Synthesis and Solvolysis of 9 Derivatives in the *exo,exo*-Dimethanonaphthalene System[1]

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Abstract: The syntheses of the epimeric outside and inside 9-alcohols of perhydro-1,4-*exo,exo*-5,8-dimethanonaphthalene (V-OH and VII-OH) and their 6,7-dehydro analogs (IX-OH and XI-OH) are described, and the solvolyses of their *p*-bromobenzenesulfonates (brosylates) or *p*-nitrobenzoates have been studied. The order of observed reactivity at 25° in the solvolysis of V, IX, VII, and XI is $1:10:10^8:10^{11}$, respectively, with the XI system 10^4 times more reactive than the already very reactive anti 7-norbornenyl system and 10^{15} times more reactive than the 7-norbornyl system. Ionization with anchimeric assistance from σ or π participation is demonstrated by these ratios. Solvolysis of XI-OPNB gave only XI-OH while solvolysis of IX-OBs gave XI-OH and two rearranged epimeric alcohols. Acetolysis of the two saturated brosylates (V-OBs and VII-OBs) gave the same four solvolysis products, and acetolysis of VII-OBs gave 44% of V-OBs by ion-pair return involving a hydrogen-bridged cation G. The deuterium scrambling in the solvolysis products from 6,7-dideuterated V-OBs and from α-deuterated VII-OBs has been studied. The proposed mechanisms in solvolysis of V-OBs, VII-OBs, IX-OBs, and XI-OPNB are discussed.

The solvolysis of the outside[4] and inside[4] pair of brosylates V-OBs and VII-OBs was of considerable interest because of the expected formation of a solvolysis product and a solvolysis mechanism similar to the one of 7-norbornyl brosylate,[5] with the additional possibility that the cationic intermediate would undergo further more complex rearrangements. Therefore, solvolysis of these two derivatives and the corresponding 6,7-dehydro analogs IX-OBs and XI-OPNB has been examined, and the results of this study are presented and discussed in the present manuscript.

Results

Materials. The commercially available insecticide aldrin[6] (I) gave only the 2,3-dihydro product II on hydrogenation over palladium/charocal in ethyl acetate at a hydrogen pressure slightly above atmospheric pressure. Dechlorination of II with lithium and *tert*-butyl alcohol in tetrahydrofuran proceeded smoothly and the *endo-exo*-monoene[6] (III) was obtained with 82% purity. Epoxidation of the olefin with monoperphthalic acid following the procedure of Royals and Harrel[7] gave the epoxide IV. Treatment of this epoxide with lithium aluminum hydride–aluminum chloride (1:1)[8a] similar to the procedure of Corey and Glass[8b] gave only the rearranged alcohol Va-OH. Oxidation of Va-OH with chromic oxide in pyridine following the procedure of Van Tamelen and Judd[9] gave the ketone VI. Reduction of VI with lithium aluminum hydride or lithium aluminum deuteride gave only the inside 9-alcohols VIIa-OH and VIId-OH, respectively. No trace of epimeric outside 9-alcohol in the reaction product could be detected by glc analysis. The *p*-bromobenzenesulfonate esters of the alcohols Va-OH and VII-OH were prepared using standard procedures.

The crude epoxide IV was used as starting material in the syntheses of the unsaturated derivatives IX–XI. The bromohydrin VIII was obtained by rearrangement of IV with dry hydrogen bromide in ether. Dehydrobromination of the pyranyl ether of VIII with potassium *tert*-butoxide in *tert*-butyl alcohol using xylene as solvent and following the procedure of Stafford[10] gave the alcohol IX-OH. Oxidation of IX-OH as before[9] gave the ketone X. The reduction of X with lithium aluminum hydride or lithium aluminum deuteride gave a mixture of the unsaturated inside 9-alcohol and the saturated outside 9-alcohol. Treatment of X with lithium aluminum hydride gave a mixture of 68% XIa-OH and 32% Va-OH in quantitative yield. Repetition of the reaction using lithium aluminum deuteride instead of lithium aluminum hydride gave in quantitative yield a mixture of 87% XIb-OH and 13% V-OH, containing 50% deuterium in the exo 6 and exo 7 positions. Treatment of X with lithium aluminum deuteride catalyzed by a trace of aluminum chloride followed by decomposition with deuterium oxide gave in quantitative yield a mixture of 69% XIb-OH and 31% Vb-OH. The saturated product Vb-OH was fully deuterated in the exo 6 and exo 7 positions, but showed no deuterium in the 9 position or in any other position. The double bond reduction by lithium aluminum hydride in 7-substituted norbornadienes and syn 7-substituted norbornenes has been studied by Franzus and Snyder[11] and our results correspond very well to theirs. The *p*-bromobenzenesulfonate esters of the alcohols IX-OH and the *p*-nitro-

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[1] Research during 1967–1969 was supported by a grant (Organic Reaction Mechanisms) from State Funds administered by the University of California.

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[3] Deceased Nov 23, 1969.

[4] The terms outside and inside are used instead of syn and anti, respectively, to indicate explicitly the orientation of the 9 derivatives.

[5] S. Winstein, F. Gadient, E. T. Stafford, and P. E. Kleinedinst, Jr., *J. Amer. Chem. Soc.*, 80, 5895 (1958).

[6] S. B. Soloway, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1955.

[7] E. E. Royals and L. L. Harrell, Jr., *J. Amer. Chem. Soc.*, 77, 1305 (1955).

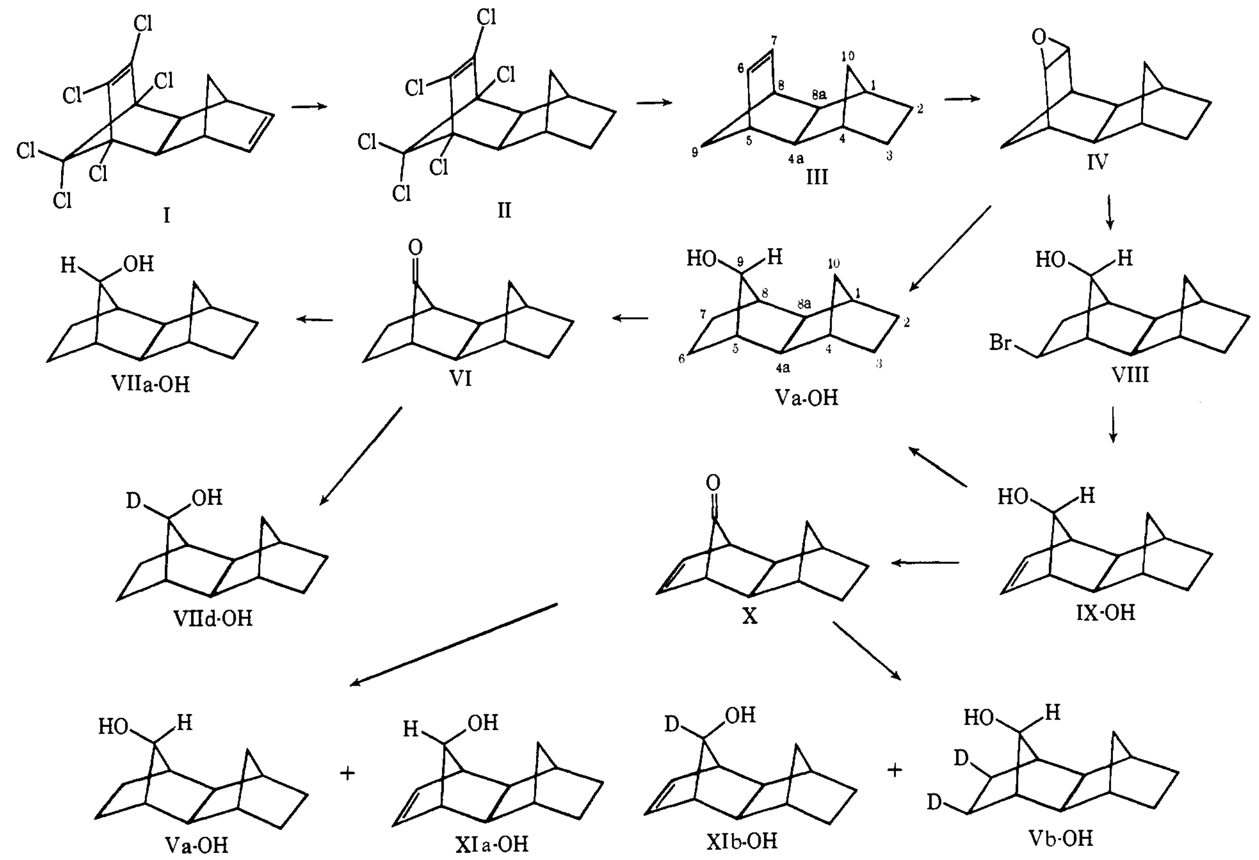
[8] (a) E. C. Ashby and J. Prather, *ibid.*, **88**, 729 (1966); (b) E. J. Corey and R. S. Glass, *ibid.*, **89**, 2600 (1967).

[9] E. E. Van Tamelen and C. I. Judd, *ibid.*, 80, 6305 (1958).

[10] E. T. Stafford, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1958.

[11] B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **87**, 3423 (1965).

Chart I



benzoates of the alcohols XI-OH were prepared using standard procedures.

Spectral Analysis. The nmr spectra (60 and 100 MHz) of the ketones, alcohols, and their esters (V–VII and IX–XI) have been interpreted on a first-order basis. The chemical shifts of the different protons of the compounds are shown in Table I.

Table I. Chemical Shifts (τ)[a]

Compd	9-H$_{ins}$	9-H$_{outs}$	10-H$_{ins}$^{b}	10-H$_{outs}$^{b}	1-H,^{c} 4-H	4a-H, 8a-H	5-H, 8-H	2-H$_{exo}$, 3-H$_{exo}$	2-H$_{endo}$,^{d} 3-H$_{endo}$	6-H$_{exo}$, 7-H$_{exo}$	6-H$_{endo}$,^{d} 7-H$_{endo}$	H$_{vinyl}$
Va-OH	5.53		8.33	9.08	7.97	8.58	8.23^e	8.71^d	9.00	8.22^d	8.89	
Va-OBs	4.88		8.49	9.01	7.96	8.55	8.01^e	8.68^f	8.93	8.32^f	8.80	
VI			8.26	9.06	7.93	8.43^g	8.27^h	8.48^d	8.85	8.38^d	8.60	
VIIa-OH		6.32	6.98	9.37	8.02	8.46	8.21^e	8.59^f	9.05	8.52^f	8.93	
VIIa-OBs		5.86	7.63	9.30	8.05	8.45	8.07^d	8.58^f	8.98	8.51^f	8.90	
IX-OH	5.56		8.16	8.95	7.86	8.69^g	7.41^h	8.53^d	8.93			4.02^i
IX-OBs	4.84		8.34	9.00	7.88	8.63^g	7.34^h	8.52^d	8.81			4.19^i
X			8.22	9.05	7.85	8.47^h	7.47^j	8.49^d	8.91			3.62^k
XIa-OH		6.55	6.84	9.30	7.95	8.52^d	7.52^h	8.53^d	8.99			4.12^k
XIa-OPNB		5.60	7.37	9.17	7.88	8.35^d	7.14^h	8.49^d	8.93			3.94^k

[a] All frequencies within 1 Hz; 15–20 w/v % solutions in CS_2 with TMS as internal standard. [b] Two quintets separated by 11 Hz. [c] Sextet. [d] Multiplet. [e] Quintet. [f] Two quintets separated by 7 Hz. [g] Doublet. [h] Quartet. [i] AA′XX′ pattern split by the α proton into two sets of four lines, all with equal height. [j] Triplet. [k] AA′XX′ pattern consisting of four strong and four weak lines.

In a special study the patterns of the vinyl protons of IX–XI were compared to vinyl patterns of *anti*-7-norborneol and *syn*-7-norbornenyl *p*-toluenesulfonate. The ketone X, the inside 9-alcohol XI–OH and the corresponding ester XI-OPNB, as well as the *anti*-7-norbornenol, all showed a similar AA′XX′ pattern, consisting of four strong and four weak lines. The *syn*-7-norbornenyl tosylate and the outside 9-alcohol IX-OH and its brosylate all showed similar vinyl patterns. The four strong lines in the AA′XX′ system were split by the 9-bridge proton into a doublet of quartets (doublet separation 0.8, 1.2, 0.9 Hz, respectively), but no weak lines of the AA′XX′ system could be detected. Such a long-range spin coupling implies that the 9-bridge proton in IX is anti to the vinyl protons with which it is coupled. The absence of any long-range coupling between the 9-bridge proton and the vinyl protons in XI implies that the 9-bridge proton is syn to the vinyl protons[12] in XI.

Solvolysis Rates. The outside 9-brosylates Va-OBs and IX-OBs as well as the inside 9-*p*-nitrobenzoate XIa-OPNB displayed good first-order behavior in solvolysis. Acetolysis of the inside 9-brosylate VIIa-OBs gave 44%

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

Table II. Summary of Rates

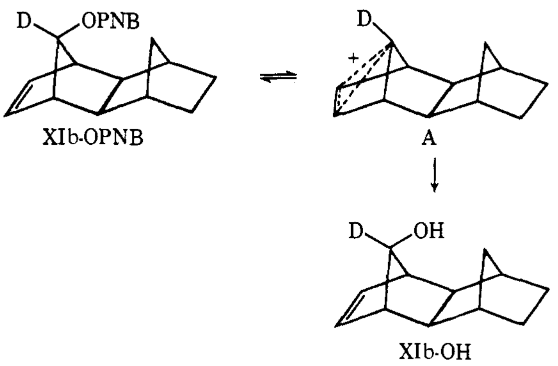
Compd	Condn	Solvent	Temp, °C	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{25}, rel
7-Norbornyl-OBs[f]	*a*	AcOH	25.0	1.91×10^{-14}			1.0
Va-OBs	*b*	AcOH	100.0	$(1.13 \pm 0.02) \times 10^{-5}$			
	b	AcOH	75.0	$(5.55 \pm 0.04) \times 10^{-7}$			
	c	AcOH	25.0	2.99×10^{-10}	30.4	−0.2	1.6×10^{4}
VIIa-OBs	*b*	AcOH	100.0	$(3.35 \pm 0.04) \times 10^{-3}$			
	b	AcOH	75.0	$(2.44 \pm 0.07) \times 10^{-4}$			
	b	AcOH	50.0	$(1.22 \pm 0.01) \times 10^{-5}$			
	c	AcOH	25.0	3.67×10^{-7}	26.2	−0.1	1.9×10^{7}
VIId-OBs	*b*	AcOH	75.0	$(2.19 \pm 0.02) \times 10^{-4}$			
IX-OBs	*b*	AcOH	100.0	$(1.02 \pm 0.02) \times 10^{-4}$			
	b	AcOH	75.0	$(5.71 \pm 0.02) \times 10^{-6}$			
	c	AcOH	25.0	4.27×10^{-9}	29.0	0.6	2.2×10^{5}
anti-7-Norbornenyl-OBs[g]	*d*	AcOH	25.0	$(2.13 \pm 0.02) \times 10^{-3}$			1.1×10^{11}
anti-7-Norbornenyl-OPNB[h]	*c*, *d*	70% Me_2CO	25.0	6.10×10^{-12}	30.0	−9.0	1.1×10^{11}
7-Norbornadienyl-OPNB[i]	*c*, *d*	70% Me_2CO	25.0	6.50×10^{-9}	25.0	−12.2	1.2×10^{14}
XIa-OPNB	*e*	70% Me_2CO	100.0	$(5.42 \times 0.05) \times 10^{-4}$			
	e	70% Me_2CO	75.0	$(5.86 \pm 0.06) \times 10^{-5}$			
	c	70% Me_2CO	25.0	2.28×10^{-7}	22.2	−14.3	4.1×10^{15}

[a] Calculated rate from the corresponding tosylate using a factor of three to relate the reactivity of the tosylate to the brosylate. [b] 0.010 *M* in ester, 0.011 *M* in sodium acetate, and 0.02 *M* in acetic anhydride. [c] Rate value extrapolated from data at higher temperatures. [d] 0.010 *M* in ester. [e] 0.005 *M* in ester. [f] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955). [g] A. Diaz, unpublished work. [h] J. Lhomme, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 1548 (1969). [i] R. K. Lustgarten, unpublished work.

of the outside 9-brosylate Va-OBs by ion-pair return independent of the temperature. Due to the large difference in reactivity it was possible to measure the rate of acetolysis of both VIIa-OBs and Va-OBs, starting from VIIa-OBs. Both VIIa-OBs and the formed Va-OBs displayed good first-order behavior. All of the esters solvolyzed with very small salt effect, and the observed infinity titers were ±2% of the theoretical ones. The rates of acetolysis of VIIa-OBs and VIId-OBs were determined under exactly the same conditions and at the same time. The isotope effect (k_H/k_D) was found to be 1.11. The first-order rate constants are summarized in Table II.

Solvolysis Products. Mainly one compound was obtained as a product of hydrolysis of the very reactive unsaturated inside 9-*p*-nitrobenzoate XIb-OPNB after 10 half-lives under kinetic conditions (0.008 *M* ester and 0.009 *M* $NaHCO_3$ in 70% aqueous acetone at 75.0°). The crude extracted product contained more than 98% of the inside 9-alcohol XIb-OH and less than 2% of hydrocarbons. No other alcohols were detected by gas–liquid chromatography. Complete retention of configuration was observed in the hydrolysis of the *p*-nitrobenzoate XIb-OPNB to the alcohol XIb-OH and no scrambling of deuterium in the alcohol was observed.

Chart II



The product from the acetolysis of the unsaturated outside 9-brosylate IX-OBs consisted of five different hydrocarbons (4:4:1:4:3) and three different acetates (1:3:5) after 1 half-life under kinetic conditions (0.034 *M* ester in 0.036 *M* NaOAc–HOAc at 75.0°). Nmr analysis of the recovered unreacted brosylate showed only the starting brosylate and no trace of an α proton of any other brosylate was found. The recovered brosylate was combined with the solvolysis product and the acetolysis was continued for 10 more half-lives. Gas–liquid chromatography showed that the acetolysis product consisted of the same five different hydrocarbons and the same three different acetates as above and in the same ratio as above. Saponification of the crude acetolysis product gave a mixture of hydrocarbons (3%) and alcohols (97%). The three alcohols and hydrocarbons were separated by chromatography. A 91% yield of isolated product was obtained, consisting of 3% hydrocarbons (4:4:3:4:2), 30% XIa-OH, 56% XII-OH, and 11% XIII-OH. The product XIa-OH was identified by its nmr spectrum. Hydrogenation of the product XII-OH gave 98% XIVa-OH and 2% of its corresponding ketone XV in quantitative yield. Oxidation of a sample of this mixture gave only the ketone XV. The nmr spectra of the product XII-OH and XIVa-OH agreed with the suggested structures of the trans 5-alcohols XII-OH and XIVa-OH. Hydrogenation of the product XIII-OH gave 70% of the cis 5-alcohol XVI-OH and 30% of its corresponding ketone XV in quantitative yield. Oxidation of this mixture gave only the ketone XV.

The acetolysis of the saturated outside and inside 9-brosylates Va-OBs and VIIa-OBs gave the same two hydrocarbons (1:9) and the same four acetates. Due to easier separation procedure of the corresponding alcohols, the acetolysis product of each run was saponified, after glc analysis and removal of more than 98%

Chart III

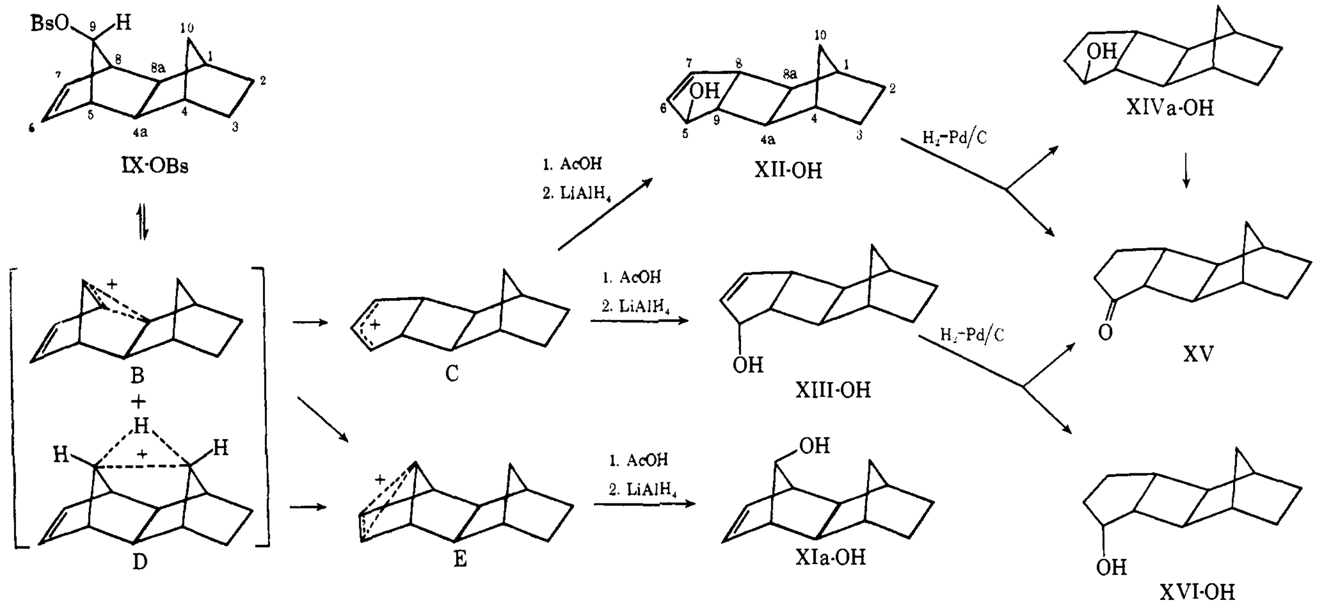
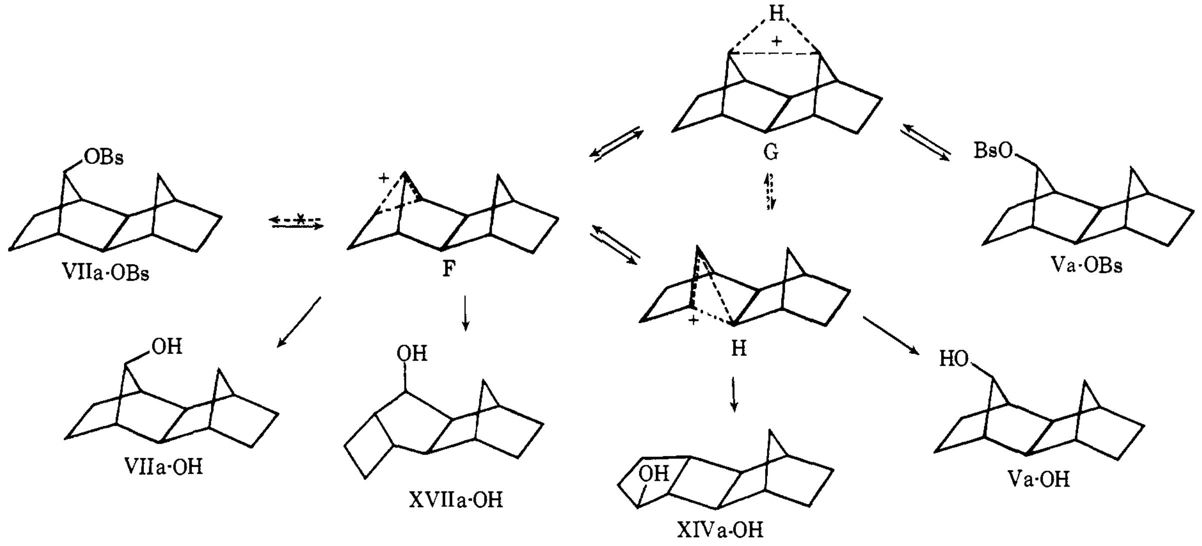


Chart IV



of the formed brosylate. The various percentages of isolated components in the different acetolyses of the saturated brosylates V-OBs and VII-OBs, after saponification and separation of the components, are summarized in Table III.

Table III. Mole Percentages of Isolated Components from the Acetolysis of the Saturated *p*-Bromobenzenesulfonates at 100.0°

ROBs	Yield,[a] %	Hydro-carbons	V-OH	VII-OH	XIV-OH	XVII-OH
			Mol % products			
Va-OBs	97	2	78.6	8	11	0.4
Vb-OBs	96	2	73.6	9	15	0.4
VIIa-OBs[b]	93	1	81.5	9	8	0.5
VIId-OBs[c]	98	1	80.4	10	8	0.6

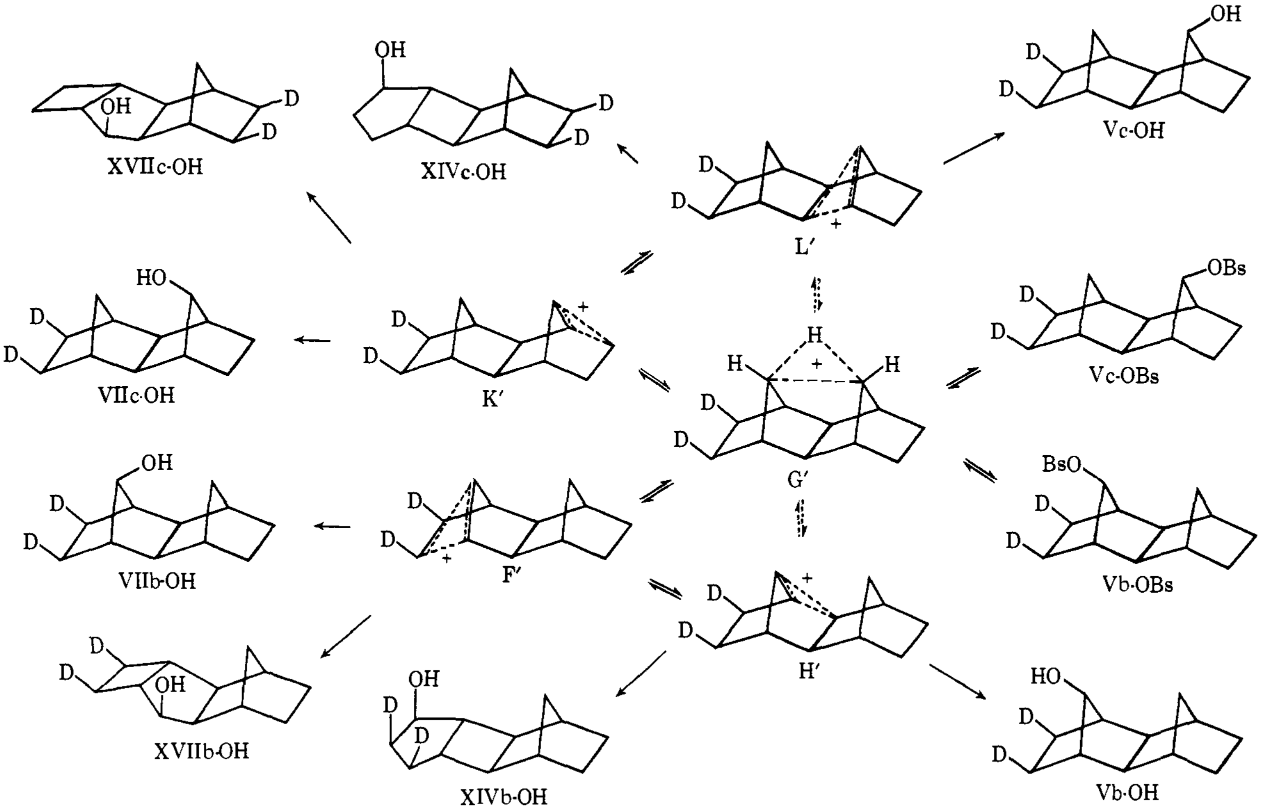
[a] Yield of isolated products after two separations, based on total saturated products only. [b] Based on 49.9% solvolysis. [c] Based on 59.0% solvolysis.

From the kinetic measurements the fraction of solvolysis for VIIa-OBs was determined to be 56%. However, in a large-scale run of VIIa-OBs the fraction of solvolysis was found to be only 50%, whereas the fraction of solvolysis for VIId-OBs was found to be 59% (calculated from the amount of recovered V-OBs from VII-OBs).

The main solvolysis products of V-OBs and VII-OBs were the three alcohols V-OH, VII-OH, and XIV-OH in the ratio 8:1:1. A higher proportion of XIV-OH was obtained from V-OBs. These three alcohols were identified by nmr analysis and by comparison with the results obtained from the solvolysis of IX-OBs. The three minor components were mainly investigated by glc analysis. The obtained alcohol with the suggested structure of XVII-OH had different retention time than the cis 5-alcohol XVI-OH (epimer of XIV-OH) on two columns. The major hydrocarbon is unsaturated as the nmr spectrum showed a vinyl peak at τ 4.3.

In a small scale experiment VIId-OBs was acetolyzed for 1.0 half-life. Nmr analysis of the recovered brosylate showed scrambled outside 9-brosylate Vd,e-OBs but no scrambling of the starting brosylate. No trace of VIIe-OBs was found by nmr after 25 scans on a

Chart V



Varian time-averaging computer (CAT) in the α proton region of VII-OBs.

Discussion

The *p*-nitrobenzoate from the unsaturated alcohol XI-OH was very reactive in solvolysis as shown by the data in Table II. In fact, XI is one of the most reactive systems of this sort and surpasses the anti 7-norbornenyl system in reactivity by more than 10^4. The order of observed reactivity in solvolysis of V, IX, VII, and XI is $1:10:10^3:10^{11}$, respectively, at 25°. The saturated inside 9-brosylate (VII-OBs) is 10^3 times more reactive than the saturated outside 9-brosylate (V-OBs), which may be explained by the assistance to ionization from the steric interaction of the inside 9-ester group and the inside 10-hydrogen in VII-OBs. The reactivities of the two brosylates with an outside ester group (V-OBs and IX-OBs) are rather similar. The double bond in IX gives a rate enhancement of only 10, whereas the double bond in the epimeric XI system gives a rate enhancement of 10^8. The large difference in reactivity of 10^{10} between the two unsaturated systems is explained partly by the steric interaction of the inside 9-ester group and the inside 10-hydrogen, but the main part of the difference (10^7) is explained by anchimerically assisted ionization of the XI-OPNB.[10] Such dramatic backside participation by a double bond or a cyclopropyl group has been well established.[13,14]

The solvolytic behavior of the unsaturated inside 9-*p*-nitrobenzoate XI-OPNB is quite analogous to the solvolytic behavior of the *anti*-7-norbornenyl toluenesulfonate.[13,14a,15] Hydrolysis of XIb-OPNB gave quantitatively XIb-OH (Chart II). The complete retention of configuration observed in the hydrolysis of XIb-OPNB is accounted for on the basis of an intermediate nonclassical "bishomocyclopropenyl" cation A. No sign of a product from attack of nucleophilic reagent at C-6 or C-7 of the cation A was observed.

The suggested mechanism for the acetolysis of the unsaturated outside 9-brosylate IX-OBs is outlined in Chart III and shows large resemblance to the solvolytic behavior of the *syn*-7-norbornenyl toluenesulfonate.[10,16] Both the allylic cation C and the "bishomocyclopropenyl" cation E are needed to explain the formed solvolysis products. Solvent attack of the cation E gives only XIa-OH, while the allylic cation C gives the trans 5-alcohol XII-OH and the cis 5-alcohol XIII-OH depending on the site of solvent attack.

As a leakage from a "bishomocyclopropenyl" cation into an allylic cation or vice versa was not observed earlier,[15,16] the two intermediate cations C and E must have been formed by rearrangement of a probably common cationic species. Mainly, there are three routes to explain the origin of the cations C and E: (i) ionization of IX-OBs with anchimeric assistance from σ participation gives the cation B, which immediately rearranges to the cations C and E by backside attack of the 6, 7 π-electron cloud at the 8 and 9 positions, respectively; (ii) the first route together with some contribution from the bridged cation D, which rearranges as soon as it is formed to the cation E; the bridged cation D arises from ionization of IX-OBs assisted by participation from the inside 10-hydrogen; (iii) unassisted ionization of IX-OBs giving a short-lived classical

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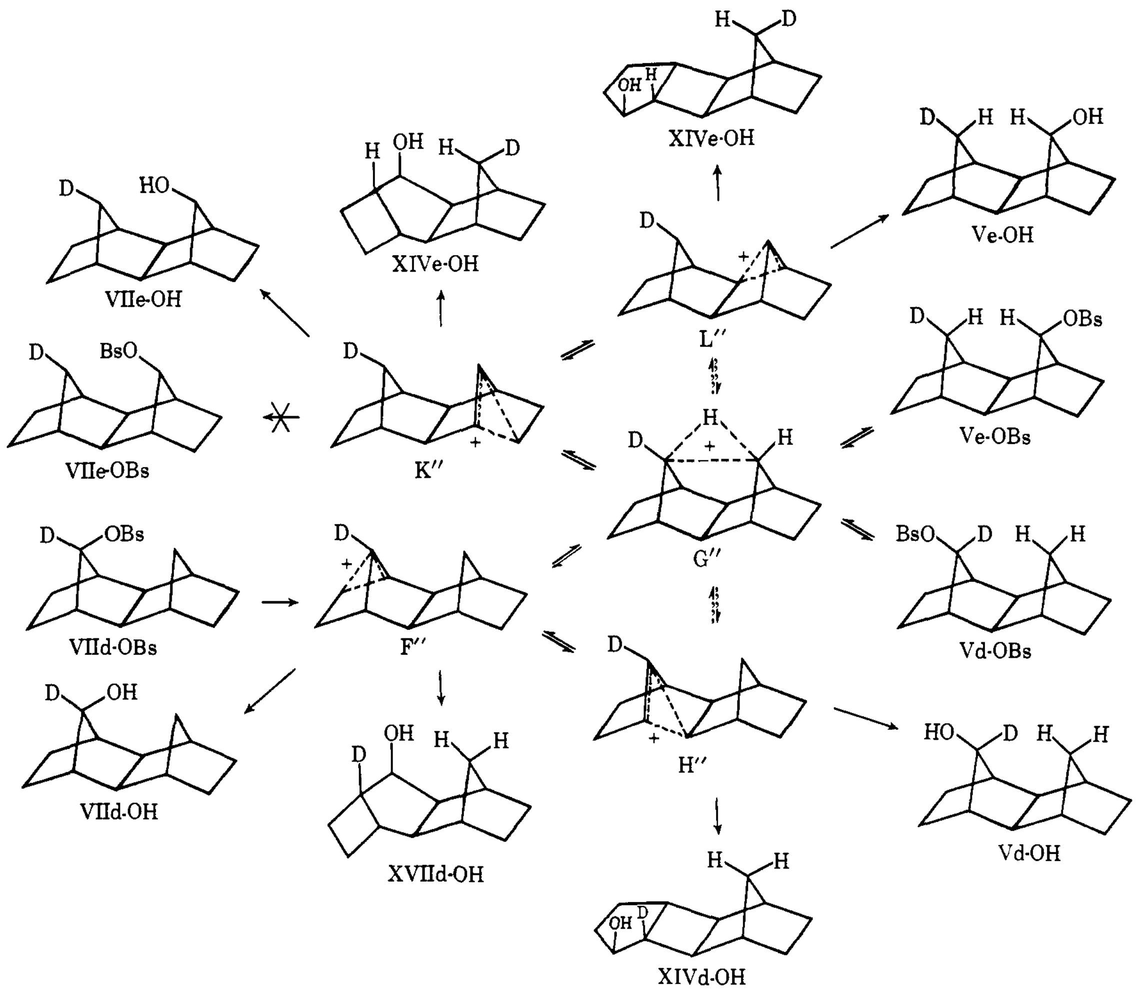
(13) See Table II, footnote *f*.

(14) (a) S. Winstein and M. Shatavsky, *J. Amer. Chem. Soc.*, **78**, 592 (1956); (b) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); (c) J. S. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

(15) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(16) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

Chart VI



cation which immediately and completely is transformed into the cations C and E in the ratio 2:1.

In our opinion the first route for the origin of the cations C and E is the most probable, but the second route might give a small contribution, if any. It is very difficult to explain the obtained kinetic data and the absence of any outside 9-alcohol IX-OH in the solvolysis product on the basis of unassisted ionization to a classical cation.

Acetolysis of the two saturated brosylates V-OBs and VII-OBs gave the same solvolysis products (see Table III and Chart IV). Although there are small differences in the obtained yields of the different components in the four runs, the combined yields of the two components arising from the same cation are constant in all runs. All of the components, except the hydrocarbons and XVII-OH, have been fully identified (see Experimental Section).

In order to get a better understanding of the proposed mechanism of the solvolysis and to question the existence of a bridged cation G, acetolysis of the deuterated brosylates Vb-OBs and VIId-OBs was carried out. Investigation of the scrambling of the deuterium by nmr of the recovered brosylate Vb,c-OBs showed 33% Vc-OBs after 1.0 solvolytic half-life at 100° starting from pure Vb-OBs. A calculated value of 34% Vc-OBs was obtained by using $k_{\text{ion}} = 2.02 \times 10^{-5}$ sec^{-1} at 100° (1.0 solvolytic half-life equals 1.74 ionization half-lives) which was obtained from the kinetic experiment and assuming return (44%) from an intermediate where the 9 and 10 positions are equivalent. Investigation of the scrambling of the deuterium by nmr of the obtained solvolysis product Vb-c-OH after complete reaction (10 solvolytic half-lives) showed 50 % Vc-OH. These results clearly indicate that the outside 9-brosylate V-OBs ionizes to a cation where the 9 and 10 positions are equivalent. The bridged cation G fulfills such a requirement. However, a hydride transfer *via* a transition state which may resemble the bridged cation G will give the same net result in the acetolysis of Vb-OBs.

Ionization of Vb-OBs assisted by participation from the inside 10-hydrogen gives the bridged cation G′, which either can give back Vb-OBs and Vc-OBs by ion-pair return or rearrange by backside attack to the cations F′ and K′. A frontside attack on the bridged cation would give the cations H′ and L′, but such rearrangement is not very probable. These latter cations are instead originated from the cations F′, respectively, K′ by backside attack, and "cross-side flipping." The four intermediates F′, H′, K′, and L′ are needed in order to explain the obtained solvolysis products.

The mechanism of the acetolysis of the inside 9-brosylate (VII-OBs) is similar to the one for the outside 9-brosylate. However, the formation of outside 9-brosylate V-OBs during the solvolysis of VII-OBs does not give rise to any complications, due to the large difference in rate between V-OBs and VII-OBs. Investigation of the formed outside 9-brosylate Vd,e-OBs

Table IV. Summary of Retention Times (Minutes)

Column	Va-OH	VI	VIIa-OH	IX-OH	X	XIa-OH	XII-OH	XIII-OH	XIVa-OH	XV	XVI-OH	XVIIa-OH
a	36	14	43	18	15	45	29	32	25	20	27	28
b	46		56				38	42	33	26	36	37

[a] Using a 1/8 in. × 16 ft column packed with 5% Carbowax 20M on Chromosorb W (80–100 mesh) at 140° and 40 psi nitrogen pressure.
[b] Using a 1/8 in. × 3 m column packed with 15% Carbowax 20M on Chromosorb W (80–100 mesh) at 162° and 40 psi nitrogen pressure.

by nmr showed even scrambling of the deuterium between the 9 and 10 positions after 10 half-lives at 100° starting from pure VIId-OBs. The results from the nmr investigation of the scrambling of the deuterium of the obtained solvolysis products Vd,e-OH and VIId-e-OH were very interesting and the analyses showed 34% Ve-OH and 42% VIIe-OH. The alcohols were converted to the corresponding brosylates and these brosylates were investigated by nmr in the same manner as for the directly formed Vd,e-OBs.

Ionization of VIId-OBs with anchimeric assistance from σ participation gives the cation F″, which either can rearrange to the bridged cation G″ by backside attack or to the cation H″ by "cross side flipping." As before the bridged cation G″ will give the cation K″ by backside attack, which then can "cross side flip" to the cation L″. The four intermediates F″, H″, K″, and L″ are needed in order to explain the obtained solvolysis products, as for the acetolysis of the saturated outside 9-brosylate. The formation of even scrambled Vd,e-OBs from VIId-OBs strongly indicates the bridged cation G″ as the intermediate (the leaving group has not traveled very far away). Frontside attack of the bridged cation G″ would give the cations H″ and L″ but such a rearrangement is not very probable as the obtained solvolysis product Vd,e-OH was not even scrambled. However, a minor leakage of G″ into H″ and L″ or a minor formation of Vd,e-OH directly from G″ does not influence the amount of scrambling of the obtained product Vd,e-OH.

It is rather difficult to give a complete explanation of the uneven scrambling of the deuterium of the solvolysis products Vd,e-OH and VIId,e-OH compared to the even scrambled Vd,e-OBs. Differences in the rates for the rearrangements of the cations of course would explain the scrambling of the obtained solvolysis products. An investigation presently in progress of the solvolytic behavior of XIV-OBs and its epimer might give further information on the mechanism of solvolysis of the saturated brosylates V-OBs and VII-OBs.

The solvolytic behavior of the saturated brosylates V-OBs and VII-OBs shows much resemblance to the solvolytic behavior of the 7-norbornyl brosylate. The solvolysis of *exo,exo*-2,3-dideuterio-*anti*-7-norbornyl tosylate was later studied by Gassman, *et al.*,[17a,b] and by Miles.[17c] These authors proposed different mechanisms in order to explain the different scrambling of the deuterium of the solvolysis products. However, Gassman, *et al.*, remarked that the leakage between two epimeric nonclassical ions would produce the same net result with respect to the scrambling of deuterium of the rearranged solvolysis product. Such a leakage would be called according to our term "same-side flipping." In our opinion the flipping between two epimeric nonclassical ions fully explains the scrambling of deuterium in the two acetolysis products, as the difference of the scrambling of only 5 ± 3% is too small to be significant. However, we would rather propose that flipping occurs from one side of the cation to the other side of the cation ("cross-side flipping") as proposed in the solvolysis of the two saturated brosylates.[17d]

Experimental Section

Melting points and boiling points are uncorrected. The nmr data were obtained at 60 MHz using a Varian A-60-D nmr spectrometer and at 100 MHz using a Varian HA-100 spectrometer operating in the field sweep mode. Samples were run as 15–20 w/v % solutions in carbon disulfide with tetramethylsilane as internal standard at the operating temperature of the instrument (*ca.* 35°). The instrument sweep was calibrated with chloroform. Resonance peaks are given in τ values. Gas–liquid chromatography (glc) analysis was carried out on a Perkin-Elmer Model 800 chromatograph. Retention times (rt) are given in minutes from injection of the sample. The retention times of the compounds are exactly comparable from one analysis to another analysis on a given column and under the given conditions, as each column was calibrated to a fixed retention time of the outside 9-alcohol Va-OH prior to use. A summary of the retention times of the compounds on two different columns is given in Table IV. Thin-layer chromatography (tlc) analysis was carried out on 3 × 20 cm Polygram SILN-HR/UV sheets (Brinkmann), eluting with ether–pentane (1:3) and detecting by spraying with sulfuric acid saturated with sodium dichromate followed by charring on a hot plate. Microanalyses were performed by Miss Heather King, Department of Chemistry, University of California at Los Angeles.

5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-*exo,endo*-5,8-dimethanonaphthalene (II). Technical grade aldrin (I) was purified by chromatography on aluminum oxide (Al_2O_3). Elution with pentane gave a white solid which was recrystallized from acetone–methanol, mp 100–101°. A solution of 73.0 g (0.20 mol) of pure aldrin in 200 ml of ethyl acetate was hydrogenated over palladium/charcoal (Pd/C; 10%). Hydrogen gas was added with the hydrogen pressure only slightly above the normal pressure at room temperature and with rapid stirring, until the uptake of hydrogen had ceased. The catalyst was filtered off through Celite. Evaporation of the filtrate gave a solid that was recrystallized from acetone–methanol to yield 72.0 g (98%) of II, mp 76–77°.

1,2,3,4,4a,5,8,8a-Octahydro-1,4-*exo,endo*-5,8-dimethanonaphthalene (III). To a stirred solution of 73.4 g (0.20 mol) of recrystallized II in 200 ml of *tert*-butyl alcohol and 1000 ml of tetrahydrofuran, under a nitrogen atmosphere in a 5-l. flask fitted with a large condenser, was added 28 g of freshly cut lithium wire. After a few minutes a vigorous exothermic reaction started, which was moderated by cooling with a Dry Ice–acetone bath. The mixture was allowed to reflux vigorously with stirring until the spontaneous reaction subsided, and then heat was applied and the mixture refluxed for 1 hr. The hot solution was poured through a screen to remove residual lithium. Ice and water were added to the filtrate, which was extracted with ether. The combined ether layers were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The ether and residual tetrahydrofuran were removed and vacuum distillation of the residue gave 26.8 g (84%) of III, bp 60–65° (1 mm). Glc analysis showed 82% monoene.

6,7-Epoxyperhydro-1,4-*exo,endo*-5,8-dimethanonaphthalene (IV). Monoperoxyphthalic acid was prepared by suspending 60 g (0.40

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(17) (a) P. G. Gassman and J. M. Hornback, *J. Amer. Chem. Soc.*, **89**, 2487 (1967); (b) P. G. Gassman, J. M. Hornback, and J. L. Marshall, *ibid.*, 90, 6238 (1968); (c) F. B. Miles, *ibid.*, **89**, 2488 (1967); 90, 1265 (1968); (d) our results do not distinguish between the two possibilities "cross-side flipping" and "same-side flipping." An investigation in progress of the solvolytic behavior of 2-deuterium, *trans*-2-brosyloxybicyclo[3.2.0]heptane might give further information. After this manuscript had been written a publication by B. Funke, *Tetrahedron Lett.*, 1477 (1971), indicates "same-side flipping" in the 7-norbornyl cation.

mol) of phthalic anhydride in 400 ml of ether and adding 200 ml of hydrogen peroxide (30%). The mixture was stirred overnight at room temperature. The clear ethereal solution was separated from the aqueous layer, washed with saturated ammonium sulfate solution, and dried over anhydrous magnesium sulfate.

The epoxidation was carried out by adding 16.0 g (0.10 mol, 82% monoene) of III in 50 ml of ether to the stirred peroxyphthalic acid solution. The mixture was stirred overnight at room temperature. The phthalic acid precipitate was filtered off and the ether solution was washed free of phthalic acid with 10% sodium bicarbonate solution. When the washings failed to give a color with KI–starch paper, the ether solution was washed with water until neutral and dried over anhydrous magnesium sulfate. The ether was removed and vacuum distillation of the residue gave 12.2 g (69%) of IV, bp 100–105° (3 mm). Glc analysis showed 82% epoxide.

outside-**9-Hydroxyperhydro-1,4-*exo*,*exo*-5,8-dimethanonaphthalene (Va-OH).** A slurry of 38 g (1.0 mol) of lithium aluminum hydride in 250 ml of ether was refluxed for 1 hr. The cooled slurry was carefully added under a nitrogen atmosphere to a previously cooled solution of 133.5 g (1.0 mol) of anhydrous aluminum chloride in 250 ml of ether. The mixture was stirred for 1 hr at room temperature. A solution of 17.6 g (0.10 mol, 82% epoxide) of IV in 200 ml of ether was added dropwise with rapid stirring and the mixture was refluxed for 20 hr. The excess reagents were decomposed by careful addition of water. The mixture was diluted with water and extracted with ether. The combined ether layers were washed with water. Evaporation of the dried ether solution left a white solid, which after recrystallization from acetone–petroleum ether yielded 12.3 g (69%) of Va-OH, mp 100–101°. Glc anlysis[18] showed only one peak (rt 36 min).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.95; H, 10.06.

The *p*-bromobenzenesulfonate of Va-OH (Va-OBs) was prepared by the standard procedure and recrystallized from ether–pentane, mp 126–127°. Tlc analysis showed only one spot and no trace of the starting alcohol.

Anal. Calcd for $C_{18}H_{21}BrO_3S$: C, 54.41; H, 5.33. Found: C, 54.61; H, 5.31.

9-Oxoperhydro-1,4-*exo*,*exo*-5,8-dimethanonaphthalene (VI). A solution of 8.9 g (0.050 mol) of Va-OH in 50 ml of dry pyridine was added dropwise during 1 hr under a nitrogen atmosphere to a stirred mixture of 20 g of chromium trioxide in 150 ml of dry pyridine. The mixture was stirred for 40 hr at room temperature. The mixture was poured into ice–water and extracted with ether. The combined ether layers were washed with water, dilute hydrochloric acid, and water. Evaporation of the dried ether solution left a white solid, that after recrystallization from pentane yielded 8.2 g (93%) of VI, mp 93–94°. Glc analysis[18] showed only one peak (rt 14 min).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.98; H, 9.28.

inside-**9-Hydroxyperhydro-1,4-*exo*,*exo*-5,8-dimethanonaphthalene (VIIa-OH).** A solution of 7.0 g (0.040 mol) of VI in 100 ml of ether was added dropwise to a stirred slurry of 3.8 g of lithium aluminum hydride in 150 ml of ether under a nitrogen atmosphere. The mixture was stirred overnight at room temperature. Water was added dropwise to decompose the complex and excess hydride, followed by 100 ml of saturated ammonium chloride solution. The layers were separated and the aqueous layer was extracted with ether. The combined ether layers were washed with water. Evaporation of the dried ether solution left a white solid, which after recrystallization from pentane yielded 6.3 g (89%) of VIIa-OH, mp 122–123°. Glc analysis[18] showed only one peak (rt 43 min).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.77; H, 10.15.

The *p*-bromobenzenesulfonate of VIIa-OH (VIIa-OBs) was prepared by the standard procedure and recrystallized from ether–pentane, mp 107–108°. Tlc analysis showed only one spot and no trace of the starting alcohol.

Anal. Calcd for $C_{18}H_{21}BrO_3S$: C, 54.41; H, 5.33. Found: C, 54.43; H, 5.40.

inside-**9-Hydroxy-9-deuterioperhydro-1,4-*exo*,*exo*-5,8-dimethanonaphthalene (VIIId-OH).** A solution of 2.65 g (0.015 mol) of VI in 50 ml of ether was added dropwise to a stirred slurry of 1.0 g of lithium aluminum deuteride (99.5% deuterium) in 75 ml of ether under a nitrogen atmosphere. The mixture was stirred overnight at room temperature and the product was worked up in the same manner as for VIIa-OH. Recrystallization of the product from pentane yielded 2.63 g (98%) of VIId-OH, mp 122–123°. Glc analysis[18] showed only one peak (rt 43 min). The nmr spectra (60 and 100 MHz) were identical with those of VIIa-OH, except that the 5,8-bridgehead protons at τ 8.21 appeared as a quartet (quintet in VIIa-OH) and no α proton at τ 6.32 could be detected after 20 scans on the CAT.

The *p*-bromobenzenesulfonate of VIId-OH (VIIId-OBs) was prepared by the standard procedure and recrystallized twice from ether–pentane, mp 107–108°. Tlc analysis showed only one spot and no trace of the starting alcohol. The nmr spectra (60 and 100 MHz) were identical with those of VIIa-OBs, except that no α-proton at τ 5.86 could be detected after 20 scans on the CAT.

outside-**9-Hydroxy-6-bromoperhydro-1,4-*exo*,*exo*-5,8-dimethanonaphthalene (VIII).** Dry ether (200 ml) was allowed to absorb 16 g of dry hydrogen bromide at 5°, and 17.6 g (0.10 mol, 82% epoxide) of IV in 100 ml of dry ether was added dropwise during 1 hr with rapid stirring. The mixture was stirred for 20 hr at room temperature. The ether solution was washed with water, sodium bicarbonate solution, and water. Evaporation of the dried ether solution left a white solid, that after recrystallization from ligroin yielded 12.5 g (49%) of VIII, mp 122–123°.

Anal. Calcd for $C_{12}H_{17}BrO$: C, 56.05; H, 6.66; Br, 31.07. Found: C, 56.81; H, 6.76; Br, 31.25.

outside-**9-Hydroxy-1,2,3,4,4a,5,8,8a-octahydro-1,4-*exo*,*exo*-5,8-dimethanonaphthalene (IX-OH).** To a mixture of 19.3 g (0.075 mol) of VIII and 75 ml of freshly distilled dihydropyran was added five drops of concentrated hydrochloric acid. All of the bromohydrin then dissolved, and the mixture was stirred overnight at room temperature. The reaction mixture was diluted with 100 ml of ether and washed with sodium hydroxide solution (10%) and water. Evaporation of the dried ethereal solution left a yellow oil (32.5 g), which was purified by chromatography on Al_2O_3 using 1.5 l. of ether–pentane (1:2) as eluent. Evaporation of the solvents left 29.0 g of a colorless oil, which was used in the dehydrobromination step.

A 22.2-g quantity (0.20 mol) of potassium *tert*-butoxide was dissolved in 500 ml of *tert*-butyl alcohol under a nitrogen atmosphere. The *tert*-butyl alcohol was distilled off until a thick paste remained, and 500 ml of xylene was added to the paste. After removal of 200 ml of this solvent by distillation, 29.0 g of the pyranyl ether in 100 ml of xylene was added dropwise, and the mixture was refluxed for 50 hr. Most of the solvent was removed by distillation and the residue was poured into water and extracted with ether. The combined ether layers were washed with water and dried over anhydrous sodium sulfate. Evaporation of the ether solution left a yellow oil (22 g), which was purified by chromatography on Al_2O_3 using 2 l. of ether–pentane (1:2) as eluent. Evaporation of the solvents left 21.5 g of a colorless oil. This oil was dissolved in 100 ml of aqueous acetone (90%) and 1 ml of perchloric acid (72%) was added. The mixture was stirred overnight at room temperature, poured into water, and extracted with ether. The combined ether layers were washed with water, saturated sodium bicarbonate solution, and water. Evaporation of the dried ether solution left a white solid, that after recrystallization from pentane yielded 10.8 g (82%) of IX-OH, mp 89–90°. Glc analysis[18] showed only one peak (rt 18 min).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.73; H, 8.94.

A 100-mg quantity of IX-OH was dissolved in 40 ml of ethyl acetate and hydrogenated over Pd/C (10%) as described for II. The absorption of hydrogen was 12.0 ml (calcd 12.6 ml). The nmr spectrum of the product (102 mg) was identical with the spectrum of earlier prepared Va-OH.

The *p*-bromobenzenesulfonate of IX-OH (IX-OBs) was prepared by the standard procedure and recrystallized from ether–pentane, mp 121–122°. Tlc analysis showed only one spot and no trace of the starting alcohol.

Anal. Calcd for $C_{18}H_{19}BrO_3S$: C, 54.69; H, 4.85. Found: 54.79; H, 5.07.

9-Oxo-1,2,3,4,4a,5,8,8a-octahydro-1,4-*exo*,*exo*-5,8-dimethanonaphthalene (X). A solution of 3.5 g (0.020 mol) of IX-OH in 50 ml of dry pyridine was added dropwise during 1 hr to a stirred mixture of 10 g of chromium trioxide in 150 ml of dry pyridine under a nitrogen atmosphere. The mixture was stirred for 20 hr at room temperature, and the product was worked up as for VI. Recrystallization from pentane yielded 2.0 g (57%) of X, mp 49–50°. Glc analysis[18] showed only one peak (rt 15 min).

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[18] See footnote *a*, Table IV.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.74; H, 8.04.

***inside*-9-Hydroxy-1,2,3,4,4a,5,8,8a-octahydro-1,4-*exo*,*exo*-5,8-dimethanonaphthalene (XIa-OH).** A solution of 2.61 g (0.015 mol) of X in 50 ml of dry ether was added dropwise to a stirred slurry of 1.0 g of lithium aluminum hydride in 100 ml of ether under a nitrogen atmosphere. The mixture was stirred overnight at room temperature, and the product was worked up as for VIIa-OH. Glc analysis[18] of the crude product (2.7 g) showed two peaks at rt 36 and 45 min, corresponding to Va-OH (32%) and XIa-OH (68%).

The two alcohols were separated by chromatography on 200 g of SilicAR (100–200 mesh), using 4 l. of ether–pentane (1:9) as eluent divided into 250-ml fractions. The progress of the separation was followed by glc analysis. In this way 600 mg of Va-OH (the nmr spectrum was identical with earlier prepared Va-OH), 139 mg of a mixture of the two alcohols, and 1.58 g of XIa-OH (pure according to glc analysis) were obtained. Recrystallization of the latter alcohol from pentane yielded 1.4 g of XIa-OH, mp 106–107°.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.63; H, 9.08.

A 100-mg quantity of XIa-OH was dissolved in 40 ml of ethyl acetate and hydrogenated over Pd/C (10%) as described for II. The absorption of hydrogen was 12.2 ml (calcd 12.6 ml). The nmr spectrum of the product (105 mg) was identical with the spectrum of earlier prepared VIIa-OH.

The *p*-nitrobenzoate of XIa-OH (XIa-OPNB) was prepared by the standard procedure and recrystallized from ether–pentane, mp 140–141°. Tlc analysis showed only one spot and no trace of the starting alcohol.

Anal. Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89. Found: C, 70.22; H, 6.02.

***inside*-9-Hydroxy-9-deuterio-1,2,3,4,4a,5,8,8a-octahydro-1,4-*exo*,*exo*-5,8-dimethanonaphthalene (XIb-OH) and *outside*-9-Hydroxy-6-*exo*,*exo*-7-dideuterioperhydro-1,4-*exo*,*exo*-5,8-dimethanonaphthalene (Vb-OH).** A solution of 1.17 g (6.7 mmol) of X in 50 ml of dry ether was added dropwise to a stirred slurry of 0.5 g of lithium aluminum deuteride (99.5% deuterium) in 50 ml of dry ether, which also contained a trace of anhydrous aluminum chloride. The mixture was stirred overnight under a nitrogen atmosphere at room temperature, and 10 ml of deuterium oxide (99% deuterium) was added dropwise. The mixture was stirred for 1 hr, and 50 ml of saturated ammonium chloride solution was added with rapid stirring. The product was worked up as usual. Glc analysis of the crude reaction product (1.2 g) showed two peaks corresponding to XIb-OH (69%) and Vb-OH (31%).

The two alcohols were separated by chromatography on 250 g of SilicAR (100–200 mesh) using 5 l. of ether–pentane (1:9) as eluent divided into 125-ml fractions. The progress of the separation was followed by glc analysis. In this way 827 mg of XIb-OH (pure according to glc analysis), 30 mg of a mixture of the two alcohols, and 331 mg of Vb-OH (pure according to glc analysis) were obtained.

The nmr spectra (100 MHz) of recrystallized XIb-OH showed no α proton at τ 6.55 after 20 scans on the CAT. The 5,8-bridgehead protons at τ 7.52 appeared as a triplet (quartet in XIa-OH), but the remainder of the spectrum was identical with that of XIa-OH. The nmr spectra (100 MHz) of recrystallized Vb-OH were identical with those of Va-OH, except that the 5,8-bridgehead protons at τ 8.23 appeared as a quartet (quintet in Va-OH) and no exo 6,7 protons at 8.22 were observed.

The *p*-nitrobenzoate of XIb-OH (XIb-OPNB) was prepared by the standard procedure and recrystallized from ether–pentane, mp 140–141°. Tlc analysis showed only one spot and no trace of the starting alcohol. The nmr spectra of this *p*-nitrobenzoate showed no α proton at τ 5.60 after 20 scans on the CAT. The 5,8-bridgehead protons at τ 7.14 appeared as a triplet (quartet in XIa-OPNB), but the remainder of the spectrum was identical with that of XIa-OPNB.

The *p*-bromobenzenesulfonate of Vb-OH (Vb-OBs) was prepared by the standard procedure and recrystallized from pentane, mp 126–127°. Tlc analysis showed only one spot and no trace of the starting alcohol. The nmr spectra of this brosylate were identical with those of Va-OBs, except that the 5,8-bridgehead protons at τ 8.01 appeared as a quartet (quintet in Va-OBs) and no exo 6,7 protons at 8.32 were observed.

Kinetics. The rates of acetolysis of the *p*-bromobenzenesulfonates were obtained in 0.011 *M* sodium acetate in acetic acid, using the common procedure.[19] For analysis a 5-ml aliquot was withdrawn and delivered into 0.013 *M* perchloric acid in acetic acid and then the mixture was backtitrated with 0.011 *M* sodium acetate in acetic acid to the bromophenol blue end point.

The rates of hydrolysis of the *p*-nitrobenzoates were measured in 70% aqueous acetone using the common ampoule technique. For analysis a 10-ml aliquot was withdrawn and the acid formed from 0.005 *M* ester was titrated with 0.0009 *M* sodium methoxide in methanol, using *p*-hydroxyazobenzene as indicator. The results of the kinetic experiments are summarized in Table II.

Hydrolysis of XIb-OPNB. A 508-mg quantity of the unsaturated inside 9-*p*-nitrobenzoate XIb-OPNB and 145 mg of sodium bicarbonate were dissolved in 200 ml of 70% aqueous acetone in a 250-ml flask with a constricted neck. The flask was flushed with nitrogen, sealed, and heated for 33 hr at 75.0° (10 half-lives). The cooled solvolysis mixture was poured into 500 ml of water and extracted with ether. The combined ether layers were washed with brine. Evaporation of the dried ether solution gave 287 mg of a white solid. Glc analysis[18] of the solvolysis product showed 98% of the inside 9-alcohol XIb-OH (rt 45 min) and 2% of three different hydrocarbons (2:1:1). No other alcohol was detected.

The alcohol was separated from the hydrocarbons by chromatography on 300 g of SilicAR (100–200 mesh) using 2 l. of pentane followed by 4 l. of ether–pentane (1:9) as eluent, divided into 250-ml fractions. The progress of the separation was followed by glc analysis. In this way 265 mg of XIb-OH (pure according to glc analysis) and 9 mg of a 1:1 mixture of the hydrocarbons and the alcohol were obtained. The total yield of isolated products was 274 mg (99%), consisting of 98.4% XIb-OH and 1.6% hydrocarbons. The recrystallized alcohol product (mp 106°) had an nmr spectrum identical with earlier recorded spectra of XIb-OH and showed no scrambling of deuterium.

Acetolysis of IX-OBs. A solution of 679 mg of the unsaturated outside 9-brosylate IX-OBs was acetolyzed in 50 ml of a 0.036 *M* solution of sodium acetate in acetic acid at 75.0° for 34.5 hr (1.0 half-life). The cooled solvolysis mixture was poured into water and extracted with ether. The combined ether layers were washed with water, sodium bicarbonate solution until the ether was free of acid, and finally with water. The dried ether solution was concentrated to 20 ml by distilling off ether through a 3-ft Claisen column. After cooling, unreacted brosylate fell out, which was filtered off and washed with cold ether.

The nmr spectra (100 MHz) of the recovered brosylate (310 mg; calcd 340 mg) were identical with the nmr spectrum of the starting brosylate. The integrations of all protons were consistent and no trace of an α proton of any other brosylate was found. Tlc analysis of the recovered brosylate showed only one spot, corresponding to IX-OBs. Tlc analysis of the residue in the mother liquor (formed solvolysis products and 30 mg of unreacted brosylate) showed two spots. The spot corresponding to IX-OBs was very small and the other was broad. Glc analysis[20] of this residue showed 4% of five different hydrocarbons (4:4:1:4:3) and 96% of three different acetates (32% XIa-OAc, rt 41 min; 54% XII-OAc, rt 48 min; 10% XIII-OAc, rt 39 min).

The recovered brosylate was combined with the solvolysis products in the mother liquor. The solvents were very carefully removed. The residue and 100 mg of sodium acetate were dissolved in 50 ml of acetic acid in a flask. The flask was flushed with nitrogen and sealed and the acetolysis was continued for 19 hr at 100.0° (10 half-lives). The acetolysis product was worked up as before. Glc analysis[20] of the concentrated ether solution showed that the acetolysis products consisted of five hydrocarbons (4%) and three different acetates (96%), with the same retention times and in the same ratio as above.

The ether solution containing the acetolysis product was added dropwise to a stirred slurry of 1 g of lithium aluminum hydride in ether under a nitrogen atmosphere. The mixture was stirred overnight at room temperature and worked up as usual. Evaporation of the dried ether solution gave 310 mg of solid. Glc analysis on two columns[18,21] showed 3% hydrocarbons (4:4:3:4:2), 33% XIa-OH, 54% XII-OH, and 10% XIII-OH, with the retention times summarized in Table IV.

Separation and Identification of the Products from IX-OBs. The three alcohols and the hydrocarbons obtained from IX-OBs were separated by chromatography on 300 g of SilicAR, using 13 l. of

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(19) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 70, 821 (1948).

(20) Using a 1/8 in. × 3 m column packed with 15% Carbowax 20M on Chromosorb W (80–100 mesh) at 150° and 40 psi nitrogen pressure.

(21) See Table IV, footnote *b*.

ether–pentane (1:19) as eluent divided into 250-ml fractions. The progress of the separation was followed by glc analysis. Fractions with the same product were combined and fractions with similar ratios of products were combined. The total yield of isolated products was 276 mg (91%), consisting of the following products: 20 mg (7%) of a mixture (9:11) of the five hydrocarbons and XIa-OH; 72 mg (26%) of pure XIa-OH; 39 mg (14%) of a mixture (1:3) of the epimeric alcohols XII-OH and XIII-OH; and 145 mg (53%) of pure XII-OH.

The nmr spectrum of the product XIa-OH was identical with the nmr spectra of earlier prepared XIa-OH. The nmr spectra (60 and 100 MHz) of the product XII-OH agreed with the suggested structure of the trans 5-alcohol XII-OH. The spectra showed a quartet at τ 8.10 (8 H and 9 H), a singlet at 5.76 (α proton), and a multiplet at 4.22 (vinyl protons).

The product XII-OH (145 mg) was hydrogenated over Pd/C (10%) in 40 ml of ethyl acetate as described for II. The absorption of hydrogen was 19.0 ml (calcd 18.0 ml). Glc analysis[21] of the hydrogenation product (150 mg) showed 2% XV and 98% saturated trans 5-alcohol XIVa-OH with the retention times shown in Table IV. No trace of any other alcohol was detected. Recrystallization of the hydrogenation product from 10 ml of pentane yielded 50 mg of pure trans 5-alcohol XIVa-OH, mp 102–103°.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.73; H, 10.07. The nmr spectra (60 and 100 MHz) of XIVa-OH agreed with the suggested structure, and showed a multiplet at τ 8.20 (8 H and 9 H) and a doublet at 6.22 (α proton). No vinyl protons were detected. Evaporation of the mother liquor from the recrystallization of the trans 5-alcohol XIVa-OH gave a solid (100 mg, consisting of 95% XIVa-OH and 5% XV). This residue was oxidized with chrominum trioxide in pyridine, and the usual work-up procedure gave 95 mg of a solid. Glc analysis[21] of the reaction product showed only one peak, corresponding to the ketone XV.

Hydrogenation as in II of the mixture of the two epimeric alcohols obtained in the above separation (39 mg; 25% XII-OH and 75% XIII-OH) gave 43 mg of a solid. Glc analysis showed 25% XIVa-OH, 23% XV, and 52% XVI-OH with the retention times of Table IV. The mixture of the crude hydrogenation product was then oxidized with chromium trioxide in pyridine as before. Glc analysis of the oxidation product showed only one peak, corresponding to the ketone XV.

Acetolysis of Va-OBs. A 3.97-g quantity of the outside 9-brosylate Va-OBs and 0.90 g of sodium acetate were dissolved in 150 ml of acetic acid in a flask with a constricted neck. The flask was flushed with nitrogen, sealed, and heated for 1 week at 100.0° (10 half-lives). The acetolysis product was worked up as before. Glc analysis of the concentrated ether solution showed 2% hydrocarbons and 98% acetates (two overlapping peaks in the ratio 5:1).

The ether solution containing the acetolysis product was added dropwise to a stirred slurry of 1 g of lithium aluminum hydride in ether under a nitrogen atmosphere. The mixture was stirred overnight at room temperature and worked up as usual. Evaporation of the dried ether solution gave 1.74 g (98%) of a white solid. Glc analysis on two columns[18,21] showed 2% hydrocarbons, 12% XIVa-OH (slight tailing peak), 79% Va-OH, and 7% VIIa-OH, with the retention times of Table IV.

Separation and Identification of the Products from Va-OBs. The products obtained above were separated by chromatography on 300 g of SilicAR (100–200 mesh) using 2 l. of pentane followed by 6 l. of ether–pentane (1:9) as eluent divided in 200-ml fractions. The progress of the separation was followed by glc analysis. Fractions with the same product were combined and fractions with a similar ratio of products were combined for rechromatography. The yield of isolated products was 1.73 g consisting of the following products: 39 mg of hydrocarbons, 140 mg of pure VIIa-OH, 988 mg of pure Va-OH, 318 mg of a mixture (9:1) of Va-OH and XIVa-OH, 247 mg of a mixture (1:4) of Va-OH and XIVa-OH. This mixture of Va-OH and XIV-OH (247 mg) was rechromatographed on 300 g of SilicAR using 7 l. of ether–pentane (1:9) as eluent in the same way as above. The following products were isolated: 42 mg of pure Va-OH, 52 mg of a mixture (3:2) of Va-OH and XIVa-OH, 142 mg of pure XIVa-OH. The total yield of isolated products after two separations was 1.72 g (97%) and the mole percentages of the isolated products are given in Table III.

Glc analysis[22] of the hydrocarbon product showed two different compounds (3% with rt 24 min and 97% with rt 29 min). The major hydrocarbon is unsaturated, as the nmr spectrum showed a peak at τ 4.3. The nmr spectra of the recrystallized product VIIa-OH (mp 122–123°) were identical with the spectra of earlier prepared VIIa-OH. Glc analysis of recrystallized VII-OH as well as of the residue left in the mother liquor showed only one peak. The nmr spectra of the recrystallized product Va-OH (mp 101–102°) were identical with the spectra of earlier prepared Va-OH. Glc analysis of the recrystallized product as well as of the residue left in the mother liquor showed only one peak.

The product XIVa-OH (142 mg) gave after recrystallization from pentane 90 mg of pure XIVa-OH, mp 102–103°. The nmr spectra (60 and 100 MHz) of the recrystallized alcohol were identical with the spectra of XIVa-OH obtained from the acetolysis of IX-OBs. Glc analysis[21] of the recrystallized alcohol showed only one peak (rt 33 min). Glc analysis[21] of the residue (52 mg) left in the mother liquor of the recrystallization showed two peaks: 86% XIVa-OH (rt 33 min) and 14% of another alcohol (rt 37 min) with the suggested structure XVII-OH (see Chart IV). Glc analysis[18,21] of a sample of this residue enriched with a sample of XIVa-OH, XV, and XVI-OH from the acetolysis of IX-OBs showed four different peaks with retention times (see Table IV) corresponding to XV, XIVa-OH, XVI-OH, and XVII-OH, respectively.

Acetolysis of Vb-OBs. A 475-mg quantity of the 6,7-dideuterio-*outside*-9-brosylate (Vb-OBs) and 110 mg of sodium acetate were dissolved in 50 ml of acetic acid in a flask with a constricted neck. The flask was flushed with nitrogen, sealed, and heated for 17.2 hr at 100.0° (1.0 half-life). The acetolysis product was worked up as before. After cooling of the concentrated ether solution the unreacted brosylate crystallized, which was then filtered and washed with cold ether.

Tlc analysis of the recovered brosylate (192 mg, calcd 237 mg) showed only one spot. Tlc analysis of the residue in the mother liquor (solvolysis products and 45 mg of unreacted brosylate) showed two spots. One small spot corresponded to V-OBs and the other broad spot corresponded to acetates. Glc analysis[20] of the above residue showed 2% hydrocarbons and 98% acetates (two overlapping peaks in the ratio 4:1). The recovered brosylate was divided into two samples and the deuterium scrambling was investigated by nmr (100 MHz; sweep width 250 Hz). The average of ten integrations and three runs of each sample showed 33 ± 1% of Vc-OBs (exo 6,7 protons at τ 8.32) for both of the two samples. The amount of the exo 6,7 protons (in the τ 8.20–8.40 interval) was measured relative to the four bridgehead protons and relative to all ten protons in the 8.20–9.20 interval. The average of ten integrations and three runs of each sample showed 73 ± 2% of Vb-OBs (exo 2,3 protons at τ 8.68) for both of the two samples. The amount of the exo 2,3 protons (in the τ 8.62–8.74 interval) was measured relative to the four bridgehead protons and relative to all ten protons in the 8.20–9.20 interval. The nmr spectra of the recovered brosylate showed no trace of an α proton of any brosylate other than the formed Vb,c-OBs.

The recovered brosylate was combined with the solvolysis products in the mother liquor. The solvents were very carefully removed. The residue and 70 mg of sodium acetate were dissolved in 50 ml of acetic acid in a flask. The flask was flushed with nitrogen and sealed and the acetolysis was continued for 1 week at 100.0° (10 half-lives). The acetolysis product was worked up as before. Glc analysis[20] of the concentrated ether solution showed 2% hydrocarbons and 98% acetates (two overlapping peaks in the ratio of 4:1).

The ether solution containing the acetolysis product was added dropwise to a stirred slurry of 200 mg of lithium aluminum hydride in ether under a nitrogen atmosphere. The mixture was stirred overnight at room temperature and the usual work-up procedure gave 220 mg of a solid (calcd 214 mg). Glc analysis on two columns[18,21] showed 2% XIV-OH (slight tailing peak), 80% V-OH, and 6% VII-OH, with the retention times of Table IV.

Separation and Identification of the Products from Vb-OBs. The products obtained above were separated by chromatography on 300 g of SilicAR (100–200 mesh), using 1.5 l. of pentane followed by 3 l. of ether–pentane (1:19) and 6 l. of ether–pentane (1:9) as eluent divided into 250-ml fractions. The progress of the separation was followed by glc analysis. Fractions that contained a mixture of products (V-OH, XIV-OH, and XVII-OH) were combined (59 mg), and rechromatographed on 300 g of SilicAR using 8 l. of ether–pentane (1:9) as eluent in the same way as above. The following products were isolated: 3 mg of hydrocarbons; 18 mg of pure VII-OH; 140 mg of pure V-OH; 28 mg of a mixture of V-OH (38%), XIV-OH (58%), and XVII-OH (4%); and 16 mg of pure XIV-OH. The total yield of isolated products was 205 mg (96%).

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[22] Using a 1/8 in. × 3 m column packed with 15% Carbowax 20M on Chromosorb W (80–100 mesh) at 90° and 30 psi nitrogen pressure.

The mole percentages of the isolated products are given in Table III.

Glc analysis[22] of the hydrocarbon product showed two hydrocarbons (6% with rt 24 min and 94% with rt 29 min). The nmr spectra and glc data of the product VII-OH corresponded to earlier obtained data of VIIa-OH. The retention times for the products XIV-OH and XVII-OH were identical with earlier obtained data of the two rearranged alcohols.

Recrystallization of the obtained product Vb,c-OH (140 mg) from pentane gave 92 mg of outside 9-alcohol, mp 101°. Glc analysis of the recrystallized alcohol as well as of the residue in the mother liquor showed only one peak. The deuterium scrambling in the product Vb,c-OH was investigated by nmr (100 MHz; sweep width 250 Hz). The average of ten integrations and four runs showed 50.0 ± 0.8% of Vc-OH (exo 6,7 protons) and 49.7 ± 1.0% of Vb-OH (exo 2,3 protons). The amount of exo 6,7 protons (from the sum of the exo 6,7 protons, 5,8-bridgehead protons, and inside 10 proton in the τ 8.10–8.45 interval, minus 3.0 protons) was measured relative to the two 1,4-bridgehead protons and relative to all twelve protons in the 8.10–9.25 interval. The amount of exo 2,3 protons (from the sum of the exo 2,3 protons and the 4a,8a protons in the τ 8.45–8.80 interval, minus 2.0 protons) was measured relative to the two 1,4-bridgehead protons and relative to all 12 protons in the τ 8.10–9.25 interval.

Acetolysis of VIIa-OBs. A solution of 7.95 g of the inside 9-brosylate VIIa-OBs was acetolyzed in 300 ml of a 0.07 *M* solution of sodium acetate in acetic acid at 100.0° for 34 min (10 half-lives of VIIa-OBs and 0.03 half-life of Va-OBs). The acetolysis product was worked up as before. After cooling the concentrated ether solution (25 ml) the formed brosylate Va-OBs crystallized, which was then filtered and washed with cold ether.

The recovered brosylate (3.98 g or 50.1%; calcd 44% or 3.50 g) was recrystallized from pentane. Tlc analysis of the recovered brosylate and of the recrystallized brosylate (mp 126–127°) showed only one spot. The nmr spectrum of the recovered brosylate was identical with the spectra of earlier prepared Va-OBs. Tlc analysis of the residue left in the ether solution after removal of the formed Va-OBs showed no spot corresponding to Va-OBs. Glc analysis[20] of this residue showed 1% hydrocarbons (two overlapping peaks in the ratio 6:1), and 99% acetates.

Treatment of the ether solution, containing the acetolysis product and less than 1% of the formed Va-OBs,[23] with 1 g of lithium aluminum hydride as before gave 1.66 g of a white solid (calcd 1.78 g, based on 3.97 g of VIIa-OBs). Glc analysis on two columns[18,21] of the solid showed 1% of two hydrocarbons (1:6), 5% XIVa-OH (slight tailing peak), 86% Va-OH, and 8% VIIa-OH, with the retention times of Table IV.

Separation and Identification of the Products from VIIa-OBs. The products obtained above were separated by chromatography on 300 g of SilicAR (100–200 mesh), using 2 l. of pentane followed by 6 l. of ether–pentane (1:9) as eluent divided into 200-ml fractions. The progress of the separation was followed by glc analysis. Fractions with the same product were combined. Fractions that contained a mixture of products (Va-OH, XIVa-OH, and XVIIa-OH) were combined (635 mg) and rechromatographed on 300 g of SilicAR, using 7 l. of ether–pentane (1:9) as eluent in the same way as above. The following products were isolated: 17 mg of hydrocarbons; 146 mg of pure VIIa-OH; 1.32 g of pure Va-OH; 70 mg of a mixture of Va-OH (40%), XIVa-OH (49%), and XVIIa-OH (11%); and 99 mg of pure XIVa-OH. The total yield of isolated products was 1.65 g (93%). The mole percentages of the isolated products are given in Table III.

Glc analysis[22] of the hydrocarbon product showed two hydrocarbons (18% with rt 24 and 82% with rt 29). The nmr spectra and glc analysis data of the product VIIIa-OH (mp 122°) were identical with earlier obtained data of VIIa-OH. The obtained product Va-OH (mp 101°) had glc analysis data and nmr spectra identical with the data of earlier prepared Va-OH. The retention times for the products XIVa-OH and XVIIa-OH were identical with earlier obtained data of the two rearranged alcohols. The nmr spectrum of XIVa-OH was identical with the spectrum of XIVa-OH obtained from the acetolysis of Va-OBs and IX-OBs.

Acetolysis of VIId-OBs. A solution of 1.20 g of the 9-deuterio-*inside*-9-brosylate (VIId-OBs) was acetolyzed in 50 ml of a 0.07 *M* solution of sodium acetate in acetic acid at 100.0° for 34 min (10 half-lives of VIIa-OBs and 0.03 half-life of Va-OBs). The acetolysis product was worked up in the same way as in the acetolysis of VIIa-OBs.

The recovered brosylate (490 mg or 41.0%; calcd 44% or 526 mg) was recrystallized from pentane. Tlc analysis of the recovered brosylate and of the recrystallized brosylate (mp 126°) showed only one spot. Tlc analysis of the residue left in the ether solution after removal of the formed Vd,e-OBs showed a weak spot corresponding to V-OBs. Glc analysis[20] of this residue showed 1% hydrocarbons (two in the ratio 1:8) and 99% acetates (two overlapping peaks in the ratio 5:1). The recrystallized recovered brosylate was divided into two samples and the deuterium scrambling was investigated by nmr (60 and 100 MHz; sweep width 500 Hz). The amount of α proton (τ 4.88) was measured relative to the four aromatic protons of the brosyl group (τ 2.40). The average of ten integrations and two runs showed 49.7 ± 0.9% Ve-OBs for one of the samples and 50.3 ± 0.7% Ve-OBs for the other sample. The nmr spectra of the recovered brosylate showed no trace of an α proton of any brosylate other than the formed Vd,e-OBs.

Treatment of the ether solution, containing the acetolysis product and about 3% of the formed Vd,e-OBs,[23] with lithium aluminum hydride as before gave 320 mg of a white solid (calcd 317 mg, based on 705 mg of VIId-OBs). Glc analysis on two columns[18,21] of the solid showed 1% of two hydrocarbons (1:7), 9% XIV-OH (slight tailing peak), 81% V-OH, and 9% VII-OH, with the retention times of Table IV.

Separation and Identification of the Products from VIId-OB. The products obtained above were separated by chromatography on 300 g of SilicAR (100–200 mesh), using 2.5 l. of pentane followed by 5 l. of ether–pentane (1:9) as eluent divided into 250-ml fractions. The progress of the separation was followed by glc analysis, and fractions with the same product were combined. Fractions that contained a mixture of products (V-OH, XIV-OH, and XVII-OH) were combined (220 mg) and rechromatographed on 300 g of SilicAR, using 7 l. of ether–pentane (1:9) as eluent in the same way as above. The following products were isolated: 3 mg of hydrocarbons; 30 mg of pure VII-OH; 222 mg of pure V-OH; and 55 mg of a mixture of V-OH (51%), XIV-OH (45%), and XVII-OH (4%). The total yield of isolated products was 310 mg (98%). The mole percentages of the isolated products are given in Table III.

Glc analysis[22] of the hydrocarbon product showed two hydrocarbons (14% with rt 24 min and 86% with rt 29 min). Glc data of the products XIV-OH and XVII-OH were identical with earlier obtained data of the two rearranged alcohols. Glc analysis[18,21] of a sample of the obtained mixture of the products V-OH, XIV-OH, and XVII-OH enriched with a sample of XIV-OH, XV, and XVI-OH from the acetolysis of IX-OBs showed five different peaks with the retention times of Table IV.

Glc analysis of the isolated product VIId,e-OH showed only one peak and the nmr spectrum (60 MHz) was identical with earlier recorded spectra of VII-OH. The deuterium scrambling was investigated by nmr (60 MHz). The area of the α proton (τ 6.32) was measured relative to the inside 10 proton (τ 6.98). The average of ten integrations showed 43 ± 2% VIIe-OH. The product VIId,e-OH was then converted to the corresponding brosylate by the usual procedure. The nmr spectrum of this inside 9-brosylate VIId,e-OBs (pure according to tlc analysis) was identical with earlier recorded spectra of VII-OBs. The deuterium scrambling was investigated by nmr (60 MHz). The area of the α proton (τ 5.86) was measured relative to the four aromatic protons of the brosyl group. The average of five integrations showed 42 ± 1% of VIIe-OBs.

Glc analysis of the isolated product Vd,e-OH showed only one peak and the nmr spectrum (60 MHz) was identical with earlier recorded spectra of Va-OH, but showed only 0.3 α proton (measured relative to the hydroxylic proton). The alcohol was converted to the corresponding brosylate (484 mg) by the usual procedure. The nmr spectra (60 and 100 MHz) of recrystallized brosylate Vd,e-OBs (pure according to tlc analysis) were identical with earlier recorded spectra of Va-OBs. The deuterium scrambling was investigated in the same way as for the brosylate formed during the acetolysis. The amount of α proton (τ 4.88) was measured relative to the four aromatic protons of the brosyl group. The average of ten integrations and two runs showed 33.9 ± 1.3% Ve-OBs (60 MHz) for one sample and 33.8 ± 0.6% Ve-OBs (100 MHz) for another sample.

Acknowledgment. The authors wish to express their appreciation to associates in these laboratories. We are indebted to Dr. Arthur Diaz for assistance in con-

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[23] Treatment of Va-OBs with $LiAlH_4$ in the usual way gave 11% hydrocarbons and 89% Va-OH.

nection with the solvolysis kinetics. Helpful discussions with Professor Göran Bergson and Dr. John Dirlam during the preparation of this manuscript are gratefully acknowledged.

Degenerate and Nondegenerate Isomerizations of 7-Norbornadienyl Cations[1]

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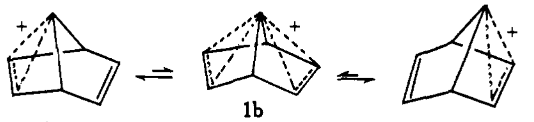
Abstract: Low-temperature nmr spectra for fluorosulfuric acid solutions of several substituted 7-norbornadienyl cations lead to assignments of unsymmetrically bridged ground states for the 7-methyl (**8**), 7-phenyl (**9**), 7-vinyl (**10**), and the three other possible methyl-substituted ions. The 7-methoxyl ion (**11**) is probably symmetrical. The activation free energy for degenerate bridge-flipping in the parent ion (**1**) is equal to or greater than 19.6 kcal/mol, for **8** it is 12.4 kcal/mol, and for **9** and **10** it is less than 5.2 and 8.2 kcal/mol, respectively. Ion **1** undergoes a degenerate isomerization which scrambles all but the "bonded" vinyl carbons. The mechanism involves a rapid equilibrium with the bicyclo[3.2.0]heptadienyl cation (**23**), the equilibrium constant at $-100°$ being $>1.2 \times 10^8$ in favor of **1**. The equilibrium constant between 2-methylbicyclo[3.2.0]heptadienyl cation (**21**) and 1-methyl-7-norbornadienyl cation (**14**) is only *ca.* 60 at $-100°$. Rate constants for the conversion of ions **1**, **9**, **10**, and **11** to the corresponding tropylium ions are reported as are the rate constants for formation of the 2-methyl-7-norbornadienyl ion (**12**) from **8**, and for decomposition of **12** and of the 5-methyl-7-norbornadienyl ion (**13**). Cation **13** may be prepared from the 7-methyl-7-quadricyclyl ion as well as from **21**, and it may be trapped to give the corresponding *syn*-7-methyl ether **24**. Ion **12** may be trapped to give the *anti*-methyl ether **25**. Mechanisms for the various degenerate and nondegenerate isomerizations are discussed.

The discovery of high solvolytic reactivity in the 7-norbornadienyl system led immediately to speculation about the structure of the apparently quite stable 7-norbornadienyl cation.[3,4] Of the several electron-delocalized possibilities envisioned in 1960,[3] the unsymmetrical one (**1a**) has since been chosen. The choice is made principally on the basis of the nmr spectrum first reported by Story and Saunders.[5] This spectrum conclusively demonstrated the nonequivalence of the two vinyl functions. It also revealed a relatively substantial coupling between the downfield ("bonded") vinyl protons and the proton at C_7. Subsequent to the nmr result, the bridged nature of the ion was indicated chemically by the observation of stereospecific endo hydride attack at C_2.[6] Further support came from the strong analogies which may be drawn from several similar observations for the 7-norbornenyl cation[7] **2** (whose structure allows straightforward determination of the stereospecificity of nucleophilic attack at C_7 as well as at C_2) and from theoretical studies.[8]



1a **1b** **1a**

(1)

In contrast to the demonstration of bridging *per se*, the stabilization that is actually afforded the 7-norbornadienyl ion by bridging has lacked experimental evaluation. The term "stabilization" may, of course, be defined in many ways, but it occurred to us that a good operational definition might derive from consideration of the energy difference between the unsymmetrical (bridged) form **1a** and the symmetrical (unbridged or symmetrically bridged) form **1b**. Couched in these terms, the problem becomes one of evaluating the activation energy for the degenerate reaction depicted in eq 1, since the transition state for this process, called bridge-flipping, would presumably be identical with the symmetrical form of the ion.[9] The techniques for generation and study of stable cations under conditions of long lifetime have attained a relatively high level of sophistication in recent years, and the bridge-flipping problem appeared quite amenable to investigation by nmr methods. Since an exchange of nonidentical vinyl functions is required, nmr line broadening and chemical tracer studies were suggested.

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(9) At least one calculation indicates that the only minimum on the potential surface for the bridge-flipping reaction is the bridged ion.[8d]