References and Notes

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(10) This correction appears to already assume a linear dependence of retention of optical purity on sodium naphthalene concentration. A nonlinear relationship could still have been detected by the graph of Figure 2 since sodium naphthalene is in a 5 mol excess.
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Synthesis and Deamination of 4-Aminospirohexane

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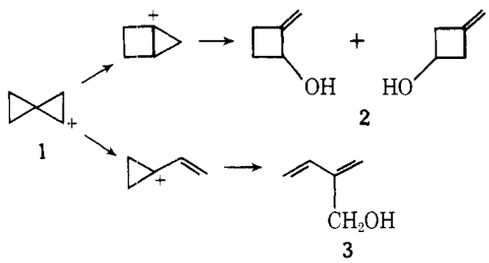
4-Aminospirohexane and 5-aminospirohexane were prepared by direct chlorocarbonylation of spirohexane followed by Curtius degradation. Deamination of 4-aminospirohexane with nitrous acid gave a mixture of spirohexan-4-ol, 2-methylenecyclopentanol, 3-methylenecyclopentanol, cyclohexanone, and several unidentified minor products. This mixture is compared with the products of the 4-spirohexyl cation as generated by solvolysis. 5-Aminospirohexane and nitrous acid gave only spirohexan-5-ol.

Rearrangements of the spiropentyl cation 1 show a remarkable dual behavior, depending upon the mode of generation.[1] When spiropentylamine is deaminated with nitrous acid, the cation rearranges like a cyclopropylcarbinyl cation, giving methylenecyclobutanols **2.** When chlorospiropentane



is allowed to hydrolyze, the cation undergoes electrocyclic ring opening like a cyclopropyl cation, leading to 2-hydroxymethylbutadiene (3). Although different ways of producing a carbonium ion generally lead to different compositions of the product mixture, the absence of any overlap in products in the above two cases is out of the ordinary, especially considering that both reactions were run in water.

In an effort to see if the same kind of duality of behavior could be found in a closely related system, it was decided to investigate the products from the 4-spirohexyl cation **4.** In this

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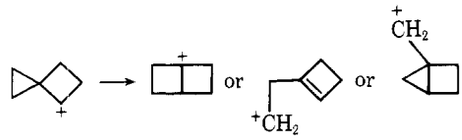
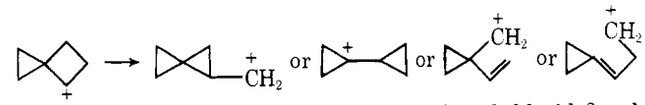
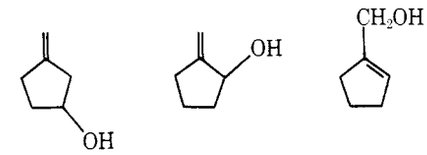
case the cation is again confronted with a competition between two favorable types of behavior. As a cyclopropylcarbinyl cation, it could give ring enlargement to a cyclobutyl cation, rearrangement to an isomeric cyclopropylcarbinyl cation, or



cleavage to an allylcarbinyl cation. As a cyclobutyl cation, it could give ring contraction or cleavage of the four-membered ring.

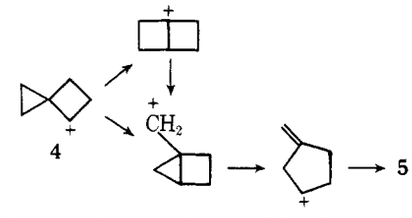


The products from hydrolysis of 4-spirohexyl chloride[2] and 3,5-dinitrobenzoate[3] have already been investigated. The rearranged products are alcohols **5–7,** with **5** making up more

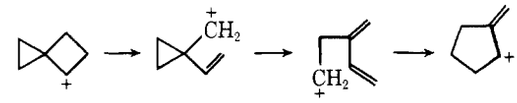


5; 52-64% **6**; 6-15% **7**; 0-5%

than half of the mixture. Product **5** seems most likely to have arisen from cyclopropylcarbinyl-type behavior of **4.** The origin



of **6** and **7** is more obscure; they could either come from a rearrangement of the 3-methylenecyclopentyl cation (from the above sequence) to the allylic 2-methylenecyclopentyl cation or from initial behavior of **4** in the other (cyclobutyl-type) mode.



We have prepared 4-aminospirohexane by a Curtius degradation procedure developed previously for aminospiro-

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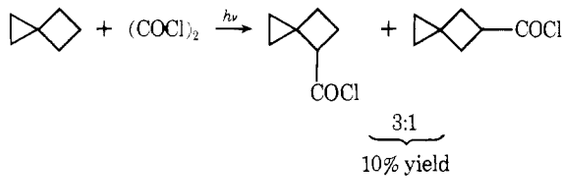
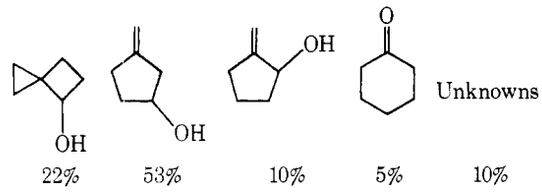
pentane.[4] The spirohexanecarboxylic acid required as starting material was prepared by the direct free-radical chlorocarbonylation of spirohexane with oxalyl chloride.[5] The two



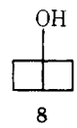
isomers obtained were identified from the NMR spectra of the ethyl esters, which were separated by preparative VPC. In particular, the NMR spectrum of the 5 isomer, except for the signals due to the ethyl group, showed a pattern closely similar to the spectrum of the acid prepared by an independent, unambiguous route, namely, a Simmons–Smith reaction on 3-methylenecyclobutanecarbonitrile followed by hydrolysis.[6] The Curtius procedure was run on both the 4 and 5 isomers to produce the corresponding amines in the form of their β-naphthylurethane derivatives, which were hydrolyzed to the amines immediately prior to diazotization.

The 4-aminospirohexane was diazotized in water at pH 4.6 to give a mixture of volatile products with the following approximate composition.



The mixture is very similar to the previously described solvolysis mixtures, except for the unexpected appearance of cyclohexanone. A repetition of the hydrolysis of 4-chlorospirohexane[2] was therefore carried out, and a minor product previously found in 4% yield but not identified was found to be, in fact, cyclohexanone. Thus, the striking sensitivity to the leaving group of the rearrangement path of the spiropentyl cation is entirely absent in the 4-spirohexyl cation. No explanation can be offered here, but the cause of the effect in the spiropentyl case is under continuing investigation and will be the subject of a future report.

The mechanism of formation of cyclohexanone was not investigated, but an obvious possibility is that it is a secondary product from rearrangement of bicyclo[2.2.0]hexan-1-ol (8)



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under the reaction conditions. Compound 8 is apparently not known, so the hypothesis could not easily be tested.

The deamination of 5-aminospirohexane was carried out and found to give only unrearranged spirohexan-5-ol, exactly the same result as obtained in the hydrolysis of 5-chlorospirohexane.[2,6]

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were recorded on Perkin-Elmer Model 521 or Model 237 grating spectrometers. NMR spectra were recorded on Varian A-60A, HA-100, and HR-220 instruments. We are indebted to Mr. Robert Thrift and associates for most of the spectra. Mass spectra were obtained with an Atlas CH-5 mass spectrometer. Preparative gas chromatography was done on an Aerograph Model A-700 Autoprep, and quantitative analysis was performed on an F&M Model 300 instrument. Elemental analyses were done by Mr. J. Nemeth and his associates.

Spirohexanecarboxylyl Chloride. The procedure followed was mainly that of Wiberg and Williams[7] in the bicyclo[1.1.1]pentane system. Spirohexane (11.366 g, 83.1% pure),[8] freshly distilled oxalyl chloride (16.774 g, 0.132 mol), and Freon 11 (20 mL) were placed in a double-walled tube equipped with a nitrogen inlet tube and a Drierite tube. The central part of the quartz tube was filled with an ice–brine mixture, and the outside area above the liquid level was covered with aluminum foil. Nitrogen was allowed to flow gently, and the reaction vessel was irradiated with a low-pressure mercury lamp (G8T5) in a Srinivasan–Griffin photochemical reactor for 25 h. The reaction mixture was transferred to a distillation flask and the solvent distilled off. After the unreacted starting materials had been recovered (15.0 g), the fraction with bp 38–48 °C (7 mm) [main fraction bp 47–48 °C (7 mm)] was collected (1.877 g). The pot residue amounted to 2.608 g.

Another run was carried out in a 200-mL round-bottom quartz flask equipped with a magnetic stirring system and a dry ice–pentane condenser. The flask was irradiated for 53 h. The result was almost the same as that of the previous run.

The yields of crude spirohexanecarboxylyl chlorides in the two runs were 11.3 and 10.4%, respectively, based on pure spirohexane. The main impurity in the starting hydrocarbon was methylenecyclobutane. The recovered unreacted starting materials were subjected to further irradiation. The IR spectrum of the crude spirohexanecarboxylyl chlorides (CS_2 solution) showed a strong carbonyl absorption at 1795 cm^{-1}, and the NMR spectrum ($CDCl_3$ solution) was similar to that of a mixture of 4- and 5-chlorospirohexanes: a multiplet at δ 3.45–4.00 (1 H, methine proton), 2.05–2.80 (4 H, cyclobutyl methylene protons), and 0.45–1.25 (4 H, cyclopropyl methylene protons).

Ethyl 4- and 5-Spirohexanecarboxylates. A mixture of the spirohexanecarboxylyl chlorides (1.67 g, 11.5 mmol) was allowed to react with 1.95 g (42 mmol) of ethanol and 1.7 g (14 mmol) of *N,N*-dimethylaniline. After the usual solvent extractions, the crude ester mixture was subjected to VPC on an 8 ft dodecyl phthalate column (3/8 in o.d.). Two peaks (other than solvents) were obtained with an uncorrected area ratio of 3.2:1.0. The major product with a shorter retention time was identified as ethyl 4-spirohexanecarboxylate and the minor product assigned to the 5 isomer based on comparison of their NMR spectra with those of 4-hydroxyspirohexane and 5-spirohexanecarboxylic acid, both reported by Bernett. The yield of the carboxylates collected by preparative GLC for several runs was 9.68% (3.768 g of the 4 isomer and 0.876 g of the 5 isomer) from spirohexane. The purities of the collected materials were checked by GLC. The 4-isomer fraction contained 3% of the 5 isomer, while the 4 isomer was not detected in the 5-isomer fraction. Elemental analysis of the 4 isomer gave satisfactory results, whereas the repeated elemental analyses of the 5 isomer did not.

The NMR spectrum of ethyl 4-spirohexanecarboxylate (CCl_4 solution) showed a multiplet at δ 0.23–0.70 (4 H, cyclopropyl methylene protons), a triplet at δ 1.25 (3 H, J = 7.2 Hz, methyl protons), a multiplet at δ 2.00–2.68 (4 H, cyclobutyl methylene protons) and 2.95–3.32 (1 H, methine proton), and a quartet at δ 4.13 (2 H, J = 7.2 Hz, methylene protons of the ethyl group).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.14; H, 9.08. Found: C, 69.88; H, 9.16.

The NMR spectrum of ethyl 5-spirohexanecarboxylate (CCl_4 solution) showed a singlet at δ 0.42 (4 H, cyclopropyl methylene protons), a triplet at δ 1.25 (3 H, J = 7.2 Hz, methyl protons), a multiplet at δ 1.98–2.70 (4 H, cyclobutyl protons) and 2.94–3.52 (1 H, methine proton), and a quartet at δ 4.15 (2 H, J = 7.2 Hz, methylene protons of the ethyl group).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.14; H, 9.08. Found: C, 69.30; H, 8.95; C, 68.92; H, 9.03; C, 68.05; H, 8.88; C, 67.71; H, 8.83.

4-Spirohexanecarboxylic Acid Hydrazide. Ethyl 4-spirohexanecarboxylate (3.730 g, 24.2 mmol) in 10 mL of absolute ethanol was added dropwise to boiling 85% hydrazine hydrate (15 mL, ca. 256 mmol) over about a 70-min period. The reaction mixture was stirred for an additional 2 h at 105 °C and evaporated to dryness under reduced pressure. Recrystallization of the residue from cyclohexane gave 2.880 g (86.5%) of white fluffy crystals: mp 89.0–90.5 °C; NMR spectrum (D_2O solution), a multiplet centered at δ 0.46 (4 H, cyclopropyl methylene protons), 2.18 (4 H, cyclobutyl methylene protons), and 3.09 (1 H, methine proton); a Me_2SO-d_6 solution showed a broad NH peak at δ 3.75 (3 H).

Anal. Calcd for $C_7H_{12}ON_2$: C, 60.05; H, 8.57; N, 20.00. Found: C, 60.05; H, 8.46; N, 19.76.

β-Naphthyl 4-Spirohexylcarbamate. The procedure followed was that of Applequist and Fanta[4] for β-naphthyl spiropentylcarbamate. To a solution of 2.740 g (19.6 mmol) of 4-spirohexanecarboxylic acid hydrazide in 50 mL of water was added 12 mL of 6 N hydrochloric

acid and 60 mL of a mixture of 5 parts benzene and 3 parts *n*-heptane (by volume). After this mixture was cooled to −5 to −10 °C, a solution of 2.90 g (36.7 mmol) of sodium nitrite in 6 mL of water was added to the rapidly stirred mixture over a 20-min period. The reaction mixture was pink during the addition and became a slightly yellow heterogeneous solution at the end of the addition. The mixture was then stirred for 10 min at −5 to −10 °C, and the organic layer was separated. The aqueous solution was extracted with a benzene–heptane mixture (4 × 20 mL), and the combined organic extracts were washed with 5% sodium bicarbonate (3 × 30 mL) and water. The solution was then dried for 10 min in the cold over calcium chloride. The dried solution was heated under reflux for 5 h. A solution of 8.60 g (59.7 mmol) of β-naphthol (purified by sublimation) in 60 mL of hot benzene and 0.1 mL of a 10% solution of tributylamine in *n*-heptane (as a catalyst) were then added, and the resulting solution was heated under reflux for 39 h. Evaporation of the reaction mixture to dryness afforded 10.296 g of a tan crystalline solid. Excess β-naphthol was removed by sublimation (1 mm, 75 °C). The residue (3.115 g) was chromatographed on a Florisil column with a mixture of chloroform and cyclohexane (30:70 by volume) to afford 2.935 g (56.1% from 4-spirohexanecarboxylic acid hydrazide) of a white solid. The chromatographed product was recrystallized from benzene–hexane solution (fine needle crystals): mp 149.0–150.0 °C; NMR spectrum (Me_2SO-d_6 solution), a multiplet at δ 7.18–8.13 (7 H, β-naphthyl protons), a triplet at δ 4.23 (J = 7.5 Hz, 1 H, methine proton), and a multiplet at δ 1.70–2.44 (4 H, cyclobutyl methylene protons) and 0.30–0.88 (4 H, cyclopropyl methylene protons). The NH proton peak was not observed due to the presence of water (the NH proton appeared as a broad peak at δ 5.05 in a $CDCl_3$ solution). The infrared spectrum (KBr) showed peaks at 3280 (with a broad shoulder), 3580–3280 (NH stretch), 1690 (amide I), 1535 (amide II), 3060, 2990, 2945, 2860, 1510, 1465, 1352, 1275, 1240, 1210, 1165, 1148, 1135, 1123, 1005, 960, 888, 867, 827, and 757 cm^{-1}. A mass spectrum ($CHCl_3$ solution) showed a parent peak at m/e 267, with other characteristic peaks having m/e 145 and 144 at 70 eV.

Anal. Calcd for $C_{17}H_{17}O_2N$: C, 76.42; H, 6.36; N, 5.24. Found: C, 76.12; H, 6.46; N, 5.37.

5-Spirohexanecarboxylic acid hydrazide was prepared by essentially the same procedure as used for the 4 isomer. From 0.850 g (5.52 mmol) of ethyl 5-spirohexanecarboxylate and 3.5 mL of 85% aqueous hydrazine was obtained 700 mg (90.6%) of recrystallized (cyclohexane) product, mp 130–131 °C. The NMR spectrum (in Me_2SO-d_6) showed a singlet at δ 0.40 with subsidiary splitting (4 H, cyclopropyl methylene protons), a symmetrical multiplet at δ 1.77–2.55 (4 H, cyclobutyl methylene protons) and 2.82–3.43 (1 H, methine proton), and a broad singlet at δ 3.86 (3 H, the protons attached to nitrogen atoms).

Anal. Calcd for $C_7H_{12}ON_2$: C, 60.05; H, 8.57; N, 20.00. Found: C, 59.89; H, 8.64; N, 20.29.

***β*-Naphthyl 5-spirohexylcarbamate** was prepared by the same procedure as used for the 4 isomer. From 0.631 g (4.5 mmol) of 5-spirohexanecarboxylic acid hydrazide, 0.610 g (8.84 mmol) of sodium nitrite, and 1.200 g (8.33 mmol) of β-naphthol was obtained 0.869 g of crude tan solid, and from that by chromatography (as described for the 4 isomer) and recrystallization from benzene–heptane was obtained 0.835 g (69.5%) of colorless needles, mp 167.0–169.0 °C. The NMR spectrum (Me_2SO-d_6) showed a singlet at δ 0.44 (cyclopropyl methylene protons), a doublet with subsidiary splitting at δ 2.31 (cyclobutyl methylene protons), and a multiplet at δ 4.30 (methine proton) and 7.16–8.03 (β-naphthyl protons). The infrared spectrum (KBr) had peaks at 3430 (broad), 3300, 3060, 2990, 2960, 2930, 1699, 1630, 1544, 1510, 1465, 1360, 1275, 1245, 1218, 1170, 1140, 1125, 993, 890, 869, 783, 758, and 484 cm^{-1}. A mass spectrum ($CHCl_3$ solution) showed a parent peak at m/e 267, with other characteristic peaks at m/e 145 and 144 at 70 eV.

Anal. Calcd for $C_{17}H_{17}O_2N$: C, 76.42; H, 6.36; N, 5.24. Found: C, 76.59; H, 6.28; N, 5.21.

Deamination of 4-Aminospirohexane. A mixture of β-naphthyl 4-spirohexylcarbamate (0.450 g, 1.68 mmol) and 1 N sodium hydroxide (40 mL) was stirred in a sealed flask for 32 h at 60 °C. (The flask had been previously purged with nitrogen and wrapped with aluminum foil.) Then the reaction mixture was cooled with ice–water and acidified with 14 mL of 3.17 N perchloric acid. The white precipitate (β-naphthol) was removed by extraction with three 35-mL portions of ether. Traces of the ether were removed by bubbling nitrogen through the aqueous solution. The acidic solution was diluted to 100 mL in a volumetric flask, and the pH was adjusted to 1.55. The acidic solution was poured into a stirred aqueous solution of sodium nitrite (15.30 g, 0.222 mol; in 25 mL of distilled water) in 15 s. The pH of the resulting solution was found to be 4.65. Then the solution was stirred at room temperature (24 °C) for 15 h in a flask (wrapped with aluminum foil) connected to a dry ice trap with a drying tube at the end. The pH of the reaction mixture was found to be 5.50 after the reaction. The reaction mixture was combined with a small amount of liquid in the cold trap, saturated with sodium chloride, and extracted with ether (5 × 80 mL). The ether extracts were combined, washed with 100 mL of 5% aqueous sodium carbonate and 50 mL of water, and then dried over magnesium sulfate. After filtration, most of the ether was removed by distillation through a 1 ft spiral wire column. The remaining solution was subjected to GLC on a Carbowax 20M column [9 ft, 20% Carbowax on Chromosorb P (base washed)] at 130 °C. Three discrete peaks were observed. The first peak had the same retention time as that of cyclohexanone. The retention times of the second and third peaks were identical with those of 4-hydroxyspirohexane and 3-methylenecyclopentanol, respectively. The peak area ratio was 2:37:61. Most of the ether-extractable product mixture was subjected to GLC to collect each fraction. The amounts collected were 2 (cyclohexanone), 14 (a mixture of 4-hydroxyspirohexane and 2-methylenecyclopentanol), and 16 mg (3-methylenecyclopentanol).

Confirmation that the first fraction was cyclohexanone was determined by a comparison of its infrared spectrum with that of an authentic sample.

The second largest peak was identified as a mixture of 4-hydroxyspirohexane, 2-methylenecyclopentanol, and at least one unknown compound (probably a carbonyl compound) based on a comparison of its NMR and IR spectra with those of authentic samples reported by Bernett.[2,6] The NMR spectrum (CCl_4 solution) showed a doublet at δ 4.99 (splitting of ca. 8 Hz (60 MHz), this splitting increased to 30 Hz (8 × 220/60) in the 220-MHz spectrum; exocyclic vinyl protons of 2-methylenecyclopentanol), a broad unsymmetrical triplet at δ 4.18 (this triplet was resolved into a broad singlet at δ 4.33 and a triplet at δ 4.16 in the 220-MHz NMR spectrum; the methine protons of 2-methylenecyclopentanol and 4-hydroxyspirohexane, respectively), complex multiplets at δ 2.50–1.50, a singlet at δ 2.09 (hydroxyl protons), and a complex multiplet at δ 1.00–0.20 (cyclopropyl methylene protons of 4-hydroxyspirohexane). The ratio of 2-methylenecyclopentanol and 4-hydroxyspirohexane was approximately 30:70 based on the NMR spectrum. The IR spectrum (CCl_4 solution) showed absorptions at 3600 (free OH stretch), 3430 (broad, associated OH stretch), 3070 (CH_2 stretch of C=CH_2 and cyclopropyl methylenes), 1655 (C=C stretch), and 900 (CH_2 out-of-plane deformation of C=CH_2) cm^{-1}. A weak carbonyl absorption was present at 1716 cm^{-1}.

The NMR spectrum (CCl_4 solution) of the largest fraction was identical with that of 3-methylenecyclopentanol reported by Bernett except for the position of the hydroxyl proton peak, which is concentration dependent: a quintet at δ 4.82 (2 H, splitting of 2.5 Hz, vinyl protons), a quintet centered at δ 4.23 (1 H, splitting of 4.5 Hz, methine proton), a singlet at δ 2.61 (1 H, hydroxyl proton), a complex multiplet at δ 2.16–2.55 (4 H), and an eight-peak multiplet at δ 1.50–2.10 (2 H). The IR spectrum (CCl_4 solution) of the largest fraction was identical with that of 3-methylenecyclopentanol reported by Bernett except for the presence of a strong absorption at 1135 cm^{-1}: 3620 (free OH stretch), 3330 (broad, associated OH stretch), 3075 (CH_2 stretch of C=CH_2), 1655 (C=C stretch), 1425 (CH_2 in-plane deformation of C=CH_2), and 881 (CH_2 out-of-plane deformation of C=CH_2) cm^{-1}.

Deamination of 5-aminospirohexane was done by the same procedure as described for the 4 isomer. When the product was analyzed on the VPC column, only one major product peak was observed in addition to the solvent peak, accompanied by a very small peak. The other detectable product peak had an intensity $^1/_{150}$th of that for the major product peak. The NMR spectrum (CCl_4 solution) of the crude product showed only the signals of diethyl ether and 5-hydroxyspirohexane. The mole ratio of the two compounds was determined based on the peak intensities of the methyl triplet of the ether and the cyclopropyl methylene singlet of the alcohol (diethyl ether/5-hydroxyspirohexane, 6:1). The amount of 5-hydroxyspirohexane determined by the mole ratio, the molecular weight ratio, and the total weight of the crude mixture was 0.226 g (92.5% based on the starting carbamate). The NMR spectrum (CCl_4 solution) of 5-hydroxyspirohexane collected by GLC showed a singlet at δ 0.38 (cyclopropyl methylene protons), a doublet at δ 2.20 (splitting of 7 Hz, cyclobutyl methylene protons), a quintet centered at δ 4.45 (splitting of 7 Hz, methine proton), and a singlet at δ 4.05 (hydroxyl proton). The IR spectrum (CCl_4 solution) showed absorptions at 3620 (sharp), 3310 (broad, strong), 3075, 3000, 2965, 2930, 2855, 1450 (w), 1425, 1328, 1220, 1115, 1055, 1010 (w), 903 (w), 840, and 694 cm^{-1}. These spectra were identical with those reported by Bernett.[6]

Control for Stability of 4-Hydroxyspirohexane. To test the possibility that any of the deamination products might be secondary rearrangement products from the 4-hydroxyspirohexane, the following experiment was done.

Perchloric acid (pH 1.55, 100 mL) was added to a stirred aqueous solution of sodium nitrite (15.35 g, 0.222 mol; plus 25 mL of water). The pH of the resulting solution was found to be 4.65. Then 4-hydroxyspirohexane (0.210 g, 2.14 mmol) was added. The mixture was stirred at room temperature (23 °C) for 40 h. The aqueous reaction mixture was saturated with sodium chloride and extracted with diethyl ether (3 × 100 mL and 1 × 50 mL). The combined ethereal solution was dried over magnesium sulfate. After filtration, the ether was distilled through a 1 ft spiral wire column. VPC on a Carbowax 20M column at 130 °C showed two product peaks in addition to those in the solvent peak region. Peaks corresponding to 3-methylenecyclopentanol and cyclohexanone were not observed. The major product peak had the same retention time as that of the starting alcohol. The retention time of the minor product peak was shorter than those of the major one and cyclohexanone. The two fractions corresponding to the two peaks were collected by VPC (13 mg and 85 mg, respectively). The NMR spectrum (CCl_4 solution) of the major product was identical with that of 4-hydroxyspirohexane. The NMR spectrum (CCl_4 solution) of the minor product showed two symmetrical pairs of multiplets centered at δ 0.96, 1.30, 2.19, and 3.00. The pattern was identical with that of 4-hydroxyspirohexane. However, some other unidentifiable peaks were present with much weaker intensities at δ 0.68 and 0.45 (a symmetrical pair of doublets), 1.56 (singlet), 1.70 (singlet), 4.26 (triplet), 5.20 (multiplet), and 7.86 (singlet). The IR spectrum (CCl_4 solution) of the minor product resembled that of spirohexan-4-one except for the presence of two additional absorptions at 1725 and 1550 cm^{-1}.

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Registry No.—**5**, 21816-24-0; **6**, 20461-31-8; 4-spirohexanecarbonyl chloride, 66036-85-9; 5-spirohexanecarbonyl chloride, 66036-85-9; spirohexane, 157-45-9; oxalyl chloride, 79-37-8; ethyl 4-spirohexanecarboxylate, 66036-86-0; ethyl 5-spirohexanecarboxylate, 66036-86-0; 4-spirohexanecarboxylic acid hydrazide, 66036-87-1; β-naphthyl 4-spirohexanecarbamate, 66036-88-2; β-naphthol, 135-19-3; 5-spirohexanecarboxylic acid hydrazide, 66036-89-3; β-naphthyl 5-spirohexanecarbamate, 66036-88-2; 4-aminospirohexane, 38772-80-4; 4-hydroxyspirohexane, 21816-25-1; 5-aminospirohexane, 38772-81-5; 5-hydroxyspirohexane, 20054-19-7.

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Synthesis of Chlorolium Ion Precursors: Solvolysis of Halobutadienes[1a]

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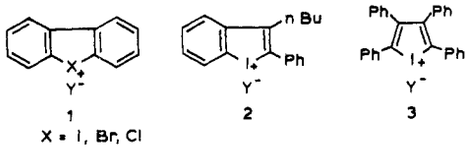
The *E,Z* and *Z,Z* isomers of 1-bromo-4-chloro-1,4-diphenyl-1,3-butadiene, 11*EZ* and 11*ZZ*, specifically deuterated in the 2 and 3 positions, were prepared. Silver-assisted solvolysis of 11*EZ* and 11*ZZ* in acetic acid and 11*EZ* in acetic anhydride gave a mixture of acetates 21*EZ* and 21*ZZ* and acetylene 9*Z*. The *E,E* isomer of 11 where chlorine participation is not possible and (*E*)-1-bromo-1-phenylpropene (29*E*) were solvolyzed in acetic acid with $AgBF_4$ to serve as model compounds. Using 29*E* deuterated in the 2 position, the isotope effect for acetylene formation from the vinyl cation was determined to be 2.0. Analysis of the deuterium distribution in the products from deuterated 11*EZ* led to the conclusion that 24 (in acetic acid) and 30% (in acetic anhydride) of the reaction proceeds through a chlorolium ion (13) intermediate. The isotope effect (k_H/k_D) for the deprotonation of 13 to give 9*Z* is 2.4 (in acetic acid) and 2.2 (in acetic anhydride). Similar results were obtained from the study of the solvolysis of 11*ZZ*. The vinyltriazenes 36*ZZ* from 11*ZZ* and its deuterated analogues were prepared and decomposed in situ with acetic acid. The deuterium content of the products showed that only 1% of the reaction involved a chlorolium ion. Even the vinyltriazene 37*ZZ* prepared from (*Z,Z*)-1-bromo-4-methylthio-1,4-diphenyl-1,3-butadiene showed little evidence (1%) of sulfur capture of the vinyl cation upon decomposition in acetic acid.

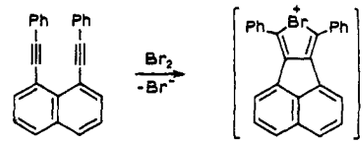
In contrast to the well studied group 7 heteroaromatic compounds furan, thiophene, selenophene, and even tellurophene, the chemistry of the analogous unsaturated halogen heterocycles, the halolium ions, has been little studied. Stable dibenzochlorolium, -bromolium, and -iodolium salts (1) were first prepared by Sandin and Hay.[2] More recently Beringer[3] has reported the synthesis of the benziodolium (2) and



1 2 3

X = I, Br, Cl

tetraphenyliodolium cations (3). A bromolium ion has been proposed by Bossenbroek and Shechter[4] as the intermediate in the bromination of 1,8-bis(phenylethynyl)naphthalene.



We report here the full details[1a] of our work on the ionization of halo- and triazenylbutadienes as a route to the 2,5-diphenylchlorolium ion (4) and related systems.

This approach to the halolium ion (4) involved the use of a halogen to trap a stabilized vinyl cation (5)[5] intramolecu-

4 5

X = Br, Cl

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