The Effect of Leaving Group Orientation on Solvolytic Cope Rearrangements. A Study of *exo*-Tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-trien-11-yl Tosylates and Derivatives

Shô Itô,* Isamu Itoh, Yutaka Fujise, Tetsuo Nakatsu,
C. A. Senkler,**,† and P. v. R. Schleyer***,†
Department of Chemistry, Tohoku University, Sendai 980
†*Department of Chemistry, Princeton University, Princeton, N.J. 08540, U.S.A.*
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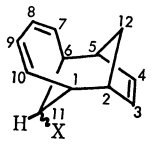
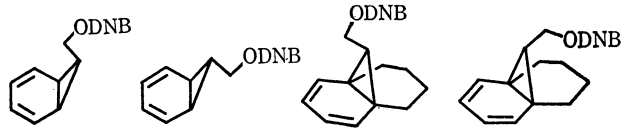
Synthesis and solvolytic behavior of derivatives of the highly hindered title compounds are described. *exo*-Tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-trien-*syn*-yl tosylate (*syn*-**18**-OTs) and the corresponding perhydro derivative, *syn*-**23**-OTs, solvolyze at rates that are in reasonable agreement with those predicted by Foote-Schleyer calculations. *syn*-**18**-OTs, and its dihydro derivatives, *syn*-**19**-OTs and *syn*-**20**-OTs, give completely rearranged products on solvolysis in acetic acid and 75% dioxane, 80% acetone, and 75% dioxane, respectively (Table 2). These products can be explained by normal cationic rearrangements, probably occurring after ionization. On the other hand, *anti*-**18**-OTs and *anti*-**23**-OTs solvolyze at rates *ca.* 10^2 times slower than those predicted by Foote-Schleyer calculations. Presumably the *anti* derivatives of **18**-OTs, **20**-OTs, **23**-OTs, and the tetrahydro tosylate (**22**-OTs) suffer steric hindrance to ionization. Product formation from *anti*-**18**-OTs (Table 3) and *anti*-**19**-OTs in acetic acid and 75% dioxane, respectively, is explained as a [3_S+3_S] sigmatropic shift induced by ionization, with formation of an allylic ion providing the driving force for rearrangement.

Molecular topologies which induce solvolysis by prior thermal rearrangement, or conversely in which thermal rearrangement is induced by ionization, have not been fully elucidated. Studies of such systems should help to clarify the relationship between reactivity and the orientation of the orbitals and the magnitude of their overlap. We now report the synthesis and solvolytic behavior of a number of derivatives of one such topology, the *exo*-tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-trien-11-yl system, **1**.††



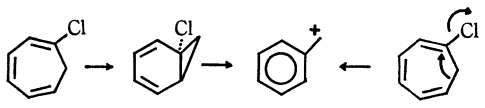
1

Several papers provide a foundation for understanding the interplay of thermal and ionic processes. In many cases, thermal process occurs prior to the ionization. (2,4,6-Cycloheptatrienyl)methyl 3,5-dinitrobenzoate solvolyzes 5.5×10^5 times faster than its fully saturated analog in 80% acetone yielding unrearranged alcohol and styrene.[1] For the rearrangment to styrene, the valence tautomerism to norcaradiene systems, **2a** and/or **2b** followed by the ionization was suggested. The similar rates of solvolysis for **3** and **4** ($k_{(4/3)}=3.4$) indicate that the 10^5 cyclopropyl-assisted rate acceleration dampens any kinetic effect due to the orientation of the leaving group with respect to the 1,3-diene system.[2] Thus, the influence of geometry, **2a** or **2b**, on the rates of solvolysis of (2,4,6-cycloheptatrienyl)methanol derivatives is probably too small to be important kinetically.[3]



2a **2b** **3** $k_{rel}=1.0$ **4** $k_{rel}=3.4$

1-, 2-, and 3-Chlorocycloheptatrienes rearrange to benzyl compounds, but the 1-chloro derivative reacts faster.[4] In addition, the rate increases with solvent polarity is slower in 80% ethanol than the rate of solvolysis of benzyl chloride. Hence, the rate determining step, though ionic, is not ionization of benzyl chloride. A probable mechanism is tautomerism to the norcaradienyl isomer, **5**, which ionizes *via* disrotatory ring opening to give the benzyl cation in the rate determining step. This mechanism accounts for the slower rates of the 2- and 3-chloro derivatives since they must first rearrange *via* 1,5-hydrogen shifts to the 1-chloro isomer. Another possible mechanism, not excluded but highly unlikely,[5] is σ participation to give the benzyl cation directly. The transition state for this process would probably not benefit from benzyl delocalization.



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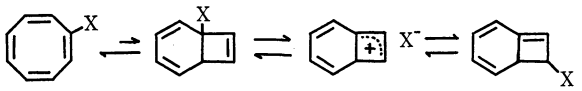
**Apart of this paper is taken from C. A. Senkler's Ph. D. Thesis, Princeton University, 1974.

***Present address: Institut für Organische Chemie der Universität Erlangen-Nürnberg, D-8520, Erlangen, West Germany.

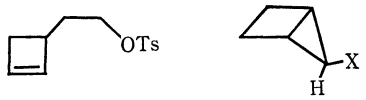
†† Although the tosylates could be named as *cis*-1-*transoid*-1,2-*cis*-2-tricyclo[4.4.1.1^{2,5}]dodeca-3,7,9-trien-11(a)-yl and -11(e)-yl *p*-toluenesulfonates following IUPAC Tentative Rules in their most extended application (IUPAC Tentative Rules for Nomenclature of Organic Chemistry, Section E: Fundamental Stereochemistry, *IUPAC Bulletin*, No. 35), we use in this paper the *exo-endo* (for carbon skeleton) and *syn-anti* (for functional groups) nomenclature for the sake of simplicity.

The rearrangement of halo- and acetoxycyclooctatetraenes **6** to the corresponding *trans*-β-halostyrenes[6] was shown to occur *via* an electrocyclic reaction to **7** followed by ionization and conrotatory ring opening.[7-9] For chloro- and acetoxycyclooctatetraenes (**6**: X=Cl or OAc), the rate determining step is ionization, **7**→**8**. For bromocyclooctatetraene (**6**: X=Br), however, ionization is rate determining in solvents of low polarity, $E_T<42$, while the electrocyclic reaction **6**→**7** is rate determining in more polar solvents. Fluorocyclooctatetraene gives a 12% yield of *trans*-β-fluorostyrene upon heating at 100 °C for 35 h, but the mechanism of this transformation has not been determined.[10]



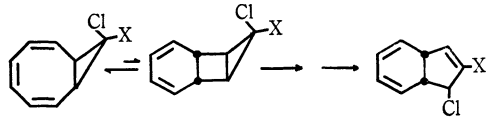
6 **7** **8**

The rate of acetolysis of 2-(2-cyclobutenyl)ethyl tosylate, **9**, reflects a competition between solvent displacement and conrotatory ring opening to a butadiene derivative, which then goes on to product.[11] The estimated rate of ring opening, 1×10^{-5} s^{-1}, in this case is greater than the rate of solvent displacement, 3×10^{-6} s^{-1}.



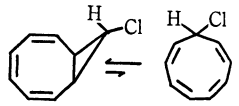
9 **10**

Investigations of the solvolysis kinetics of *anti*-5-bicyclo[2.1.0]pentyl derivatives, **10** (X=OTs, or OPNB),[12] have revealed a remarkable insensitivity to solvent polarity and leaving group. The products, however, are cyclopentadiene and 2-cyclopentenol, typical of cationic intermediates. The expalanation involves rate-limiting epimerization of **10** to the corresponding *syn* isomers, presumably *via* diradical.[13] *syn* Isomers then undergo disrotatory solvolytic ring opening to give the observed products.



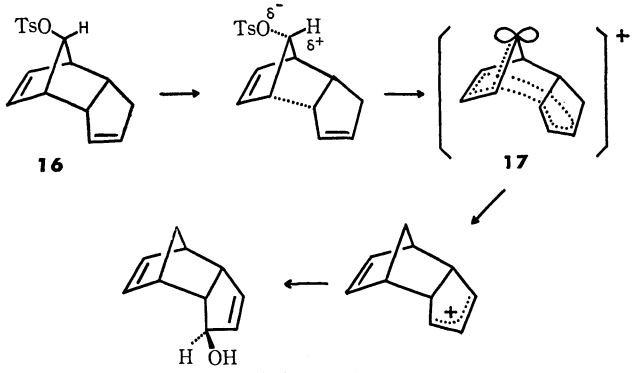
11 **12** **13**

In agreement with Vogel's original proposal,[14] both 9,9-dichlorobicyclo[6.1.0]nonatriene (**11**: X=Cl), and *syn*-9-chlorobicyclo[6.1.0]nonatriene-9-*d* (**11**: X=D), rearrange at a rate independent of solvent to give dihydroindenyl chlorides **13**.[15] An attractive mechanistic proposal is a rate determining electrocyclic reaction to a tricyclo[6.1.0.0^{2,7}]nonadiene ring system **12** followed by rapid disrotatory solvolytic ring opening to an allylic dihydroindenyl cation which gives the observed products. *anti*-9-Chlorobicyclo[6.1.0]nonatriene, **14**, also solvolyzes at a rate independent of solvent to give the same dihydroindenyl chloride. However, the reaction of **14**-*d* revealed the complete deuterium scrambling.[15] This result eliminates an epimerization mechanism similar to that found in **10**, and culminates to a mechanism which involves the rate-determining rearrangement of **14** to 9-chlorocyclononatetraene, **15**, followed by rapid solvolysis *via* the cyclononatetraenyl cation. The mechanism is consistent with the observation that 9-chlorocyclononatetraene **15** behaves exactly same way at −60° in SO_2 while **14** is inert at −20 °C in SO_2.[16]



14 **15**

Apart from these instances in which isomerization takes place prior to solvolysis, Breslow's work on derivatives of dicyclopentadiene has provided an interesting example of the converse process, an electrocyclic reaction induced by solvolysis (Scheme 1).[17] The ionization of **16** to ion pair weakens the β bonds antiparallel to the leaving group and induces a Cope rearrangement (transition state; **17**), the driving force being formation



16 **17**

Scheme 1.

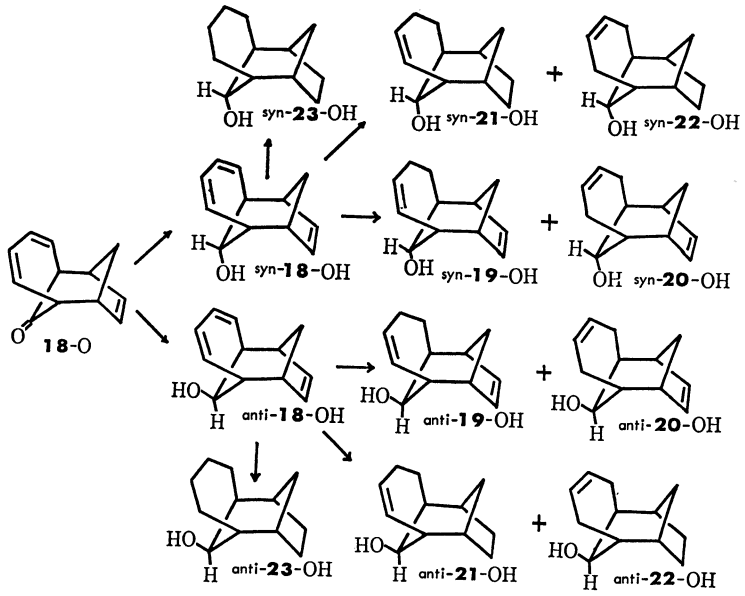
of an allylic ion. Supporting evidence for this mechanism is the fact that the C-8 ketones related to **16** undergo relatively rapid Cope rearrangement which are facilitated by protonation of the carbonyl oxygen.[18]

After the completion of the present study, Haywood-Farmer *et al.* published their preliminary result on the acetolysis of very similar brosylates, with no implication on product analysis.[19] The paper includes the kinetic data of brosylate of our *anti*-**23**-OH (*vide infra*).

Results

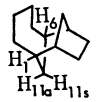
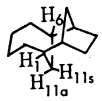
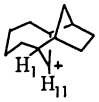
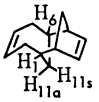
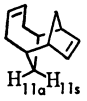
Synthesis of Substrates. Ketone **18**-O, the product of [6+4] cycloaddition of tropone with cyclopentadiene,[20] underwent Meerwein-Ponndorf reduction to give 21% of *syn*-**18**-OH and 74% of *anti*-**18**-OH. The conjugated double bonds of these alcohols were selectively reduced by Na/*n*-BuOH to give alcohols, *syn*- and *anti*-**19**-OH and *syn*- and *anti*-**20**-OH. Allowing *syn*- and *anti*-**18**-OH to react with two moles of hydrogen each gave four alcohols, *syn*- and *anti*-**21**-OH and *syn*- and *anti*-**22**-OH, while complete hydrogenation resulted in *syn*- and *anti*-**23**-OH (Scheme 2). Tosylates of these alcohols were obtained by the standard procedure.

Configuration of the alcohols were assigned by correla-

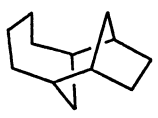


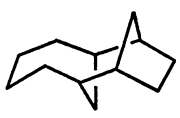
Scheme 2.

Table 1. Molecular mechanics calculations[21]

Structure	Engler force field				Allinger force field			
	ΔH_f (kcal/mol)	Strain (kcal/mol)	Steric energy (kcal/mol)	ϕ (°) H_1–C_1–C_{11}–H_{11} H_6–C_6–C_{11}–H_{11}	ΔH_f (kcal/mol)	Strain (kcal/mol)	Steric energy (kcal/mol)	ϕ (°) H_1–C_1–C_{11}–H_{11} H_6–C_6–C_{11}–H_{11}
	−16.71	32.97	41.61	H_{11a} {72.3 / 70.8	−16.63	33.51	34.15	H_{11a} {72.5 / 71.0
				H_{11s} {41.8 / 43.3				H_{11s} {40.5 / 41.9
	−18.20	31.48	40.12	H_{11a} {64.8 / 64.8	−21.03	29.11	29.75	H_{11a} {63.7 / 63.6
				H_{11s} {48.0 / 47.8				H_{11s} {47.1 / 47.0
anti-**23**-OH (a-form)	—	—	43.88	H_{11s} {43.5 / 44.5	—	—	—	—
anti-**23**-OH (b-form)	—	—	44.37	H_{11s} {49.8 / 49.8	—	—	—	—
syn-**23**-OH (a-form)	—	—	44.42	H_{11a} {74.8 / 73.7	—	—	—	—
syn-**23**-OH (b-form)	—	—	43.63	H_{11a} {66.7 / 66.7	—	—	—	—
	—		37.35	16.1	—	—	—	—
	—		—	—	—	—	21.19	H_{11a} {78.1 / 78.2
								H_{11s} {37.0 / 36.9
	—		—	—	—	—	25.66	H_{11a} {64.2 / 64.2
								H_{11s} {46.6 / 46.6

tion of the magnitude of $J_{\underline{C}HOH\text{-bridgehead }\underline{H}}$ with dihedral angle. Molecular mechanics calculations[21] on alcohols *syn*-**23**-OH and *anti*-**23**-OH (Table 1) reveal both the dihedral angles, ϕ, and preferred conformations. *anti*-**23**-OH is less strained by 0.5 kcal/mol in the chair (a) than the boat-like (b) conformation, while *syn*-**23**-OH is less strained by 0.8 kcal/mol in b- form than in

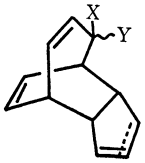

a


b

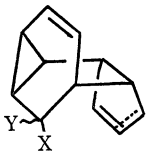
a-form. Thus, both conformers are likely present in each alcohol and tosylate. Dihedral angles for *anti*-**23**-OH range from 43 to 50°, for which J=3.5—4.0 Hz is expected, while dihedral angles of 66° to 75° for *syn*-**23**-OH suggest J=0—0.8 Hz.[22] NMR data described in experimental part agree with the expectations, showing a broad singlet for *syn* compounds and a triplet (J=4—7 Hz) for *anti* compounds.

That the ketone **18**-O is somewhat sterically hindered was evidenced by its failure to react with sodium borohydride or sodium in ethanol. However, reduction by lithium aluminium hydride in tetrahydrofuran yielded a single alcohol *syn*-**18**-OH.[20a] The result is supported by calculations. Thus, hindrance calculations[23] suggest that both *anti* and *syn* sides of the ketone are quite hindered. However, congestion is substantially larger on the *syn* side (116.1) than on the *anti* side (77.5), and therefore kinetically-controlled reduction would be expected to give *syn*-**18**-OH.

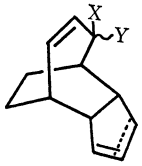
Solvolysis. *anti*-**18**-OTs was heated at 110 °C in acetic acid buffered with sodium acetate for 24 h. The resulting acetate mixture (75% yield) was reduced with lithium aluminium hydride and then oxidized with chromium(VI) oxide–pyridine. The products, separated by column chromatography, consisted of known ketones: **24**-O[24a] and **25**-O.[24b] Thus, the original acetates must have been **24**-OAc and **25**-OAc (Table 2).



24-O: X, Y=O
24-OAc: X=H, Y=OAc
24-OH: X=H, Y=OH,



25-O: X, Y=O
25-OAc: X=H, Y=OAc
25-OH: X=H, Y=OH

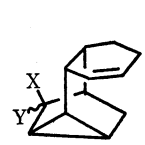


26-O: X, Y=O
26-OH: X=H, Y=OH

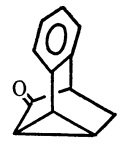
A mixture of *anti*-**19**-OTs and *anti*-**20**-OTs was heated at 90 °C for 5 h in 75% aqueous dioxane. The latter was unreactive under these conditions and was recovered quantitatively. The alcohol product from *anti*-**19**-OTs was oxidized to give a mixture of α,β-unsaturated ketones, **26**-O, ν_{CO}=1657 cm^{-1}. The NMR spectrum of the mixture featured absorptions at δ 5.5 (m) and 5.83 ppm (dt, J=6.0 and 2.0 Hz), due to the isolated double bond, and δ 6.15 (d, J=11.0 Hz) and 7.25 ppm (dd, J=11.0 and 9.0 Hz), due to the conjugated double bond. Catalytic hydrogenation of the mixture gave the corresponding, fully saturated ketone.[24a,c] Thus, the original alcohol products consist of **26**-OH.

syn-**19**-OTs was heated for 4.5 h in 80% aqueous acetone. The resulting alcohol, **27**-OH, was oxidized to a single ketone, **27**-O, ν_{CO}=1727 cm^{-1}, whose NMR featured a 2H multiplet at δ 6.01 ppm. Dehydrogenation of **27**-O gave the known ketone **28**.[25]

Refluxing *syn*-**20**-OTs in 75% aqueous dioxane resulted in three alcohols. The major alcohol, *syn*-**29**-OH, and the minor alcohol, *anti*-**29**-OH, showed NMR absorptions for two vinyl hydrogens and were oxidized



27-O: X, Y=O
27-OH: X=H, X=OH



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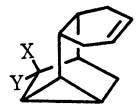
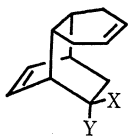
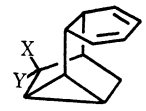


29-O: X, Y=O
syn-**29**-OH: X=H, Y=OH
anti-**29**-OH: X=OH, Y=H



30-O: X, Y=O
30-OH: X=OH, Y=H

31



syn-**32**-OAc: X=H, Y=OAc
anti-**32**-OAc: X=OAc, Y=H

to the same ketone, **29**-O, ν_{CO}=1729 cm^{-1}. Dehydrogenation of this ketone gave **28**. The structure of *syn*-**29**-OH was assigned on the basis of the singlet at δ 4.00 ppm for the >CHOH proton, while that of *anti*-**29**-OH was based on a quartet nature of the same proton at δ 4.46 ppm (dd, J=5.5 and 3.2 Hz). The third alcohol, **30**-OH, featured a carbinyl proton, δ 3.87 ppm, split into a multiplet and vinyl absorptions integrating for four protons: δ 6.08 (2H, m), 6.23 (1H, t, J=5.0 Hz) and 6.37 ppm (1H, t, J=5.0 Hz). Oxidation to a ketone, **30**-O, caused a significant shift only in the last two vinyl absorptions: δ 6.25 (1H, tt, J=7.0 and 1.5 Hz) and 6.67 ppm (1H, tt, J=7.0 and 1.2 Hz). Dehydrogenation of **30**-O gave the aromatic compound **31**.

The solvolysis of *syn*-**18**-OTs afforded *syn*- and *anti*-**32**-OAc and **33**-OAc. While the result of acetolysis has been published,[25] hydrolysis also gave the major product, *syn*-**32**-OH with no trace of fragmentation product. Product data for all compounds are summarized in Table 2. Rates of solvolysis in 60% aqueous acetone with *syn*/*anti* rate ratios and relative rates are presented in Table 3.

Table 2. Solvolysis products

Compound	Condition	Product
anti-**18**-OTs	HOAc, NaOAc 110 °C, 24 h	**24**-OAc (55%) **25**-OAc (12%)
anti-**19**-OTs	75% aq dioxane 90 °C, 5 h	**26**-OH (51%) Cycloheptatriene (trace)
syn-**18**-OTs	HOAc, NaOAc 110 °C, 3 h	*syn*-**32**-OAc (80%) *anti*-**32**-OAc (10%) **33**-OAc (6%)
	75% aq dioxane 95 °C, 5 h	*syn*-**32**-OH (95%) (as *N*-Phenylmaleimide adduct)
syn-**19**-OTs	80% aq acetone reflux, 4.5 h	**27**-OH (80%)
syn-**20**-OTs	75% aq dioxane reflux, 18 h	*syn*-**29**-OH (42%) *anti*-**29**-OH (10%) **30**-OH (24%)

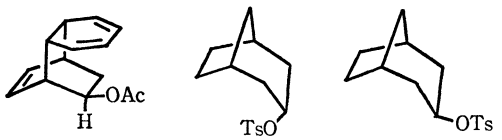
Table 3. Rates of solvolysis[a] and relative rates

Compound	k[b] (s^{-1})	T (°C)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)	$k(syn/anti)$ (75 °C)	k_{rel} (75 °C) *anti*	k_{rel} (75 °C) *syn*
syn-**23**-OTs	$(5.23\pm0.14)\times10^{-4}$	30.0	17.8	−14.8	122	—	1.0
	$(3.48\pm0.05)\times10^{-3}$	50.0					
	3.13×10^{-4} c)	25.0					
	2.76×10^{-2} c)	75.0					
anti-**23**-OTs	$(2.25\pm0.04)\times10^{-4}$	74.9	23.2	−8.9	1.0	1.0	—
	$(2.16\pm0.10)\times10^{-3}$	100.1					
	$(2.97\pm0.05)\times10^{-3}$	102.2					
	7.03×10^{-7} c)	25.0					
	2.27×10^{-4} c)	75.0					
syn-**22**-OTs	$(6.32\pm0.32)\times10^{-5}$	49.9	25.3	0.3	580	—	4.2×10^{-2}
	$(1.18\pm0.06)\times10^{-3}$	75.2					
	1.16×10^{-3} c)	75.0					
	2.17×10^{-6} c)	25.0			980		
anti-**22**-OTs	$(2.04\pm0.40)\times10^{-6}$	75.2	27.4	−6.1	1.0	8.8×10^{-3}	—
	$(3.81\pm0.35)\times10^{-5}$	102.2					
	2.00×10^{-6} c)	75.0					
	2.20×10^{-9} c)	25.0					
syn-**20**-OTs	$(8.19\pm0.25)\times10^{-5}$	49.7	25.9	2.9	400	—	6.1×10^{-2}
	$(1.72\pm0.02)\times10^{-3}$	75.3					
	1.67×10^{-3} c)	75.0					
	2.67×10^{-6} c)	25.0					
	$(7.58\pm0.35)\times10^{-5}$	102.0					
anti-**20**-OTs	$(6.79\pm0.21)\times10^{-4}$	125.3	27.2	−5.4	1.0	1.8×10^{-2}	—
	4.16×10^{-6} c)	75.0					
	4.89×10^{-9} c)	25.0					
syn-**18**-OTs	$(1.40\pm0.15)\times10^{-4}$	75.0	23.8	−8.2	53	—	5.1×10^{-3}
	$(1.52\pm0.15)\times10^{-3}$	100.2					
	3.75×10^{-7} c)	25.0					
anti-**18**-OTs	$(4.86\pm0.20)\times10^{-5}$	100.2	29.0	−1.0	1.0	1.2×10^{-2}	—
	$(6.04\pm0.20)\times10^{-4}$	125.2					
	2.66×10^{-6} c)	75.0					
	2.00×10^{-9} c)	25.0					
anti-**21**-OTs	$(3.18\pm0.30)\times10^{-4}$	75.3	25.4	−1.9	—	1.4	—
	$(8.32\pm0.03)\times10^{-4}$	84.4					
	3.07×10^{-4} c)	75.0					
	5.56×10^{-7} c)	25.0					

a) 60% acetone, 2,6-lutidine buffer. b) Determined conductimetrically, rate is average of at least two determinations. c) Calculated from data at other temperatures.

Discussion

Using the Foote-Schleyer treatment,[26] the unassisted rates of solvolysis for *syn*-**18**-OTs, *anti*-**18**-OTs, *syn*-**23**-OTs and *anti*-**23**-OTs in 60% acetone, along with several related compounds, can be calculated (Table 4). The difference in strain between chair and boat conformers for both *syn*- and *anti*-**23**-OH is less than 1 kcal/mol[21] (Table 1). Since the effect on conformer population of replacing -OH with -OTs should be small, it seems reasonable that both *syn*- and *anti*-**23**-OTs exist as a chair–boat mixture. Thus, as a crude estimate, rates were calculated for both chair and boat conformers. Dihedral angles for the chair conformation of the hydrocarbon **20**-H were used to approximate those of *syn*- and *anti*-**18**-OTs. The chair form of **20**-H is more stable than the boat form by 4.5 kcal/mol.[21a]



33-OAc **34** **35**

Table 4 reveals that the observed rate of *syn*-**23**-OTs in 60% acetone is $10^{1.4}$ and $10^{0.8}$ times slower than the rates calculated for the chair and boat conformations, respectively. *syn*-Bicyclo[3.2.1]oct-3-yl tosylate, **34**, which lacks only the four-carbon bridge of *syn*-**23**-OTs, would seem to be a plausible model. Jefford, *et al.*,[27] have observed that **34** undergoes acetolysis *ca.* 6 times slower than calculated, perhaps due to the "reflex" effect[28] or steric hindrance to ionization by the ethylene bridge. Although the Foote-Schleyer parameters used in Table 4 differ somewhat from those of Jefford, *et al.*,[27]

Table 4. Foote-schleyer calculations[26]

Compd	Ketone ν_{CO} (cm^{-1})	ϕ, deg	GS-TS (kcal/mol)	log k_{rel} (reference: cyclohexyl OTs) Calcd Foote-Schleyer (25 °C)	Obsd 60% acetone[f] (25 °C)
syn-**23**-OTs (a-form)	1705	36, 35[a]	0.8	+3.73	+2.34
syn-**23**-OTs (b-form)	1705	40, 40[a]	0.8	+3.16	
anti-**23**-OTs (a-form)	1705	50, 48[a]	0.6[i]	+2.91	−0.31
anti-**23**-OTs (b-form)	1705	56, 56[a]	0.8	+1.89	
anti-**18**-OTs	1715	37, 37[b]	0.3	−0.82[g]	−2.85
syn-**18**-OTs	1715	38, 38[b]	0.4	−0.87[g]	−0.58
					Obsd AcOH (25°)
34	1714[d]	45, 45[c]	3.8[d]	+3.59	+2.04[d]
35	1714[d]	45, 45[c]	0.6[i]	+1.31	+1.00[d]
36	1700[e]	45, 45[c]	0.6[i]	+1.16[h]	+0.46[e]
37	1700[e]	45, 45[c]	1.9	+3.09[h]	+1.86[e]

a) Determined by molecular mechanics calculations on the alcohol. b) Dihedral angles of the chair conformation of **20**-H, used as approximation, see text. c) Determined by molecular mechanics calcuations on bicyclo[3.2.1]-octane. d) Ref. 27. e) Ref. 32. f) Rate of cyclohexyl tosylate in AcOH (0.001 M Ac_2O) $k=4.88\times10^{-8}$ s^{-1}: S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952). This was converted to the reference rate constant in 60% acetone, $k=1.42\times10^{-6}$, using $m=0.6$, $Y_{60\%\ acetone}=+0.80$, $Y_{AcOH}=-1.64$: S. Winstein and A. H. Fainberg, *ibid.*, **78**, 2770 (1956). g) Includes inductive factor 3/8, Ref. 26b. h) Includes inductive factor 1/8, Ref. 26b. i) Axial cyclohexyl strain energy, E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw Hill Book Co., New York, N. Y. (1962), p. 236.

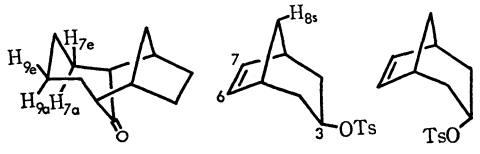
the indication is similar: **34** is $10^{1.5}$ times slower than expected.[29] Hence neither *syn*-**23**-OTs nor **34** solvolyzes *via* σ participation, and both may be somewhat slowed by steric interactions. The rates of *syn*-**23**-OTs and **34** in 60% acetone at 25 °C are quite comparable; $k_{syn\text{-}23\text{-}OTs}/k_{34}=2.0$.[30]

Inclusion of a Δ^8 double bond (*syn*-**22**-OTs), causes a 24 fold rate decrease relative to *syn*-**23**-OTs at 75 °C (Table 3). This seems large for an inductive effect of a γ double bond, as β double bonds usually cause only a 10 fold decrease in rate.[26b] In any case, the double bond in *syn*-**22**-OTs does not seem to be participating.

The observed rate for *anti*-**23**-OTs is $10^{2.2}$ and $10^{3.2}$ times slower than the rates calculated for the boat and chair conformers, respectively. Calculations by Jefford, *et al.*,[27] and those in Table 4 reveal that model compound **35** solvolyzes at a normal, largely unassisted rate in acetic acid. Comparison of the relative rates for *anti*-**23**-OTs and **35** in 60% acetone at 25 °C, $k_{anti\text{-}23\text{-}OTs}/k_{35}=0.003$, seems to indicate that steric hindrance to ionization by the four-carbon bridge in the former may be responsible for its slow rate. Steric effects of a similar magnitude have been observed in crowded norbornanes.[31]

Hindrance calculations[23] on the ketone **23**-O formed on oxidation of *syn*- or *anti*-**23**-OH show a pronounced reversal of congestion, relative to unsaturated ketone **18**-O. Attack by a nucleophile from the *syn* direction is much less hindered (62.4) than attack from the *anti* direction (1441.1). In fact, the ketone **23**-O yielded *anti*-**23**-OH quantitatively on the reduction with lithium aluminium hydride. The value of 1441.1 is quite large; therefore H_{9a} must be displaced 0.7 Å to allow attack of the nucleophile from the *anti* direction.[23] Clearly these observations support the idea that steric hindrance to ionization is a major contributor to the rate deceleration observed in *anti*-**23**-OTs.

Inclusion of a Δ^8 double bond (*anti*-**22**-OTs) causes a rate decrease relative to *anti*-**23**-OTs by a factor of 0.0088 which again seems quite large for an inductive effect (Table 3). This deceleration might be due to steric hindrance to ionization as in the case of *anti*-**23**-OTs. One of the two most hindering atoms in the ketone **23**-O, H_{9a} and H_{7a},[23] remains intact in *anti*-**22**-OTs, while the other has become vinylic. Since molecular mechanics calculations indicate that the twisted form of **22**-O, a similar system, is more stable than the boat by 4.5 kcal/mol,[21] it would seem that the preference for the twisted form in *anti*-**22**-OTs might be even larger due to substitution of -OTs for=O. In contrast, the Δ^7 double bond in *anti*-**21**-OTs causes a rate enhancement of 1.4 over *anti*-**23**-OTs. The actual rate enhancement is probably *ca.* 14 if one assumes that a β-double bond in a nonparticipating system should slow the rate by a factor of 10.[26b] In this case, migration of one of the σ bonds *trans* to the leaving group



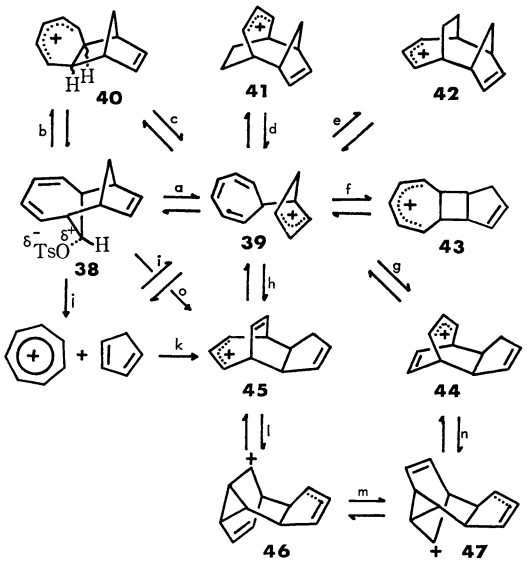
23-O **36** **37**

results in formation of an allyl cation. This is likely the mode of participation. However, products were not determined for this compound.

The rates of *anti*-**22**-OTs, *anti*-**20**-OTs and *anti*-**18**-OTs are within a factor of 2.1 of one another at 75 °C. Since the last tosylate reacts 10^2 times slower than the Foote-Schleyer calculation predicts, and the calculation estimates for the first two should be faster than for *anti*-**18**-OTs, all three seem to be anomalously slow. Since a model compound for *anti*-**18**-OTs and *anti*-**20**-OTs, bicyclic **36** also solvolyzes at a rate which agrees with that calculated by the Foote-Schleyer equation (Table 4), the distance between the double bond and the carbon containing the leaving group in **36** has been postulated to be too far to permit participation.[32] In the *endo* conformation with the 6-membered ring in a chair form of bicyclo[3.2.1]octane, molecular mechanics calculations indicate the distances C-3 to C-6 and C-3 to C-7 to be 2.999 and 2.997 Å, respectively,[21b] while, in the olefin, these would probably be *ca.* 0.1 Å shorter. On the other hand, participation by a double bond has occurred over greater distances. For example, in (*endo*-bicyclo[3.3.1]non-6-en-3-yl)methyl tosylate, in which the rate enhancement is *ca.* 10^4, [33] the distances between the olefinic carbons and the carbon bearing the leaving group are 3.313 and 3.280 Å.[21b] Therefore, it seems also possible that **36** solvolyze from the *exo* conformation (boat form), for which the distances in bicyclo[3.2.1]octane are 3.425 and 3.437 Å.[21b] This conformation would probably not allow "edge-on" interaction[34] of the double bond with the developing cationic center. The *exo* conformation in bicyclo[3.2.1]octane, however, is less stable than the *endo* by ≈5 kcal/mol.[21b] Replacing –H by –OTs should provide increased steric interaction with the H_{8s}, thus accentuating the energy difference between *endo* and *exo*. Compounds *anti*-**18**-OTs and *anti*-**20**-OTs, however, do not have such conformational freedom and the distance from the double bond carbons to C–OTs is only 2.854 Å. Thus, it seems likely that the source of the decelerations for *anti* unsaturated derivatives also lies in the four-carbon bridge.

The rate of *syn*-**18**-OTs shows good agreement with that calculated at 25 °C in 60% acetone. The 12.0 fold rate acceleration of *syn*-**20**-OTs (Table 3) is generally consistent with its having one less double bond than *syn*-**18**-OTs. Thus, neither compound seems to be benefiting from participation to a large degree, as in the model compounds **37**.[32]

Table 2 shows that *anti*-**18**-OTs gives completely rearranged products on acetolysis. Kinetic analysis seems to indicate that rearrangement occurs after ionization. Scheme 3 depicts possible rearrangement pathways available to the ion pair **38**. Breaking the σ bond *trans* to the leaving group (**a**) gives allylic ion **39**. Rotation about the bond joining the two rings of **39** permits reclosure six ways (**c**—**h**) to give six isomeric resonance stabilized cations, **40**—**45**. Ion **40** may also result from **38** directly *via* a Wagner-Meerwein rearrangement or a [1,5] sigmatropy (**b**). Both **38** and **39** may undergo fragmentation (**i**, **j**) to give tropylium ion and cyclopentadiene, which can undergo [4+2] cycloaddition giving **45**.[24b] Finally, **38** can undergo a Cope rearrangement (**o**) also giving **45**. Ions **44** and **45** can be interconverted through vinyl–cyclopropylcarbinyl rearrangements (**l**—**m**—**n**).



Scheme 3.

According to Table 2, however, products form only from **45** and **46**. Formation of **45** *via* reclosure of **39** (**h**) requires a *ca.* 180° rotation about the σ bond joining the rings of the initially formed ion. Since **45** should be similar in stability to **40**—**44**, the failure to observe products deriving from these latter ions argues against reclosure of **39** *via* **h**.

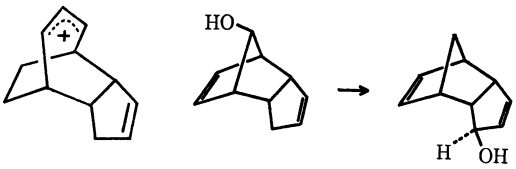
The tropylium ion and cyclopentadiene undergo [4+2] cycloaddition in 66% dioxane or acetic acid to give, after reduction of the acetates in the latter case, **24**-OH and **25**-OH in a ratio of 4.6 to 1.0.[24b] Notably, this is the same ratio in which **24**-OAc and **25**-OAc are formed on acetolysis of *anti*-**18**-OTs (Table 2). Therefore, both the fragmentation-recombination sequences (**j**—**k**) and the Cope rearrangement (**o**) can account for the stereospecific formation of **45**, which in turn forms **46** *via* path **l**.

In order to establish the fragmentation–recombination pathway for *anti*-**18**-OTs, trapping experiments were carried out. Acetylacetone trapped the tropylium ion as tropylacetylacetone (86% in hydrolysis and 51% in acetolysis) and *N*-phenylmaleimide captured cyclopentadiene as its cycloadduct (91%) in acetolysis. Furthermore, acetolysis with constant addition of methylcyclopentadiene resulted in a 6% incorporation of the latter, although this figure is somewhat inaccurate because of extensive polymerization of methylcyclopentadiene during the reaction. Thus, the pathway **j**—**k** was established.

Since the partially hydrogenated derivative, *anti*-**19**-OTs, can react *via* the Cope mechanism but cannot form the highly stable tropylium ion *via* fragmentation, its solvolysis products should help reveal the former pathway (**o**). In this case, fragmentation of the ion corresponding to **39** would form the cycloheptadienyl cation and cyclopentadiene which are incapable of cycloaddition reaction. Furthermore, the fragmentation

would have a driving force comparable to that of the bond rotation-recombination pathways. Accordingly, a mixture of products with various carbon skeleton is expected from *anti*-**19**-OTs, if *anti*-**18**-OTs were reacting by the fragmentation-recombination mechanism. The fact that tricyclic product derived only from **48** (Table 2) implied that the Cope rearrangement path is operative. In addition, the detection of cycloheptariene which is the deprotonation product of cycloheptadienyl cation implied the fragmentation process is also operative to some extent.

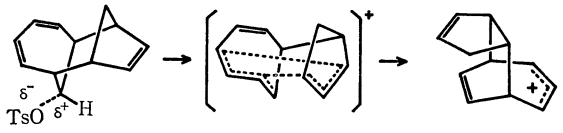
Thus, *anti*-**18**-OTs and *anti*-**19**-OTs solvolyze through the Cope rearrangement and fragmentation, the difference between these cases being that, in the former, the fragmentation products cycloadd to give the same products with those of internal process, while in the latter the fragmentation products are incapable of recombination and are detected as such.



48 **49**

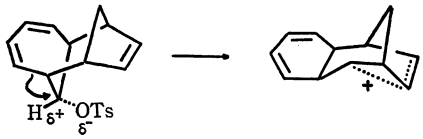
An alternative pathway for the intramolecular rearrangement is initial Cope rearrangement of these tosylates to the allyl tosylate followed by rapid solvolysis. The thermal Cope rearrangement of a similar systems **49**, is rapid only above 140 °C [17b] and *anti*-**18**-OH and its tosylate are stable at 120 °C. Thus, the rate of solvolysis of *anti*-**18**-OTs, if is were indicative of a thermal rate-determining step, should be much slower than that of *anti*-**20**-OTs or *anti*-**22**-OTs which do not contain the 1,5-diene system. At 75 °C, however, the rates of solvolysis for these three are within a factor of 2.1 (Table 3).

Thus, one of the rearrangement pathway for both *anti*-**18**-OTs and *anti*-**19**-OTs appears to be a rather remarkable $[3_s+3_s]$ sigmatropic shift induced by ion pair formation[35] which weakens the σ bonds *trans* to the leaving group.[36] This bond weakening may permit the skew orientation of the 1,5-diene system to distort towards the preferred chair orientation.[37] The aromatic Cope transition state **50** can conjugate with the external carbenium ion, thus stabilizing both;[38] this is similar to the stabilization of an adjacent carbonium ion by a benzene ring.



38 **50** **45**

If the facility with which the *anti* compounds, *anti*-**18**-OTs and *anti*-**19**-OTs, undergo the Cope rearrangement and fragmentation is due chiefly to the weakening of the σ bonds *trans* to the leaving group, then the *syn* compounds should not rearrange in this manner. The data in Table 2 confirm this premise. *syn*-**18**-OTs, *syn*-**19**-OTs, and *syn*-**20**-OTs rearrange completely to the products of the same tetracyclic skeleton and, for *syn*-**18**-OTs, essentially no difference was observed by the change of the solvent. Furthermore, any attempt to trap cyclopentadiene or the tropylium ion failed. The Foote-Schleyer treatment has implied that the *syn* compounds solvolyze at an unassisted rate. To account for >99% rearranged products due to σ participation, a rate enhancement of at least 100 over the calculated unassisted rate is necessary.[39] Clearly such a rate enhancement is lacking. Hence, *syn* compounds likely rearrange after ionization. A possible rearrangement path for *syn*-**18**-OTs is given below. Participation of the Δ^3 double bond gives the cyclopropylcarbinyl ion derivative **51**, solvent capture of which accounts for both tetracyclic *syn*- and *anti*-**32**-OAc as well as tricyclic *anti*-**33**-OAc.



51

Conclusion

Comparison of the kinetic data in Table 3 with the rates calculated *via* the Foote-Schleyer equation and the rates of model compounds seems to indicate that the *anti* compounds solvolyze anomalously slow. In the case of *anti*-**23**-OTs, this is probably due to steric hindrance to ionization by the four-carbon bridge. Steric hindrance to ionization also seems to be a factor also for unsaturated *anti* derivatives. *syn* Compounds solvolyze at rates which agree with those predicted by Foote-Schleyer calculation. Since *syn*-**18**-OTs, *syn*-**19**-OTs and *syn*-**20**-OTs give completely rearranged products but a very small rate enhancement, it seems probable that rearrangement follows ionization. Products from these *syn* tosylates result from normal carbenium ion rearrangements.

anti-**18**-OTs and *anti*-**19**-OTs undergo both fragmentation and a $[3_s+3_s]$ sigmatropic rearrangement induced by ionization. The ease of the latter process results from two factors: (1) The σ bond *trans* to the leaving group, which is weakened on ionization, is also the σ bond broken in the Cope rearrangement; and (2) the Cope transition state can conjugate with the external carbenium ion, thus allowing for mutual stabilization.

Experimental

General. Infrared spectra were taken in a film for liquids and KBr pellets for solids using Hitachi EPI-S2 IR spectrometer. All NMR spectra were measured in $CDCl_3$ solution with TMS internal standard using a Varian HA-100 or A-60D instrument. Tosylation of alcohols was carried out by the standard method.[40]

Rate Measurement. All rates were determined in 60% acetone conductimetrically with a Wayne-Kerr Model B331 Impedence Bridge capable of 0.1% accuracy. The acetone

was purified by refluxing with potassium permanganate, drying with Drierite, and distilling through a 60 cm Vigreux column prior to use. The conductivity cells used had bright platium electrodes, cell constants of 0.2—0.4 and volumes of *ca.* 25 ml. In a typical run, enough tosylate to make a 10^{-3} M solution was placed in the conductivity cell and 20 ml of 60% acetone was added. The cell was sealed and equilibrated with shaking for 4 min in the constant temperature bath. The usual number of measurements was 35. Each reaction was run at least in duplicate, and was followed for at least two half-lives. Good first-order rate plots were obtained in all cases.

Synthesis. Meerwein-Ponndorf Reduction of exo-*Tricyclo*[*4.4.1.1*^{2,5}]*dodeca-3,7,9-trien-11-one (18-O). Preparation of* syn-*18-OH and* anti-*18-OH*: Ten grams of **18**-O[20] in 200 ml of 2-propanol was heated unser reflux with 10 g of aluminium isopropoxide for 10 h and 100 ml of solvent was distilled during further refluxing for 10 h. The reaction mixture was poured into 50 ml of 2M HCl and extracted with ether. After the ether solution was washed with water and dried, the solvent was removed to yield 10 g of a semisolid material which was recrystallized from petroleum ether to give 5.7 g of *anti*-**18**-OH.

anti-**18**-OH: Mp 80—82 °C. IR: 3500 cm^{-1}. NMR (δ): 1.18 (1H, m), 1.53 (1H, d, J=11 Hz), 1.80 (1H, br. d, $J\approx$ 9 Hz), 2.7—3.0 (4H, complex)[41], 4.10 (1H, m),[41] 5.7—6.3 ppm (6H, complex). Found: C, 82.30; H, 7.99%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

anti-**18**-OTs: Mp 114—115 °C. NMR (δ): 1.18 (1H, m), 1.65 (1H, d, J=11 Hz), 2.44 (3H, s), 2.60—3.00 (4H, complex), 5.05 (1H, t, J=5.5 Hz), 5.5—6.2 (6H, complex), 7.33 (1H, d, J=8.5 Hz), 7.70 ppm (1H, d, J=8.5 Hz). Found: C, 69.51; H, 6.08%. Calcd for $C_{19}H_{20}O_3S$: C, 69.49; H, 6.14%.

The filtrate from the recrystallization of *anti*-**18**-OH was subjected to silica gel chromatography. Elution with a mixed solvent system of petroleum ether–ether gave 1.7 g of *anti*-**18**-OH and 2g of *syn*-**18**-OH.

syn-**18**-OH: Mp 32.5—34.5 °C. UV (MeOH) λ_{max}: 243 nm (ε=4552, sh), 252 (5720), 262 (5668), 273 (3173). IR: 3490 cm^{-1}. NMR (δ): 1.49 (1H, m), 2.21 (1H, d, J=10.4 Hz), 2.74 (5H, br.m), 3.90 (1H, br.s), 5.83 (4H, m), 6.21 ppm (2H, br.s). Found: C, 82.48; H, 8.16%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

syn-**18**-OTs: Mp 138—139.5 °C. NMR (δ): 1.40 (1H, m), 1.98 (1H, d, J=11 Hz), 2.43, (3H, s), 2.70 (4H, m), 4.76 (1H, br.s), 5.90 (6H, m), 7.30 (1H, d, J=9 Hz), 7.68 ppm (1H, d, J=9 Hz). Found: C, 69.23; H, 6.04%. Calcd for $C_{19}H_{20}O_3S$: C, 69.49; H, 6.14%.

Bouveault-Blanc Reduction of exo-*Tricyclo*[*4.4.1.1*^{2,5}]*dodeca-3,7,9-trien*-syn-*11-ol* (syn-*18-OH). Preparation of* syn-*19-OH and* syn-*20-OH*: To 3.63 g of *syn*-**18**-OH in 100 ml of 1-butanol were added, in several portions, 2 g of sodium at room temperature. The reaction mixture was refluxed gently and 3 g of sodium was added over 0.5 h. The cooled solution was diluted with water, neutralized with 5% HCl and extracted with ether. After the ether solution was washed with water and dried, the solvent was removed to yield 4.5 g of oil. The oil was separated by silica gel chromatography. Elution with a mixture of hexane and ether gave 1.0 g of *syn*-**19**-OH and 1.5 g of *syn*-**20**-OH.

syn-**19**-OH: Oil. IR: 3560, 3460 cm^{-1}. NMR (δ): 4.03 (1H, d, J=10 Hz),[41] 5.65 (2H, complex), 6.39 ppm (2H, m). Found: C, 81.58; H, 9.18%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

syn-**19**-OTs: Mp 96 °C (dec). NMR (δ): 1.60 (1H, dt, J=12 and 5 Hz), 2.45 (3H, s), 4.90 (1H, br.s), 5.60 (2H, m), 6.03 (2H, m), 7.32 (2H, d, J=8.5 Hz), 7.73 ppm (2H, d, J=8.5 Hz). Found: C, 68.91; H, 6.82%. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71%.

syn-**20**-OH: Mp 37—38 °C. IR: 3586, 3450 cm^{-1}. NMR (δ): 1.45 (1H, dt, J=11 and 5.5 Hz), 3.85 (1H, s,) 5.50 (2H, br.s), 6.40 ppm (2H, br.s). Found: C, 81.71; H, 9.12%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

syn-**20**-OTs: Mp 126.5—128 °C. NMR (δ): 1.45 (1H, dt, J=11 and 5 Hz), 2.45 (3H, s), 4.70 (1H, br.s), 5.45 (2H, br.s), 6.10 (2H, d, J=1 Hz), 7.32 (2H, d, J=8.5 Hz), 7.55 ppm (2H, d, J=8.5 Hz), Found: C, 68.89; H, 6.65%. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71%.

Bouveault-Blanc Reduction of exo-*Tricyclo*[*4.4.1.1*^{2,5}]*dodeca-3,7,9-trien*-anti-*11-ol* (anti-*18-OH). Preparation of* anti-*19-OH*: The alcohol *anti*-**18**-OH was reduced similarly to 1: 1 mixture of *anti*-**19**-OH and *anti*-**20**-OH. Separation of these alcohols was unsuccessful. A mixture of *anti*-**19**-OH and *anti*-**20**-OH was also prepared by sodium reduction of **18**-O. As the solvolysis rates of tosylates of *anti*-**19**-OH and *anti*-**20**-OH differ greatly, the mixture was used without separation. The mild solvolysis yielded pure *anti*-**20**-OTs, $LiAlH_4$ reduction of which produced *anti*-**20**-OH.

anti-**20**-OH: Mp 101.5—103 °C. IR: 3450 cm^{-1}. NMR (δ): 1.40 (1H, dt, J=11 and 5 Hz), 4.00 (1H, t, J=6.5 Hz), 5.60 (2H, t, J=2 Hz), 6.02 ppm (2H, m). Found: C, 81.00; H, 8.97%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

anti-**20**-OTs: Mp 132—133 °C. NMR (δ): 1.38 (1H, dt, J=10 and 6 Hz), 2.44 (3H, s), 4.98 (1H, t, J=7 Hz), 5.48 (2H, br.s), 6.03 (2H, d, J=1 Hz), 7.32 (2H, d, J=8.5 Hz), 7.76 ppm (2H, d, J=8.5 Hz). Found: C, 68.93; H, 6.65%. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71%.

Catalytic Reduction of exo-*Tricyclo*[*4.4.1.1*^{2,5}]*dodeca-3,7,9-trien*-syn-*11-ol* (syn-*18-OH). Prepartaion of* syn-*21-OH and* syn-*22-OH*: Two grams of *syn*-**18**-OH was hydrogenated in 50 ml of methanol with 10% Pd–C catalyst (200 mg) at room temperature. After 2.1 mol of hydrogen uptake, the catalyst and the solvent were removed, giving 2 g of an oil. *syn*-**21**-OH and *syn*-**22**-OH were partly separated by silica gel chromatography eluted with a mixture of hexane and ether.

syn-**21**-OH: Oil. IR: 3300 cm^{-1}. NMR (δ): 1.0 (1H, m), 4.13 (1H, br.s), 5.62 ppm (2H, m). Found: C, 81.02; H, 10.06%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

syn-**21**-OTs: Mp 121—122 °C. NMR (δ): 1.0 (1H, m), 2.44 (3H,s), 4.85 (1H, br.s), 5.60 (2H, complex), 7.46 (2H, d, J=8 Hz), 7.90 ppm (2H, d, J=8 Hz). Found: C, 68.75; H, 7.16%. Calcd for $C_{19}H_{24}O_3S$: C, 68.64; H, 7.28%.

syn-**22**-OH: Oil. IR: 3300 cm^{-1}. NMR (δ): 1.0 (1H, m), 1.5—2.4 (14H, complex), 3.95 (1H, br.s), 5.45 ppm (2H, br.s). Found: C, 80.88; H, 10.08%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

syn-**22**-OTs: Mp 113—114.5 °C. NMR (δ): 1.0 (1H, m), 2.44 (3H, s), 4.73 (1H, br.s), 5.50 (2H, br.s), 7.44 (2H, d, J=8.5 Hz), 7.90 ppm (2H, d, J=8.5 Hz). Found: C, 68.68; H, 7.35%. Calcd for $C_{19}H_{24}O_3S$: C, 68.64; H, 7.28%.

Catalytic Reduction of exo-*Tricyclo*[*4.4.1.1*^{2,5}]*dodeca-3,7,9-trien*-anti-*11-ol* (anti-*18-OH). Preparation of* anti-*21-OH and* anti-*22-OH*: Compound *anti*-**18**-OH was reduced similarly to a 1: 1 mixture of *anti*-**21**-OH and *anti*-**22**-OH. These alcohols were partly separated by silica gel chromotography.

anti-**21**-OH: Oil. IR 3370 cm^{-1}. NMR (δ); 1.05 (1H, m), 1.4—2.7 (14H, complex), 4.03 (1H, t, J=5.2 Hz), 5.65 (1H, ddd, J=11, 6.5, and 2.5 Hz), 6.90 ppm (1H, dd, J=11 and 4.5 Hz). Found: C, 81.02; H, 10.07%, Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

anti-**21**-OTs: Mp 99—100.5 °C. NMR (δ): 1.05 (1H, m), 2.46 (3H, s), 4.90 (1H, t, J=5 Hz), 5.10 (1H, ddd, J=12, 5, and 2 Hz), 5.88 (1H, dt, J=12 and 4.5 Hz), 7.47

(2H, d, J=8 Hz), 7.89 ppm (2H, d, J=8 Hz). Found: C, 68.62; H, 7.25%. Calcd for $C_{19}H_{24}O_3S$: C, 68.64; H, 7.28%.

anti-**22**-OH: Oil. IR: 3350 cm^{-1}. NMR (δ): 1.00 (1H, m), 1.55 (4H, m), 2.1—2.50 (9H, complex), 4.05 (1H, t, J=5.5 Hz), 5.54 ppm (2H, t, J=2 Hz). Found: C, 81.00; H, 10.10%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

anti-**22**-OTs: Mp 120—121 °C. NMR (δ): 1.0 (1H, m), 1.45—2.20 (13H, complex), 2.42 (3H, s), 4.92 (1H, t, J=5.5 Hz), 5.48 (2H, t, J=2 Hz), 7.35 (2H, d, J=8 Hz), 7.80 ppm (2H, d, J=8 Hz). Found: C, 68.54; H, 7.37%. Calcd for $C_{19}H_{24}O_3S$: C, 68.64; H, 7.28%.

Catalytic Reduction of syn-***18-OH*** *and* anti-***18-OH***. *Preparation of* syn-***23-OH*** *and* anti-***23-OH***: 500 mg of *syn*-**18**-OH was hydrogenated in methanol (10 ml) with 10% Pd–C catalyst (100 mg) at room temperature for two days and the catalyst and solvent were removed. Recrystallization of the residue from petroleum ether yielded 450 mg of *syn*-**23**-OH.

syn-**23**-OH: Mp 80—81 °C. IR: 3350 cm^{-1}. NMR (δ): 0.8—2.3 (18H, complex), 3.92 ppm (1H, s). Found: C, 79.67; H, 11.19%. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18%.

syn-**23**-OTs: NMR (δ): 2.46 (3H, s), 4.68 (1H, br.s), 7.43 (2H, d, J=8 Hz), 7.88 ppm (2H, d, J=8 Hz). Unstable in air.

Catalytic reduction of *anti*-**18**-OH was performed exactly the same way to give *anti*-**23**-OH.

anti-**23**-OH: Mp 73—75 °C. IR: 3400 cm^{-1}. NMR (δ): 1.0 (1H, br.d, J=11 Hz), 1.2—2.2 (18H, complex), 4.15 ppm (1H, br.t, J=4 Hz). Found: C, 79.26; H, 10.99%. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18%.

anti-**23**-OTs: Mp 96.5—97.5 °C. NMR (δ): 0.95 (1H, br.d, J=12 Hz), 1.2—2.2 (17H, complex), 2.45 (3H, s), 4.87 (1H, t, J=5 Hz), 7.35 (2H, d, J=8.7 Hz), 7.80 ppm (2H, d, J=8.7 Hz). Found: C, 68.34; H, 7.89%. Calcd for $C_{19}H_{26}O_3S$: C, 68.23; H, 7.84%.

Solvolysis of anti-***18-OTs***. *anti*-**18**-OTs (4 g) was heated at 110 °C for 24 h in acetic acid (150 ml) with sodium acetate (1.3 g). The resulting cooled solulon was neutralized with sodium hydrogencarbonate and extracted with a mixed solvent of ether and benzene. After the extract was washed with water and dried, the solvent was removed to yield 2 g of an oil. The residue was chromatographed on silica gel (100 g) to give an acetate mixture (1.73 g). No product originated from fragmentation was detected.

The acetate (1.73 g) in dry ether (40 ml) was treated at room temperature for 5 h with $LiAlH_4$ (250 mg) in dry ether (30 ml). After excess reagent was decomposed, the reaction mixture was washed with 2 M HCl and water, dried, and the solvent was removed to give an alcohol mixture (1.16 g).

The alcohol (1.16 g) in dry pyridine (50 ml) was oxidized overnight at room temperature with chromium(VI) oxide-pyridine (1.2 eqv.), poured into ice water (50 ml), neutralized with 2 M HCl and extracted with ether. The extract was washed with water, dried and evaporated, leaving an oil (1.06 g). The residue was chromatographed on silica gel (600 g) to give a mixture of **24**-O[24a] (760 mg), and **25**-O (165 mg).[24b] **24**-O was further chromatographed on silica gel impregnated with $AgNO_3$ afforded the two previously known ketones.[24a]

Solvolysis of anti-***19-OTs***. The mixture of *anti*-**19**-OTs and *anti*-**20**-OTs (550 mg) was solvolyzed in 75% dioxane (20 ml) at 90° for 5 hr. After addition of water (20 ml), the reaction mixture was extracted with a mixed slvent of benzene and ether. The extract was washed with water, dried and evaporated, leaving an oil (400 mg). The residue was chromatographed on silica gel (250 g) to give hydrocarbons (20 mg), *anti*-**20**-OTs (220 mg) and alcohols (120 mg).

The alcohols (100 mg) in dry pyridine (5 ml) were oxidized with chromium(VI) oxide–pyridine complex (2.0 eqv.) to give an oily ketone (90 mg). The oil was purified by chromatography on silica gel (5 g) to give **26**-O (75 mg).

26-O: Oil. MS m/e: 174 (M^+). IR: 1657 cm^{-1}. NMR (δ): 1.4—2.2 (5H, m), 2.5—2.9 (5H, m), 5.5 (1H, m), 5.83 (1H, dt, J=6 and 2 Hz), 6.15 (1H, d, J=11 Hz), 7.25 ppm (1H, dd, J=11 and 9 Hz). Found: C, 82.68; H, 8.16%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%. Cycloheptatriene was identified by GLC examination of the hydrocarbon fraction.

Catalytic Hydrogenation of ***26-O***. A methanol (10 ml) solution of **26**-O (20 mg) was hydrogenated with 10% Pd–C catalyst (10 mg) at room temperature and the catalyst and the solvent were removed to give previously konwn saturated ketone quantitatively.[24]

Solvolysis of syn-***19-OTs and Oxidation of the Product to 27-O***. The mixture of *syn*-**19**-OTs and *syn*-**20**-OTs (2.2 g) was heated for 4.5 h under reflux in 80% acetone (37 ml), and poured into ice water (20 ml), leaving a crystalline substance (720 mg) which was unchanged *syn*-**20**-OTs. The filtrate was extracted with a mixed solvent of benzene and ether, washed with water, dried and evaporated the solvent to give 800 mg of an oil. The oil was chromatographed on silica gel (40 g) to give *syn*-**20**- OTs (100 mg) and an oil (570 mg).

The oil (320 mg) was oxidized (10 min) at room temperature with chromium(VI) oxide–pyridine complex (6 eqv.) in dichlormethane (30 ml), and filtered through silica gel layer, evaporated the solvent to give **27**-O (300 mg).

27-O: Oil. MS m/e: 174 (M^+). IR: 1727 cm^{-1}. NMR (δ): 1.7—2.3 (12H, m), 6.08 ppm (2H, m). Found: C, 82.81; H, 8.06%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

Dehydrogenation of ***27-O***. **27**-O (50 mg) and DDQ (10 eqv.) were heated for 2 days in dry benzene (10 ml), under reflux. The reaction mixture was filtered through alumina layer, evaporated to give semicrystalline material (40 mg). Purification by recrystallization yielded the ketone **28** (38 mg).

28: Mp 70.5—71 °C. NMR (δ): 1.5 (1H, d, J=10.5 Hz), 1.8 (1H, ddd, J=7, 4.5, and 1.4 Hz), 2.3—2.7 (2H, complex), 2.8 (1H, t, J=7 Hz), 3.1 (1H, d, J=6 Hz), 7.0—7.3 ppm (4H, AA′BB′).

Solovolysis of syn-***20-OTs***. *syn*-**20**-OTs (720 mg) in 75% dioxane (20 ml) was heated for 18 h under reflux and cooled reaction mixture was extracted with ether. The extract was dried and evaporated to give an oil (490 mg). The residue was chromatographed on silica gel (300 g) to yield *syn*-**29**-OH (162 mg), *anti*-**29**-OH (40 mg) and **30**-OH (90 mg).

syn-**29**-OH: Mp 80—81 °C. MS m/e: 176 (M^+). IR: 3300 cm^{-1}. NMR (δ): 0.94 (1H, tt, J=8 and 1.5 Hz), 1.2—2.0 (12H, m), 4.00 (1H, s), 5.97 ppm (2H, m). Found: C, 81.62; H, 9.20%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

anti-**29**-OH: Oil. MS m/e: 176 (M^+). IR: 3350 cm^{-1}. NMR (δ): 0.81 (1H, tt, J=7 and 1.5 Hz), 1.2—2.3 (12H, m), 4.46 (1H, dd, J=5.5 and 3.2 Hz), 6.05 ppm (2H, m). Found: C, 81.81; H, 9.15%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

30-OH: Mp 86—87 °C. MS m/e: 158 (M^+-H_2O). IR: 3300 cm^{-1}. NMR (δ): 1.6—2.6 (11H, m), 3.87 (1H, m), 6.08 (2H, m), 6.23 (1H, t, J=5 Hz), 6.37 ppm (1H, t, J=5 Hz). Found: C, 81.98; H, 9.21%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

Oxidation of ***30-OH to 30-O***. **30**-OH (50 mg) in dichloromethane (13 ml) was oxidized for 10 min. at toom temper-

ature with chromium(VI) oxide–pyridine complex (6 eqv.) and filtered through silica gel layer, evaporated to give the ketone **30**-O (45 mg).

30-O: Oil. MS *m/e*: 174 (M^+). IR: 1723 cm^{-1}. NMR (δ): 1.5—3.0 (10H, m), 6.00 (2H, m), 6.25 (1H, tt, $J=7$ and 1.5 Hz), 6.67 ppm (1H, tt, $J=7$ and 1.2 Hz). Found: C, 82.66; H, 8.14%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

Dehydrogenation of ***30***-O. **30**-O (30 mg) was dehydrogenated to the known ketone **31**[25] (27 mg), by the same procedure as for **27**-O.

Oxidation of syn-***29-OH*** *and* anti-***29-OH***. *syn*-**29**-OH (10 mg) and *anti*-**29**-OH (110 mg) were oxidized to the same ketone **29**-O by the oxidation with chromium(VI) oxide-pyridine complex under the conditions described previously.

29-O: Oil. MS *m/e*: 174 (M^+). IR: 1729 cm^{-1}. NMR (δ): 1.7—2.4 (12H, m), 6.03 (2H, m). Found: C, 82.88; H, 8.09%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

29-O was oxidized to **28**[25] with DDQ in refluxing benzene for 48 h.

Solvolysis of anti-***18-OTs*** *in the Presence of Trapping Reagents. Hydrolysis in the Presence of Acetylacetone*: *anti*-**18**-OTs (135 mg) was heated at 130 °C for 10 days in dioxane–H_2O (3: 1) with sodium acetate (38 mg) and acetylacetone (2 ml). After cooling, sodium *p*-toluenesulfonate (66 mg) was filtered off and the solvent was evaporated. Tropylacetylacetone[42] mp 126—126.5 °C (8 mg) was obtained from the concentrated mixture. NMR spectrum of mother liquor shows to contain *anti*-**18**-OTs (51%), tropylacetylacetone (44%) and acetylacetone (4.5%). Thus, total yield of tropylacetylacetone was 57% with 33% recovery of *anti*-**18**-OTs.

Acetolysis in the Presence of Acetylacetone. *anti*-**18**-OTs (200 mg) was heated at 105 °C for 24 h in acetic acid (10 ml) with sodium acetate (62 mg) and acetylacetone (2 ml). The resulting solution was neutralized with sodium hydrogencarbonate to pH 6, extracted twice with chloroform, washed with brine and dried over sodium sulfate. Removal of solvents under reduced pressure gave 127 mg of oil, NMR spectrum of which revealed the presence of 51% of tropylacetylacetone[42] and 41% of acetate mixture correspond to **24**-OAc.

Acetolysis in the Presence of N-*Phenylmaleimide.* *anti*-**18**-OTs (202 mg) was heated at 105 °C for 15 h in acetic acid (10 ml) with sodium acetate (63 mg) and *N*-phenylmaleimide (500 mg). The resulting reaction mixture was neutralized with sodium hydrogencarbonate and extracted 3 times with chloroform. Organic layer was washed twice with water, once with brine and dried over sodium sulfate. Removal of solvents under reduced pressure, followed by column chromatography on silica gel, gave 134 mg (91%) of cyclopentadiene-*N*-phenylmaleimide adduct.[43]

Acetolysis in the Presence of Methylcyclopentadiene. *anti*-**18**-OTs (500 mg) was solvolyzed for 13 h as in the previous section, with the dropwise addition of methylcyclopentadiene (500 mg) in acetic acid (10 ml). The reaction mixture turned dark immediately. The work up, treatment with $LiAlH_4$ and chromic acid oxidation, carried out exactly as in the previous section, furnished 65 mg of an α,β-unsaturated ketone mixture. NMR spectra of the mixture showed small broad singlet at 1.69 ppm. Mass spectrum (at 15 eV) showed *m/e* 172 with the 1/15 intensity of *m/e* 158.

Solvolysis of syn-***18-OTs***. *syn*-**18**-OTs (204 mg) was heated in 75% aq dioxane in the presence of *N*-phenylmaleimide (525 mg) and sodium acetate (62 mg) for 5 h at 95 °C yielded *N*-phenylmaleimide adduct of *syn*-**32**-OH (667 mg) in 95% yield. No cyclopentadiene adduct was detected.

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