exo-phenylbicyclo[3.1.0]hexan-3-ol, mp 185–186 °C (lit.[3] 185.5–186.5 °C) was isolated.

The mother liquors obtained after extensive crystallization of the other isomers were rechromatographed and the fractions which were shown by NMR to be largely 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hex-2-ene were then hydroborated to give a quantitative yield of the 2- and 3-ols; 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-ol, mp 83–85 °C (lit.[3] mp 87–88 °C), was isolated.

Hydroboration of 6-*endo*-*p*-methylphenyl-6-*exo*-phenylbicyclo-[3.1.0]hex-2-ene, mp 59–61 °C, gave a quantitative yield of the 2- and 3-ols; 6-*endo*-*p*-methylphenyl-6-*exo*-phenylbicyclo-[3.1.0]hexan-3-ol, mp 138.5–139.5 °C, was isolated with NMR δ ($CDCl_3$) 7.32 (5 H Ph pseudo s), 7.25 (4 H, C_6H_4 pseudo s), 3.02 (1 H t, J = 7 Hz, HCOH), 2.40 (3 H s, CH_3), 2.75–1.65 (6 H m, CH_2 and cyclopropyl H), 1.33 (1 H s, OH); ir (mull) 3350 (OH), 3050, 1600, 1500, 1480, 1360, 1320, 1120, 1080, 1040, 980, 860, 760, 700 cm^{-1}.

Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 85.55;[19] H, 7.67.

Hydroboration of 6-*endo*-*p*-methoxyphenyl-6-*exo*-phenylbicyclo[3.1.0]hex-2-ene, mp 90–91 °C, gave a good yield of the 2- and 3-ols; 6-*endo*-*p*-methoxyphenyl-6-*exo*-phenylbicyclo[3.1.0]hexan-3-ol, mp 151–152 °C, was isolated with NMR δ 6.8–7.4 (9 H Ar m with Ph at 7.10 covering the lower side of the A_2B_2 quartet), 3.82 (3 H s, CH_3), 2.95 (1 H t, J = 7 Hz, HCOH), 1.7–2.6 (6 H m CH_2 and cyclopropyl H), 1.33 (1 H s, OH); ir (mull) 3350 (OH), 3080, 3050, 1600, 1490, 1440, 1365, 1280, 1230, 1160, 1060, 1010, 830, 730, 690 cm^{-1}.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 80.99; H, 7.32.

Europium Shift Reagent Studies. A sample of 20–25 mg of the 3-ol was dissolved in 0.5 ml of deuteriochloroform and the spectrum recorded at 1000-Hz sweep width. A weighed sample of commercially available $Eu(fod)_3$ (180–220 mg) was dissolved in a minimum volume of deuteriochloroform and the total solution was taken up in a 250-μl syringe so that the total volume of the solution could be measured. Then individual 5–20-μl aliquots were added to the tube and a spectrum was recorded. Additions were continued until the signal attributed to H_{at} was clearly delineated between the doublet due to H_{no} and the doublet due to H_{xo}. The induced shifts were plotted against the mole ratio (see Figure 1). The shifts were shown to correlate with $1/r^2$ where r is the distance from the oxygen lone pair lobes to the hydrogen atom as measured on Prentice–Hall models for the shallow chair conformation. Then distance and angle factors from the europium ion were included in the correlation. The europium ion center was positioned 3.0 Å from the alcohol oxygen so that the Eu–O axis was 130° from the C–O bond[14]. Then R, the distance from the europium ion to the hydrogen atom on the model, was measured with dividers, and θ, the angle between that vector and the Eu–O axis, was measured with a protractor. The results are given in Table I. The induced shifts at ca 1.4/1 mole ratio were extrapolated to 1/1 following the reported method.[13] Using his technique only 1/1 complexes are formed. Least-squares correlation coefficients were calculated on a standard program available with the cps package for an IBM 360-65.

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Registry No.—**1a**, 22524-13-6; **1b**, 57774-37-5; **1c**, 21884-57-1; **1d**, 21884-61-7; **1e**, 57774-38-6; **1f**, 57774-39-7; **3a**, 57774-40-0; **3b**, 57774-41-1; **3c**, 57774-42-2; **3d**, 57774-43-3; **3e**, 57774-44-4; **3f**, 57774-45-5.

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(19) This alcohol shows no trace of impurity by TLC, ir, or NMR, and it produces good needles on crystallization. However, three independent analyses even after drying overnight at 120 °C at 0.1 mm still gave low carbon analyses.

An Unexpected Decomposition of Triphenyl(methyl)stibonium Bromide under Mild Conditions

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In the course of a routine examination of the electrical conductance of a series of triphenyl(methyl)stibonium salts in acetonitrile at 25 °C, we observed that the electrical conductivity of triphenyl(methyl)stibonium bromide solutions decreased slowly with time (Table I).[2] In aged solutions, the ^1H NMR signals of triphenylstibine and methyl bromide as well as the signals of the triphenyl(methyl)stibonium cation were observed. The decomposition reaction[3]

$$(C_6H_5)_3SbCH_3{}^+Br^- \rightarrow (C_6H_5)_3Sb + CH_3Br$$

was studied conductimetrically. The kinetic results were initially baffling, but when ion-pairing and salt effects were accounted for, the data (Table II) were found to fit a second-order rate law of the form

$$\text{rate} = k^0\alpha^2C^2\frac{\gamma_A\gamma_B}{\gamma_{\neq}}$$

where k^0 is the rate constant, α is the degree of dissociation of the salt at total concentration C, and γ_A, γ_B, $\gamma_{\neq}$ are the activity coefficients of the ions (A, B) and transition state ($\neq$).

Table I. Decomposition of Triphenyl(methyl)stibonium Bromide in Acetonitrile at 25 °C

Run	Concn (C) × 10^3 mol/l.	Initial conductance × 10^7 ohm^{-1}	$\frac{mol/l.}{ohm^{-1}}$	Rate × 10^9 ohm^{-1}/s	Rate × 10^9 mol/l. s
3	5.987	36 249	1.6516	1.616	2.670
1	5.234	33 897	1.5450	1.475	2.278
1	3.604	22 446	1.4062	0.8483	1.193
3	3.085	22 459	1.3742	0.8225	1.130
2	2.849	21 255	1.3404	0.7848	1.052
1	1.802	14 750	1.2230	0.3883	0.4749
3	1.462	12 157	1.2025	0.2863	0.3443
2	1.425	12 000	1.1875	0.2458	0.2919
3	0.7803	7 041	1.1082	0.1107	0.1226
1	0.7208	6 758	1.0670	0.1233	0.1316

Table II. Behavior of Triphenyl(methyl)stibonium Bromide in Acetonitrile at 25 °C[a]

Run	Concn (C) × 10^3 mol/l.	Λ	Λ_x	α	k = rate/α^2C^2 × 10^5 l mol^{-1} s^{-1}	$\sqrt{\alpha C}$ × 10^2
3	5.987	80.0	126.4	0.633	18.60	6.16
1	5.234	85.4	127.0	0.672	18.40	5.93
1	3.604	93.4	129.3	0.723	17.58	5.10
3	3.085	96.0	130.1	0.737	21.82	4.77
2	2.849	98.3	130.5	0.752	22.98	4.63
1	1.802	107.0	132.7	0.806	22.52	3.81
3	1.462	109.8	133.7	0.821	23.90	3.46
2	1.425	110.7	133.7	0.828	20.98	3.43
3	0.7803	118.6	136.0	0.872	26.48	2.61
1	0.7208	121.1	136.2	0.889	32.03	2.53

[a] Λ = observed molar conductance; Λ_x = molar conductance expected in the absence of ion pairing; Λ_x was determined by an iterative process using the Kohlrausch–Onsager equation $\Lambda_x = \Lambda_0 - S[\Lambda/\Lambda_x C]^{1/2}$, $S = 0.7374\Lambda_0 + 233.6$, Λ_0 for $(C_6H_5)_3SbCH_3Br = 143$; α = degree of dissociation = $\Lambda/\Lambda_x = [Br^-]/C = [(C_6H_5)_3SbCH_3^+]/C$; C = total salt concentration; $\alpha C = \mu$ = ionic strength.

In agreement with the Debye–Hückel theory,[4] we found that a plot of log (rate/α^2C^2) vs. the square root of ionic strength gives a straight line plot for the data from which $k^0 = 3.4 \times 10^{-4}$ M^{-1} s^{-1} was determined by extrapolation of the data for run 3. The theoretical slope based on the dielectric constant of acetonitrile (35.95)[5] is −3.28; the experimental slope was −4.32.

$$\log \frac{\text{rate}}{\alpha^2C^2} = \log k^0 + \log (\gamma_A\gamma_B/\gamma_{\neq})$$

$$\log \gamma_A\gamma_B = 2Z_AZ_BA\sqrt{\mu}$$

where $\gamma_{\neq} = 1$, $A = 1.64$ for dielectric constant 35.95, Z_A and Z_B are the ionic charges (+1, −1), and μ is the ionic strength which in this case is equal to αC at any concentration.

In theory k^0 is the sum of two contributions in the form $k^0 = k_1{}^0k_A + k_2{}^0$, where $k_1{}^0$ is the rate constant for collapse of ion pairs, k_A is the ion association constant, and $k_2{}^0$ is the rate constant for direct reaction of free ions. However, it is impossible to separate k^0 into its parts for the reasons discussed by Pocker and Parker.[3]

As calculated from electrical conductance measurements, the degree of dissociation of the salt varied from 0.633 at 5.99×10^{-3} M to 0.889 at 0.721×10^{-3} M. During the course of the study, the limiting ionic conductances of triphenyl(methyl)stibonium cation (47 ± 5), tetraphenylstibonium cation (41 ± 4), and BF_4^- anion (104 ± 7) were estimated. The values are reasonable compared to the ionic conductances of tetraphenylarsonium cation (55.8) and perchlorate anion (103.8) reported in the literature.[6,7]

Experimental Section

Triphenyl(methyl)stibonium tetrafluoroborate was prepared by treating triphenylstibine with trimethyloxonium tetrafluoroborate in boiling methylene chloride for 2.5 h. Anal. Calcd for $C_{19}H_{18}SbBF_4$: C, 50.17; H, 4.00; Sb, 26.76. Found: C, 50.45; H, 4.06; Sb, 26.51. The bromide salt was prepared by adding the corresponding potassium salt to a solution of the stibonium tetrafluoroborate in 95% ethanol and removal of the precipitated KBF_4 by filtration. Anal. Calcd for $C_{19}H_{18}SbBr$: C, 50.94; H, 4.05; Sb, 27.18. Found: C, 50.67; H, 4.11; Sb, 27.32. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and antimony analyses were performed by Mrs. D. E. Knight at N.C.S.U.

Acetonitrile was purified for conductance measurements by standing over NaOH pellets and molecular sieve for several days followed by distillation through a column packed with molecular sieve. The specific conductance of the solvent used in the measurements was usually 30×10^{-7} ohm^{-1} cm^{-1} at 25 °C, but no significant difference was noted using solvent with specific conductance as high as 200×10^{-7} ohm^{-1} cm^{-1} provided this correction was applied to the measured conductances of salt solutions.

Conductance and kinetic measurements were made in an enclosed fill-type Beckman cell with cell constant 0.1320 ± 0.0003 cm^{-1}. The cell was kept in a bath which was maintained at 25.0 ± 0.2 °C. A Beckman RC-18A bridge was used to measure conductance.

The kinetic runs were made by two different techniques. Preliminary runs (1 and 2) were made by making up a large volume of stock solution from which dilutions were made. The diluted solutions were stored in a thermostated Dewar flask and their conductances were measured periodically by transferring samples into the conductance cell. All manipulations were made in the air. Later runs (run 3) were made by accurately weighing samples of the salt into 25-ml volumetrics and transferring the volumetrics into a nitrogen-flushed glove box. Acetonitrile was added and the salt rapidly dissolved. The cell was rinsed with three small portions (~3 ml each) of the solution and the remaining solution was just sufficient to fill the cell. The cell was closed with its ground glass thermometer, taken out of the glove box, and placed in the thermostated bath. The first conductance measurements were made approximately 15 min after adding solvent and the sample was monitored continuously for up to 1500 min without disruption. While the preliminary runs showed some scatter in the results, the latter technique produced a very consistent set of data.

Registry No.—Triphenyl(methyl)stibonium bromide, 58074-28-5; triphenyl(methyl)stibonium tetrafluoroborate, 3802-09-3; triphenylstibine, 603-36-1; trimethyloxonium tetrafluoroborate, 420-37-1.

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Photocyclization of 3-(3-Methyl-2-butenyloxy)- and 3-(3-Methyl-2-butenylamino)-5,5-dimethyl-2-cyclohexen-1-ones to 7-Oxa- and 7-Azabicyclo[4.3.0]nonan-2-ones

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In a preceding paper,[1] we have shown that the photocycloaddition reaction of 1,5-hexadienes to bicyclo[2.1.1]hexanes[2] [**1** (X = CH_2) → **2**] can be extended to the syntheses of 2-oxa- and 2-azabicyclo[2.1.1]hexane ring systems [**1** (X