular Diels-Alder reaction to give cation 5, has been suggested.[1] (Rearrangement Mode I)



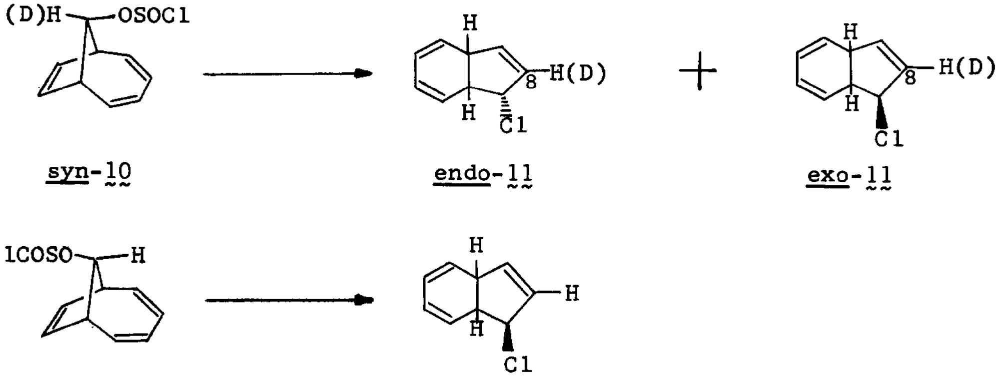
syn-1(X=D, Y=OTs)
anti-1(X=OTs, Y=D)   4   5   3   2

By contrast, Kirmse et al. reported that the cation 7, generated by the photolysis of the tosylhydrazone (6) in methanol-d, provided as the major rearranged product exo-9-methoxy derivative 9 with half a deuterium located exclusively at C-1 and C-6 as a result of 1,2-alkyl shift in 7 to give 8.[2] (Rearrangement Mode II) The inconsistency with Mode I was noted by the criticism that the solvolysis of 1 should not involve cation 4 in the rate-determining step.



6   7   8   9

We wish to report an example of the title rearrangement which is formally regarded as Mode I and which nevertheless involves virtually non-ionic rate-determining step. Thermolysis of *syn*-bicyclo[4.2.1]nona-2,4,7-trien-9-yl chlorosulfite (*syn*-10)$^{5)}$ in carbon tetrachloride at 46°C/10^{-6}Torr provided initially a 3:2 mixture of *endo*- and *exo*-9-chlorobicyclo[4.3.0]nona-2,4,7-trienes (11) which upon prolonged heating reached 1:9 ratio. By contrast, *anti*-10 afforded *exo*-11 and less than 10% *endo*-11, the ratio being unchanged throughout thermolysis under identical conditions. Less than 2% indene was detected in both cases. Taking into account the previously reported observation that *endo*-11 epimerizes into *exo*-11 under these conditions,$^{5)}$ the above results suggest that the [4.2.1]→[4.3.0] rearrangement(10→11) is at least partially stereospecific. Furthermore *syn*-10-9-d produced 11 with effectively all of the deuterium at C-8, suggesting that the rearrangement mechanism of 10 should closely resemble Mode I rather than Mode II.



syn-10 *endo*-11 *exo*-11

anti-10 *exo*-11

This expectation was further substantiated by the measurements of rate constants as shown in TABLE 1. First order kinetics were observed in each case and the rate was concentration-independent, indicating that thermolysis is an intramolecular process. The resemblance of the kinetic profile between 1 and 10 is significant despite the fact that 10 is more reactive than 1. Thus the *syn*-isomer is more reactive than the *anti*-isomer in both cases. The difference in the kinetic parameters between *syn*- and *anti*-10($\Delta\Delta H^{\ddagger}$=7.9 kJ/mol and $\Delta\Delta S^{\ddagger}$= 19.3 J/K·mol) is remarkably similar to the corresponding difference between the tosylate epimers (1)($\Delta\Delta H^{\ddagger}$=7.1 kJ/mol and $\Delta\Delta S^{\ddagger}$=17.1 J/K·mol). This as well as deuterium labelling experiment strongly suggest that the decomposition of 10 is mechanistically identical with Mode I.

The ionic character in the rate-determining step of the thermolysis of *syn*-10 was estimated from its solvent-sensitivity. As seen in TABLE 2, the largest solvent effect on rate(relative rate=3.1) was observed in thionyl

TABLE 1 Summary of Rate Constants for Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Chlorosulfites (**10**)[a] and Tosylates (**1**)[b]

ROSOCl[a]				ROTs[b]			
Solvent	Temp.(°C)	$k(10^{-6}s^{-1})$		Solvent	Temp.(°C)	$k(10^{-6}s^{-1})$	
		syn	*anti*			*syn*	*anti*
CCl_4	46.0	76	38	AcOH	50	63.7	35.0
CCl_4	61.2	201	132	AcOH	75	901	600
CCl_4	71.0	871	427	AcOH	125	6.8×10^4	-
$\Delta H^{\ddagger}$(kJ/mol)		79.1	87.0	$\Delta H^{\ddagger}$(kJ/mol)		96.2	103.3
$\Delta S^{\ddagger}$(J/K·mol)		-67.4	-48.1	$\Delta S^{\ddagger}$(J/K·mol)		-28.0	-10.9

[a]This work. [b]Reference 2.

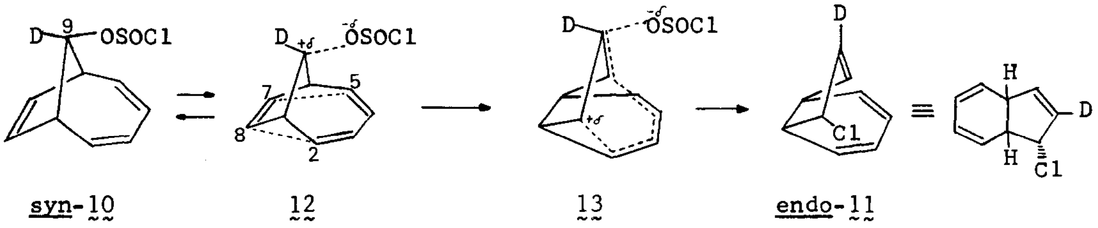
TABLE 2 Solvent sensitivity of Rate Constants for *syn*-Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Chlorosulfite (**10**)[a]

Solvent	$k(10^{-4}s^{-1})$	Rel. rate	Solvent	$k(10^{-4}s^{-1})$	Rel.rate
Cyclohexane-d_{12}	1.66	1.0	1,4-dioxane-d_8	3.92	2.4
CCl_4	2.01	1.2	THF-d_8	4.34	2.6
Benzene-d_6	3.62	2.2	Thionyl chloride	5.12	3.1
Pyridine-d_5	3.68	2.4			

[a]At 61.2°C.

chloride, a solvent of high ionizing power. The magnitude of solvent effect for the *syn*-**10** in these solvents is by far smaller than that of other secondary alkyl chlorosulfites.7) While these secondary alkyl chlorosulfites react in 1,4-dioxane at least 16 times faster than they do in iso-octane,6,7) *syn*-**10** reacts in the former solvent only 2.4 times faster than in cyclohexane, a nonpolar solvent. Moreover allyl chlorosulfite decomposes 270 times faster in thionyl chloride than in iso-octane,7) whereas *syn*-**10** reacts only 3.1 times faster in thionyl chloride than in cyclohexane. Interestingly the thermolysis does not seem greatly enhanced in pyridine in which significant tertiary amine catalysis is generally observed for secondary alkyl chlorosulfites.8) Since it has been established that these previously known chlorosulfites involve rate-determining C-O bond ionization as revealed by significant secondary β-deuterium isotope effect,9) it seems reasonable that the rate-determining step of the thermolysis of **10** is marginally ionic, or virtually non-ionic. Thus we conclude that the discrete cation like **4** or **7** cannot intervene in the rate-determining step in the thermolysis of **10**.

We *tentatively* propose the following mechanism for the thermolysis of **10** as shown in Scheme 1. In this mechanism, the interaction between the monoene and diene begins synchronously with the C-O bond ionization as partial positive charge develops at C-9. Subsequently as the sufficient interaction is achieved between C-2(C-5) and C-8(C-7) bond to generate an intermediate like **13**, which then rapidly collapses into *endo*-**11**, the observed stereospecific product. It may be noted that such a one-step concerted mehcanism should not require the intervention of cation **4** or **7**.



SCHEME 1

Whatever the mechanistic details of this reaction, because of the remarkable resemblance between the chlorosulfite thermolysis and tosylate solvolysis as shown by both kinetic and deuterium labelling studies, it has become increasingly clear that Mode I represented by the solvolysis of the tosylate **1** would not involve the discrete cation **4** in the rate-determining step as Kirmse has pointed out previously.2)

Further mechanistic studies are now in progress.

REFERENCES AND NOTES

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