Experimental Section

Hydrocarbons 6,[19] 9,[9,20] and 12[21] were prepared according to the literature methods.

2,3-Benzobicyclo[6.1.0]nona-2,4,6-triene (11).[22] Benzocyclooctatetraene (1.53 g, 0.01 mol)[23] was dissolved in liquid ammonia (*ca.* 250 ml) at −33° under a nitrogen atmosphere. Clean potassium metal (1.4 g, 0.036 g-atom) was added in small pieces and the mixture was stirred for 2 hr at this temperature. To the dark brown solution of the dianion was added dichloromethane (30 ml) dissolved in anhydrous ether (50 ml). The solution became light orange and no further change was observed during stirring at −33° for 6 hr. Solid ammonium chloride was introduced, after which most of the ammonia was allowed to evaporate from the resulting colorless solution under a stream of nitrogen. The residue was dissolved in water (100 ml) and the hydrocarbon product was extracted into pentane (2 × 30 ml). The pentane layer was washed several times with water, dried, and concentrated to a volume of 10 ml. This solution was passed through a small column of Florisil and the eluate was evaporated to yield a pale yellow oil (1.47 g, 87.5%). Nmr and vpc analysis of this material indicated it to be >95% pure. An analytical sample was obtained by preparative vpc purification on a 6 ft × 0.25 in. column packed with 5% SE-30 on Chromosorb W; $\lambda_{max}^{cyclohexane}$ two shoulders on long tailing absorption at 240 nm (ϵ 6250) and 215 (19,400); nmr $\delta_{TMS}^{CDCl_3}$ 7.0–7.6 (m, 4, aryl), 5.6–6.75 (m, 4, olefinic), and 0.4–2.85 (series of four overlapping m, 4, cyclopropyl).

Anal. Calcd for $C_{13}H_{12}$: C, 92.80; H, 7.20. Found: C, 92.58; H, 7.33.

Polarographic Measurements. The electrochemical apparatus employed in these experiments has been described previously.[12,13] Techniques for purifying solvents and background electrolytes and experimental procedures were identical with those utilized in the earlier work.[12,13]

(19) (a) E. Vogel, *et al.*, *Justus Liebigs Ann. Chem.*, **653**, 55 (1962); *Tetrahedron Lett.*, **11**, 673 (1963); (b) T. H. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 5194 (1964).

(20) E. Vogel, W. Grimme, and W. E. Bleck, private communication of unpublished work at Köln.

(21) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969).

(22) Subsequent to the completion of this work, **11** was reported as a thermolysis product of 8,9-benzobicyclo[5.2.0]nona-2,4,8-triene: M. Kato, T. Sawa, and T. Miwa, *Chem. Commun.*, 1635 (1971). No spectral or analytical data were given.

(23) L. Friedman and D. F. Lindow, *J. Amer. Chem. Soc.*, **90**, 2329 (1968).

exo-Tricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-yl Carbonium Ion. A New $[CH]_9^+$ Species from Rearrangement of *anti*-Tricyclo[5.2.0.$0^{2,5}$]nona-3,8-dien-6-yl Derivatives[1]

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Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received July 31, 1972*

Abstract: Acetolysis of *anti*-tricyclo[5.2.0.$0^{2,5}$]nona-3,8-dien-6-yl tosylate (**1**-OTs) proceeds with stereospecific rearrangement to *exo,syn*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-yl acetate (**2**-OAc) and 6.8 × 10^4-fold rate enhancement compared with that of *endo*-bicyclo[3.2.0]hept-6-en-2-yl tosylate (**14**-OTs). The intermediate *exo*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-yl carbonium ion (**8**), a new $[CH]_9^+$ species, as well as its 1-deuterio (**8**-*1-d*), 1-methyl (**9**), and 1-phenyl (**10**) derivatives, were generated in fluorosulfonic acid at −78° from *anti*-tricyclo[5.2.0.$0^{2,5}$]nona-3,8-dien-6-ol (**1**-OH) and the respective 6-deuterio (**1**-*6-d*-OH), 6-methyl (**6**), and 6-phenyl (**7**) alcohols, and observed by nmr spectroscopy. The simplified, time-averaged nmr spectrum exhibited by the phenyl-substituted carbonium ion (**10**) at +10° in fluorosulfonic acid is attributed to a twofold degenerate rearrangement of **10** by way of the stabilized 6-phenyltricyclo[5.2.0.$0^{2,5}$]nona-3,8-dien-6-yl cation (**12**).

Recent investigations with polycyclic compounds of the type $[CH]_n$–X (n = odd integer) have revealed unusual solvolytic reactivities, numerous skeletal rearrangements, and novel degenerate isomerizations.[3] Although a substantial proportion of the lower members (n = 5, 7) in these ethynylogous families of structures have been prepared and studied,[3] relatively few of the more numerous, higher polycycles are known.[3,4] In view of the interesting properties uncovered thus far in the $[CH]_9$–X group,[3,5] we decided to examine the behavior of *anti*-tricyclo[5.2.0.$0^{2,5}$]nona-3,8-dien-6-yl derivatives (**1**-OR), a new representative recently made available through the synthetic work of Cargill, King, Sears, and Willcott.[6] At the outset it seemed likely that this highly strained ring system would undergo a ring-expansion rearrangement to its bridged ring isomer, the *exo*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-yl carbonium ion, as is observed with other 2-bicyclo[3.2.0]heptyl deriva-

(1) Taken in part from Ph.D. Thesis of K. Yano, University of Illinois, 1972.

(2) A. P. Sloan Foundation Fellow, 1971–1973.

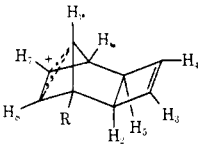
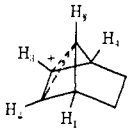
(3) Recent review: R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).

(4) Disregarding stereochemistry, the number of isomeric structures are as follows: 1 $[CH]_3$–X, 3 $[CH]_5$–X, 15 $[CH]_7$–X, and 90 $[CH]_9$–X: A. T. Balaban, *Rev. Roum. Chim.*, **11**, 1097 (1966).

(5) Some examples are (a) homocubyl [P. v. R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, **89**, 698 (1967); J. C. Barborak and R. Petit, *ibid.*, **89**, 3080 (1967)], (b) 9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl [R. M. Coates and J. L. Kirkpatrick, *ibid.*, **92**, 4883 (1970)], (c) bicyclo[3.2.2]nona-3,6,8-trien-2-yl and barbaralyl [M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967); W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967); J. C. Barborak, J. Daub, D. M. Follweiler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 7760 (1969); P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 4454 (1970); J. B. Grutzner and S. Winstein, *ibid.*, **94**, 2200 (1972)].

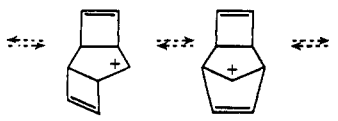
(6) R. L. Cargill, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Org. Chem.*, **36**, 1423 (1971). We are grateful to Professor Cargill for providing a sample of ketone **5** and experimental details concerning its synthesis.

Table I. Pmr Spectral Data[a] for Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl Carbonium Ions in Fluorosulfonic Acid

Carbonium ion		Temp, °C	Vinyl H_7 H_8	Vinyl H_8 H_4	Bridgehead H_1 H_6	Cyclobutane H_2 H_5	Bridge H_9	Other
	R = H (**8**)	−70	7.22 (unsym qnt, $J \sim 2.5$)	6.27 (s)	4.34 (qnt, $J \sim 2.5$)	3.18 (s)[b]	~3.1[b]	
	R = D (**8-*1-d***)	−45	7.22 (2 d, J = 2,4)[c]	6.27 (s)[c]	4.34 (t of d, J = 2,4)[c]	3.18 (s)[b,c]	~3.1[b,c]	
	R = CH_3 (**9**)	−20	7.10 (unsym qnt, $J \sim 2.5$)[d]	6.35 (s)	4.31 (br qnt, $J \sim 3$)	3.24 (br s)	3.04 (m)	CH_3 1.72 (s)
	R = C_6H_5 (**10**)	−60	7.2–7.5[b]	6.44 (d, J = 2.8) 6.23 (d, J = 2.8)	4.52 (br m)	3.65 (br m) 3.40[e]	3.40[e]	C_6H_5 7.46[b]
			H_2 H_3		H_1 H_4		H_7	
			7.07 (qnt)[f]		4.24 (m)[f]		3.24 (m)[f]	

[a] Chemical shifts given as δ values from internal $CHCl_3$ (δ 7.28) with **8** and **9** and CH_2Cl_2 (δ 5.29) with **10**. Relative peak area corresponded to the appropriate number of protons. J values refer to the observed line spacings in Hz and not necessarily the true coupling constants (except for **8-*1-d***). [b] Overlapping peaks. [c] $J_{6,9(1,9)} = J_{7,9(8,9)} = 2$; $J_{6,7(1,8)} = J_{6,8(1,7)} = 4$; $J_{2,3(4,5)} = J_{5,6(1,2)} = 0$. [d] Multiplet pitched toward high field. [e] Overlapping peaks. [f] Reference 16, $J_{1,7(4,7)} = 2.6$; $J_{2,7(3,7)} = 2.5$; $J_{1,2(4,2)} + J_{1,3(4,2)} = 8.7$.

tives.[7] This rearrangement, if reversible, could lead to multiple degeneracy (eq 1).

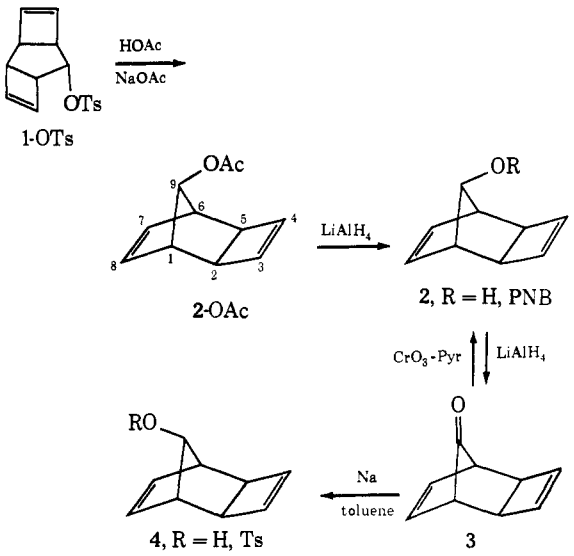


(1)

Buffered acetolysis (35°, 6 hr) of **1**-OTs gave rise to a major rearranged acetate which was isolated in 82% yield. A minor product (<3%) was detected by glpc analysis. The identity of this compound as *exo-syn*-tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl acetate (**2**OAc) follows from the chemical transformations summarized in Chart I and consideration of the nmr spectra of this new series of $[CH]_9X$ isomers.[8,9]

It is evident from the nmr spectra that there must be two pairs of equivalent vinyl protons and two pairs of equivalent protons bound to saturated carbon, although the latter are not always resolved. Further, since there is no coupling between either type of vinyl protons, each of these equivalent pairs of hydrogens must reside on the same carbon–carbon double bond. These restrictions, taken together with the existence of two different alcohols epimeric about the carbinyl carbon, require that the corresponding ketone possess one symmetry plane which is perpendicular to the plane defined by the carbonyl group and its adjacent carbon atoms with all protons symmetrically disposed on either side. Of the 19 structurally different tricyclic ketones of the type $[CH]_8C{=}O$ possible (disregarding stereochemistry),[10,11] only one, tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one (*exo*- or *endo*-**3**), satisfies these criteria.

Chart I



The exo orientation of the cyclobutene ring is required by the lack of significant coupling between H_1 and H_2,[12] the sensitivity ($\Delta\delta$ = 0.42) of the chemical shift for the cyclobutene vinyl protons to the hydroxyl stereochemistry, and the high selectivity observed in the lithium aluminum hydride reduction of the ketone.[13]

(7) (a) S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedienst, Jr., *J. Amer. Chem. Soc.*, 80, 5895 (1958); (b) S. C. Lewis and G. H. Whitham, *J. Chem. Soc. C*, 274 (1967); (c) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2347 (1972).

(8) The endo isomers of **2**-OH, **3**, and **4**-OH have been reported: M. Sakai, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4452 (1970); see also footnote 13.

(9) The 1,6-dimethyl-7,8-diphenyl derivatives of **2**-OH and **3** have been described: C. M. Anderson, I. W. McCay, and R. N. Warrener, *Tetrahedron Lett.*, 2735 (1970).

(10) The possible structures are generated by insertion of a carbonyl group into each different single bond of the five tricyclic $[CH]_9$ isomers given in ref 4.

(11) Although the possibility of hydrogen rearrangement is not formally considered in this analysis, there appear to be no such structures with the requisite molecular symmetry.

(12) See D. H. R. Barton and N. H. Werstiuk, *J. Chem. Soc. C*, 148 (1968), and pertinent references cited therein.

(13) Unfortunately, neither physical properties nor spectral data were mentioned in the preliminary communication reporting the endo isomers of **2**–**4**.[8] Nmr spectral data recently reported for the endo isomer of **3** are distinctly from those of ketone **3**. Particularly significant is the 4-Hz coupling between H_1 and H_2; *cf.* T. A. Antkowiak, D. C.

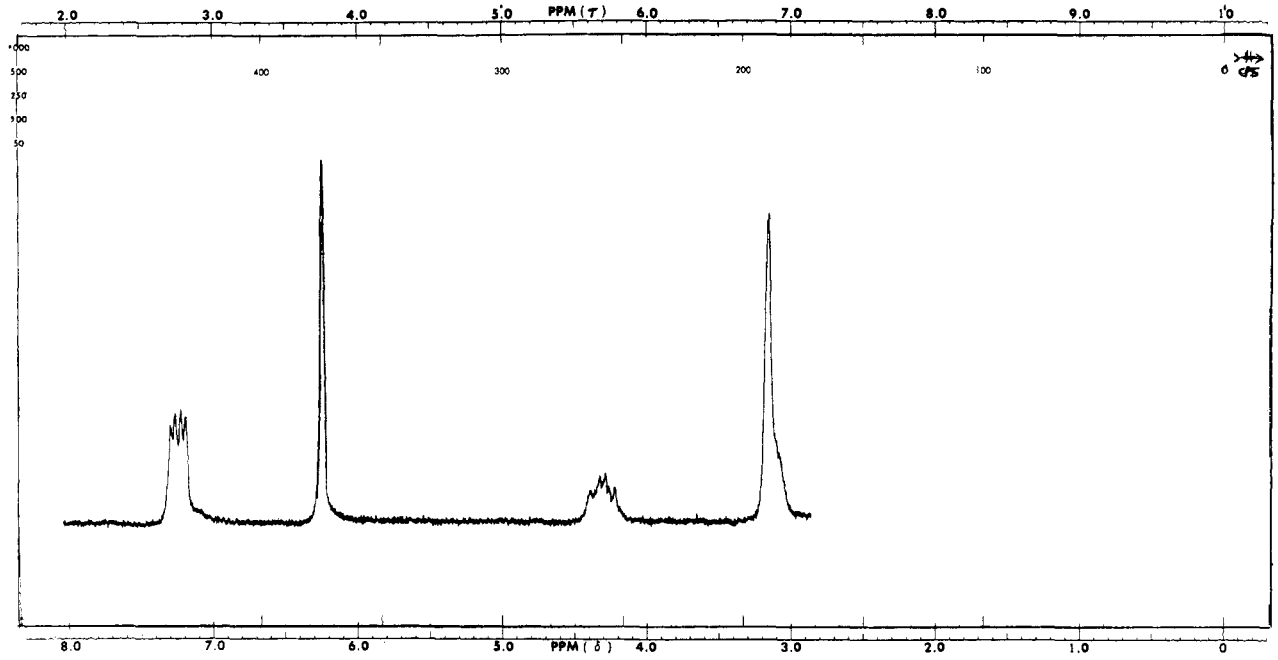


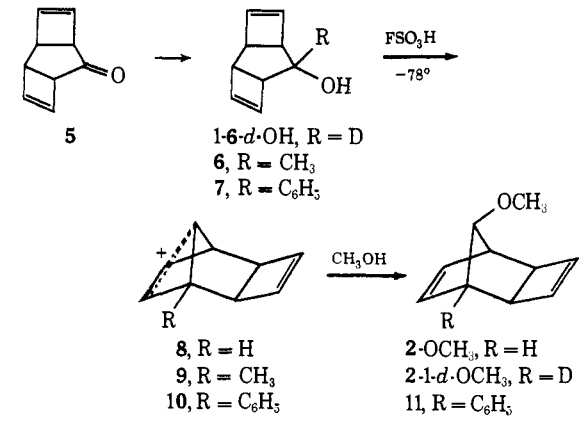
Figure 1. Pmr spectrum of *exo*-1-deuteriotricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl carbonium ion (**8**-1-*d*) in fluorosulfonic acid at −45°.

The stereochemical disposition of the hydroxyl group in **2** also follows from the selectivity in the hydride reduction and is supported by the clean triplet (J = 2 Hz) observed for the vinyl protons H_7 and H_8 in the syn series as opposed to more complex pattern in the anti isomers. The additional splitting in the latter arises from a long range coupling to H_9.[14] The individual chemical shifts and coupling constants correspond well with data for the bicyclic *syn*- and *anti*-7-norbornenyl derivatives.[14]

The stereospecific rearrangement of **1**-OTs to **2**-OAc with acetate capture from the more hindered syn direction implicates a nonclassical carbonium ion intermediate **8** analogous to the highly stabilized 7-norbornenyl carbonium ion.[15] In order to obtain additional evidence on the matter and possibly observe further rearrangement(s) of the intermediate, we generated the long-lived carbonium ions **8**, **8**-*1-d*, **9**, and **10** by extraction of the alcohols **1**-OH, **1**-*6-d*-OH, **2**-OH, **6**, and **7** from chloroform or methylene chloride solution into fluorosulfonic acid at −78°. Nmr spectral data for the stable carbonium ions so formed are collected in Table I along with literature data for the 7-norbornenyl carbonium ion[16] for comparison. The nmr spectrum of the deuterium labeled ion (**8**-*1-d*) is reproduced in Figure 1. The parent ion **8** was formed from either **1**-OH or **2**-OH. Quenching of the solutions of **8**, **8**-*1-d*, and **10** with methanol afforded the rearranged methyl ethers **2**-OCH_3, **2**-*1-d*-OCH_3, and **11**-OCH_3.

The close correspondence of the nmr spectral data with literature values reported for the 7-norbornenyl, 7-norbornadienyl, and 1-methyl-7-norbornadienyl carbonium ions[7,16] leaves little doubt that the analogous

Chart II



bishomocyclopropenyl ions **8**, **8**-*1-d*, **9**, and **10** were observed. In the spectrum of the labeled ion (**8**-*1-d*, Figure 1), the patterns from the vinyl protons (H_7 and H_8) and the bridgehead proton (H_1) simplified and sharpened, permitting assignment of approximate coupling constants (Table I, footnote *c*). These coupling data also agree with constants reported for the bicyclic ion (Table I, footnote *f*).

The observation of distinct resonances for the two types of vinyl protons ($H_{7,8}$ and $H_{3,4}$) and two types of protons on saturated carbons ($H_{1,6}$ and $H_{2,5}$) for **8** proves that this ion is not in rapid equilibrium with the isomeric tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-yl cation (see eq 1) on the nmr time scale. Warming either the parent ion **8** or the methyl derivative **9** leads to decomposition above −20° with no evidence of the degenerate rearrangement. However, the spectrum of the phenyl-substituted ion **10** exhibited reproducible line broadening (−30 to −10°), coalescence ($t_c \sim -12°$), and eventual collapse (+10°) to a time-averaged spectrum (see Figure 2). These spectral changes were shown to be reversible by cooling again to −60°, although not without the appearance of some decomposition.

A degenerate rearrangement **10a** ⇄ **10b** by way of

Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5366 (1972).

(14) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).

(15) For a leading reference, see R. K. Lustgarten, M. Brookhart, S. Winstein, P. G. Gassman, D. S. Patton, H. G. Richey, Jr., and J. D. Nichols, *Tetrahedron Lett.*, 1699 (1970).

(16) M. Brookhart, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, 88, 3135 (1966).

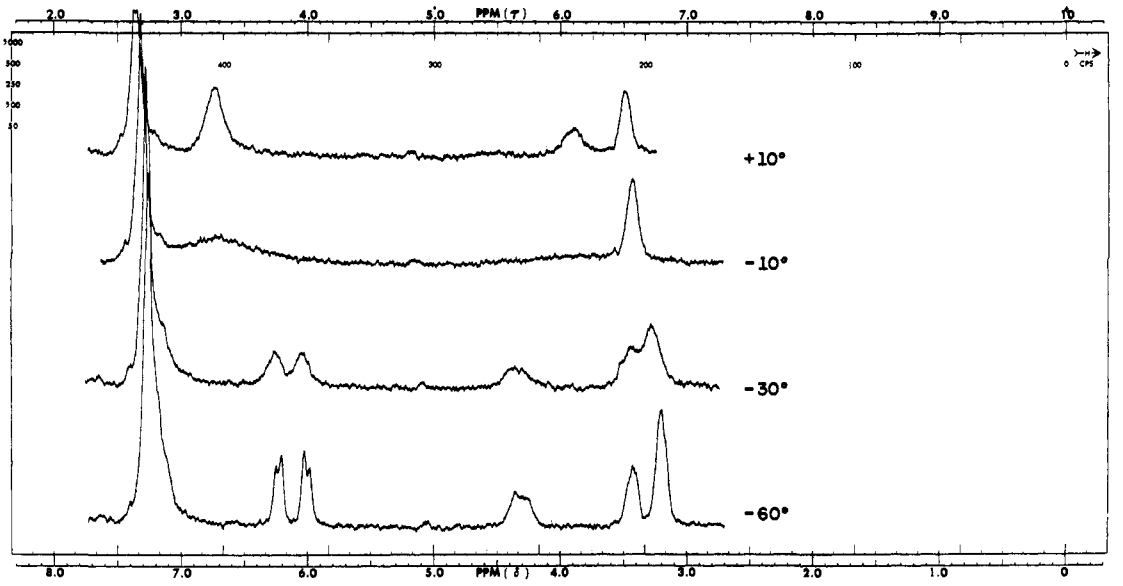
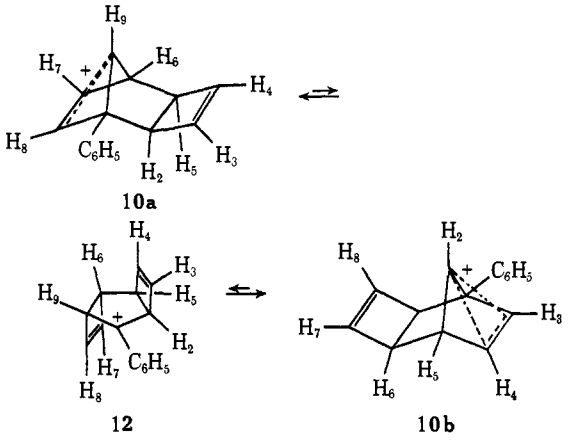


Figure 2. Pmr spectra of *exo*-1-phenyltricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl carbonium ion (**10**) in fluorosulfonic acid at various temperatures.



10a ⇌ **12** ⇌ **10b**

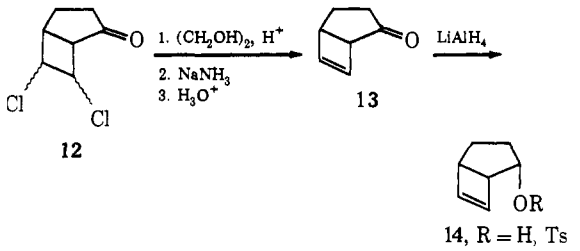
the phenyl-stabilized ion **12** provides a fully satisfactory explanation for the time-averaged spectrum recorded at +10°. The calculated and observed positions for the four two proton positional exchanges (the two vinyl proton exchanges were not resolved) given in Table II are in good agreement. The free energy of activation for this process is approximately 14 kcal/mol.

Table II. Calculated and Observed Chemical Shifts for the Time-Averaged Nmr Spectrum of 1-Phenyltricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl Carbonium Ion (**10**) in Fluorosulfonic Acid at +10°

Exchanging protons	Time-averaged chemical shift[a] Calcd	Obsd
$H_2 \rightleftarrows H_9$	3.52	3.46
$H_3 \rightleftarrows H_8$	6.7-6.9	6.83
$H_4 \rightleftarrows H_7$	6.8-7.0	
$H_5 \rightleftarrows H_6$	3.96	3.98

[a] δ value relative to internal $CHCl_3$ (7.28).

The solvolytic reactivities of **1**-OTs, **2**-OPNB, and **4**-OTs were determined for comparison with related bicyclic and tricyclic compounds. Bicyclic tosylate **14**-OTs was prepared from dichloro ketone **12**[6] by way of the known ketone **13**[17] in order to calibrate the reactivity of **1**-OTs. The endo orientation of the hydroxyl group in **14**-OH is ensured by the fact that lithium aluminum hydride reduction of bicyclo[3.2.0]-



heptan-2-one (dihydro **13**) affords 99% endo alcohol.[18] The kinetic data are summarized in Table III.

The rate of acetolysis of **1**-OTs is considerably enhanced ($k_{rel}^{25°}$ = 6.8 × 10^4) compared with the bicyclic model **14**-OTs. Factors which should be considered with regard to the increased reactivity of **1**-OTs are relief of ring strain[19] in the transition state (**1**-OR is estimated to contain approximately 13 kcal/mol of strain energy beyond that of **2**-OR)[20] and the ultimate formation of the very stable 7-norbornenyl-type carbonium ion **8**. However, **1**-OTs is actually somewhat less reactive than the less strained *anti*-7-norbornenyl tosylate (**15**-OTs, $k_{15\text{-OTs}}/k_{1\text{-OTs}}$ = 1.9 at 25°)[22] and thus even less reactive than **2**-OTs would be, indicating that the transition state involved in solvolysis of **1**-OTs resembles carbonium ion **8** considerably less than in the

(17) C. G. Scouten, F. E. Barton, Jr., J. R. Burgess, P. R. Story, and J. F. Garst, *Chem. Commun.*, 78 (1969).
(18) B. Funke and S. Winstein, *Tetrahedron Lett.*, 1477 (1971).
(19) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Amer. Chem. Soc.*, 90, 1014 (1968).
(20) This figure is the difference between the strain energy of norbornene (22.8 kcal/mol)[21a] and an estimated strain energy for bicyclo[3.2.0]hept-6-ene (35.5 kcal mol), the latter being the sum of the strain of the component cyclopentane (7.0 kcal mol)[21b] and cyclobutene (28.5 kcal mol)[21a] rings.
(21) (a) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Colburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, 90, 4315 (1968); (b) S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *ibid.*, 92, 3109 (1970).
(22) $k^{25°}$ = 3.7 × 10^{-4} sec^{-1}: S. Winstein and M. Shatavsky, *J. Amer. Chem. Soc.*, 78, 592 (1956).

Table III. Kinetic Data for Solvolysis of Tricyclo[4.2.0.0^{2,5}]nona-3,8-dien-6-yl Tosylate (**1**-OTs), *exo-syn*-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl *p*-Nitrobenzoate (**2**-OPNB), *exo-anti*-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl Tosylate (**4**-OTs), and Related Compounds

Substrate	Temp, °C	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$	k_{rel}
1-OTs[a]	16.9	$(6.0 \pm 0.2) \times 10^{-5}$ [b]			
	25	$(1.97 \pm 0.13) \times 10^{-4}$ [c,d]	25.2 ± 1.4	+9.0 ± 4.8	6.8×10^{4}
14-OTs[a]	25	2.7×10^{-9} [e]			(1.0)
	100	$(4.90 \pm 0.27) \times 10^{-5}$ [b]			
	125	$(5.63 \pm 0.03) \times 10^{-4}$ [d,f]	28.1 ± 0.6	−3.6 ± 1.5	
2-OPNB[g]	110	$(2.69 \pm 0.12) \times 10^{-5}$ [b]			
	125	$(1.14 \pm 0.01) \times 10^{-4}$ [d,h]	28.7 ± 0.8	−5.3 ± 2.0	0.34
7-Norbornadienyl	110	$(7.4 \pm 0.4) \times 10^{-4}$ [b]			
p-nitrobenzoate[g]	125	$(3.3 \pm 0.2) \times 10^{-3}$ [b]			(1.0)
4-OTs[a]	125	$(2.21 \pm 0.02) \times 10^{-6}$ [b]	36.4 ± 2.0	+6.5 ± 5.0	0.13
	150	$(3.39 \times 0.63) \times 10^{-5}$ [d,i]			
syn-7-Norbornenyl tosylate	125	1.67×10^{-5} [j]			(1.0)

[a] 0.015–0.023 *M* in acetic acid buffered with 0.045 *M* sodium acetate. [b] One run; error indicates average deviation of individual points from the line. [c] Average of two runs: $(2.10 \pm 0.04) \times 10^{-4}$, $(1.84 \pm 0.03) \times 10^{-4}$. [d] Error in table indicates deviation from the average. [e] Value extrapolated from data at higher temperatures. [f] Average of two runs: $(5.66 \pm 0.08) \times 10^{-4}$, $(5.60 \pm 0.41) \times 10^{-4}$. [g] *Ca.* 0.006 *M* in 50% acetone–50% water by volume. [h] Average of two runs: $(1.13 \pm 0.08) \times 10^{-4}$, $(1.15 \pm 0.05) \times 10^{-4}$. [i] Average of two runs: $(2.76 \pm 0.12) \times 10^{-5}$, $(4.03 \pm 0.52) \times 10^{-5}$. [j] Extrapolated from data given by S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.*, **79**, 505 (1957).

case of **2**-X. This seems reasonable in view of the extensive structural changes required to reach **8** from **1**-OTs and the fact that the developing positive charge cannot be symmetrically delocalized in the transition state from **1**-OTs. It is entirely possible that a different carbonium ion (or ion pair) intermediate is formed initially and subsequently rearranges to **8**.

The bridged ester **2**-OPNB undergoes hydrolysis at one-third the rate of 7-norbornadienyl *p*-nitrobenzoate and accordingly is about 50 times more reactive than *anti*-7-norbornenyl *p*-nitrobenzoate (**15**-OPNB).[23] The increased reactivity of **2**-OPNB compared with the **15**-OPNB is in line with the rate enhancements resulting from the fusion of strained rings onto the 5,6 positions of various *anti*-7-norbornenyl and 7-*syn*-benzonorbornenyl derivatives.[24]

The exo,anti tosylate (**4**-OTs) is the least reactive of the series, undergoing acetolysis at about one-eighth the rate of *syn*-7-norbornenyl tosylate. The cyclobutene double bond in **4**-OTs is thus unable to participate in the ionization in this case.

Experimental Section[25]

***anti*-Tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-yl *p*-Toluenesulfonate (1 OTs).** To a solution of tricyclic alcohol **1**-OH (1.2 g, 9 mmol)[6] in 100 ml of dry pyridine was added *p*-toluenesulfonyl chloride (3.46 g, 18 mmol) in small portions at 0°. The resulting solution was allowed to stand for 4 days in a refrigerator. The mixture was poured onto 400 g of ice and 15 ml of concentrated hydrochloric acid and stirred briefly, and the white solid was filtered and dissolved in ether. The ethereal solution was washed with 5% sodium carbonate and water. During filtration and extraction, the temperature was kept at 0° by cooling with ice. After drying ($MgSO_4$), evaporation, and recrystallization from pentane, 2 g (78%) of **1**-OTs was obtained: mp 94.0–95.5°; nmr (CCl_4) δ 7.75 and 7.29 (2 d, A_2B_2, 4 H, J = 8.1 Hz, aromatic), 6.00 (quintet, 4 H, vinyl, J = 3.0 Hz), 4.65 (2 d, 1 H, J = 1.5, 7.7 Hz), 3.90 (2 d, 1 H, J = 3.1, 7.7 Hz), 3.60 (m, 1 H), 3.14 (m, 2 H, H_1 and H_2), 2.46 (s, 3 H, CH_3).

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.66; H, 5.59; S, 11.10. Found: C, 66.55; H, 5.86; S, 11.20.

***exo-syn*-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl Acetate (2-OAc).** A solution of tosylate **1**-OTs (900 mg, 3.1 mmol) in 100 ml of anhydrous acetic acid buffered with 410 mg of sodium acetate was allowed to stand for 6 hr at 35°. The solution was neutralized with saturated sodium carbonate at 0° and extracted with ether. The ethereal solution was washed with saturated sodium chloride, dried ($MgSO_4$), and evaporated under reduced pressure. The product was purified by chromatography on a silica gel column, eluting with 5% ether in petroleum ether to give 451 mg (82%) of the rearranged acetate (**2**-OAc) as a clear liquid: ir (film) 3010, 2950, 2890, 1735 (C=O), 1240, 1050, 725 cm^{-1}; nmr (CCl_4) δ 6.25 (s, 2 H, H_8 and H_4), 6.10 (t, 2 H, H_7 and H_8, J = 2.0 Hz), 4.31 (m, 1 H, H_9), 2.85 (2 d, 2 H, H_1 and H_6, J = 1.5, 2.0 Hz), 2.61 (d, 2 H, H_2 and H_5, J = 1.5 Hz), 1.84 (s, 3 H, CH_3).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.11; H, 6.93.

***exo-syn*-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-ol (2-OH).** Acetate **2**-OAc (451 mg, 2.57 mmol) in 4 ml of ether was added dropwise to a suspension of lithium aluminum hydride (87 mg, 2.3 mmol) in 8 ml of ether at room temperature. The reaction mixture was worked up as described below for **1**-*6-d*-OH to yield 271 mg (79%) of the alcohol as a clear liquid: ir (film) 3350, 3400, 3010, 2950, 2900, 1420, 1290, 1264, 1209, 1093, 809, 713 cm^{-1}; nmr (CCl_4) δ 6.66 (s, 2 H, H_3 and H_4), 6.09 (t, 2 H, H_7 and H_8, J = 2.0 Hz), 3.33–3.72 (br, m, 1 H, H_9), 2.66–2.90 (m, 4 H).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.52; H, 7.42.

***exo*-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one (3).** A solution of alcohol **2**-OH (100 mg, 0.75 mmol) in 1 ml of dry pyridine was added to Sarett's reagent (450 mg, 4.5 mmol, of chromium trioxide in 4 ml of dry pyridine).[26] The reaction mixture was heated at 45–50° for 10 min and then allowed to stir at room temperature for 7 hr. The dark solution was poured into 50 ml of water and extracted with ether. The ethereal solution was washed with water, dilute sulfuric acid and water and dried ($MgSO_4$). After removal of the ether, the crude product was purified by chromatography on a silica gel column. Elution with 5% ether in petroleum ether gave the volatile ketone **3** (82 mg, 83%): mp 49.5–51.0°; ir (CCl_4) 3010, 2950, 2900, 1780 (C=O), 1280, 845, 722, 679 cm^{-1}; nmr (CCl_4) δ 6.64 (t, 2 H, H_7 and H_8, J = 2.1 Hz), 6.38 (t, 2 H, H_3 and H_4, J = 0.9 Hz), 2.73 (t, 2 H, H_1 and H_6, J = 2.1 Hz), 2.62 (d, 2 H, H_2 and H_5,

(23) 7-Norbornadienyl *p*-nitrobenzoate hydrolyzes 156 times faster than the *anti*-7-norbornenyl ester at 126.2° in 70% aqueous acetone.[24]

(24) M. A. Battiste, P. F. Ranken, and R. Edelman, *J. Amer. Chem. Soc.*, 93, 6276 (1971).

(25) Spectra were recorded with the following instruments: Perkin-Elmer Model 202 ultraviolet-visible spectrophotometer, and Models 137 and 137B infrared spectrophotometers; Varian Associates A-60A, A-56/60, HA-100, and HA-220 nmr spectrumeters (tetramethylsilane as internal standard); Atlas CH_4 and CH_5 mass spectrometers. The nmr spectra at 100 and 220 MHz were determined by R. Thrift and associates and the mass spectra by J. C. Cook and associates. Microanalyses were performed in the University of Illinois microanalytical laboratory by J. Nemeth and associates. Gas–liquid chromatography (glpc) was carried out with Varian Aerograph 90-P3 and Hy-Fy 600D instruments.

(26) (a) G. I. Poos, G. E. Arth, R. E. Beyler, and L. A. Sarett, *J. Amer. Chem. Soc.*, 75, 422 (1953); (b) J. Meinwald, J. C. Shelton, G. L. Buchanan, and A. Courtin, *J. Org. Chem.*, 33, 99 (1968).

J = 0.9 Hz). The low per cent carbon is attributed to sublimation during analysis.

Anal. Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.12; H, 6.19.

Reduction of *exo*-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one (3). **A.** Ketone **3** (80 mg, 0.606 mmol) was reduced with lithium aluminum hydride as described below for **5** to give 62 mg (77%) of an alcohol identified as **2**-OH by nmr spectral comparison with a sample prepared as described above.

B. Sodium chips (85 mg, 3.7 mg-atoms) in 1 ml of toluene were melted at 110° with stirring under nitrogen. A solution of ketone **3** (170 mg, 1.29 mmol) and 2-propanol (232 mg, 3.87 mmol) was then added, and the resulting suspension was allowed to stir under reflux for 1.5 hr.[27] Ice–water (5 ml) was added carefully to the cooled reaction mixture. Extraction with ether and purification by chromatography on a silica gel column gave 50 mg (29%) of the anti alcohol (**4**-OH) as a clear liquid: ir (film) 3360 (OH), 3010, 2950, 2900, 1410, 1280, 1210, 1085, 790, 746, 700 cm^{-1}; nmr (CCl_4) δ 6.24 (s, 2 H, H_3 and H_4), 6.13 (m, 2 H, H_7 and H_8), 3.95 (br m, 1 H, H_9), 2.47 (s, 4 H), 1.64 (br s, 1 H, OH).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.45; H, 7.46.

***anti*-6-Deuteriotricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-ol (1-6-*d*-OH).** Ketone **5**[6] (261 mg, 1.95 mmol) in 10 ml of anhydrous ether was added dropwise to a suspension of lithium aluminum deuteride (1.05 mmol) in 10 ml of ether at room temperature under nitrogen. The resulting mixture was allowed to stir for 14 hr at room temperature. The product was isolated by ether extraction and purified by chromatography on a silica gel column. Elution with 5% ether in petroleum ether gave the labeled alcohol **1**-*6*-*d*-OH (170 mg, 65%). The nmr spectrum is identical with that of **1**-OH[6] except for the proton intensity at δ 4.0.

***anti*-6-Methyltetracyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-ol (6).** Ethereal methyllithium (1.5 mmol) was added dropwise to a solution of ketone **3** (100 mg, 0.76 mmol) in 2 ml of ether at room temperature under nitrogen. After 12 hr the excess methyllithium was destroyed with saturated ammonium chloride, and the product was extracted into ether. The ethereal solution was washed with water, dried ($MgSO_4$), and concentrated. Purification of the product on a silica gel column, eluting with 5% ether in petroleum ether, afforded 79 mg (71%) of **6** as a yellow oil: ir (firm) 3350, 3010, 2900, 1450, 1360, 1270, 1240, 1190, 1145, 1120, 963, 935, 910, 856, 825, 757 cm^{-1}; nmr (CCl_4) δ 6.12 (m, 3 H, vinyl), 5.97 (d, 1 H, vinyl), 3.48 (m, 2 H, H_5 and H_6), 3.12 (m, 2 H, H_1 and H_2), 1.67 (s, 1 H, OH), 1.25 (s, 3 H, CH_3). Although this material appeared to be pure according to tlc analysis, the nmr spectrum indicated the presence of a minor impurity.

***anti*-6-Phenyltricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-ol (7).** Phenyllithium (1.8 mmol) in a mixture of benzene and ether (70:30) under nitrogen was added to a solution of **3** (200 mg, 1.52 mmol) in 10 ml of ether. After *ca.* 12 hr at room temperature, 5 ml of 5% sodium hydroxide was added and the product was extracted with ether. The ethereal solution was washed with water, dried ($MgSO_4$), and evaporated. The product was placed on a silica gel column and eluted with benzene to yield 257 mg (75%) of **7** as a yellow oil: ir (film) 3360 (OH), 3000, 2900, 1600, 1440, 1270, 1080, 1038, 820, 750, 700 cm^{-1}; nmr (CCl_4) δ 7.05–7.55 (m, 5 H, aromatic), 6.18 (d, 2 H, H_3 and H_9, J = 0.9 Hz), 5.91 (2 d, 1 H, J = 2.8 Hz), 5.49 (d, t, 1 H, J = 0.9, 2.8 Hz), 4.11 (d, 1 H, J = 3.1 Hz), 3.61 (d, t, 1 H, J = 0.9, 3.1 Hz), 3.25 (m, 2 H, H_1 and H_2), 1.98 (br s, 1 H, O*H*); mass spectrum *m/e* 210 (M$^+$, 2.36), 191 (1.63), 165 (2.07), 105 (16.51), 75 (13.79), 69 (100.00), 55 (14.46), 37 (46.16). Attempts to crystallize or to purify this material by glc failed; it was used for the nmr experiments in fluorosulfonic acid without further purification.

Stable Carbonium Ions. A typical experiment proceeded as follows. About 40 mg of the alcohol was dissolved in 0.5 ml of solvent (CCl_4, $CDCl_3$, CH_2Cl_2, CD_2Cl_2) in a nmr tube. Distilled fluorosulfonic acid (0.5 ml), cooled to −78°, was introduced into the solution at −78°. The resulting mixture was carefully shaken at −78°; then the layers were allowed to separate. The upper layer was removed by a pipet, and the yellow fluorosulfonic acid solution was used directly for the nmr measurements using residual CH_2Cl_2 or $CHCl_3$ as an internal standard. The nmr data for the carbonium ions obtained from **1**-OH, **1**-*6*-*d*-OH, **6**, and **7** are summarized in Table I.

Quenching of the Stable Carbonium Ions. The stable carbonium ion from **7** (60 mg) in 1 ml of fluorosulfonic acid at −78° was added in small portions to 3 ml of methanol cooled to −78°. After completion of the addition, the resulting solution was neutralized with 5% sodium bicarbonate, and saturated with sodium chloride. The product was separated by ether extraction and purified by chromatography on a silica gel giving 22 mg (33%) of *exo-syn*-9-methoxy-1-phenyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**11**) as a liquid: ir (CCl_4) 3050, 2950, 2900, 1600, 1490, 1290, 1279, 1200, 1120, 700 cm^{-1}; nmr (CCl_4) δ 7.10–7.55 (m, 5 H, aromatic), 6.52 (d, 1 H, J = 2.7 Hz), 6.33 (d, 1 H, J = 2.7 Hz), 6.10–6.30 (m, 2 H, H_7 and H_8), 3.50 (m, 1 H, H_9), 2.76–3.06 (m, 6 H); mass spectrum *m/e* 224 (M$^+$, 25.5), 210 (12.8), 209 (13.7), 165 (58.1), 115 (61.7).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.18; H, 7.16.

A similar methanol quench of **8**-*1*-*d* afforded **2**-*1*-*d*-OCH_3 (27% after preparative glpc): nmr (CCl_4) δ 6.21 (s, 2 H, H_8 and H_4), 6.05 (d, 2 H, J = 2 Hz, H_7 and H_8), 3.29 (quartet, 1 H, J ~1.5, H_9), 3.06 (s, 3 H, OCH_3), 2.71 (quintet (?), 1 H, J ~2 Hz, H_6), 2.58 (d, 2 H, J = 1.5 Hz, H_2 and H_5). The unlabeled methyl ether (**2**-OCH_3) was similarly obtained: nmr (same as **2**-*1*-*d*-OCH_3 except as indicated) 6.05 (t, J = 2 Hz), 3.29 (m), 2.71 (m, 2 H).

***exo-syn*-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl *p*-Nitrobenzoate (2-OPNB).** To a solution of **2**-OH (170 mg, 1.28 mmol) in dry pyridine (4 ml) was added *p*-nitrobenzoyl chloride (280 mg, 1.51 mmol) in small portions at 0°. The resulting solution was allowed to stand in a refrigerator for 3 days and then poured into ice–water (20 g) containing 1 ml of concentrated hydrochloric acid. The product was isolated by ether extraction and recrystallized from hexane yielding 326 mg (91%) of **2**-OPNB: mp 130–132°; ir (CCl_4) 2920, 1730, 1610, 1530, 1280, 1120, 1025 cm^{-1}; nmr (CCl_4) δ 8.17 (A_2B_2, 4 H, aromatic, J = 9.0 Hz), 6.40 (s, 2 H, H_3 and H_4), 6.25 (t, 2 H, H_7 and H_8, J = 2.0 Hz), 4.73 (m, 1 H, H_9), 3.02 (m, 2 H, H_1 and H_6), and 2.75 (m, 2 H, H_2 and H_5).

Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94. Found: C, 67.71; H, 4.72; N, 5.04.

***exo-anti*-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl *p*-Toluenesulfonate (4-OTs).** The *anti* alcohol (**4**-OH, 48 mg) was converted to the tosylate as described above for **1**-OH: yield 59 mg (58%); mp 71–72°; ir (CCl_4) 3010, 2950, 1600, 1470, 1190, 1180, 1008, 860 cm^{-1}; nmr (CCl_4) δ 7.25 and 7.70 (2 d, A_2B_2, 4 H, aromatic, J = 8.0 Hz), 6.28 (s, 2 H, H_3 and H_4), 5.98 (m, 2 H, H_7 and H_8), 4.65 (m, 1 H, H_9), 2.60 (m, 2 H, H_1 and H_6), 2.44 (s, 5 H).

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.06; H, 5.59. Found: C, 66.70; H, 5.78.

***endo*-Bicyclo[3.2.0]hept-6-en-2-yl *p*-Toluenesulfonate (14-OTs).** A solution of 3.7 g (0.02 mmol) of dichloro ketone **12**[6] in 70 ml of ethylene glycol and 125 ml of benzene containing a few drops of concentrated sulfuric acid was allowed to reflux for 40 hr. After addition of 200 ml of 5% sodium bicarbonate solution, the aqueous layer was extracted with ether. The ethereal solution was dried and concentrated. The residue was dissolved in 50 ml of ether and added to 400 ml of aqueous ammonia. Sodium metal was added to the solution until the blue color persisted for 20 min The reaction was quenched with ammonium chloride, water added, and the product extracted with ether. The ethereal solution was allowed to stir at room temperature overnight with 100 ml of 1.5 *M* hydrochloric acid. The aqueous layer was extracted with ether, and the combined ethereal extract was washed with dilute sodium carbonate and water and dried ($MgSO_4$). After removal of the ether, the product was purified by chromatography on a silica gel column giving 1.01 g (46%) of bicyclo[3.2.0]hept-6-en-2-one (**13**):[18] ir (film) 1730 (C=O) cm^{-1}.

Ketone **13** (218 mg, 1.97 mmol) was reduced with lithium aluminum hydride in ether to give 206 mg (95%) of the endo alcohol (**14**-OH) as a clear liquid. This alcohol (206 mg, 1.87 mmol) was converted to the crystalline tosylate (**14**-OTs) by the previously described procedure (360 mg, 74%): mp 52.5–54.0°; ir (CCl_4) 3050, 2910, 1350, 1180, 980 cm^{-1}; nmr (CCl_4) δ 7.14 and 7.59 (A_2B_2, 4 H, aromatic, J = 8.0 Hz), 5.81 (2 d, 2 H, H_3 and H_4, J = 3.0 Hz), 4.43 (2 t, 1 H, H_2, J = 9.0, 7.0 Hz), 2.90–3.25 (m, 2 H, H_2 and H_5), 2.40 (s, 3 H, CH_3), 1.70–2.10 (m, 2 H), 1.10–1.55 (m, 2 H).

Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.63; H, 6.10. Found: C, 63.29; H, 6.03.

Kinetic Measurements. A. Acetolysis. The acetic acid solvent was heated at reflux with acetic anhydride and sodium acetate for 24 hr and distilled. For runs at 100° or less, solutions of the tosylate (23–34 mg) in acetic acid containing sodium acetate (0.045 *M*) diluted to 5 ml (0.016–0.023 *M* in tosylate) were heated at the indicated temperature (Table III). Aliquots (4–5) were removed at appropriate intervals and cooled (0°) and the uv absorbance was

(27) S. Dev, *J. Indian Chem. Soc.*, 33, 769 (1956).

measured (room temperature) at 272 mμ.[28] The absorbance generally decreased by about 60% during the acetolysis. For runs at higher temperatures, aliquots of tosylate solutions similarly prepared were heated individually in sealed ampoules. The rate constants were determined graphically.

B. Hydrolysis. The *p*-nitrobenzoates were hydrolyzed in 50% aqueous acetone (volume per cent before mixing) and the rates measured as previously described.[5b]

The kinetic data are summarized in Table III.

(28) M. L. Sinnott, *J. Org. Chem.*, **34**, 3638 (1969).

Preparative Solvolysis of 2-OPNB. The *p*-nitrobenzoate (83 mg) in 25 ml of 50% aqueous acetone containing 1.5 equiv of 2,6-lutidine was sealed in 2 test tubes under nitrogen and heated for 24 hr at 125°. The cooled solution was concentrated and the product (15 mg, 44%,) isolated by ether extraction was identified as **2**-OH by nmr comparison.

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Additions to Bicyclic Olefins. V. The Effect of 7,7-Dimethyl Substituents on the Stereochemistry and Rates of Cyclic Additions to Norbornenes

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Abstract: Various cyclic additions to norbornene (**1**) and 7,7-dimethylnorbornene (**2**) have been studied to determine the effects of 7,7-dimethyl substituents on the stereochemistry and rates of additions to norbornyl systems. The 7,7-dimethyls exerted very large steric hindrance to exo attack, equal to or even greater than the hindrance to endo attack arising from the endo-5,6-hydrogen atoms. Certain reactions, such as silver ion complexation, addition of nitrosyl chloride, and addition of dichlorocarbene, proceed quite satisfactorily with **1**, but fail with **2**, presumably because the attack of the adding moiety is severely hindered by both the 7,7-dimethyl groups and the endo-5,6-hydrogen atoms. Comparative rate studies of exo attack of **1** *vs.* **2** indicate substantial rate retardations for reactions involving exo addition *via* cyclic processes in such reactions as epoxidation (1000), hydroboration with 9-BBN (480), diimide reduction (950), and addition of benzenesulfenyl chloride (1820), whereas the retardation factor is smaller for additions not involving cyclic species, such as the free radical reaction of thiophenol (30). The importance of the steric influence of 7,7-dimethyl substituents is also revealed by the stereochemistry of addition. For all known additions to **1**, the adding moieties come in preferentially from the exo side. Even the introduction of 7,7-dimethyl substituents does not reverse this exo stereoselectivity for additions proceeding through noncyclic processes. Thus, the two-stage addition of thiophenol is 99.5% exo with **1**, and 95% exo with **2**. However, for additions involving three- and four-membered ring cyclic processes, the preference for exo reaction is not retained in **2**, presumably because of the large steric crowding by the 7,7-dimethyl groups. For instance, hydroboration of **1** with 9-BBN gives 99.5% *exo*-norbornanol (**11**) but only 3% of 7,7-dimethyl-*exo*-norbornanol (**15**) from **2**. Similarly, addition of benzenesulfenyl chloride to **1** gives nearly 100% *exo*-2-phenylthio-*endo*-3-chloronorbornane *via exo*-episulfonium ion, but gives only 4% 7,7-dimethyl-*exo*-2-phenylthio-*endo*-3-chloronorbornane *via* the *exo*-episulfonium ion from **2**. Diimide, however, adds exo to both **1** and **2**. This exception is attributed to the larger six-membered cyclic transition state which does not interact as strongly as the three- and four-membered rings with the *syn*-7-methyl group.

It is generally accepted that the exo side of the norbornyl system is less hindered than the endo side toward attack by a wide variety of reagents. Introduction of bulky substituents on the bridge carbon, such as the *gem*-7,7-dimethyl groups, has long been recognized as causing a reversal in the preferred direction of reaction, as in the preferred transfer of hydride from complex hydrides to the endo side of camphor.[3] On the other hand, solvolysis of 7,7-dimethylnorbornyl derivatives leads to predominant exo substitution, and it has been argued that this requires the intermediacy of a σ-bridged species,[4,5] which blocks reaction from the endo direction. However, recent data indicate that the large endo preference for nonsolvolytic reactions is not the rule, providing the steric requirements of the attacking reagent are not too large. For example, the reduction of camphor by lithium aluminum hydride proceeds with 92% endo attack,[6,7] whereas reduction with borane in tetrahydrofuran involves approximately equal attack from both directions.[8]

It therefore appeared desirable to investigate the

(1) Graduate research assistant on grants (G 19878 and GP 6492X) supported by the National Science Foundation.

(2) Postdoctoral research associate (1968–1970) on a grant (GP 6492-X) supported by the National Science Foundation.

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(5) (a) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Amer. Chem. Soc.*, 87, 378 (1965); (b) R. Howe, E. C. Friedrich, and S. Winstein, *ibid.*, 87, 379 (1965).

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