absorbed with an extinction coefficient which was measured to be 138 whereas the substrate, 1-methoxyacenaphthene, and the base solution, 0.37 *M* KO-*t*-Bu–HO-*t*-Bu, did not absorb appreciably. **5** gave a linear Beer's law plot of absorbance *vs.* concentration at 412 nm over the concentration range used in the experiment. The density of the 1-methoxyacenaphthene solution in 0.37 *M* KO-*t*-Bu–HO-*t*-Bu was 0.773 g/ml at 65°. This was calculated from the specific gravity of the solution at 25° and the density of water at 25° and corrected for the change in density of *tert*-butyl alcohol on heating to 65°.

Acknowledgment. The authors wish to thank the National Research Council of Canada for their financial support and J. F. King for useful discussions.

Nature of the Carbonium Ion. XI. The 2-Homobrendyl Cation[1a]

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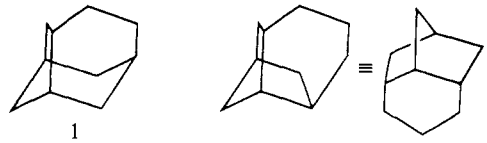
Contribution from the Metcalf Research Laboratories, Brown University, Providence, Rhode Island 02912. *Received June 25, 1973*

Abstract: The syntheses of 3-(5-norbornen-*endo*-2-yl)propyl *p*-nitrobenzenesulfonate (**11a**) and its saturated analog **13a** are described. Product studies for the acetolysis, trifluoroacetolysis, and trifluoroethanolysis of **11a** were conducted. The acetolysis derived products were the corresponding acetate **11c**, or the products of acid-catalyzed acetic acid addition to **11c** (**34a** and **34b**), depending on the buffer present in the medium. Only the structurally identical acetate **13b** was obtained from **13a**. Rate measurements of the acetolyses of **11a** and **13a** revealed no π-orbital participation in ionization of the unsaturated compound. Also described are the syntheses of 2-*endo*- (**32b**) and 2-*exo*-tricyclo[3.3.1.1^{3,9}]decyl ("2-homobrendyl") *p*-bromobenzenesulfonates (**33b**). Solvolysis product studies were conducted in the manner utilized for **11a**. Acetolysis products from **32b** and **33b** were nearly identical in proportion and consisted of only two compounds, *exo*-2-homobrendyl acetate (**33c**) and 4-*exo*-tricyclo-[4.4.0.0^{3,7}]decyl ("4-homobrexyl") acetate (**35b**). Despite the similarity of products a substantial exo:endo rate ratio (**33b**:**32b** = 953) was detected by kinetic measurements of the acetolyses. Trifluoroacetolyses of **32b** and **33b** afforded considerably more complex product mixtures which underwent a slow transformation toward 2-adamantyl trifluoroacetate due to secondary ionizations of the initial products with prolonged reaction times. A consolidated interpretation of the cationic pathways from the 2-homobrendyl cations is given.

The discovery by Schleyer and Donaldson of a simple and effective route to the adamantyl ring system *via* multiple carbonium ion rearrangements of polycyclic materials[3] has allowed the syntheses and studies of large numbers of derivatives of this complex rigid skeleton. Of particular interest and importance were the observations of biological activities for a number of these compounds.[4]

It has been apparent to us that polycyclic structural isomers of adamantyl derivatives should also be of chemical and biological interest. For this reason we have explored means of synthesizing these isomers and have detailed their rearrangements under ionizing conditions. Of primary concern to us have been skeletons whose ions were implicated[3] as precursors to the adamantyl ions derived from Lewis acid catalyzed "adamantanization" of perhydrodicyclopentadiene. In earlier work we therefore studied derivatives of protoadamantane (**1**)[5] since ions of this isomer are viewed as the immediate precursors of adamantyl ions. Having



1 2

shown that the adamantyl skeleton (and several other isomers) can indeed be obtained from solvolysis-generated σ- and π-route 2-protoadamantyl cations, we have next turned our attention to a ring skeleton, homobrendane (**2**),[6] unrepresented in the rearrangement products from the protoadamantyl cations, and presumably precedent to these in the routes from perhydrodicyclopentadienyl to adamantyl cations.

The choice of the 2-homobrendyl derivatives (**3**) as targets for synthesis and study was dictated by the pos-

3 4

sibility that their ionizations would be related to those of the easily accessible 3-(5-norbornen-*endo*-2-yl)propyl derivatives (**4**) in a fashion similar to the σ route, π route relationship which we had observed in the aforementioned protoadamantyl studies. It was hoped

(1) (a) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstracts, ORGN-155. (b) Taken in part from the Ph.D. Thesis of J. G. Henkel, Brown University, 1972.

(2) Alfred P. Sloan Fellow, 1973–1975.

(3) For a review, see R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); V. V. Sevost'yanova, M. M. Krayushlein, and A. G. Yurchenko, *Usp. Khim.*, **39**, 1721 (1970); R. C. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971).

(4) See, for example, E. W. Davies, *et al.*, *Science*, **144**, 862 (1964); H. Wendel, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **23**, 387 (1964); Grunert, *et al.*, *Virology*, **26**, 262 (1965).

(5) Paper X of this series: L. A. Spurlock and K. P. Clark, *J. Amer. Chem. Soc.*, **94**, 5349 (1972); also **92**, 3829 (1970).

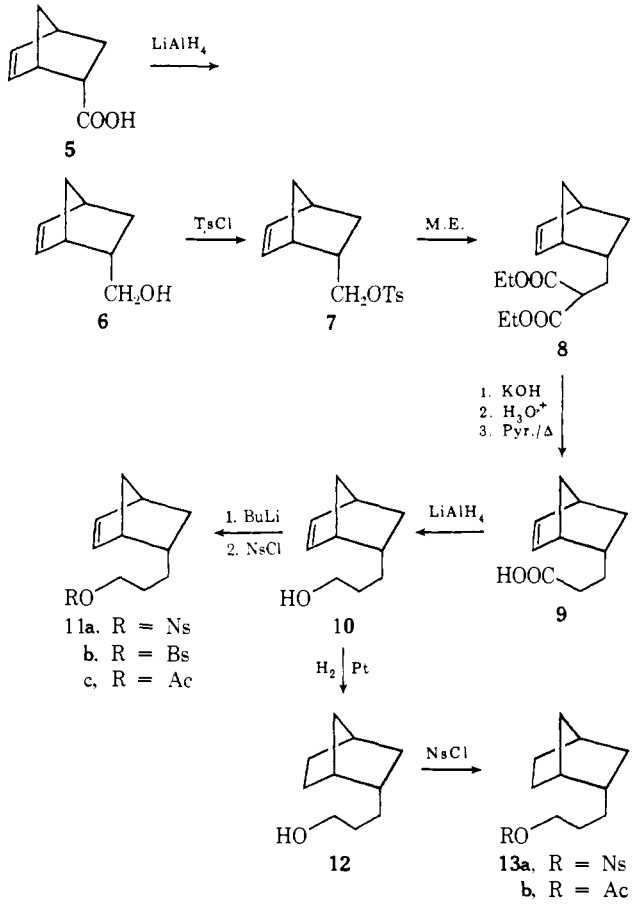
(6) We have adopted the trivial name "homobrendane" for tricyclo-[3.3.1.1^{3,9}]decane, "homobrexane" for tricyclo[4.4.0.0^{3,7}]decane, and "cristane" for tricyclo[5.3.0.0^{3,9}]decane to facilitate reference.

furthermore that solvolyses of **4** would afford cyclization followed by rearrangements which would render this a means of easily generating protoadamantanes and adamantanes under fairly mild conditions. We now describe our exploration of these postulates.

Results

Starting with the known[7] *endo*-5-norbornene-2-carboxylic acid **5**, treatment with lithium aluminum hydride in ether followed by treatment of **6** with *p*-toluenesulfonyl chloride in pyridine gave the *p*-toluenesulfonate ester **7**. Subjection of this ester to nucleophilic displacement by potassium diethyl malonate, followed by saponification of **8** and decarboxylation of the diacid, afforded the 5-norbornenepropionic acid **9** in excellent yield. Reduction of this acid by lithium aluminum hydride in ether produced alcohol **10**, which was converted into its *p*-nitrobenzenesulfonate ester **11a**, and its *p*-bromobenzenesulfonate ester **11b**, by the action of *p*-nitrobenzenesulfonyl chloride and *p*-bromobenzenesulfonyl chloride, respectively, on the lithium alkoxide of **10** (Scheme I).

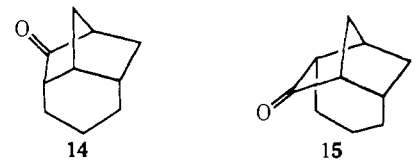
Scheme I



The saturated analog of **11a** was prepared by hydrogenation of 3-(5-norbornen-*endo*-2-yl)propanol **10** over platinum oxide in ethanol. Treatment of a solution of the resulting 3-(*endo*-2-norbornyl)-1-propanol **12** with *n*-butyllithium in hexane, followed by *p*-nitrobenzenesulfonyl chloride in tetrahydrofuran, afforded the 3-(*endo*-2-norbornyl)propyl *p*-nitrobenzenesulfonate (**13a**).

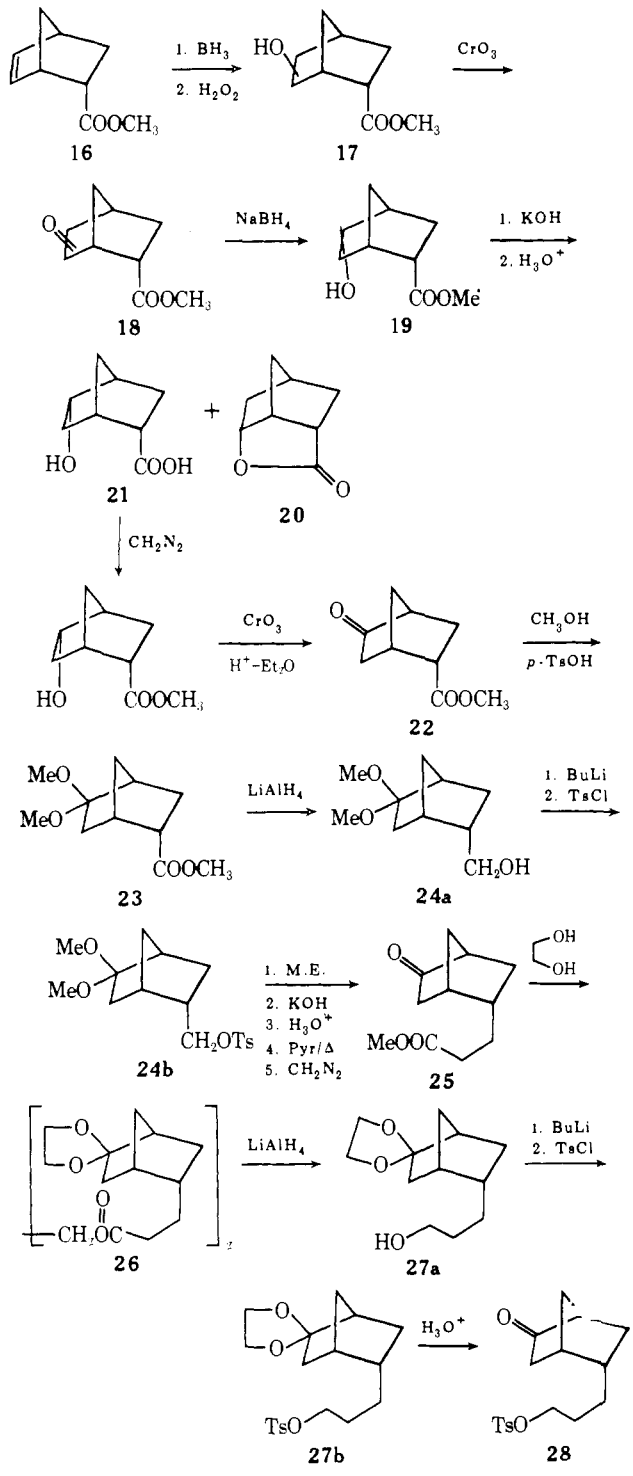
(7) J. A. Berson and D. A. Ben-Efraim, *J. Amer. Chem. Soc.*, 81, 4083 (1959).

To obtain authentic samples of the expected products resulting from π-route ring closure of **11a**, it was decided to synthesize the ketonic derivatives of the two conceivable tricyclic ring systems. Different routes were taken for the syntheses of pure samples of 2-homobrendanone (**14**) and 6-cristanone[6] (**15**). In the case



of the homobrendanone (see Scheme II), the starting

Scheme II



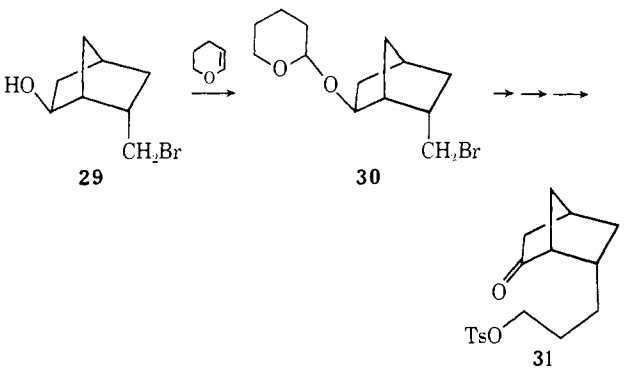
point was again *endo*-2-norbornenecarboxylic acid **5**. After esterification with diazomethane to form the methyl ester **16**, borane in tetrahydrofuran was used to form a mixture of *exo*-hydroxy esters (**17**). Further treatment of this crude mixture with chromic acid by the method of Brown[8] produced a mixture of the two keto esters **18** in a ratio of 56:44 (by gc analysis). The lesser component was the desired methyl 5-oxo-*endo*-2-norbornanecarboxylate (**22**).

Separation of the two isomers was accomplished chemically, utilizing their differing steric properties. Reduction of the mixture, **18**, with sodium borohydride in methanol afforded an excellent yield of the two *endo,endo*-hydroxy esters (**19**). Shaking this mixture with concentrated potassium hydroxide solution for 1 hr, followed by acidification in the cold, produced the two *endo,endo*-hydroxy acids. The 2,6 isomer spontaneously formed the known[9] *endo*-6-hydroxy-*endo*-2-norbornanecarboxylic acid lactone (**20**); thus treatment of the mixture with sodium bicarbonate solution permitted the neutral lactone to be extracted, leaving the pure sodium *endo*-5-hydroxy-*endo*-2-norbornanecarboxylate in solution. Reacidification and extraction with ether produced the pure hydroxy acid **21**. Esterification of this material with diazomethane and oxidation with sodium dichromate afforded pure methyl 5-oxo-*endo*-2-norbornanecarboxylate (**22**) (99% pure by gc).

Protection of the ketone in **22** was accomplished by treatment with excess methanol and a trace of *p*-toluenesulfonic acid, giving the dimethyl ketal **23**. Alcohol **24a** then resulted from reduction of the ester group by lithium aluminum hydride. Treatment of the lithium alkoxide of **24a** with *p*-toluenesulfonyl chloride in tetrahydrofuran produced *p*-toluenesulfonate ester **23b** in 99% yield. Subjection of the crude *p*-toluenesulfonate to malonic ester alkylation, as previously described, followed by saponification, decarboxylation, and esterification with diazomethane, afforded methyl 3-(5-oxo-*endo*-2-norbornyl)propionate (**25**) in 93% overall yield from **24a**. The ketone carbonyl was again protected, this time by treatment with 1.5 equiv of ethylene glycol and a trace of *p*-toluenesulfonic acid in benzene solvent. This reaction gave the ethylene bis-(3-(5,5-ethylenedioxy-*endo*-2-norbornyl)propionate) (**26**) in 96% yield. Reduction of this diester with lithium aluminum hydride in ether yielded 3-(5,5-ethylenedioxy-*endo*-2-norbornyl)propan-1-ol (**27a**). The lithium alkoxide of this alcohol was converted to its *p*-toluenesulfonate ester **27b** by treatment with *p*-toluenesulfonyl chloride in tetrahydrofuran. Aqueous acid treatment afforded **28**.

With this compound on hand, several base and solvent combinations were investigated, including potassium *tert*-butoxide in tetrahydrofuran and *tert*-butyl alcohol, sodium hydride in dimethylformamide, lithium triphenylmethide in dimethoxyethane, sodium methylsulfinylmethide in dimethyl sulfoxide, sodium amide in diethyl ether, and sodium bis(trimethylsilyl)amide in diethyl ether and tetrahydrofuran. Ultimately, sodium bis(trimethylsilyl)amide, which has been shown to react quantitatively with ketones to produce the corresponding enolates,[10] gave the best results of all the bases studied. The pure keto ester **28**, when treated with 1 equiv of this base in tetrahydrofuran, afforded a 52% yield of 2-homobrendanone (**14**) (along with some unreacted starting material, which was separated by chromatography on silica gel).

Quite disappointingly, the isomeric keto-*p*-toluenesulfonate **31** (which was prepared from the tetrahydropyranyl ether, **30**, of *exo*-6-hydroxy-*endo*-2-bromomethylnorbornane (**29**)[11] *via* a route analogous to that used for the conversion of **24b** to **28**) totally failed to



afford any 6-cristanone (**15**) when treated with the base–solvent combination utilized in study of the cyclization of **28**.

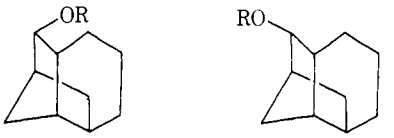
Conversion of 2-homobrendanone **14** to the desired exo and endo alcohols was attempted with a variety of reducing agents. The results are summarized in Table I. Epimerization of the endo alcohol **32a** to the exo

Table I. Reductions of 2-Homobrendanone (**14**)

Method	% *endo*-**32a**[a]	% *exo*-**33a**[a]
$LiAlH_4/Et_2O$	100	0
$NaBH_4/CH_3OH$	100	0
$NaBH_4$/pyridine	100	0
Na/CH_3OH	54	46

[a] Determined by gas chromatography of the corresponding trimethylsilyl ethers of **32a** and **33a**.

isomer **33a** by equilibration was accomplished only with



32a, R = H
b, R = Bs

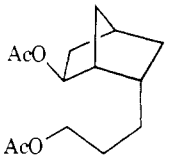
33a, R = H
b, R = Bs
c, R = Ac

difficulty despite the apparent greater thermodynamic stability of the latter. Ultimately, a mixture of **32a** and **33a** resulting from reduction of **14** with sodium in methanol was heated with sodium methoxide in methanol at reflux for 145 hr in the presence of a trace of **14**. This procedure afforded a mixture which was found to be 69% **33a** and 31% **32a**. Further heating seemingly resulted in decomposition of **33a**, as the ratio of products decreased and the overall yield of product was less. Separation of the alcohols was accomplished by liquid chromatography on neutral alumina to afford pure **33a**.

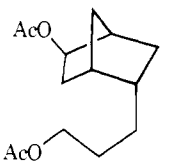
(8) H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 83, 2952 (1961).
(9) S. Beckmann and H. Geiger, *Chem. Ber.*, **94**, 48 (1961).
(10) C. Kruger, E. G. Rochow, and U. Wannagat, *Chem. Ber.*, **96**, 2131 (1963).
(11) D. E. Gwynn and K. Skillern, *Chem. Commun.*, 490 (1968).

Conversions of the two tricyclic alcohols to their corresponding *p*-bromobenzenesulfonate esters **32b** and **33b** were effected, as usual, by successive treatment with *n*-butyllithium in hexane and *p*-bromobenzenesulfonyl chloride in tetrahydrofuran.

Solvolytic studies of *p*-nitrobenzenesulfonate **11a** were undertaken, with rather unexpected results (no cyclized products could be detected from acetolyses at 80 and 100°). In fact, the only detectable product from sodium acetate buffered acetolysis was uncyclized acetate **11c**, which was identified by comparison with an authentic sample synthesized from **10** by treatment with acetic anhydride in pyridine. Even more unusual was the solvolytic behavior of **11a** under urea buffered acetolysis conditions. In the presence of urea, the rate of addition of acetic acid to the norbornyl double bond became competitive with that of solvolysis, thus, after 8 solvolysis half-lives, the only products isolated were the diacetates **34a** and **34b**. In a control experiment it could be shown that norbornylene does not undergo reaction with the urea buffered acetic acid solution under the acetolysis conditions. The conclusion must be that the protonated urea generated by liberation of *p*-nitrobenzenesulfonic acid is a sufficiently strong acid to catalyze the attack of acetic acid on the norbornyl double bond.



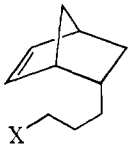
34a



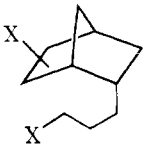
34b

The results from product studies of solvolyses of **11a** are summarized in Table II. The identification of the trifluoroethanolysis product was accomplished by spectroscopic comparison with an authentic sample synthesized by the action of the alkoxide of **10** on 2,2,2-trifluoroethyl *p*-nitrobenzenesulfonate.

Table II. Solvolysis Products from 3-(5-Norbornen-*endo*-2-yl)propyl *p*-Nitrobenzenesulfonate (**11a**)



A



B

Solvent	Buffer	Temp, °C	A	Cyclized products	B
CH_3COOH	NaOAc	80	100		
		100	100		
	Urea	80			100
		100			100
	None	80			100
		100			100
CF_3CH_2OH	Collidine	100	>99	Trace	
	Urea	100	Trace	Trace	>99
CF_3COOH	CF_3COONa	25		Trace	100

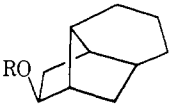
In order to determine the magnitude of anchimeric assistance to solvolysis associated with the double bond, kinetic studies of the acetolyses of **11a** and its saturated analog **13a** were undertaken. Both compounds exhibited good first-order kinetic behavior at 80 and 100°. The results are summarized in Table III.

Table III. Kinetic Data for Acetolyses in 0.01 *M* Sodium Acetate Buffer

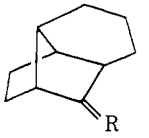
Compd	Temp, °C	k, $sec^{-1} \times 10^5$	$\Delta H^{\pm}$	$\Delta S^{\pm}$
11a	80.0	1.20 ± 0.01	21.3	−21
	100.1	6.10 ± 0.15		
13a	80.0	1.25 ± 0.01	20.9	−22
	100.1	6.21 ± 0.23		
33b	25.0	4.07 ± 0.03	25.4	+7
	35.2	16.6 ± 0.1		
32b	59.8	0.676 ± 0.005	27.9	+1
	80.0	7.35 ± 0.05		
	75	4.35[a]		
	25	0.0033[a]		
k_u/k_s = 0.95				
k_{exo}/k_{endo} = 953				

[a] Extrapolated from data obtained at other temperatures.

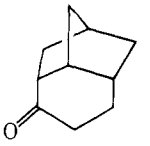
With the failure of **11a** to solvolyze with cyclization, attention was next turned to the solvolytic behavior of the 2-homobrendyl *p*-bromobenzenesulfonates **32b** and **33b**. Interestingly, both the exo and endo esters underwent acetolysis (see Table III) with rates similar to those of the respective norbornyl isomers. Under all acetolysis conditions, both **32b** and **33b** afforded only two products (see Table IV). The acetate products were not cleanly resolvable by gas chromatography, and so were reduced to the corresponding alcohols with lithium aluminum hydride. The resultant alcohol mixture was also poorly resolved, but conversion to the trimethylsilyl ethers afforded quite clean gc separation. The identity of the *exo*-2-homobrendyl product was established by comparison to an authentic sample of the trimethylsilyl ether of **33a**. Since an authentic sample was not available, the other product was assigned as *exo*-4-homobrexyl acetate **35b** by the following procedure. 2-Homobrendanone (**14**) was treated with potassium *tert*-butoxide in *tert*-butyl alcohol at 185° for 120 hr[12] to afford an equilibrium mixture of **14** and 2-homobrexanone **36a**. Wolff–Kishner reduction of this equilibrium mixture produced a mixture of the hydrocarbons homobrendane **2** and homobrexane **36b**. The alcohols derived from acetolysis were oxidized to the corresponding ketones and then converted to the hydrocarbons as above. Identity of retention times for the minor component of each reaction mixture was established by gas chromatography. Because the major component was clearly **2**, the homobrexane skeleta for **35** and **36** were thereby established.



35a, R = H
b, R = Ac



36a, R = O
b, R = H_2

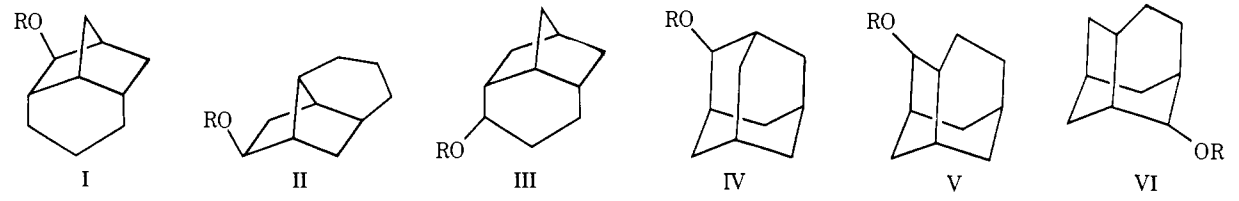


37

As a check on the product ratios from acetolysis, the

(12) These conditions were used previously for equilibration of a brexanone with a brendanone, see A. Nickon, H. Kwasnik, T. Schwartz, R. O. Williams, and J. B. DiGiorgio, *J. Amer. Chem. Soc.*, 87, 1615 (1965).

Table IV. Solvolysis Products from *exo*- (**33b**) and *endo*-2-Homobrendyl *p*-Bromobenzenesulfonates (**32b**)



I II III IV V VI

ROBs	Solvent	Temp, °C	Time, hr	Relative product ratio I	II	III	IV	V	VI	"A"	Other cyclic products
33b	AcOH	25	40	86	14						
		35	9	85	15						
	CF_3COOH	35	4	75	1	1				23	1[a]
		80	1	66		23	1	1	2	4	3
			8	19		47	2	2	4	10	16
			24	8		40	9	4	7	3	29
32b	AcOH	60	232	85	15						
		80	24	87	13						
	CF_3COOH	35	168	85		1				14	
		60	96	23	4	44	4	4	7	2	12[b]
		80	1	80		11	tr	1	1	3	4
			26	5	5	36	16	3	11	3	21[c]

[a] Consisted of five separable components. [b] Consisted of 12 gc separable components. [c] Consisted of 14 gc separable components.

acetate-derived alcohol mixture was oxidized to the corresponding ketone mixture. Gas chromatographic analysis showed excellent agreement with the analysis of the silyl ethers.

In order to gain further insight into the isomerization processes of the 2-homobrendyl system and evaluate its suitability as an adamantyl precursor, trifluoroacetolysis studies of **32b** and **33b** were undertaken. In marked contrast to acetolysis, trifluoroacetolysis produced an extremely complex mixture of products, both from primary ionization of the *p*-bromobenzenesulfonates and from secondary ionizations of the resulting trifluoroacetates. The compositions of the product mixtures were, as a result, highly dependent upon the reaction conditions, and in the most complicated case, 22 products were detectable. The minute quantities of material present precluded the detailed analysis of each product; however, several compounds could be identified on the basis of prior work[5] (see Table IV). For the most part analyses were carried out by comparison of gas chromatographic retention times of the ketones,[13] derived from sequential reduction and oxidation of the trifluoroacetate mixtures, with those of authentic samples. Of the seven major products of interest, authentic samples of five of the ketones were available, the structure of one was deduced by methods to be subsequently discussed, and one was not identified ("A").

An authentic sample of 6-homobrendanone (**37**) was not available, so an indirect spectroscopic identification was undertaken. A mixture of ketones derived from trifluoroacetolysis of **32b** at 60° was found to contain 44% of the compound suspected to be **37**, along with 23% of **14** plus other minor components. High-resolution infrared spectral analysis of this mixture showed a carbonyl absorption maximum at 1725 cm^{-1}, characteristic of a six-membered ring ketone, and a second less intense band at approximately 1745 cm^{-1}. The ketone mixture was passed through a gas chromatographic deuterating column[14] which exchanged active α hydrogens for deuteriums, and the effluent was fractionally collected. A fraction was collected which contained 89% 6-homobrendanone (also present was a small amount of **14**). Mass spectral analysis of this mixture showed a major parent peak at *m/e* 152, with a minor parent peak at *m/e* 150, indicating the predominant incorporation of two deuteriums into the molecule. On this basis the structure of **37** was assigned, since it is the only easily accessible (resultant from <two bond shifts) product which can exhibit this behavior.[15] The actual solvolysis product was assumed to be *exo*-6-homobrendyl trifluoroacetate based on the probability of nucleophilic attack on the carbonium ion from this less hindered face.

The wide variation in product distribution from trifluoroacetolysis prompted an investigation of the availability of secondary ionization pathways after cation ion capture by trifluoroacetate. These results are also shown in Table IV. The studies on **33b** were accomplished by running three simultaneous solvolyses at 35°. Two of the tubes were transferred to a bath at 80°, while one was worked up immediately. Clearly a secondary ionization occurred in both the exo and endo cases which served to enhance the process of adamantanization, albeit rather slowly. This was interesting since adamantanization normally occurs very rapidly in the strongly acidic medium of antimony pentafluoride–fluorosulfuric acid, but is not generally observed in trifluoroacetic acid.

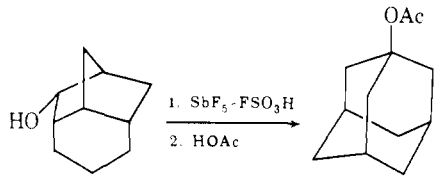
The behavior of the homobrendyl system in superacid media was investigated with the use of antimony pentafluoride and fluorosulfuric acid in liquid sulfur dioxide. Treatment of *endo*-2-homobrendanol (**32a**) with the solution of superacid, followed by quenching of the reaction with glacial acetic acid, resulted in the

(13) Infrared spectra of the ketone mixtures indicated the absence of alcoholic products, thus eliminating products derived from tertiary (bridgehead) ions as possibilities.

(14) We are indebted to Dr. T. E. Parks for the instructions and discussion on the use of the deuterating column.

(15) The possibility of ring-opened products was considered, but under the analysis procedure, these products would be oxidized to substituted carboxylic acids, none of which were detected. Furthermore, no unsaturation was visible in the spectra of the product esters.

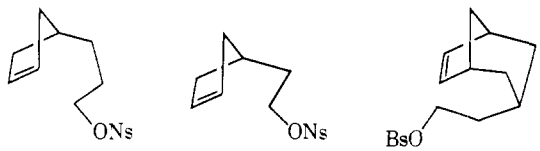
formation of only one product, 1-adamantyl acetate, which was identified by gas chromatography. This



rapid isomerization was not very informative as to the energy barriers between the two skeletons. More enlightening was the behavior of homobrendane (**2**) itself toward Lewis acid catalyzed isomerization. Homobrendane, when heated at 70° for 2 hr with a suspension of aluminum chloride in hexane,[16] isomerized smoothly and completely to adamantane. The fact that this isomerization was effected under these relatively mild conditions indicated that the homobrendyl cations are indeed separated from the adamantyl ones by lower energy barriers than those of tetrahydrocyclopentadiene, which undergoes only exo–endo isomerization under these conditions.

Discussion

The extreme reluctance of 3-(5-norbornen-*endo*-2-yl)-propyl *p*-nitrobenzenesulfonate (**11a**) to undergo solvolytic π-route cyclization was somewhat unexpected. Although **11a** bears a strong structural resemblance to 3-(Δ^3-cyclopentenyl)propyl *p*-nitrobenzenesulfonate (**38**) which has been shown by Bartlett[17] not to cyclize under acetolysis conditions, it was felt that the more reactive norbornyl double bond of **11a** would have a positive



38 **39** **40**

influence on cyclization, and at least some π participation would be observed.

Bartlett attributed the noncyclization of **38** (as compared to the facile cyclization of its ethyl analog **39**) to a combination of enthalpy and entropy factors. The entropy increase was related to the greater number of degrees of freedom present in **38**, while the unfavorable enthalpy factor was thought to arise from the required eclipsing of the C_2 and C_3 hydrogens on the propyl chain of **38** when the developing positive charge is in the most favorable position to receive anchimeric assistance from the π orbital. An examination of molecular models revealed that *no* appreciable eclipsing interactions of this type are found in **11a**.

Initially we felt that the rigidity of the system in the *endo*-norbornyl configuration would impart to **11a** a conformational advantage over **38**, if slight, by holding the propyl chain in reasonable proximity to the double bond. In actuality, it is this *endo*-norbornyl alignment that may provide some explanation for the observed unreactivity. Attack of electrophilic agents on the norbornyl double bond is known to proceed with a remarkable stereospecificity for the exo face. Examples of this phenomenon include reduction with borane and oxymercuration, as well as additions of acids. In the case of **11a**, the ring would constrain any intramolecular interaction of the developing positive charge to the disfavored endo face of the double bond. This apparently is enough to severely retard any association between the carbonium ion and the electrons of the π bond. A further indication of the conformational restriction on this kind of interaction may be found in the utter failure of keto-*p*-toluenesulfonate **31** to cyclize to 6-cristanone (**15**). Seemingly any propyl attachment, partial or full, between C_3 and C_6 of the norbornane ring is energetically disfavored.

It is instructive to compare the reactivity of the present system with that of the isomeric 2-(*endo*-bicyclo-[3.2.1]oct-6-en-3-yl)ethyl *p*-bromobenzenesulfonate[3] (**40**). This compound, upon acetolysis, underwent ring closure to tricyclic products (mainly adamantyl) to the extent of 94%, and with an 18-fold rate enhancement over its saturated analog. It exhibited the greatest degree of π-orbital influence on ionization observed for any arenesulfonate with a double bond separated by a minimum of four carbons from the site of dissociation.[5] Reference to molecular models indicates that **40** also need suffer no side chain eclipsing interactions, and possesses only one less degree of freedom than **11a**. Presumably this latter entropy factor coupled with the increase in stability gained through formation of the protoadamantane ring serves to enhance the cyclization of **40**.

It is consistent with the absence of cyclized products from **11a** that a slight rate retardation exists in its acetolysis when compared to the acetolysis rate of its saturated analog **13a** (Table III). This is the expected effect of a π bond in which no anchimeric assistance to ionization is present, and only the slight negative inductive effect is operational. A similar behavior was observed for the solvolytic rate of **38** and its saturated analog, where k_u/k_s was 0.9 and no cyclization occurred.

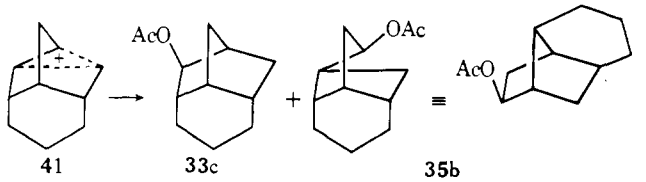
Fortunately, examination of the σ-route cations from **33b** and **32b** offered insight into the originally expected rearrangements. The synthesis of 2-homobrendanone (**14**) was a facile one proceeding in good yield, indicating the absence of any significant additional strain provided by the introduction of the 3,5-propyl bridge to the norbornyl molecule. In fact, molecular models indicate that the new six-membered ring is almost completely strain free in a chair conformation similar to those of the adamantyl system. As has been previously observed in similar geometric alignments,[5a] reductions of the carbonyl with metal hydrides afforded only the endo alcohol **32a**, thereby indicating that the carbonyl has two quite different diastereotopic faces, one of which, the endo face, is extremely hindered. Dissolving metal reductions overcame this steric hindrance to some degree, but equilibration of endo alcohol **32a** to the thermodynamically more stable exo alcohol **33a** was still accomplished with some difficulty. Quite obviously the steric factors operating in the reduction of the carbonyl group of **14** were also influential during equilibration with sodium methoxide in methanol, and only a slow buildup of exo product was observed. From examination of molecular models, the source of the steric hindrance is likely to be a combination of the endo C_2 proton (the major source), which is 2.4 Å from

(16) H. W. Whitlock and M. W. Siefken, *J. Amer. Chem. Soc.*, 90, 4929 (1968).
(17) P. D. Bartlett, *et al.*, *J. Amer. Chem. Soc.*, 87, 1314 (1965).

C_2, and the endo C_7 proton, which in the probable chair conformation is 2.5 Å from the carbonyl carbon of **14**. These same steric controls may be expected to operate on the cations derived from **33b** and **32b** as well, thereby serving to inhibit attack of any external nucleophile from the endo face of the ion.

Studies of the acetolyses of **32b** and **33b** showed clearly that the 2-homobrendyl esters behave primarily as bridged norbornyl derivatives, with no tendency under these moderately nucleophilic conditions to undergo the ring expansions required for access to protoadamantyl and adamantyl ions. That homobrendane has indeed a reaction pathway to adamantane was, however, easily demonstrated by its facile isomerization to adamantane in the presence of aluminum chloride in hexane, and by the rapid formation of 1-adamantyl products when **32a** was treated with antimony pentafluoride and fluorosulfuric acid.

The fact that the common products **33c** and **35b** are formed in the same ratio from acetolyses of both **32b** and **33b** can be envisaged as the result of conventional norbornyl ionization pathways, affording ion **41** (or its



41 33c 35b

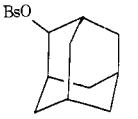
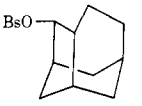
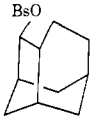
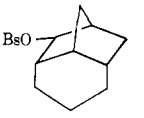
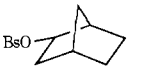
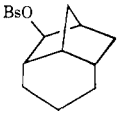
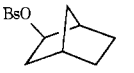
localized equivalents), from both endo and exo esters. The most interesting feature of this product ratio is the indication which it gives of the asymmetry afforded the norbornyl ion (which ordinarily suffers a 50:50 ratio of attack at C_1 and C_2) by the introduction of the C_3,C_5-propyl bridge. Clearly in this case attack at C_1 is somewhat restricted.

Also, consistent with the mechanistic picture of these ionizations as norbornyl type is the exo:endo rate ratio of 953 (the corresponding unsubstituted esters show a rate ratio of 350). The factors influencing the ionization process in systems of this type have been postulated as anchimeric assistance and steric hindrance.[18] Whether one subscribes to either the localized ion or delocalized ion theory, it is clear that both rate influencing factors are in operation in this substituted norbornyl case. As previously discussed, a large degree of steric hindrance does exist around C_2. This undoubtedly causes resistance to the expulsion of the leaving group in the ionization of **32b**. Furthermore, σ-route anchimeric assistance to ionization in **33b**, by the C_3–C_4 bond, should enhance the rate of solvolysis of this exo derivative. The data of Table V compare the acetolysis rates of various esters related to **32b** and **33b**.

As the acetolysis results suggested a barrier to rearrangements toward protoadamantyl and adamantyl ions, the better indication of the relationship of the homobrendyl cations to the adamantanization pathway is seen in the more ionizing and less nucleophilic solvent trifluoroacetic acid. The most striking feature is the wide deviation in the trifluoroacetate distributions resulting from the exo and endo isomers **33b** and **32b**.

(18) For a comprehensive review, see J. A. Berson in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 3.

Table V. Comparison of Selected Acetolysis Rates

ROBs	10^5k, sec^{-1}	Temp, °C	k_{exo}/k_{endo}
	1.8	75	
	7.2	75	.040
	0.04	75	
	4.34	75[a]	
	15.4	75	
	4.1	25	953[a]
	8.8	25	350

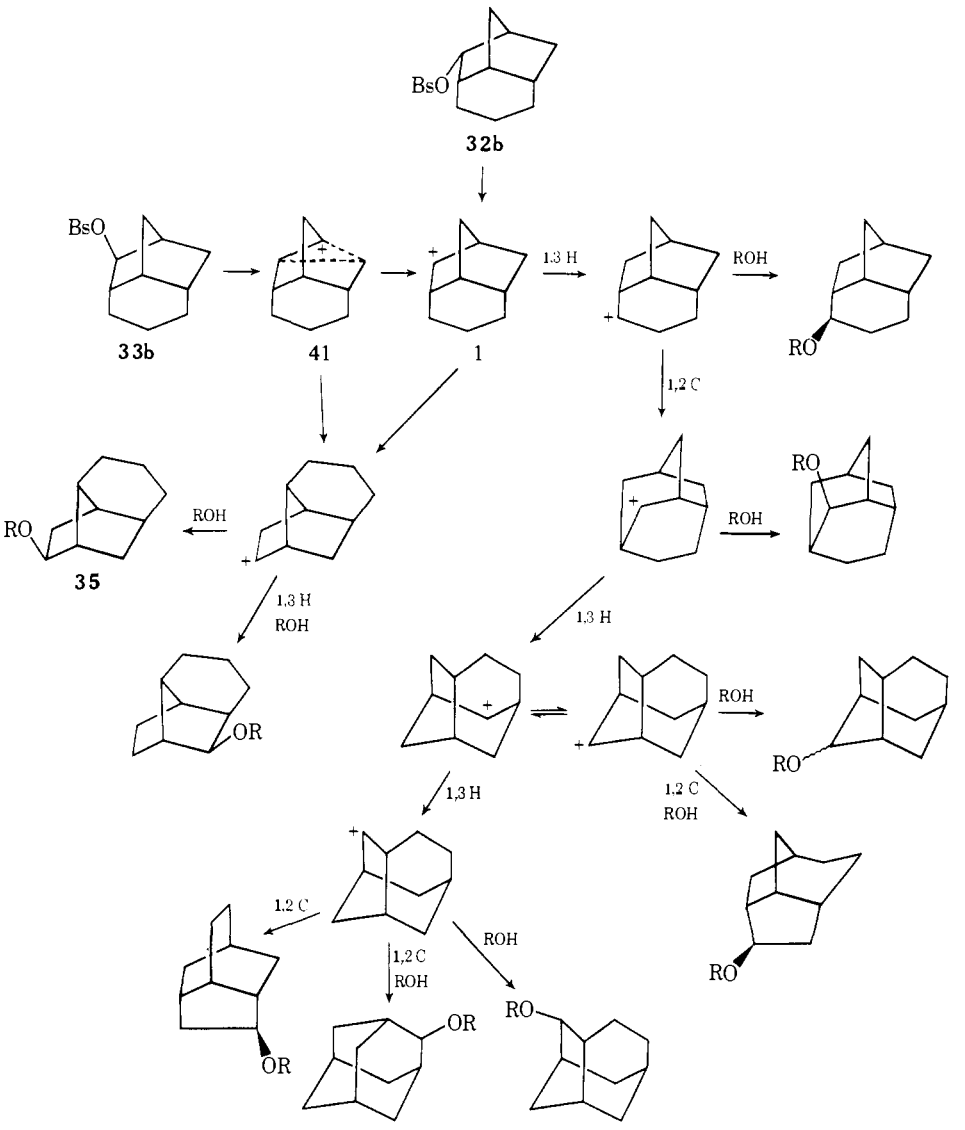
[a] Extrapolated from kinetic data at other temperatures. See Table IV.

This seems to be due more to temperature effects than to substrate configurational effects, however, for the product distributions became quite similar when **32b** and **33b** were subjected to trifluoroacetolysis under similar conditions (Table IV). The minor differences then observed can more realistically be attributed to solvent stabilization effects on the two initial cations, and the position of the counterion.

The partition of ions from both of the homobrendyl isomers in trifluoroacetic acid is apparently quite similar to that of acetolysis, before temperature and secondary ionization effects become operative. The observation that solvolyses of both **32b** and **33b** below 35° afford no products resulting from major skeletal rearrangement tends to support the existence of an energy barrier to further rearrangement from the norbornyl ion **41**. Furthermore, logic and the subsequent product distributions indicate that the barrier may lie in the 1,3-hydride shift required to afford the 6-homobrendyl cation (Scheme III). It is interesting to note that the proportion of 4-homobrexyl product is significantly lower from trifluoroacetolysis than from acetolysis (1% *vs.* 15%). This greater selectivity for homobrendyl product is due presumably to the low nucleophilicity of the solvent and to the greater strain present in the transition state leading to homobrexane. It therefore may reflect, at least qualitatively, the lower stability of this ring structure relative to homobrendane.

Given time and sufficient energy, the process of adamantanization ultimately occurs, as seen from the prod-

Scheme III



uct distributions of prolonged heating. Scheme III summarizes some probable mechanistic pathways from **32b** and **33b** toward protoadamantanes and adamantane. That such a great number of isomeric products appear is in keeping with the extensive rearrangements undergone by the 2-protoadamantyl ions.[5] The fact that adamantyl product is not particularly dominant in the product distributions, even at longer reaction times, is most likely indicative of the rather involved reaction pathways through which the ions must travel before encountering the adamantyl "energy well." The 1,2-carbon migrations and 1,3-hydride shifts necessarily involved are thus not given sufficient time, prior to capture, to undergo the necessary rearrangements. This fact is strongly supported by the complete isomerization of **32a** to the 1-adamantyl cation in antimony pentafluoride–fluorosulfuric acid, a solvent in which carbonium ion lifetimes are considerably longer.

In summary, these studies have established the inaccessibility of tricyclic products from solvolyses of the 3-(5-norbornen-*endo*-2-yl)propyl derivatives, and the limited accessibility of adamantyl derivatives from solvolyses of 2-homobrendyl derivatives. The latter phenomenon is seemingly related to a relatively inefficient 1,3-hydride transfer process affording the 6-homobrendyl cation, and the comparatively high stability of the norbornyl-type 2-homobrendyl cation. In addition, solvolytic adamantanization of the homobrendanes requires a rather large number of rearrangements to occur in not exceptionally low nucleophilic media. It is nevertheless conceivable that homobrendyl cations are involved in the Lewis acid catalyzed adamantanization of perhydrodicyclopentadiene.

Experimental Section[19]

5-Norbornene-*endo*-2-carboxylic acid (5) was prepared from dicyclopentadiene and acrylic acid by the method of Berson.[7] Four recrystallizations from pentane yielded pure endo acid, mp 44.5–45.5° (lit.[7] mp 44–45°).

***endo*-2-Hydroxymethyl-5-norbornene (6).** To a suspension of 25

(19) Infrared spectra were determined with either a Perkin-Elmer 247 grating infrared spectrometer or a Perkin-Elmer 237 spectrometer using sodium chloride optics. Infrared carbonyl absorption bands were determined utilizing a Perkin-Elmer 301 spectrometer. The nmr determinations were carried out on a Varian Associates A60-A spectrometer, approximately 20% solutions with tetramethylsilane as the internal standard. Gas chromatography was accomplished with a Perkin-Elmer 881 flame ionization gas chromatograph fitted with a Golay capillary column adapter. Columns used were all 50-ft Support Coated Open Tubular (SCOT) capillary columns with supports as noted. Microanalyses were performed by Microanalysis, Inc., of Wilmington, Del., and Baron Consulting Co. of Orange, Conn. Melting points and boiling points are uncorrected.

g (0.65 mol) of lithium aluminum hydride in 800 ml of ether was added 89.0 g of **5** (0.649 mol) in 300 ml of ether. The mixture was allowed to stir for 3 hr. The excess hydride was destroyed by addition of 25 ml of water, followed by 75 ml of 15% potassium hydroxide solution and 25 ml of water. Filtration and evaporation of solvent yielded 81 g of crude alcohol **6** (100%). Gc analysis (50-ft SCOT Carbowax 20M) showed a purity of 99.8% endo alcohol. Further purification was not necessary.

(*endo*-**2-Norbornen-5-yl)methyl** *p*-**Toluenesulfonate** (**7**). To a stirred solution of 80.0 g (0.65 mol) of **6** in 150 ml of pyridine maintained at 0° was added 128 g of commercial *p*-toluenesulfonyl chloride (0.67 mol) in 200 ml of pyridine. The mixture was allowed to stir overnight. Addition of 500 ml of water followed by acidification at 0° and extraction with ether yielded 145 g (80%) of the ester, mp 47.5–48.5°, after recrystallization from ether–pentane.

3-(*endo*-**2-Norbornen-5-yl)propionic Acid** (**9**). To a stirred and heated solution of 1 l. of 0.206 *M* potassium *tert*-butoxide in *tert*-butyl alcohol, prepared from 8.06 g of potassium metal (0.206 mol), was added 35.20 g (0.22 mol) of diethyl malonate, producing a white precipitate of potassium diethyl malonate. After 0.5 hr, 52 g (0.187 mol) of *p*-toluenesulfonate **7** was added in solid form and excess *tert*-butyl alcohol was distilled off until a thick slurry remained (*ca.* 200 ml in volume). This was allowed to stir at reflux for 48 hr. The reaction mixture was dumped into 400 ml of ice–water, acidified, and extracted with ether. The ether extract was washed with water and bicarbonate solution, and dried over magnesium sulfate. Evaporation of solvent yielded 59.5 g of crude diester **8**. Saponification of the diester was accomplished by heating with 150 ml of 8 *M* potassium hydroxide solution for 1.5 hr. The alkaline solution was acidified after extraction with ether to remove any unreacted *p*-toluenesulfonate, and further extraction with ether followed by evaporation produced the crude diacid. This geminal diacid was heated in 100 ml of pyridine at reflux until carbon dioxide ceased to be evolved (*ca.* 1.5 hr). The pyridine–acid solution was poured into ice–water, acidified with 6 *N* hydrochloric acid, and extracted with ether. The ether extract was washed once each with 10% hydrochloric acid and water, and dried over magnesium sulfate. Evaporation of solvent and distillation yielded 22.9 g (74%) of acid **9**: bp 135–137° (0.1 mm); ir (film) 3300–2800 (br) and 1710 cm^{-1}; nmr (CCl_4) δ 11.92 (1 H, s), 6.00 (2 H, m), 2.90–0.90 (m), 0.55 (q).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.30; H, 8.49. Found: C, 72.03; H, 8.48.

3-(*endo*-**Bicyclo[2.2.1]hept-5-en-2-yl)-1-propanol** (**10**). To a stirred suspension of 5.23 g (0.138 mol) of lithium aluminum hydride in ether was added dropwise 22.9 g (0.151 mol) of acid **9** dissolved in 50 ml of ether. The mixture was stirred overnight. A 5-ml portion of water was slowly added, followed by 15 ml of 15% potassium hydroxide solution and 5 ml of water. The precipitated salts were removed by filtration and the filtrate was dried and concentrated to obtain 20.97 g of crude alcohol **10**. Distillation afforded 19.57 g (93.3%): bp 75–78° (0.1 mm); ir (film) 3450, 3020, and 2900 cm^{-1}; nmr (CCl_4) δ 6.00 (2 H, m), 4.28 (1 H, s), 3.50 (2 H, tr), 2.50 (2 H, br s), 2.16–0.32 (m).

3-(*endo*-**2-Norbornyl)-1-propanol** (**12**). A 0.500-g (3.3 mmol) portion of alcohol **10** in 50 ml of absolute ethanol was shaken with 30 mg of platinum oxide (Adams catalyst) in a Parr shaker for 2 hr at 40 psi and room temperature. The catalyst was removed by filtration and the solvent evaporated under reduced pressure. The resulting crude alcohol was distilled under reduced pressure to yield 0.43 g of **12**: bp 80–82° (0.2 mm); ir (film) 3340, 2950, 1455, 1060 cm^{-1}; nmr ($CDCl_3$) δ 3.5 (tr), 2.3–0.5 (m).

3-(*endo*-**2-Norbornyl)propyl** *p*-**Nitrobenzenesulfonate** (**13a**). To a stirred ice-cold solution of 0.308 g (0.002 mol) of alcohol **12** in 10 ml of dry tetrahydrofuran was added 1.41 ml of 15.2% *n*-butyllithium in hexane. After the mixture was stirred for 20 min, 0.486 g (0.0022 mol) of *p*-nitrobenzenesulfonyl chloride in 10 ml of dry tetrahydrofuran was added. The mixture was stirred for 2 hr at 0°, then poured into 100 ml of ice–water and extracted three times with ether. The ether extracts were combined and washed with water, dried, and evaporated to yield 0.657 g of yellow crystals, which were recrystallized from ether–pentane: mp 92.5–93°; ir (Nujol) 3110, 2960, 1540, 1350, 1195 cm^{-1}; nmr ($CDCl_3$) δ 8.25 (4 H, q), 4.1 (2 H, tr), 2.7 (2 H, br s), 2.0–0.3 (m).

3-(5-Norbornen-*endo*-**2-yl)propyl** *p*-**Nitrobenzenesulfonate** (**11a**). To a stirred solution of 2.00 g (0.013 mol) of alcohol **10** in 10 ml of dry tetrahydrofuran at 0° was slowly added 11.0 ml of 15.2% *n*-butyllithium in hexane. After the mixture was stirred for 20 min, 3.20 g (0.014 mol) of freshly recrystallized *p*-nitrobenzenesulfonyl chloride in 10 ml of dry tetrahydrofuran was added dropwise. The clear yellow solution was stirred for 1 hr at 0° and dumped into 75 ml of ice–water, producing a flocculent yellow precipitate. The mixture was extracted five times with ether. The combined extracts were washed twice with saturated sodium chloride solution and dried over magnesium sulfate. Evaporation of solvent yielded a yellow oil which solidified upon standing. Recrystallization from ether–pentane afforded 3.46 g of yellow crystals: mp 86.5–87°; ir (CCl_4) 3310, 3060, 2960, 1355, 1190, 940 cm^{-1}; nmr ($CDCl_3$) δ 8.25 (4 H, q), 6.0 (2 H, q), 4.1 (2 H, tr), 2.7 (2 H, br s), 2.0–0.3 (m).

3-(5-Norbornen-*endo*-**2-yl)propyl** *p*-**Bromobenzenesulfonate** (**11b**). To a stirred, ice-cold solution of 18.0 g (0.112 mol) of alcohol **10** in 50 ml of pyridine was slowly added 33 g (0.13 mol) of *p*-bromobenzenesulfonyl chloride, mp 74–75°, in 50 ml of pyridine. The mixture was allowed to stir overnight. It was then poured into 100 ml of ice–water and acidified. Extraction with ether yielded 43 g of crude ester, which was recrystallized from ether–pentane to give 32.8 g (75%) of pure *p*-bromobenzenesulfonate: mp 51–52°; ir (CCl_4) 3025, 2950, 1570, 1375, and 1195 cm^{-1}; nmr (CCl_4) δ 7.7 (4 H, s), 6.0 (2 H, m), 4.0 (2 H, tr), 2.7 (2 H, br s), 2.0–0.8 (m).

Anal. Calcd for $C_{16}H_{19}O_3BrS$: C, 51.76; H, 5.16. Found: C, 51.95; H, 5.12.

Methyl 5-Norbornen-*endo*-**2-carboxylate** (**16**). To a cold, stirred ethereal solution of diazomethane, prepared from 33 g of DIAZALD, was added dropwise 9 g of acid **5** in 50 ml of ether. After nitrogen evolution had ceased, the solution was washed with sodium bicarbonate solution, dried, and evaporated. Distillation of the product yielded 9.26 g (94%) of clear colorless liquid, bp 64–65° (7 mm) (lit.[20] bp 70° (10 mm)).

Methyl *exo*-**5(6)-Hydroxy-***endo*-**2-norbornanecarboxylate** (**17**). To 70 ml of 1 *M* borane in tetrahydrofuran (0.07 mol) at 0° was added dropwise 21.6 g (0.14 mol) of ester **16** in 30 ml of ether. The solution was allowed to stir for 1 hr, after which time water was added slowly to destroy the excess borane. A 15-ml portion of 3 *N* sodium hydroxide (45 mmol) was added, followed by slow addition of 18 ml of 30% hydrogen peroxide (180 mmol). The mixture was stirred for 0.5 hr. Solid sodium chloride was added and the mixture was continuously extracted with ether overnight. Evaporation of solvent yielded a colorless oil which was distilled to give 16.6 g (60%) of **17**: bp 94–96° (0.1 mm); ir (film) 3410, 2970, and 1730 cm^{-1}; nmr ($CDCl_3$) δ 3.8 (2 H, br s), 3.62 (3 H, s), 2.95–1.0 (m).

Methyl 5(6)-Oxo-*endo*-**2-norbornanecarboxylate**[21] (**18**). A 16.2-g portion of hydroxy esters **17** was oxidized to the keto esters by the procedure of Brown and Garg.[8] Yield of crude esters was 15.2 g (95%). Distillation afforded 14.0 g of **18**: bp 74–76° (0.2 mm) (lit.[21] bp 64–65° (0.2 mm)); ir (film) 2960 and 1740 (br) cm^{-1}; nmr ($CDCl_3$) δ 3.63 (unsym d), 3.30–1.18 (m); gc analysis showed two peaks, ratio 56:44 (50-ft SCOT column).

Methyl 5-Oxo-*endo*-**2-norbornanecarboxylate** (**22**). A freshly prepared solution of 3.5 g (0.09 mol) of sodium borohydride in methanol was added to a solution of 16.0 g (0.09 mol) of **18** in 300 ml of methanol and allowed to stir for 4 hr. Most of the methanol was removed under reduced pressure and the resulting hydroxy ester was saponified with 7.20 g (0.18 mol) of sodium hydroxide in 75 ml of water. The strongly alkaline solution was cooled to 0°, acidified with 6 *N* hydrochloric acid, and then made weakly basic with saturated sodium bicarbonate solution. Continuous extraction of the aqueous solution with ether produced 7.7 g of *endo*-6-hydroxy-*endo*-2-norbornanecarboxylic acid lactone (**20**), mp 155–156° (lit. mp 155–156°).[22] The bicarbonate solution was then acidified to pH 2 with hydrochloric acid and continuously extracted with ether overnight to yield the crude *endo*-5-hydroxy-*endo*-2-norbornanecarboxylic acid **21**. Treatment of an ether solution of this acid with diazomethane as above, followed by a two-phase oxidation with acidic sodium dichromate as above[8] afforded 6.5 of **22** which was purified by distillation: bp 80–82° (0.4 mm); ir (film) 2960 and 1740 (br); nmr ($CDCl_3$) δ 3.68 (s), 3.0 (br d), 2.60 (br s), 2.18–1.60 (m); gc analysis (50-ft DC SCOT column) showed the material to be 98.5% pure.

Methyl 5,5-Dimethoxy-*endo*-**2-norbornanecarboxylate** (**23**). A 10.64-g (0.063 mol) portion of **22** was mixed with 200 ml of absolute methanol and two small crystals of *p*-toluenesulfonic acid, and the solution was heated at reflux for 4 hr. Upon cooling, the solution was made basic by addition of a few drops of sodium methoxide in methanol. Evaporation of the methanol under reduced pressure

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(21) E. Crundwell and W. Templeton, *J. Chem. Soc.*, 1400 (1964).

(22) J. D. Roberts, E. R. Trumball, Jr., W. Bennett, and W. Armstrong, *J. Amer. Chem. Soc.*, 72, 3116 (1950).

yielded a mixture of ketal and ketone, as indicated by infrared. A second treatment produced 10.80 g of ketal (80%): bp 90–95° (0.3 mm); ir (film) 2970, 2840, and 1740 cm^{-1}; nmr (CCl_4) δ 6.40 (s), 6.92 (d), 7.10–9.00 (m).

5,5-Dimethoxy-*endo*-2-hydroxymethylnorbornane (24a). To a mechanically stirred suspension of 4.6 g (0.12 mol) of lithium aluminum hydride in 500 ml of ether was added 33.7 g (0.16 mol) of **23**. After the mixture was stirred for 1 hr, the excess hydride was destroyed by addition of 4 ml of water, followed by 12 ml of 15% potassium hydroxide solution and another 4 ml of water. After the mixture was stirred for 1.5 hr, a quantity of anhydrous sodium sulfate was added to the white slurry. The precipitated salts were removed by filtration and the filtrate was dried and concentrated to yield 30.0 g of **24a** as a colorless oil. Gc analysis of the product (as the silyl ethers 50-ft DC 550 SCOT column) showed that 28.7% of the mixture was the diol resulting from the reduction of unreacted **22**. The crude product mixture was chromatographed in two 15-g batches on silica gel (20:1), eluting with 50% ether–hexane. The first twenty-five 125-ml fractions contained pure **24a**. The eluent was then changed to 100% ether, pure diol being eluted after 20 fractions. The appropriate fractions were combined to yield 22.57 g of **24a** as a pale yellow oil, which was not purified further: ir (film) 3400, 2960, 2840, 1110, 1050, and 860 cm^{-1}; nmr ($CDCl_3$) δ 3.60 (4 H, s), 3.08 (2 H, d), 2.90–1.00 (m).

(5,5-Dimethoxy-*endo*-2-norbornyl)methyl *p*-Toluenesulfonate (24b). To a cold, stirred solution of 10.1 g (0.05 mol) of **24a** in 20 ml of dry tetrahydrofuran was added 37.5 ml of 1.6 *M* *n*-butyllithium in hexane (0.06 mol). After the mixture was stirred for 20 min to allow anion formation, 11.3 g of recrystallized *p*-toluenesulfonyl chloride (0.06 mol) in 20 ml of tetrahydrofuran was added. The mixture was stirred for 2 hr, poured into 100 ml of water, and extracted with ether. The ether solution was washed with water, dried, and evaporated to yield 18.4 g of **24b** (99%) as a very pale yellow, viscous oil. Further purification was unnecessary: ir (film) 2970, 2840, 1600, and 1190 cm^{-1}; nmr ($CDCl_3$) δ 7.58 (q), 4.04 (d), 3.05 (s), 2.42 (s), 2.37–0.77 (m).

Methyl 3-(5-Oxo-*endo*-2-norbornyl)propionate (25). To 500 ml of dry *tert*-butyl alcohol was added 4.50 g (0.115 g-atom) of freshly cut potassium metal. After heating at reflux until all the metal had dissolved, 19.0 g (0.119 mol) of diethyl malonate was added in one portion and the mixture stirred for 30 min to allow for anion formation. **24b** (37.4 g, 0.110 mol) was mixed with 50 ml of dry *tert*-butyl alcohol and added in one portion to the white suspension at room temperature. The mixture was then heated to reflux and *tert*-butyl alcohol was removed by distillation until a thick slurry remained. The slurry was heated at reflux for 72 hr. After cooling, the slurry was poured into 400 ml of ice–water and extracted with five portions of ethyl ether. The ether solutions were evaporated under reduced pressure and the crude diester residue was saponified with 40 g of potassium hydroxide in 80 ml of water. Extraction of the basic solution with ether afforded 1.43 g of neutral material. The aqueous basic solutions were cooled to 0°, acidified with 12 *N* hydrochloric acid, saturated with sodium chloride, and continuously extracted with ether for 24 hr. The resulting ether solution of diacid was evaporated and the residue decarboxylated by heating in 75 ml of pyridine at reflux for 2 hr. After cooling and acidification, the crude keto acid was continuously extracted with ether for 24 hr.

The ether solution of the keto acid was esterified with an ethereal solution of diazomethane, the solvent evaporated, and the crude **25** distilled, bp 91–93° (0.2 mm), affording 18.89 g (92.9%) of product: ir (film) 2960, 1740, 1415, and 1170 cm^{-1}; nmr ($CDCl_3$) δ 3.56 (s), 2.67–0.75 (m).

Ethylene Bis(3-(5,5-Ethylenedioxy-*endo*-2-norbornyl)propionate) (26). A mixture of 6.00 g (0.032 mol) of **25**, 3.05 g (0.049 mol) of ethylene glycol, and 80 ml of dry benzene was heated at reflux in the presence of two small crystals of *p*-toluenesulfonic acid until the benzene–water azeotrope ceased to distil. During the distillation of the azeotrope, more benzene was added periodically, the total solution volume being kept at approximately 90 ml. After heating for 15 hr, approximately 300 ml of liquid had distilled.

One pellet of sodium hydroxide was added to the cooled solution and stirred for 15 min. A quantity of anhydrous sodium sulfate was added and the mixture was stirred for 1 hr. The pale yellow benzene solution of **26** was decanted into a separatory funnel and washed twice with 5% sodium bicarbonate solution, once with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Evaporation of solvent yielded 7.43 g (96%) of **26** as a pale yellow liquid: ir (film) 2950, 2880, and 1740 cm^{-1}; nmr (CCl_4) δ 3.70 (8 H, d), 3.1 (4 H, d), 2.50–0.85 (m).

3-(5,5-Ethylenedioxy-*endo*-2-norbornyl)propanol (27a). To a mechanically stirred suspension of 0.71 g (0.019 mol) of lithium aluminum hydride in ether was added a solution of 7.43 g (0.016 mol) of **26** in 30 ml of ether. The mixture was stirred for 0.5 hr, after which 1 ml of water was slowly added, followed by 3 ml of 15% potassium hydroxide solution and 1 ml of water. Filtration of the precipitated salts followed by drying and evaporation of solvent yielded 6.38 g of **27a** (97%) as a colorless oil: ir (film) 3400, 2960, 2840, 1340, 1100, 1060, and 1020 cm^{-1}; nmr ($CDCl_3$) δ 3.8–3.05 (m), 2.45–0.83 (m).

3-(5,5-Ethylenedioxy-*endo*-2-norbornyl)propyl *p*-Toluenesulfonate (27b). A 6.323-g (0.30 mol) sample of **27a** was mixed with 25 ml of dry tetrahydrofuran, cooled to 0°, and treated with 13.4 ml (0.031 mol) of 2.34 *M* *n*-butyllithium in hexane. After the mixture was stirred for 30 min, 5.700 g (0.030 mol) of recrystallized *p*-toluenesulfonyl chloride in 10 ml of tetrahydrofuran was added dropwise. The reaction was stirred for 2 hr at 0°.

The product was poured into 150 ml of ice–water and extracted with three portions of ether. The extracts were combined and washed twice with 5% sodium bicarbonate solution and once with saturated sodium chloride solution. After drying over magnesium sulfate, evaporation of solvent yielded 10.60 g of **27b** as a pale yellow oil, used without further purification: ir (film) 2960, 1600, 1365, 1195, 1180, and 660 cm^{-1}.

3-(5-Oxo-*endo*-2-norbornyl)propyl *p*-Toluenesulfonate (28). A 10.60-g (0.029 mol) portion of **27b** was mixed with 70 ml of reagent acetone and a solution of 1 ml of concentrated sulfuric acid in 20 ml of water. The clear solution was heated to 50° for 1 hr, then stirred at room temperature for 1 hr. Most of the solvent was evaporated under reduced pressure, and the resulting two-phase mixture of product and water was extracted with three portions of ether. The combined extracts were washed twice with water and once with 5% sodium bicarbonate solution, then dried over magnesium sulfate. Evaporation of solvent afforded 9.44 g of pure **28** (98%) as a pale yellow oil, which solidified upon prolonged standing at 6°. Recrystallization was attempted, but without success: ir (film) 2960, 1745, 1600, 1370, 1200, 1180, 950, and 660 cm^{-1}; nmr ($CDCl_3$) δ 7.6 (4 H, q), 4.1 (2 H, tr), 2.45 (3 H, s), 2.4–0.7 (m). 2,4-Dinitrophenylhydrazone: mp 179–180°.

Anal. Calcd for $C_{23}H_{26}O_7N_4S$: C, 54.97; H, 5.22; N, 11.15; S, 6.38. Found: C, 55.11; H, 5.24; N, 11.00; S, 6.29.

Sodium Bis(trimethylsilyl)amide.[23] To a suspension of 3.90 g (0.1 mol) of fresh sodium amide in 25 ml of benzene under nitrogen was added 16.20 g (0.1 mol) of commercial hexamethyldisilazane. The mixture was heated at reflux until no more ammonia was evolved (approximately 6 hr). The benzene solution was filtered under nitrogen, the gray residue being washed with two portions of dry benzene. The solvent was removed under reduced pressure, producing 18.1 g of product as a white solid which was stable under nitrogen.

Tricyclo[3.3.1.1^{3,9}]decan-2-one (2-Homobrendanone) (14). To 2.05 g (0.011 mol) of sodium bis(trimethylsilyl)amide under nitrogen was added 100 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride); 3.60 g (0.011 mol) of **28** was dissolved in the dry tetrahydrofuran and added to the solution of base dropwise. The mixture was stirred at room temperature for 30 min, then heated under nitrogen for 30 hr at 45°. The cooled suspension was poured into 200 ml of ice–water, made weakly acidic with dilute hydrochloric acid, and extracted with four portions of pentane. The combined extracts were washed once with 100% hydrochloric acid, twice with water, and twice with 5% sodium bicarbonate solution and dried over magnesium sulfate. Evaporation of solvent afforded 2.04 g of crude yellow oil.

The crude product was chromatographed on silica gel (activity 5), eluting with 1% ether–pentane. Ketone **14** was eluted in the first ten fractions, after which the solvent was switched to 50% ether–pentane, with recovered starting material eluting after six fractions. A total of 0.848 g of starting material was recovered, along with 0.905 g of 2-homobrendanone (70% based on 2.76 g of **28**): mp 122–124° (sealed tube); ir (CCl_4) 2970 and 1750 cm^{-1}; nmr ($CDCl_3$) δ 2.50–0.77 (m).

(5-Norbornen-*endo*-2-yl)methyl Bromide. An 8.4-g (0.03 mol) portion of **7** was combined with 2.88 g (0.03 mol) of dry lithium bromide in 75 ml of dry acetone in a large test tube. The tube was sealed and placed on a steam bath for 16 hr, cooled, and poured into 200 ml of ice–water. The mixture was extracted with three portions of pentane. The pentane extracts were combined, washed two

(23) U. Wannegat and H. Niederprum, *Chem. Ber.*, **94**, 1540 (1961).

times with water, and dried over magnesium sulfate. The solvent was evaporated to yield 5.55 g (99%) of crude product, which was distilled, bp 70–72° (9 mm), to afford 3.98 g of pure bromide: ir (film) 3060, 2960, and 720 cm^{-1}; nmr (CCl_4) δ 6.1 (2 H, sym mult), 3.5–1.0 (m), 0.6 (1 H), d of d); gc analysis (50-ft SCOT Carbowax 20M column) showed >99% purity.

(*exo*-**6-Hydroxy-*endo*-2-norbornyl)methyl Bromide**[11] **(29).** To 200 ml (0.20 mol) of a cold, stirred 1 *M* solution of borane in tetrahydrofuran was slowly added 96.9 g (0.52 mol) of (5-norbornen-*endo*-2-yl)methyl bromide in 100 ml of dry tetrahydrofuran. The solution was stirred for 2 hr at room temperature, then cooled again in ice. To this cooled solution was added 54.75 ml (0.16 mol) of 3 *N* sodium hydroxide in one portion, followed by 65.70 ml (0.58 mol) of 30% hydrogen peroxide dropwise. The addition of hydrogen peroxide generated a significant amount of heat. Following addition, the mixture was stirred at room temperature for 1 hr and 10 g of sodium chloride was then added, to produce a separation of layers. The aqueous phase was separated and extracted with three portions of ether. The ether extracts were combined with the original organic phase and the solution was dried over magnesium sulfate. Evaporation of solvent yielded 109.9 g of crude **29** as a yellow mixture of isomers. Gc analysis of the trimethyl silyl ethers (50-ft DC 550 SCOT column) indicated that **29** was present in a ratio of 65:35 to the *exo*-5-hydroxy isomer. The neat oil was allowed to stand for 4 days in an open flask at 20°, after which time crystallization began to take place. Within 24 hr, crystallization was essentially complete. Filtration of the mixture produced 37 g of crude white crystals, which were recrystallized once from ether–pentane to afford 27 g of pure **29**: mp 76–77° (lit.[11] mp 74–75°); ir (Nujol) 3250 and 2950 cm^{-1}; nmr ($CDCl_3$) δ 4.05 (1 H, br d), 3.34 (2 H, d of d), 2.33 (2 H, br s), 2.20 (1 H, s), 2.20–1.0 (m), 0.6 (1 H, br d); gc analysis (as the trimethylsilyl ethers, 50-ft DC 550 SCOT column) indicated that <1% of the 2,5 isomer was present.

exo-**6-(*endo*-2-Norbornylmethyl Bromide) 2′-Tetrahydropyranyl Ether (30).** To 4.00 g (0.020 mol) of **29** was added 2.50 g (0.024 mol) of freshly distilled dihydropyran and 10 ml of dry ether. Two crystals (~1 mg) of *p*-toluenesulfonic acid monohydrate was added, and the solution was allowed to stir for 12 hr. Two pellets of sodium hydroxide were added, and after 1 hr the ethereal solution was decanted, washed two times with 15% potassium hydroxide solution, dried over sodium sulfate, and evaporated to yield 5.63 g (100%) of **30** as a colorless liquid: ir (film) 2960, 1135, and 1020 cm^{-1}; nmr ($CDCl_3$) δ 4.62 (1 H, br s), 4.15–3.20 (5 H, br m), 2.7–1.0 (13 H, m), 0.64 (1 H, br d).

Methyl 3-(*endo*-2-Norbornyl-*exo*-6-(2′-tetrahydropyranyl ether))-propionate. To 50 ml of freshly distilled *tert*-butyl alcohol was added 0.78 g (0.02 mol) of freshly cut potassium metal with stirring. This mixture was heated at reflux until all of the potassium had dissolved. To this solution was then added 3.36 g (0.02 mol) of diethyl malonate in one portion which formed a white precipitate of potassium diethyl malonate. After heating and stirring the mixture for 15 min, 5.63 g (0.02 mol) of **30** in 10 ml of *tert*-butyl alcohol was added in one portion and the reaction mixture was concentrated by distillation of solvent until a thick slurry remained. This slurry was heated at gentle reflux with stirring for 45 hr. The reaction mixture was cooled, poured into 100 ml of ice–water, and extracted with four 25-ml portions of ether. The ether extracts were combined, dried over magnesium sulfate, and evaporated to yield 7.6 g of crude diester. The crude product was heated with 8 g of potassium hydroxide in 20 ml of water for 2 hr with intermittent agitation. The basic mixture was extracted with three portions of ether which after drying over magnesium sulfate and evaporation produced 1.74 g of unreacted **30**. The aqueous alkaline solution was cooled to 0° and carefully acidified to pH 3 with 6 *N* hydrochloric acid. The resulting diacid was quickly extracted with four portions of ether which were combined and dried over magnesium sulfate. Evaporation of solvent afforded 5.0 g of crude diacid. This crude product was heated at reflux with 20 ml of anhydrous pyridine until evolution of carbon dioxide ceased (approximately 2 hr). The pyridine was evaporated under reduced pressure, the product was taken up in 50 ml of ether, and the solution was washed with two portions of cold 6 *N* hydrochloric acid to remove the last traces of base. After drying over magnesium sulfate, ethereal diazomethane was added until nitrogen evolution ceased. The solvent was evaporated to afford 3.79 g of product (97% yield, based on 3.90 g (0.014 mol) of **30**): bp 131–132° (0.05 mm); ir (film) 2960, 1740, and 1010 cm^{-1}; nmr ($CDCl_3$) δ 4.50 (1 H, br s), 4.05–3.15 (3 H, mult), 3.58 (3 H, s), 2.45–0.95 (18 H, m), 0.54 (1 H, br d).

3-(*endo*-2-Norbornyl-*exo*-6-(2′-tetrahydropyranyl ether)) propanol. To a mechanically stirred suspension of 0.38 g (0.010 mol) of lithium aluminum hydride in 30 ml of ether was added dropwise a solution of 3.78 g (0.013 mol) of the above ester in 10 ml of ether. As the ester was added, a thick suspension formed which dissipated upon stirring for 10 hr. The excess hydride was decomposed by dropwise addition of 0.5 ml of water followed by 1.5 ml of 15% potassium hydroxide and another 0.5 ml of water. After salt formation, a small portion of magnesium sulfate was added to the stirred suspension to remove excess water. Filtration of the solution followed by evaporation of solvent afforded 3.36 g (99%) of alcohol: ir (film) 3425, 2950, and 1010 cm^{-1}; nmr ($CDCl_3$) δ 4.55 (1 H, br s), 4.10–3.20 (5 H, m), 2.90 (1 H, br s), 2.4–1.0 (18 H, m), 0.50 (1 H, br d).

3-(*endo*-2-Norbornyl-*exo*-6-(2′-tetrahydropyranyl ether))propyl *p*-Toluenesulfonate. To an ice-cold, stirred solution of 3.37 g (0.013 mol) of alcohol in 15 ml of dry tetrahydrofuran was added 5.94 ml (0.014 mol) of 2.34 *M n*-butyllithium in hexane. After the mixture was stirred for 30 min, 2.54 g (0.013 mol) of *p*-toluenesulfonyl chloride in 10 ml of dry tetrahydrofuran was added dropwise. The pale yellow solution was allowed to stir at room temperature for 1 hr. The product was poured into 100 ml of ice–water and extracted with four portions of ether. The ether extracts were combined, washed two times with 5% sodium bicarbonate solution, and dried over magnesium sulfate. Evaporation of solvent afforded 5.42 g (100%) of crude *p*-toluenesulfonate as a very pale yellow oil: ir (film) 2960, 1600, 1365, 1190 (d), 1010, and 660 cm^{-1}; nmr ($CDCl_3$) δ 7.45 (4 H, q), 4.50 (1 H, br s), 4.15–3.20 (5 H, mult), 2.40 (3 H, s), 2.35–1.0 (18 H, m), 0.45 (1 H, br d).

3-(6-Oxo-*endo*-2-norbornyl)propyl *p*-Toluenesulfonate (31). To a solution of 5.42 g (0.013 mol) of the above ester in 50 ml of acetone was added a solution of 0.2 ml of 96% sulfuric acid in 20 ml of water. The stirred reaction mixture was heated at 65° for 3 hr. The acetone was removed under reduced pressure and the crude product taken up in ether. The aqueous phase was washed twice with ether and all of the ether extracts were combined. The ether solution was then washed with two portions of water and once with 5% sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to yield 4.38 g of crude hydroxy ester. This crude product was taken up in 100 ml of ether, and to the stirred solution at 0° was added 20 ml of a dichromate oxidation mixture.[8] The dark, two-phase system was stirred at 0° for 1 hr, then at room temperature for 12 hr. The lower aqueous phase was separated and extracted once with ether, and the extract was added to the ether solution of product. This solution was washed with two portions of water and two portions of 5% sodium bicarbonate solution, then dried over magnesium sulfate. Evaporation of solvent afforded 3.46 g (82%) of **31** as a very pale yellow oil which resisted all attempts at crystallization: ir (film) 2960, 1740, 1600, 1360, 1190, and 660 cm^{-1}; nmr ($CDCl_3$) δ 7.45 (4 H, q), 5.92 (2 H, tr), 2.38 (3, H, s), 2.6–0.6 (13 H, m).

Reductions of 2-Homobrendanone (14). (A) Lithium Aluminum Hydride in Ether. To a suspension of 0.100 g (2.6 mmol) of lithium aluminum hydride in 15 ml of ether was added 0.500 g (3.3 mmol) of ketone **14** in 10 ml of ether. The reaction was allowed to stir for 5 hr, at which time the excess hydride was decomposed by addition of 10 drops of water followed by 25 drops of 15% potassium hydroxide solution and 10 drops of water. The mixture was allowed to stir overnight. Filtration of the lithium salts followed by evaporation of the filtrate afforded 0.497 (98%) of solid alcohol which was 100% *endo*-2-homobrendanol (**32a**). Recrystallization afforded 0.450 g (89%) of pure **32a**: mp (sealed tube) 169.5–170°; ir (CCl_4) 3620, 3350, 2940, 1460, 1065, 1050, and 1013 cm^{-1}; nmr (CCl_4) δ 4.08 (1 H, br d), 2.58 (1 H, br s), 2.28–0.85 (14 H, m).

(B) Sodium Borohydride in Methanol. To a stirred solution of 0.020 g (0.13 mmol) of **14** in 3 ml of methanol was added a solution of 0.010 g (0.22 mmol) of sodium borohydride in 2 ml of methanol and 0.5 ml of water. After 4 hr, 2 ml of water and 2 ml of 15% potassium hydroxide solution were added. The mixture was diluted to 20 ml with water and extracted with three portions of ether. The ether extracts were washed with water, dried, and concentrated to yield 0.017 g (84%) of alcohol which analyzed as pure **32a**.

(C) Sodium Borohydride in Pyridine. To a stirred solution of 0.017 g of **14** (0.13 mmol) in 4 ml of dry pyridine was added 0.015 g of solid sodium borohydride. The resulting solution was stirred for 24 hr. The reaction was worked up as above to afford 0.017 g (99%) of alcohol which analyzed as 100% **32a**, plus some unreacted ketone **14**.

(D) Sodium in Methanol. To 0.150 g (1.0 mmol) of ketone **14** in 40 ml of dry methanol was added 6.0 g of sodium metal in small pieces over a period of 2 hr. The mixture was allowed to reflux

during the reaction. After the mixture was stirred overnight, the excess sodium was destroyed by the addition of more methanol. The solution was poured into 100 ml of water and extracted with five portions of pentane. These combined extracts were washed once with water, dried, and evaporated to afforded 0.133 g (88%) of an alcohol mixture which upon analysis was shown to be 54% **32a** and 46% **33a**.

Equilibration of *endo*-2-Homobrendanol (32a). To a solution of 0.91 g (6.0 mmol) of the above mixture of alcohols in 100 ml of methanol was added 1.50 g (65 mmol) of sodium in small pieces. After all of the sodium had reacted, approximately 2 mg of ketone **14** was added and the solution was heated at reflux under argon for 145 hr. The product was isolated as above, giving 0.820 g (90%) of a mixture of alcohols which was composed of 69% **33a** and 31% **32a**. Further reaction times caused a decrease in the percentage of **33a**, presumably through decomposition.

Trimethylsilation of Alcohol Mixtures. To approximately 10 mg of alcohol in a 1 dram vial fitted with a micro stirring bar was added 1 ml of a silylating mixture composed of one part trimethylsilyl chloride, two parts hexamethyldisilazane, and ten parts pyridine. The vial was capped and the mixture stirred at room temperature overnight. The crude product was poured into 20 ml of water and extracted with three 15-ml portions of pentane. The combined extracts were washed once with 10% hydrochloric acid, twice with water, and once with saturated sodium bicarbonate solution. Drying over magnesium sulfate and evaporation of solvent afforded samples used for gc analysis. Retention times for the trimethylsilyl ethers of **32a** and **33a** were 10.6 and 11.8 min, respectively.

***exo*-2-Homobrendanol (33a).** The sodium in methanol equilibrium mixture of alcohols (0.820 g) was chromatographed on 80 g of activity grade II Woelm neutral alumina (4% H_2O), using pentane and various amounts of ether as eluents. The 25% ether–pentane solution eluted 0.471 g of pure **33a**: mp 127–129°; ir (CCl_4) 3630, 3350, 2950, 1460, 1065, 1055, and 1015 cm^{-1}; nmr ($CDCl_3$) δ 3.52 (1 H, br s), 2.2–0.65 (15 H, m).

***endo*-2-Homobrendyl *p*-Bromobenzenesulfonate (32b).** To a cold, stirred solution of 0.497 g (3.3 mmol) of **32a** in 5 ml of dry tetrahydrofuran under nitrogen was added 1.40 ml of 2.34 *M* *n*-butyllithium in hexane. The solution was stirred for 30 min, then 0.835 g (3.27 mmol) of recrystallized *p*-bromobenzenesulfonyl chloride in 5 ml of tetrahydrofuran was added dropwise and the solution stirred for 2 hr at 0°. The mixture was poured into 30 ml of ice–water and extracted with four portions of pentane. The combined extracts were washed with water and dried to afford 1.17 g of colorless oil (97%) which solidified upon standing. Recrystallization from ether–pentane produced pure **32b**: mp 86–87°; ir (CCl_4) 2950, 1580, 1475, 1400, 1380, 1195, 1100, 1070, 990, 930, 880, and 840 cm^{-1}; nmr ($CDCl_3$) δ 7.60 (4 H, s), 4.75 (1 H, d of d), 2.40–1.05 (14 H, m).

Anal. Calcd for $C_{16}H_{19}O_3SBr$: C, 51.74; H, 5.16; S, 8.64. Found: C, 51.76; H, 5.14; S, 8.45.

Isomerization of 32a in Antimony Pentafluoride–Fluorosulfuric Acid. To a magnetically stirred solution of 1 ml of antimony pentafluoride and 1 ml of fluorosulfuric acid in 7 ml of liquid sulfur dioxide under nitrogen was added 13 mg (0.9 mmol) of **32a** in one portion. The solution was allowed to stir for 10 min, then quenched by the rapid addition of 10 ml of glacial acetic acid. The sulfur dioxide was allowed to evaporate at room temperature and the residue taken up in several portions of pentane and several portions of water. The aqueous phase was extracted with three additional portions of pentane; the extracts were combined and washed with saturated sodium bicarbonate solution until basic. The pentane solution was then dried over magnesium sulfate and evaporated to afford 10 mg of a colorless oil which solidified upon standing. Gc analysis (50-ft butanediol succinate SCOT column) showed only a single peak, corresponding in retention time to 1-adamantyl acetate.

Isomerization of Homobrendane (2) to Adamantane.[16] A mixture of 50 mg of aluminum chloride and a solution of 5 mg of homobrendane in 2 ml of reagent hexane was placed in a sealed tube under nitrogen and heated at 70° for 2 hr. The mixture was cooled, poured into 10 ml of ice–water, and extracted with three 5-ml portions of pentane. The combined extracts were washed with 5% sodium bicarbonate solution, dried over magnesium sulfate, and evaporated at atmospheric pressure with a stream of dry nitrogen. Gc analysis of the hydrocarbon residue (100-ft DC 550 SCOT column) indicated the presence of only adamantane.

***exo*-2-Homobrendyl *p*-Bromobenzenesulfonate (33b).** The procedure used for preparation of **32b** was followed exactly, using 0.370 g (2.4 mmol) of **33a** in 4 ml of tetrahydrofuran, 1.1 ml of 2.34 *M* *n*-butyllithium in hexane, and 0.646 g of *p*-bromobenzenesulfonyl chloride in 3 ml of tetrahydrofuran. As the product was only slightly soluble in ether, addition of some extra tetrahydrofuran to the ether allowed extraction to occur. The combined extracts were dried over sodium sulfate and carefully evaporated to produce 0.921 g of crude white solid which slowly turned pale yellow. The crude product was triturated with two 3-ml portions of pentane and one 3-ml portion of 10% ether–pentane. This afforded 0.651 g of a white solid, mp 119.5–120°. The reactive product was stored at Dry Ice temperature to minimize decomposition: ir (Nujol mull) 3090, 2950, 1570, 1470, 1380, 1195, 1095, 1068, 920, 910, 900, 840, 820, 790, and 740 cm^{-1}.

Acetolysis Product Studies. To 0.080 g (0.2 mmol) of ester in a Pyrex combustion tube was added 10.0 ml of 0.05 *M* sodium acetate in acetic acid containing 1% acetic anhydride. The tube was flushed with nitrogen, cooled, sealed, and heated at constant temperature for approximately 8 half-lives. Duplicate samples were utilized for each temperature and ester. For *p*-nitrobenzenesulfonate **11a**, samples were run at 80 and 100°. Studies were conducted with unbuffered solvent as well as with sodium acetate and urea buffers. Acetolyses of *exo*- and *endo*-2-homobrendyl *p*-bromobenzenesulfonates, **33b** and **32b**, were conducted at 25 and 35° and at 60 and 80°, respectively. The solutions were buffered with sodium acetate. After cooling, the contents of each tube was poured into 30 ml of water and extracted with three 10-ml portions of pentane. The combined extracts were washed with water and 5% sodium bicarbonate solution, and dried over magnesium sulfate. The resulting acetates were poorly resolved by gas chromatography, so the products were converted to the corresponding alcohols in quantitative yield by treatment of each sample with lithium aluminum hydride in ether (0.050 g, 0.14 mmol). Approximately 5 mg of the resultant alcohol mixture was converted to the corresponding trimethylsilyl ethers by the procedure previously described. The remaining alcohol mixture was oxidized to the corresponding mixture of ketones by the following method.[8] To a solution of approximately 25 mg of the alcohol mixture in 10 ml of ether was added 3 ml of chromic acid oxidizing mixture (2.5 g of $Na_2Cr_2O_7 \cdot 2H_2O$ and 1.9 ml of 96% sulfuric acid diluted to 12.5 ml with water). After the mixture was stirred overnight, the layers were separated and the ether layer was washed with water and 5% sodium bicarbonate solution and dried over magnesium sulfate. Evaporation of solvent afforded the desired products in 90% yield.

The acetates, trimethylsilyl ethers, and ketones were analyzed by gc, using a 50-ft DC 550 support coated open tubular (SCOT) capillary column. A 50-ft Carboxwax 20M SCOT capillary column was also utilized for analysis of the ketone mixtures, and a 50-ft butanediol succinate SCOT capillary column was used for the acetates. The following columns and conditions were utilized: trimethylsilyl ethers, 50-ft DC 550, temperature, 110°, pressure, 10 psi, retention times (min), *exo*-4-homobrexyl, 14.5, *exo*-2-homobrendyl, 12.0; ketones, 50 ft DC 550, temperature, 110°, pressure, 10 psi, retention times (min), 2-homobrendyl, 13.6, 4-homobrexyl, 17.3; acetates, 50-ft butanediol succinate, temperature, 130°, pressure, 15 psi, retention times (min), **35b**, 4.7, **33c**, 6.3.

Trifluoroacetolysis Product Studies. A 0.05 *M* solution of sodium trifluoroacetate in trifluoroacetic acid was prepared from 1.700 g of sodium trifluoroacetate and 250 ml of freshly distilled trifluoroacetic acid containing 1% trifluoroacetic anhydride by weight. Solutions were again prepared from 0.080 g of *p*-bromobenzenesulfonate and solvolyzed as previously described. After standard work-up as above, the resulting trifluoroacetates were converted into the corresponding ketones for analysis. Gc analysis of the product mixture was accomplished using a 100-ft DC 550 SCOT capillary column, temperature 120°, carrier pressure 15 psi. Retention times were: unknown "A," 12.2 min; **37**, 14.0 min; **14**, 19.3 min; 2-protoadamantanone, 21.9 min; 2-adamantanone, 23.6 min; 4-homobrexanone, 25.0 min; 10-protoadamantanone, 25.8 min.

Separation of Solvolysis Derived Products. The samples for each temperature from acetolysis kinetic runs of *exo*-2-homobrendyl *p*-bromobenzenesulfonate (200 ml) were combined and poured into 400 ml of water. The mixture was extracted with three 50-ml portions of pentane. The pentane extracts were combined and washed with saturated sodium bicarbonate solution until basic. Drying over magnesium sulfate followed by evaporation of solvent afforded 52 mg of crude acetate mixture, the composition of which was analyzed by gas chromatography. The mixture was then treated with 0.02 g (0.5 mmol) of lithium aluminum hydride in ether to afford 38 mg of tricyclic alcohol mixture following normal

base work-up. A 5-mg sample of this mixture was converted to the corresponding trimethylsilyl ethers, while the remainder was oxidized to the mixture of ketones by the procedure described above.

Structure Identification Procedures. (A) Conversion of Solvolysis Products to Hydrocarbons. The procedure of Whitlock and Siefken[16] was used to convert the ketones derived from solvolysis into their respective hydrocarbons. A representative procedure is: to a solution of 25 mg of ketone mixture in 4 ml of freshly distilled triethylene glycol was added 0.25 ml of 99% hydrazine hydrate and four drops of glacial acetic acid. The solution was heated at 80–90° for 24 hr under nitrogen, after which time 0.5 g of potassium hydroxide was added. The mixture was stirred and heated to 200° for 6 hr. The reaction mixture was then cooled, mixed with water, and washed with pentane. The pentane washings and extracts were combined, washed with saturated sodium chloride solution, and dried over magnesium sulfate. The solvent was removed at atmospheric pressure and room temperature with a stream of dry nitrogen. The resulting hydrocarbons (yield 50–70%) were examined by gc, utilizing a 100-ft DC 550 capillary column (SCOT): temperature 90°, carrier pressure 10 psi. Retention times: homobrendane, 15.0 min; homobrexane, 15.8 min; adamantane, 1.64 min; isotwistane, 17.9 min; protoadamantane, 19.0 min.

(B) Isotopic Labeling of Solvolysis Derived Ketones. A gc column was prepared for the deuteration of the active α positions of carbonyl compounds. A mixture of ketones containing a large amount of 6-homobrendanone was passed through the column and fractionally collected in cooled capillary tubes. Reinjection under analysis conditions revealed one fraction containing 89% of **37**, along with 11% 2-homobrendanone **14**. Mass spectrometry of this fraction revealed two parent peaks, the major one at *m/e* 152, the minor one at *m/e* 150. The major parent peak corresponded to incorporation of two deuteriums into the molecule, indicating two exchangeable α protons. **37** is the only easily accessible structure consistent with these observations.

(C) Structure Proofs of Solvolysis Derived Ketones. 2-Homobrendanone (14) was identified by comparison with an authentic sample previously prepared. Gc retention time (19.3 min) was identical with that of the authentic sample.

6-Homobrendanone (37). Due to the inability to obtain an authentic sample of this compound, the following information was used to deduce the structure. The product mixture resulting from 60° trifluoroacetolysis, which contained 44% of **37** and 23% of **14**, exhibited an infrared carbonyl stretching band with a maximum at 1725 cm^{-1}, consistent with a six-membered, cyclic ketone, and a secondary band at approximately 1745 cm^{-1}, attributed to 2-homobrendanone. Exchange experiments indicated that two deuteriums were incorporated into the major component of the mixture, confirming the presence of two exchangeable α protons. These observations are consistent with only one structure easily derived from the 2-homobrendyl ion.

2-Adamantanone was identified by comparison to a commercially obtained authentic sample. Gc retention time (23.6 min) was identical with that of the authentic sample.

4-Homobrexanone was identified in the following manner. Wolff–Kishner reduction of 25 mg of the mixture of acetolysis derived ketones afforded approximately 10 mg of a mixture of two hydrocarbons, the major component of which was identical with homobrendane in gc retention time. The minor component was identical in retention time with the minor component of the hydrocarbon mixture derived from homoenolization and equilibration of 2-homobrendanone. Into an 8 × 10 × 200 mm Carius combustion tube was placed 3 ml of dry *tert*-butyl alcohol and 45 mg (1.2 mg-atoms) of freshly cut potassium metal. The tube was warmed with a heat gun until all of the potassium had reacted. Then 45 mg (0.3 mmol) of 2-homobrendanone was added; the tube was flushed with nitrogen, cooled, and sealed. The solution was heated at 185° for 115 hr, cooled, and poured into 30 ml of ice–water. The mixture was extracted with four 10-ml portions of pentane. The combined extracts were washed with water, dried over magnesium sulfate, and evaporated to yield 43 mg of ketone mixture which was treated as above. Gc analysis of the mixture showed 98:2 ratio of **14** to 2-homobrenanone.

2-Protoadamantanone was identified by comparison to an unambiguously synthesized[5] authentic sample. Gc retention times were identical (21.8 min) for both samples.

9-Protoadamantanone was identified by comparison to a mixture of tricyclic ketones of known composition[5] using gas chromatographic analysis. Gc retention times were identical on both DC 550 and Carbowax 20M capillary columns.

Unknown ketone "A" was the first peak in the gc spectrum and was present in significant amounts only in the low temperature solvolyses. It did not correspond to any authentic sample, and infrared analyses of mixtures in which it was present showed no evidence for alcoholic or unsaturation absorptions. Hydrocarbon products such as adamantane showed retention times which were much shorter under the conditions of analysis (3 min *vs.* 12 min). Conversion to the hydrocarbon by previously described methods indicated the ring structure to be different from that of any other product. The possibility that this structure was cristane could not be verified.

Kinetic Studies. Either J. T. Baker or Target (Lehigh Valley Chemical Co.) reagent grade glacial acetic acid, to which was added 1% acetic anhydride by weight, was used for the acetolysis rate determinations. Standard perchloric acid (0.0114 *N*) in glacial acetic acid was prepared and standardized against potassium hydrogen phthalate. A standard solution of sodium acetate (0.0099 *N*) in glacial acetic acid was prepared and standardized against the perchloric acid.

All determinations were made titrimetrically with a 5-ml microburet precise to 0.01 ml, using a 0.2% solution of crystal violet in glacial acetic acid as an indicator, the end point of each titration being taken at blue-green. Constant temperature was maintained with a Neslab TEX9-H isothermal bath filled with Dow-Corning 200 silicone fluid. Temperatures were determined with a calibrated National Bureau of Standards thermometer.

The general procedure for each kinetic run was as follows, except for **33b**: the *p*-bromobenzenesulfonate was weighed into a 50-ml volumetric flask and diluted to volume with standard sodium acetate in glacial acetic acid. Aliquots (one-tenth of total volume) of this solution were sealed in ampoules (Kimble Neutraglas, No. 12012-L) and immersed in the isothermal bath. At appropriate intervals, a tube was withdrawn, cooled in ice–water, opened, and the contents titrated with standard perchloric acid.

The reaction was followed through approximately 3 half-lives, with zero time being taken as the time the tubes were immersed in the bath.

Due to the rapid rate of solvolysis of **33b**, the following procedure was utilized: into a 50-ml volumetric flask was weighed 80.0 mg of **33b**, 40.0 ml of the sodium acetate buffered glacial acetic acid at run temperature was added and the flask capped and shaken to dissolve the ester. The flask was fitted with a loose-fitting serum cap which held a 5-ml syringe and 6-in. flat-tipped needle. The flask was immersed in an isothermal bath and at various time intervals 4.0-ml aliquots of solution were withdrawn and diluted into 10 ml of glacial acetic acid. Titration of this solution was conducted as above.

The first-order rate constants were determined by the use of PLSTSQR, a specially written computer program (APL language) which plots at a terminal the graph of ln [ROBs] *vs.* time, then calculates the best rate fit to the valid points by the method of least squares.

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