

reactions are carried out for longer periods than 8 h, *trans*-stilbene is formed in appreciable amounts possibly through dimerization of carbene intermediates. Similar results have been reported.<sup>7</sup> The low yields may be attributed in part to steric hindrance of bulky *sec*-alkyl groups. *tert*-Butyl formate, for example, does not react with any of the phosphoranes mentioned.

Our attempts to obtain vinyl ethers from the reaction of stabilized ylides as well as benzylidenetriphenylphosphorane with esters of acetic, butyric, and benzoic acids proved to be unsuccessful under a variety of conditions of temperature and reaction medium. Reactive ylides have been reported to give  $\beta$ -ketoalkylidenephosphoranes.<sup>8</sup>

In all cases, the products are mixtures of *cis* and *trans* isomers but the proportions vary depending upon the nature of the ylide. The stable ylide carbethoxymethylenetriphenylphosphorane gave *cis* and *trans* vinyl ethers in a 10:90 ratio, while with benzylidenephosphorane the proportion of *cis* isomer increased to 22% of the product. A *cis*-*trans* ratio of 45:55 was observed with the reactive ylide 3-methylbutylidenetriphenylphosphorane. The ratios were based on the vinylic absorptions in the NMR spectra of products.

It appears that substituted vinyl ethers may be conveniently synthesized by reaction of phosphoranes with ethyl formate under suitable conditions, thereby providing a general method for the conversion of alkyl and aralkyl halides to vinyl ethers.

### Experimental Section

NMR spectra were recorded on a Varian T-60 instrument in CDCl<sub>3</sub>. Chemical shifts are reported in  $\delta$  units from internal Me<sub>4</sub>Si, and are followed by parentheses giving multiplicity of signal, coupling constant if applicable, and number of protons. Spin multiplicity is given by s = singlet, d = doublet, t = triplet, q = quartet. All compounds showed satisfactory analytical data ( $\pm 0.4\%$  for C and H). Boiling points are uncorrected.

**2-Carboethoxyethenyl Ethyl Ether (6).** Carbethoxymethylenetriphenylphosphorane was prepared according to the published procedure.<sup>9</sup> A mixture of 17.5 g (0.05 mol) of the phosphorane and 40 ml of ethyl formate was heated under reflux for 4 h. The reaction mixture was cooled in ice and the triphenylphosphine oxide formed was separated by filtration. Excess ethyl formate was removed by distillation at atmospheric pressure. Distillation of the residual liquid at 0.5 Torr gave 6.8 g (95% yield) of a pleasant-smelling liquid boiling at 60–61 °C.

NMR spectrum:  $\delta_{\text{Me}_4\text{Si}}$  1.25 and 1.33 (t, t, 3 H, 3 H, -CH<sub>3</sub> of the two ethyl groups), 3.9 and 4.1 (q, q, 2 H, 2 H, -CH<sub>2</sub>- of the two Et), 4.78 and 5.17 (d, d,  $J = 7$  and 13 Hz, together 1 H, =CHOEt), 6.57 and 7.57 (d, d,  $J = 7$  and 13 Hz, together 1 H, =CHCO<sub>2</sub>Et).

**Ethyl Styryl Ether (7).** Benzylidenetriphenylphosphorane was generated, according to the method of Corey et al.,<sup>10</sup> from 39.0 g (0.1 mol) of benzyltriphenylphosphonium chloride and 2.6 g (0.11 mol) of sodium hydride in 400 ml of dimethyl sulfoxide. Ethyl formate (15 g, 0.2 mol) was added to the phosphorane and stirred at room temperature for 3 h, during which the red color gradually changed to pale brown. The reaction mixture was thrown into 800 ml of water, the mixture was extracted exhaustively with pentane, and the combined pentane extract was dried over anhydrous MgSO<sub>4</sub>. Pentane was distilled off under reduced pressure. A clear, colorless liquid boiling at 63 °C (1 mmHg) was obtained in 90% yield (13.3 g).

NMR spectrum:  $\delta_{\text{Me}_4\text{Si}}$  1.25 (t, 3 H, CH<sub>3</sub> of Et), 3.75 (q, 2 H, -CH<sub>2</sub>- of Et), 5.18 and 5.8 (d, d,  $J = 7$  and 13 Hz, together 1 H, =CHOEt), 6.1 and 6.93 (d, d,  $J = 7$  and 13 Hz, together 1 H, =CHC<sub>6</sub>H<sub>5</sub>), 7.08 (broad s, 5 H, C<sub>6</sub>H<sub>5</sub>-).

**4-Methyl-1-pentenyl Ethyl Ether (8).** A suspension of 20.7 g (0.05 mol) of 3-methylbutyltriphenylphosphonium bromide in 250 ml of anhydrous ether was stirred with 21 ml of a 2.4 M solution of *n*-butyllithium (0.05 mol) at room temperature in an atmosphere of N<sub>2</sub>. After 0.5 h it was cooled in a bath of dry ice-acetone for 10 min. A solution of 4.1 g (0.055 mol) of ethyl formate in 10 ml of ether was slowly added with stirring. The red color discharged slowly. The reaction mixture was allowed to warm to room temperature. About 10 ml of alcohol was added and the slurry filtered.

The filtrate was washed with water, dried with MgSO<sub>4</sub>, and solvent removed by distillation at atmospheric pressure. The residue was distilled from a small flask and 1.4 g (22% yield) of compound 8 was obtained as a colorless liquid boiling at 132–133° (760 mm).

NMR spectrum:  $\delta_{\text{Me}_4\text{Si}}$  0.9 [d, 6 H, methyls of -CH(CH<sub>3</sub>)<sub>2</sub>], 1.23 (t, 3 H, -CH<sub>3</sub> of OEt), 1.73 and 1.85 (m, m, together 3 H, -CH- and -CH<sub>2</sub>- of C-4 and C-3 respectively), 3.66 and 3.73 (q, q, together 2 H, -CH<sub>2</sub>- of OEt, *trans* and *cis* isomers, respectively), 4.27, 4.37, 4.60, and 4.82 (t, t, t, t, together 1 H,  $J = 7$  and 13 Hz, respectively, =CHCH<sub>2</sub> *cis* and *trans*), 5.93, 6.17 (d, d, together 1 H,  $J = 7$  and 13 Hz, respectively, -CH= of EtOCH=).

***sec*-Butyl styryl ether (9) and cyclohexyl styryl ether (10)** were prepared by the same procedure used for making compound 7 from 0.05 mol of the benzylidenetriphenylphosphorane and obtained in 24 and 27% yields, respectively.

**Registry No.**—(E)-6, 5941-55-9; (Z)-6, 40648-44-0; (E)-7, 20565-86-0; (Z)-7, 13294-31-0; (E)-8, 16969-14-5; (Z)-8, 16969-29-2; (E)-9, 57967-99-4; (Z)-9, 14371-22-3; (E)-10, 57901-31-2; (Z)-10, 57901-32-3; carbethoxymethylenetriphenylphosphorane, 1099-45-2; ethyl formate, 109-94-4; benzylidenetriphenylphosphorane, 16721-45-2; 3-methylbutyltriphenylphosphonium bromide, 28322-40-9.

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### Europium Shift Reagents.

#### The Assignment of Aryl Stereochemistry in 6,6-Diarylbicyclo[3.1.0]hexan-3-*exo*-ols

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As part of our studies on remote electronic interactions, we have studied the stereoselectivity of cyclopropanation by substituted diarylcarbenoids.<sup>1</sup> The assignment of *endo/exo* aryl stereochemistry on the isomeric 6-phenyl-6-arylbicyclo[3.1.0]hex-2-ene products was a tremendous problem that could not be solved by uv spectroscopy,<sup>2</sup> <sup>13</sup>C NMR,<sup>2</sup> or OH- $\pi$  bonding studies<sup>3</sup> on alcohol derivatives. CNDO calculations indicated that photoelectron spectroscopy would not be helpful.<sup>2</sup> Although <sup>1</sup>H NMR has been used to study the stereochemistry of various 6,6-disubstituted bicyclo[3.1.0]hexane derivatives<sup>4</sup> and a great number of phenylcyclopropanes,<sup>5</sup> the small (ca. 0.1 ppm) but regular shifts of the center of each aryl pattern seen here were not definitive. Europium shift reagents have been applied to a variety of stereochemical problems<sup>6</sup> and the necessary alcohol derivatives could be readily prepared<sup>3</sup> via hydroboration of the bicyclic olefins (eq 1). We therefore present a europium shift reagent study that clearly defines the aryl stereochemistry in 6,6-diarylbicyclo[3.1.0]hexan-3-*exo*-ols (3) and suggests the principal conformation of the 5 ring. We

Table I. Observed and Calculated Induced Shift Ratios in 6-Aryl-6-phenylbicyclo[3.1.0]hexan-3-*exo*-ols

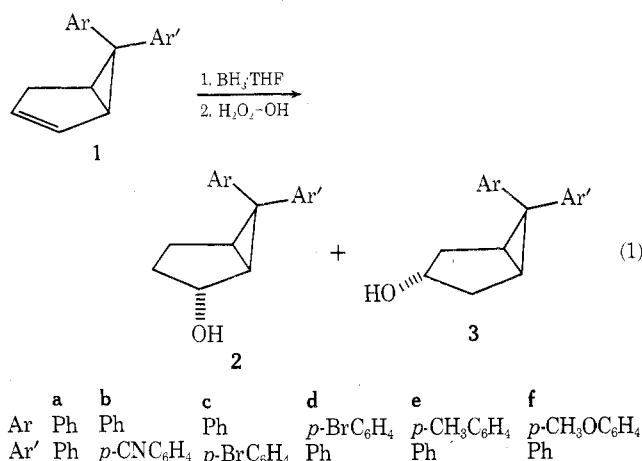
Proton <sup>a</sup>	Calcd <sup>b</sup>	PhPh (1.35/1) <sup>c</sup>	<i>p</i> -Br <sub>endo</sub> (1.5/1)	<i>p</i> -Br <sub>exo</sub> (1.63/1)	<i>p</i> -CN <sub>exo</sub> (1.45/1)	<i>p</i> -Me <sub>endo</sub> (0.85/1)	<i>p</i> -MeO <sub>endo</sub> (1.5/1) <sup>f</sup>
H <sub>ac</sub>	12.8	5.25	4.90	5.10	5.48	5.16	5.19
H <sub>at</sub>	7.47	3.56	3.26	3.43	3.71	3.48	3.30
H <sub>cp</sub>	5.77	2.24	1.93	2.02	2.40	2.05	2.13
H <sub>no</sub>	2.52	0.368	0.324	0.306	0.377	0.320	0.314
H <sub>xo</sub>	2.28	0.260	0.226	0.158	0.332	0.212	0.206
H <sub>nm</sub>	1.07	0.143 <sup>d</sup>	0.125	0.101	0.154	0.098	0.132
H <sub>xm</sub>	1.16	0.150 <sup>d</sup>	0.125	0.164	0.228	0.319	0.103
Corr coeff		0.988	0.989	0.987	0.988 <sup>e</sup>	0.986	0.991

<sup>a</sup> See designations in Figure 2. <sup>b</sup>  $10^3(3 \cos^2 \theta - 1)/R^3$ . <sup>c</sup> Mole ratio of Eu(fod)<sub>3</sub> to substrate from which extrapolation to 1/1 was made following ref 13. <sup>d</sup> Assignment is uncertain since both rings have a para hydrogen. <sup>e</sup> If H<sub>np</sub> is included, the correlation coefficient is still 0.988. <sup>f</sup> For the methoxy protons 0.061.

will also discuss the origin and interpretation of the aryl absorption patterns in the spectra before shift reagent was added.

### Results and Discussion

The bicyclic olefins **1a-f** were prepared by zinc chloride catalyzed cyclopropanation of cyclopentadiene with the corresponding diaryldiazomethane.<sup>7</sup> The pure bicyclic olefins **1a-f** were individually hydroborated to give a mixture



of the corresponding 6,6-diarylbicyclo[3.1.0]hexan-*exo*-2-ols **2** and 6,6-diarylbicyclo[3.1.0]hexan-*exo*-3-ols **3** which were chromatographically separated. The *exo* hydroxyl stereochemistry was confirmed for the 2-ols by comparison to the bromo cases where both *endo*-2-ols and *exo*-2-ols are known<sup>3</sup> and for the 3-alcohols by comparison to the diphenyl case where both isomers are known.<sup>3,8</sup> In both cases the *endo* methine on the carbon bearing the *exo* hydroxyl has a <sup>1</sup>H NMR absorption at higher field than the *exo* methine on the other isomer as one would expect since the *endo* methine can be shielded by both the cyclopropyl ring<sup>9</sup> and the *endo* phenyl ring.<sup>10</sup>

The aryl region of the unshifted spectra was interesting enough that we attempted to assign stereochemistry on the basis of the relative shift of the center of the aryl patterns following Closs' comment on the phenyl absorption of the *syn*- and *anti*-7-phenylbicyclo[4.1.0]heptanes.<sup>5b</sup> For simple geminal diphenyl cases, the lower phenyl pseudosinglet can be attributed to the *endo* phenyl moiety. The origin of this shift difference is interesting. Since it is essentially unchanged by different substituents in the 5 ring such as a double bond, a carbonyl at C-2 or C-3, or hydroxyls at C-2 or C-3, it probably originates from the *exo* phenyl group spending part of its time in a bisected conformation which has maximum overlap with the cyclopropyl ring. In this conformation the cyclopropyl ring shields<sup>9</sup> the ortho protons and causes an overall upfield shift for the *exo* aryl pattern.<sup>5</sup> However, the shift reagent work demonstrated that,

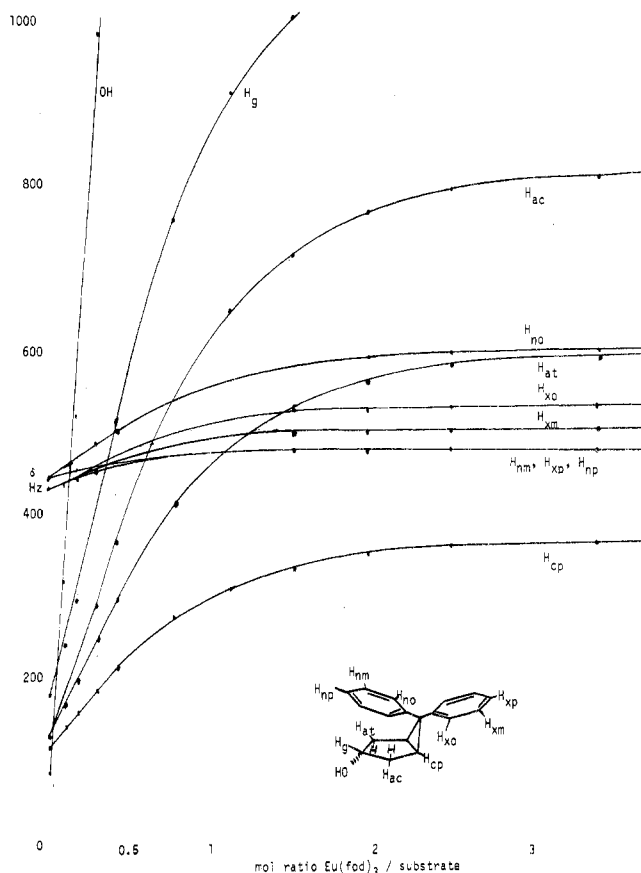


Figure 1. Europium induced shifts for 6,6-diphenylbicyclo[3.1.0]hexan-3-*exo*-ol.

for substituted cases, such interpretations were frequently false since electron-donating substituents tend to raise and electron-withdrawing substituents tend to lower the average aryl chemical shift.<sup>10</sup> These substituent shifts are sufficient to void any simple interpretation.

The Eu(fod)<sub>3</sub><sup>11</sup> studies on the *exo*-3-ols **3a-f** were run in deuteriochloroform solution. Spectra were recorded after each addition and shifts were plotted vs. mole ratio of shift reagent to substrate (see Figure 1 for a sample plot of the diphenyl data for **3a**). Signal assignments depended on integration, signal multiplicity, and careful following of each signal as increments of shift reagent were added. The aliphatic protons H<sub>g</sub>, H<sub>ac</sub>, H<sub>at</sub>, and H<sub>cp</sub> were easily assigned. In each case, two aromatic doublet patterns with ca. 8 Hz ortho coupling moved measurably faster than the rest of the aromatic signals. If the pattern showed no further coupling it was assigned to the protons ortho to the cyclopropyl ring on a para-substituted phenyl ring, and if a ca. 2 Hz meta coupling was visible it was assigned to the protons ortho to the cyclopropyl ring on an unsubstituted phenyl

ring. The faster moving aromatic doublet was assigned to the endo phenyl ring ( $H_{no}$ ), and the slower moving doublet was assigned to the exo phenyl ring ( $H_{xo}$ ) in agreement with predictions of both the crude distance ( $1/R^2$ ) as well as the more exact McConnell treatments.<sup>6,12</sup>

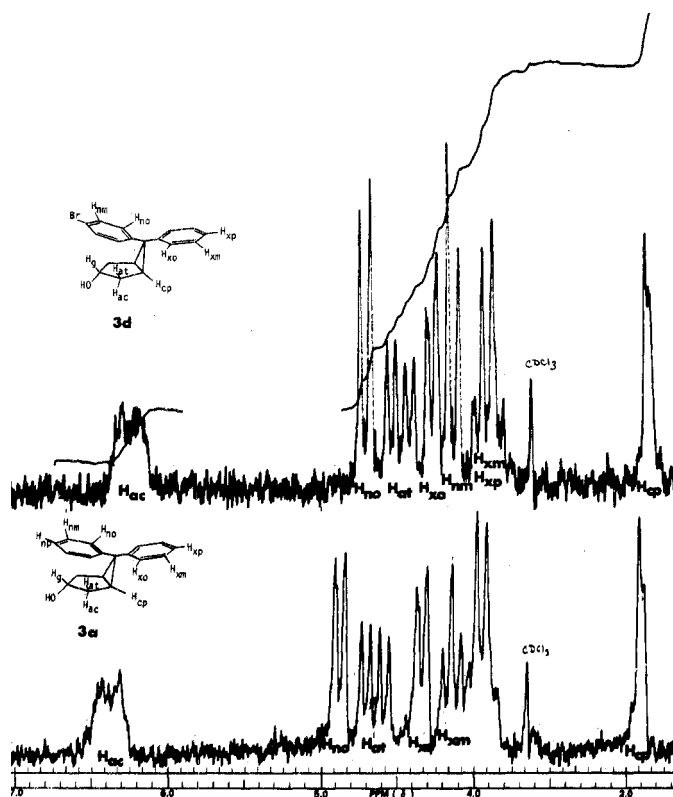


Figure 2. Portions of the shifted spectra for 3a and 3d (1000-Hz sweepwidth).

At ca. 1.4:1 mole ratio the lower field ortho doublet showed no meta coupling and the higher field doublet showed coupling allowing assignment of *endo-p*-bromophenyl 3d, *endo-p*-methylphenyl 3e, and *endo-p*-methoxyphenyl 3f stereochemistry in these cases (for an example see Figure 2.) At similar mole ratios, the high-field doublet was clean but the lower field doublet showed a ca. 2 Hz meta coupling allowing assignment of endo phenyl stereochemistry in 3b and 3c. As shown in Figure 2, the diphenyl case 3a showed meta coupling in both doublets. This analysis is consistent with the observation of marked changes in the aromatic signals assigned to the endo aryl group during the first few additions of shift reagent. The greater shifts induced in the endo ortho protons are first noticed as changes in apparent line width of the endo aryl signals when little or no change is seen in the line width of the exo aryl signals.

The observed values of  $\Delta\nu_i/\nu$  are collected in Table I and were compared to McConnell calculations<sup>12</sup> on a variety of 1/1 molecular arrangements.<sup>13</sup> Positioning the europium ion was aided by the clear order  $\Delta\nu_i/\nu = H_{ac} > H_{at} > H_{cp}$  for the aliphatic protons, as well as the small positive shifts observed for the *endo-p*-methyl and *endo-p*-methoxyl absorptions in 3e and 3f. This small but nearly linear shift of the methoxyl protons even at 1.48/1 mole ratio rules out any second site complexation occurring here in preference to the hydroxyl oxygen. This order is reproduced only for the conformation shown in Figure 3 where the 5 ring has a shallow chair conformation with 10–12° of pucker and the europium is located 3 Å from the oxygen with the Eu–O

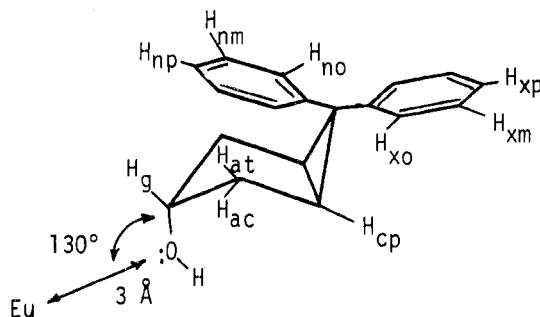


Figure 3. Best molecular arrangement for europium-substrate complexation.

axis at 130° to the C–O bond.<sup>14</sup> The observed relative induced shifts  $\delta\nu_i/\nu$  for each of the 3-ols are collected in Table I along with the calculated values using this conformation and the correlation coefficients.

The hydroxyl protons and  $H_g$  were not included in the correlation since they are known to correlate poorly because of their closeness to the europium ion.<sup>15</sup> Only in the *exo-p*-cyanophenyl case 3b was a para proton sufficiently resolved to allow assignment. The overall order of induced shifts is calculated to be  $H_{ac} > H_{at} > H_{cp} > H_{no} > H_{xo} > H_{xm} > H_{nm} > H_{xp} > H_{np}$ , but small changes in conformation can change the order among the meta and para protons. The experimental values seem to reflect this sensitivity. For acyclic unsubstituted phenyl systems<sup>16</sup> the order of induced shifts is  $H_o > H_m > H_p$  in agreement with our work, but for benzo systems interpretation<sup>17</sup> is more difficult.

### Experimental Section

All melting points were determined on a hot stage apparatus and are corrected. The ir spectra were determined on a Beckman Acculab 1 or Perkin-Elmer 700. NMR spectra were recorded on a Varian A-60A using tetramethylsilane as internal standard and deuteriochloroform solvent. Aldrich  $BH_3 \cdot THF$  and  $Eu(fod)_3$  from Kary Laboratories were used as received. The diarylbicyclic olefins 1a–f were prepared by zinc chloride catalyzed cyclopropanation of cyclopentadiene with the corresponding diaryldiazomethane.<sup>18</sup> Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

**Hydroboration of the 6-Phenyl-6-aryl-bicyclo[3.1.0]hex-2-enes.** The olefins were dissolved in dry THF and hydroborated with commercial  $BH_3 \cdot THF$  solution.<sup>3</sup> The best yields involved use of a 1/1.5 mole ratio instead of 1/0.33. Some of the 3-ol often crystallized out when the reaction mixture was poured into water before ether extraction. The remainder of the reaction mixture was then chromatographed on a slurry packed column of deactivated silica gel using 50% ether–hexane eluent. The 3-ol eluted first and was recrystallized and characterized. The later fractions containing the 2-ol were saved for later work. The product ratio by HPLC analysis was about 1.3:1 favoring the 3-ol and showing little substituent effect. Individual details and characterizations follow.

Hydroboration of 6,6-diphenylbicyclo[3.1.0]hex-2-ene, mp 80–81 °C (lit.<sup>3</sup> mp 79–80 °C), gave a quantitative yield of the 2- and 3-ols; 6,6-diphenylbicyclo[3.1.0]hexan-3-ol, mp 156–157 °C (lit.<sup>3</sup> 157–158 °C), was isolated.

Hydroboration of 6-*endo*-phenyl-6-*exo-p*-cyanophenylbicyclo[3.1.0]hex-2-ene, mp 95–96 °C, gave a quantitative yield of the 2- and 3-ols; 6-*endo*-phenyl-6-*exo-p*-cyanophenylbicyclo[3.1.0]hexan-3-ol, mp 70 °C, was isolated with NMR ( $CDCl_3$ )  $\delta$  7.55–6.85 (9 H ar m with Ph peak at 7.28), 2.88 (1 H t,  $J = 7$  Hz, HCOH), 2.65–1.62 (6 H m,  $CH_2$  and cyclopropyl H), 1.47 (1 H s, OH); ir (mull) 3340 (OH), 3060, 3030, 2240 (CN), 1600, 1500, 1490, 1460, 1360, 1280, 1180, 1070, 1040, 960, 800, 780, 750, 720, 700  $cm^{-1}$ .

Anal. Calcd for  $C_{19}H_{17}NO$ : C, 82.88; H, 6.23; N, 5.09. Found: C, 82.96; H, 6.46; N, 4.97.

Hydroboration of 6-*endo-p*-bromophenyl-6-*exo*-phenylbicyclo[3.1.0]hex-2-ene, mp 104–105 °C (lit.<sup>3</sup> mp 105–106 °C), gave a quantitative yield of the 2- and 3-ols; 6-*endo-p*-bromophenyl-6-

*exo*-phenylbicyclo[3.1.0]hexan-3-ol, mp 185–186 °C (lit.<sup>3</sup> 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.<sup>3</sup> 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  $\delta$  (CDCl<sub>3</sub>) 7.32 (5 H Ph pseudo s), 7.25 (4 H, C<sub>6</sub>H<sub>4</sub> pseudo s), 3.02 (1 H t,  $J = 7$  Hz, HCOH), 2.40 (3 H s, CH<sub>3</sub>), 2.75–1.65 (6 H m, CH<sub>2</sub> 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<sup>-1</sup>.

Anal. Calcd for C<sub>19</sub>H<sub>20</sub>O: C, 86.32; H, 7.63. Found: C, 85.55;<sup>19</sup> 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  $\delta$  6.8–7.4 (9 H Ar m with Ph at 7.10 covering the lower side of the A<sub>2</sub>B<sub>2</sub> quartet), 3.82 (3 H s, CH<sub>3</sub>), 2.95 (1 H t,  $J = 7$  Hz, HCOH), 1.7–2.6 (6 H m CH<sub>2</sub> 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<sup>-1</sup>.

Anal. Calcd for C<sub>19</sub>H<sub>20</sub>O<sub>2</sub>: 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)<sub>3</sub> (180–220 mg) was dissolved in a minimum volume of deuteriochloroform and the total solution was taken up in a 250- $\mu$ l syringe so that the total volume of the solution could be measured. Then individual 5–20- $\mu$ l aliquots were added to the tube and a spectrum was recorded. Additions were continued until the signal attributed to H<sub>at</sub> was clearly delineated between the doublet due to H<sub>no</sub> and the doublet due to H<sub>so</sub>. 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<sup>14</sup>. Then  $R$ , the distance from the europium ion to the hydrogen atom on the model, was measured with dividers, and  $\theta$ , 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.<sup>13</sup> 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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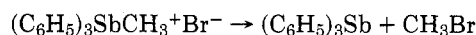
### An Unexpected Decomposition of Triphenyl(methyl)stibonium Bromide under Mild Conditions

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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).<sup>2</sup> In aged solutions, the <sup>1</sup>H NMR signals of triphenylstibine and methyl bromide as well as the signals of the triphenyl(methyl)stibonium cation were observed. The decomposition reaction<sup>3</sup>



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

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

where  $k^0$  is the rate constant,  $\alpha$  is the degree of dissociation of the salt at total concentration  $C$ , and  $\gamma_A$ ,  $\gamma_B$ ,  $\gamma_{\neq}$  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 <sup>3</sup> mol/l.	Initial conductance × 10 <sup>7</sup> ohm <sup>-1</sup>	mol/l. ohm <sup>-1</sup>	Rate × 10 <sup>9</sup> ohm <sup>-1</sup> /s	Rate × 10 <sup>9</sup> 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