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REACTIONS OF DISPIRO[2.0.2.2]OCT-7-ENE. ELECTROPHILIC AND FREE RADICAL ADDITIONS†

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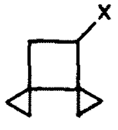
Abstract—Dispiro[2.0.2.2]oct-7-ene 1 was synthesized by debromination of *cis*- and *trans*-7,8-dibromodispiro[2.0.2.2]octane 3a with LAH and by dechlorination of *cis*- and *trans*-7,8-dichlorodispiro[2.0.2.2]octane 3b with magnesium. Stepwise electrophilic additions to 1 of HBr, HI, Br_2 and Cl_2 were studied. The major products (and yields) from these reactions were: 7-bromodispiro[2.0.2.2]octane 2a (43%), 4-iodo-4,5-ethanospiro[2.3]hexane 4b (*ca.* 50%); *trans*-3a (40%); and *cis*-3b (20%). Free-radical addition of hydrogen bromide to 1 gave an 80% yield of 7-bromodispiro[2.0.2.2]octane 2a. At −10°, hydroboration-oxidation of 1 was found to give mainly 7-hydroxydispiro[2.0.2.2]octane 2a in *ca.* 90% yield; at 25°, near equal amounts of 2c and 4-(2-hydroxyethyl)spiro[2.3]hex-4-ene 14 were obtained.

The highly strained molecule dispiro[2.0.2.2]oct-7-ene 1 is of interest, among other reasons, because "it possesses the minimum energy bisected geometry[1] in which the planes of both cyclopropane rings are normal to the nodal plane of the adjacent double bond. This should allow maximum interaction between the π system and the p-character bonds of the cyclopropane rings."[2] Because of similar geometrical considerations, 7-substituted dispiro[2.0.2.2]octanes 2 derivable from 1, as well as the transition states in their formation and reactions, are also of interest. In 1968, Dolbier, Lomas, and Tarrant reported the synthesis of 1 in >60% yield in 3 steps from 2,2-dichloromethylenecyclopropane,[2,3] which can be prepared in ~20% yield by addition of dichlorocarbene to allene.[2-4] Because of the tendency of 1 to polymerize, little has been learned of its chemistry[3] other than its remarkable but unsurprising thermal stability[2] and its straightforward ozonization.[2,3]


1



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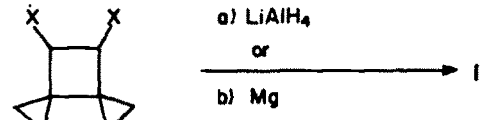
a, X = Br; b, X = I; c, X = OH

We have found that 1 can be prepared conveniently in 80% yield in 4 steps from methylenecyclopropane, which can be obtained in a high state of purity in 68% yield from relatively inexpensive β-methallyl chloride.[5] In following up an observation of Dolbier *et al.*,[3] we have also found that 1 is reasonably stable as a *ca.* 10% solution in common organic solvents. Consequently, we have been able to study some additional reactions of 1, which we describe here.

Dispiro[2.0.2.2]oct-7-ene 1 is prepared readily and in quantitative yield by treatment of *cis*- and *trans*-7,8-dibromodispiro[2.0.2.2]octane 3a[6] with lithium aluminum hydride (eqn 1a). Although the *trans* isomer undergoes more rapid conversion to 1, its reactivity is only slightly greater than that of the *cis* isomer. Consequently, 1 can be prepared conveniently by treating the mixture of *cis*- and *trans*-3 obtained directly from thermally-induced dimerization of bromomethylenecyclopropane.[6] Compound 1 can also be prepared in quantitative yield by dechlorination with magnesium in ether of *cis*- and *trans*-7,8-dichlorodispiro[2.0.2.2]octane 3b, the thermal dimerization of bromomethylenecyclopropane.[6] Compound 1 can also be prepared in quantitative yield by dechlorination with magnesium in ether of *cis*- and *trans*-7,8-dichlorodispiro[2.0.2.2] octane 3b, the thermal dimer of chloromethylenecyclopropane (eqn 16).[6] This reaction is somewhat less convenient than the preparation using the dibromide. A more important objection to this alternate route is that the yield of chloromethylenecyclopropane from methylenecyclopropane is much poorer than the yield of bromomethylenecyclopropane.[6]

(1)


3a, X=Br; 3b, X=Cl

Ionic additions of hydrogen bromide and hydrogen iodide to 1 in dry carbon tetrachloride gave mixtures of the corresponding 7-halodispiro[2.0.2.2]octane 2 and 4-halo-4,5-ethanospiro[2.3]hexane 4 in total yields of 75% and 60%, respectively (eqn 2). Interestingly, the dispiroöctane 2 was the major product from the addition of hydrogen bromide and the minor product from the addition of hydrogen iodide; the 2:4 product ratios throughout the reactions were 1.0:0.74 and 1.0:3.2. After they were isolated the iodides were noted to be relatively unstable compared with the bromides, and 7-iododispiro[2.0.2.2]octane 2b appeared to be more unstable than 4b.

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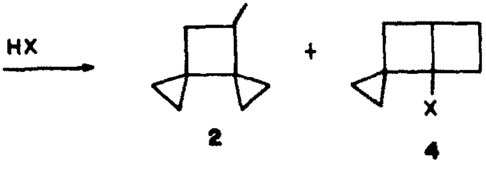

a, X=Br; b, X=I

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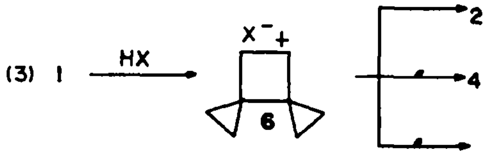
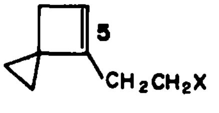
†Taken in part from the Ph.D. Dissertation of L. J. Cabral, University of California, Davis (1975).

7-Bromodispiro[2.0.2.2]octane **2a** has also been obtained from cycloaddition of methylenecyclopropane and bromomethylenecyclopropane.[6] The structural assignment to the iodide **2b** was made on the basis of its mass and ^{1}H NMR spectra, which were similar to those of **2a**. The mass and ^{1}HNMR spectra of **4a** and **4b** established that they had the same carbon skeleton and that they were isomers of **2a** and **2b**. In addition to the near symmetrical bands centered between δ 0.7 and 0.8 ppm due to the cyclopropyl protons (4H), the ^{1}H NMR spectra of **4a** and **4b** consisted of similar complex patterns between *ca.* δ 1.6 and 3.6 ppm (7H), which confirmed that they had no vinyl protons. In light of what is known about cyclopropylcarbinyl cation rearrangements,[7a] these data and the stability of the compounds in the presence of excess hydrogen halide seem consistent only with structure **4**.

Early in the reaction of **1** with hydrogen bromide (<10% conversion), a third product was noted with glpc retention time similar to that of **2a** and **4a**, and it constituted about 15% of the product mixture. As the reaction proceeded, the amount of this third product relative to **2a** and **4a** decreased until only a trace could be noted at the end of the reaction. This evidence of unsaturation leads us to conclude that the unstable product is 4-(2-bromoethyl)spiro[2.3]hex-4-ene **5a**, which can arise together with **2a** and **4a** from the cyclopropylcarbinyl-like ion pair (depicted as **6**) formed by proton transfer to **1** (eqn 3).[7]



a, X=Br b, X=I

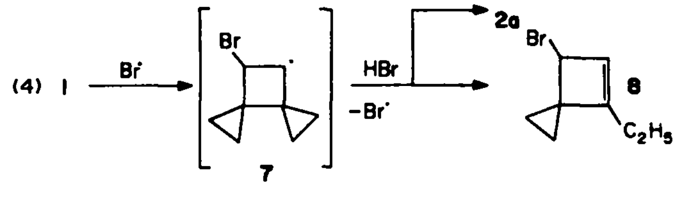


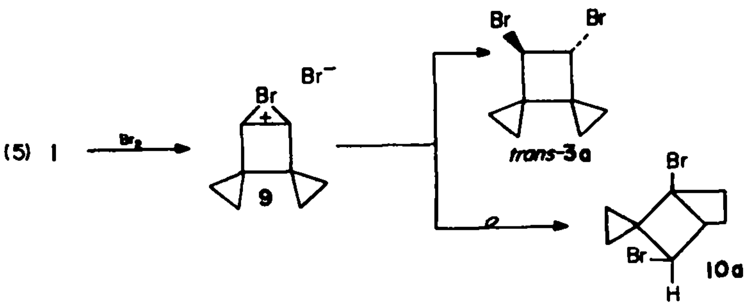
The 1-hydrogen iodide reaction mixture was also examined by glpc at low conversions of **1**, and no evidence was obtained to indicate the presence of iodide **5b**. These observations require that **5b**, if formed, is significantly more nucleophilic than **1**. In this regard, **1** did not react with hydrogen chloride in dry carbon tetrachloride at 0° or 60°. The dispiroöctene **1** would be expected to form **6**, as opposed to a delocalized ion pair, more easily with hydrogen iodide than with hydrogen bromide; and once **6** were formed, the iodide would be expected to collapse to 7-halodispiro[2.0.2.2]octane **2** more readily than the bromide. In other words, reaction of **1** *via* **6** should give less rearrangement with hydrogen iodide than with hydrogen bromide. Conceivably, some proton transfer is assisted by a cyclopropyl ring to give a delocalized ion pair directly. More assistance would be required for proton transfer from hydrogen bromide than from hydrogen iodide, and again addition via this pathway would give more rearrangement with hydrogen bromide. The results can be rationalized as follows. Reaction of **1** with hydrogen iodide occurs mainly by a bimolecular route to give **6b**, which undergoes extensive rearrangement; with hydrogen bromide, reaction occurs in large part by a trimolecular process in which proton and bromide ion transfer occur simultaneously. Determination of the stereochemistry of addition of the deuterium halides to **1** would provide one test of this rationalization.

Free-radical addition of hydrogen bromide in the presence of benzoyl peroxide to **1** gave 7-bromodispiro[2.0.2.2]octane **2a** in 80% yield together with small amounts of 2 other products with similar glpc retention times. The ratio of these minor products changed from 1:5 at 10% conversion of **1** to 1:0.5 at 95% conversion, while the ratio of **2a** to what was at first the minor side product remained constant throughout the reaction at *ca.* 50:1. (This shows that very little if any of the **2a** formed in the previously described reaction of **1** with hydrogen bromide arises by a free-radical pathway.) In light of what is known of the behavior of cyclopropylcarbinyl free radicals,[8] it seems likely that the unstable minor product is 6-bromo-4-ethylspiro[2.3]hex-4-ene **8**, which can be formed by rearrangement of the initially-formed cyclopropylcarbinyl-like free radical **7** (eqn 4). The stable minor product was not characterized beyond observation of its glpc behavior, which was very similar to that of **4a** relative to **2a**.

Bromination of dispiro[2.0.2.2]oct-7-ene **1** in pentane at either −75° or 0° yielded about 40% *trans*-7,8-dibromodispiro[2.0.2.2]octane **3a** and 30% of an isomer (mass spectra) with 4 cyclopropyl protons and no vinyl protons (^{1}H NMR). In addition, the presence of at least 7 minor products was noted by glpc examination of the concentrated reaction mixture. The only one of these minor products that was tentatively identified was *cis*-**3a** (glpc), and its yield was estimated as <3%. The stereoselectivity seen in this reaction indicates that most of the reaction occurs via the cyclic bromonium ion **9**, as is typically obtained from electrophilic attack of bromine on a double bond (eqn 5).[7b] Attack in a *trans* manner on **9** by bromide ion provides the best explanation for the large *trans* : *cis*-**3a** product ratio. An alternative mode of attack on the bromonium ion center is by the cyclopropyl ring from the side opposite the bromine. Such a route, assisted or followed by attack of bromide ion, would lead to *cis*-4,6-dibromo-4,5-ethanospiro[2.3]hexane **10a** (eqn 5), which we believe is the structure of the second major product.

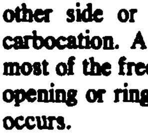
Chlorination of **1** was carried out in carbon tetrachloride in the presence of oxygen[9] at both −75° and 0°, and these reactions gave at least 10 products with glpc retention times similar to or identical with those of *cis*- and *trans*-7,8-dichlorodispiro[2.0.2.2]octane **3b**.[6] For comparable conversions of **1**, the product compositions at the 2 temperatures were very similar. Of the 10 products observed by glpc, 4 were unstable under the





reaction conditions and are presumed to be unsaturated. At conversions of **1** of 75% or less, 5 of the products, including 2 that were unstable under the reaction conditions, each made up at least 10% of the product mixture. The only 2 products that were identified were *cis*-7,8-dichlorodispiro[2.0.2.2]octane (*cis*-**3b**), the major product, and its *trans* isomer. At the conclusion of the reaction at 0° (75% conversion of **1**), *cis*- and *trans*-**3b** accounted for 30% and 4%, respectively, of the product mixture, and their yields were estimated by NMR as 20% and 3%.

The observation that about 7 times as much *cis*-7,8-dichlorodispiro[2.0.2.2]octane (*cis*-**3b**) was formed as *trans*-**3b** is most significant. A simple carbocation mechanism involving an intermediate that can be pictured most simply as **11** is ruled out because it would give at least as much *trans*- as *cis*-**3b**. Intermediacy of a cyclic chloronium ion **12** similar to **9** would favor the formation of *trans*-**3b** even more. The most reasonable explanation for the large *cis* : *trans*-**3b** ratio is that an ion pair **13** is formed which collapses[10] to form *cis*-**3b** to an appreciable extent before the chloride ion diffuses to the other side or away from the cyclopropylcarbinyl-like carbocation. A complete explanation also requires that most of the free carbocations formed undergo either ring opening or ring expansion before attack by chloride ion occurs.



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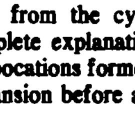

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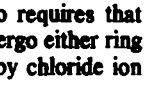

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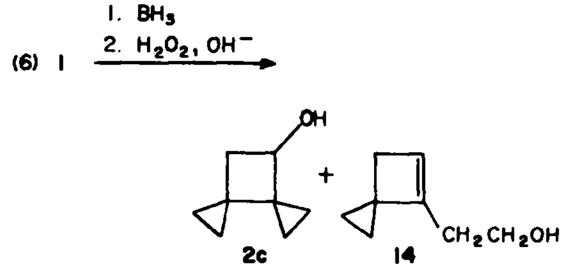
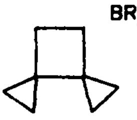
Hydroboration-oxidation of **1** at 25° gave a 90% yield of a near equal mixture of 7-hydroxydispiro[2.0.2.2]octane **2c** and 4-(2-hydroxyethyl)spiro[2.3]hex-4-ene **14** (eqn 6). The 60-MHz ^1H NMR spectrum of **2c**, which is similar to that of 7-chlorodispiro[2.0.2.2]octane[6] and the corresponding bromide **2a** and iodide **2b**, consisted of complex cyclopropyl proton resonances at δ −0.25 to 0.90 ppm, the variable OH proton resonance at *ca* 2.8 ppm, the C_8-proton resonances interpretable as the AB part of an ABM pattern, δ_A 2.39, δ_B 2.21 ppm, $J_{AB} = |11|$ Hz,[11] $J_{AM} = 6.5$ Hz,[11] $J_{BM} = 6.0$ Hz,[11] and the C_7-proton resonance, a broadened apparent triplet at δ 4.31 ppm. That of **14** consisted of a broadened single line at δ 0.68 ppm due to the cyclopropyl protons, the variable OH proton resonance at *ca.* 2.7 ppm, finely split bands at δ 2.40–2.55 and 5.70–5.80 ppm due respectively to the C_6- and C_5-protons, and triplets, $J = 6.6$ Hz, at δ 2.00 and 3.56 ppm due respectively to the β- and α-protons of the 2-hydroxyethyl group; the triplet at δ 2.00 ppm was finely split, $J \approx 1.8$ Hz,by across-the-ring coupling with the C_6 protons.[12]



When the hydroboration-oxidation reaction of **1** was carried out at −5° to −10° rather than 25°, the yield remained high (>90%), but the **2c** : **14** product ratio was *ca.* 20 : 1 rather than *ca.* 1 : 1. Apparently the tri(7-dispiro[2.0.2.2]octyl)borane isomerizes in part at the higher temperature to the borane corresponding to **14**, probably *via* the cyclopropylcarbinyl-like free radical **15**.[8] Variation in the time between the hydroboration and oxidation steps from 1 to 24 hr at 25° did not change the **2c** : **14** product ratio. In this regard, hydroboration of methylenecyclopropane with tetraethyldiborane at below 0° has been observed to give diethyl(cyclopropylmethyl)borane, which isomerizes rapidly at room temperature to diethyl-3-butenyl-borane.[13]



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Bromohydration with N-bromosuccinimide in water and oxymercuration-reduction reactions of **1** were also carried out. Because of the complexity of the product mixtures, they were given only cursory examination. Details of these reactions, as well as of the attempts to add hydrogen chloride to **1**, are given elsewhere.[14]

EXPERIMENTAL

Temps are uncorrected. NMR spectra were obtained at 60 MHz with a Varian Associates A-60A system; NMR spectra of purified compounds were taken of 10–20% solns in CCl_4 containing 1–2% TMS. Routine low-resolution mass spectra were determined with a Consolidated Electrodynamics Corporation Type 21-104 Mass Spectrometer by Mr. J. L. Voth; high resolution mass spectral analyses for exact mass determinations were obtained with a Varian M-66 mass spectrometer by Mr. K. Miyano. Selected values of *m/e* are given; the complete mass spectra are recorded elsewhere.[14] Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona. Glpc work was done with a Varian Aerograph Model 90-P gas chromatograph. Columns used were: *A*—5′ 20% Carbowax 20 M; *B*—3′ 20% FFAP; *C*—10′ 20% FFAP; *D*—5′ 20% FFAP. Columns were 3/8″ o.d., and 30/60 Chromosorb W was the solid support. THF was distilled from LAH through a column packed with glass helices immediately before use. Other distillations were carried out using a 45 × 0.9 cm Nester-Faust spinning band column with platinum band. Preparative reactions were run under a positive N_2 atmosphere.

Dispiro[2.0.2.2]*oct-7-ene* (1)

(A) *Debromination of* cis- *and* trans-7,8-*dibromodispiro*[2.0.2.2]*octane with lithium aluminum hydride in ether.* To a magnetically-stirred soln of 0.596 g (2.26 mmole) of *trans*-7,8-dibromodispiro[2.0.2.2]octane[6] in 3.0 ml of dry ether contained in a 15-ml flask equipped with an ice-water cooled condenser was added, in *ca.* 1 equiv portions, 3.8 ml of a 0.75 M soln of LAH (2.83 mmoles, 5 equiv). Examination of the mixture by glpc (Column *C* at 150° and 80°) indicated that all of the dibromide had reacted to give a single volatile product, the dispiroöctene 1. Water (0.5 ml) was added dropwise to destroy the excess LAH and the mixture was rinsed into a separatory funnel with ether. The ether soln was washed with 10^{-3} N HCl (30 ml) and ice water (3 × 40 ml), dried (K_2CO_3), and concentrated by distillation of most of the ether. Compound 1 (0.16 g, 67%) was isolated by prep glpc of the residue (Column *A* at 80°): NMR δ 5.95 (s, 2H) and 0.15–0.80 (m, symm about δ 0.47 ppm, 8H) (lit.[3] NMR δ 6.13 (s, 2H), 0.73 (symm m, 4H), and 0.47 ppm (symm m, 4H); ms, *m/e* (rel intensity) 107 (1.6), 106 (18), 105 (25), 91 (100), 79 (32), 78 (36), 77 (29), 39 (47), 27 (36).

Use of the same procedure with 0.28 g of *cis*-7,8-dibromodispiro[2.0.2.2]octane[6] and *ca.* 7 equiv of LAH gave an apparently quantitative conversion (glpc) to 1.

A preparative scale reaction was carried out with 6.67 g of 0.9:1.0 mixture of *cis*- and *trans*-7,8-dibromodispiro[2.0.2.2]octane.[6] Aliquots were taken from time to time, at least 30 min following the addn of LAH, and examined by glpc. The *cis*:*trans* ratio rose during the course of the reaction, and virtually all of the *trans* isomer had reacted following the addition of 6 equiv of LAH. An additional 2 equiv of LAH was required to bring about complete reaction of the remaining *cis*-dibromide. Both NMR and glpc analysis indicated that the 2 isomers were converted quantitatively to 1.

(B) *Dechlorination of* cis- *and* trans-7,8-*dichlorodispiro*[2.0.2.2]*octane with magnesium in ether.* To a 15-ml, 2-necked flask equipped with magnetic stirrer, serum-capped entry port, and ice-water cooled condenser, was added 0.354 g (2.0 mmole) of *trans*-7,8-dichlorodispiro[2.0.2.2]octane[6] and 7 ml of dry ether. Mg turnings (0.243 g, 10 mmole) were added, and the mixture was stirred vigorously. After 1 hr, glpc analysis (Column *D* at 148°) indicated that no reaction had occurred. Ether together with a few Mg turnings, which had been activated by the addition of a drop of 1,2-dibromoethane, were then added to the stirred mixture. Shortly afterwards, glpc analysis indicated that some 1 had formed. Several more additions of Mg turnings that had been activated in the same way were made during the next 2 days until conversion of the dichloride to the dispiroöctene was complete. The mixture was filtered, and the filtrate was rinsed into a separatory funnel with ether. The ether soln was washed several times with ice water, dried ($MgSO_4$), and concentrated by distillation of most of the ether. Analysis of the residue by NMR and glpc indicated that the dichloride had been converted quantitatively to 1.

In the same manner, 0.243 g of *cis*-7,8-dichlorodispiro[2.0.2.2]octane was converted quantitatively in 2 days to 1.

A prep scale reaction was carried out with 10.6 g of a 0.9:1.0 mixture of *cis*- and *trans*-7,8-dichlorodispiro[2.0.2.2]octane in 150 ml of dry ether. Over a period of 3 days, portions of *ca.* 0.5 g of Mg turnings, which had been activated by addition to 0.1 ml of 1,2-dibromoethane in 2 ml of ether, were added from time to time until the reaction was complete. There appeared to be no significant difference in the reactivity of the 2 isomers with Mg. The mixture was worked up in the usual manner, and NMR and glpc analysis indicated that 1 was formed in >90% yield.

Stability of 1 *in solution.* A *ca.* 40% soln of 1 in ether was separated by prep glpc (Column *C* at 80°), and 1 was collected directly in dry pentane until the soln was 14.0 mole % in 1. The soln was transferred to an NMR tube, benzene to 4.0 mole % was added, and the tube was sealed. No change detectable by NMR occurred in the amount of dispiroöctene in 10 days.

In the same way, a 9.5 mole % soln of 1 in THF was prepared. Benzene to 2.5 mole % was added. No change detectable by NMR occurred in the amount of 1 in 10 days.

A *ca.* 40 mole % soln of 1 containing a pellet of KOH was allowed to stand at −4° for 12 months. The soln deposited a small amount of white solid, but glpc examination (Column *C* at 80°) failed to show the presence of any volatile component other than ether and 1.

Reactions of 1.

(A) *Free radical addition of hydrogen bromide.* In a 25-ml, 3-necked flask equipped with serum-capped entry port, ice-water cooled condenser, thermometer, and magnetic stirrer, was placed 0.316 g (3.0 mmole) of freshly purified 1 in 12 ml dry CCl_4 and 21 mg (0.15 mmole) benzoyl peroxide. Anhyd HBr was passed slowly into the mixture, and the extent of reaction was monitored closely by glpc analysis (Column *D* at 115°) of removed aliquots. At 10% conversion of 1, 3 products with similar retention times were noted in relative amounts of *ca.* 0.2:10:1. The relative amounts of products remained constant until about 70% conversion, when the relative amount of the more abundant minor product began to decrease. At 85% conversion, the relative amounts were *ca.* 0.2:10:0.5, and at 95% conversion, when the addition of HBr was stopped, the relative amounts were *ca.* 0.2:10:0.1. Most of the CCl_4 was removed by distillation, and the major product was isolated by prep glpc (Column *D* at 115°) and shown to be identical with 2a;[6] its yield, estimated by glpc, was 80%.

(B) *Ionic addition of hydrogen bromide.* A reaction similar to that described under A was carried out, *except* 15 mg of hydroquinone was used in place of benzoyl peroxide, and the mixture was cooled below 0° with an ice salt bath. At <10% conversion of the dispiroöctene 1, 3 products were observed with similar retention times in the relative amounts of *ca.* 7:10:3. As the reaction proceeded, the relative amounts of the 2 major products remained constant (0.74:1.0), but the relative amount of the minor product decreased until it was barely detectable at >98% conversion. The 2 remaining products were isolated by prep glpc (Column *D* at 105°) and identified as 2a (the major product) and 4a. The total yield of these 2 products, estimated by glpc and NMR, was 75%.

4-Bromo-4,5-ethanospiro[2.3]*hexane* 4a. NMR δ 1.60–3.53 (m's, 7H), 0.50–1.02 ppm (m, 4H); ms, *m/e* (rel intensity) 188 (0.8), 186 (0.8), 107 (59), 91 (7.5), 79 (100), 77 (57), 65 (49), 62 (69), 53 (30), 51 (56), 41 (36); exact mass, 186.0048 (Calc. for $C_8H_{11}Br^{79}$ 186.0045); C, 51.34; H, 5.66; Br, 42.03 ($C_8H_{11}Br$ requires: C, 51.36; H, 5.93; Br, 42.71).

(C) *Addition of hydrogen iodide.* A reaction similar to that described under B was carried out, except that anhyd HI was used in place of HBr. Early in the reaction, 2 products in the ratio of 3.2:1 with similar retention times were noted by glpc (Column *D* at 110°), and this ratio remained constant throughout the reaction. On concentration of the CCl_4 mixture, a small amount of dark tar separated. The two products were isolated by prep glpc and identified as 4b, the major product, and 2b. The yields, estimated by glpc, were *ca.* 50% and 15%. Both products decomposed slowly on standing.

4-Iodo-4,5-ethanospiro[2.3]*hexane* 4b. NMR δ 1.53–3.65 (m's 7H), 0.55–0.95 ppm (m, 4H); ms, *m/e* (rel intensity) 234 (0.2), 107 (40), 91 (60), 79 (100), 77 (47), 67 (26), 65 (27), 53 (32), 51 (41), 41 (44); exact mass, 233.9921 (Calc. for $C_8H_{11}I$, 233.9905). I, 54.21% ($C_8H_{11}I$ requires I, 54.35%).

7-Iododispiro[2.0.2.2]*octane* **2b**. NMR δ 4.78 (app t, J = 7.0 Hz, 1H), 2.65–2.95 (m, 2H), 0.10–1.05 ppm (m, 8H); ms, *m/e* (rel intensity) 234 (2.9), 107 (47), 91 (70), 78 (26), 77 (48), 53 (30), 51 (41); exact mass, 233.9919. An elemental analysis was not obtained.

(D) *Addition of bromine.* In a 100-ml, 3-necked flask equipped with serum-capped entry port, cold finger condenser cooled with dry ice-acetone, low temp thermometer, and magnetic stirrer, was placed 0.316 g (3.0 mmole) of **1** in 50 ml of "unsaturate-free" pentane. The stirred soln was cooled to −75° with a dry ice-acetone bath, and 162 μl (1.0 equiv) of Br_2 in 5 ml pentane was added slowly by syringe. The Br_2 color was discharged immediately on addition. The reaction was monitored by glpc (Column *B* at 120°), and a very slight amount of **1** remained unreacted when addition was complete. The soln was allowed to warm to room temp., and most of the pentane was removed by distillation. Analysis of the residue by glpc showed the presence of 2 major products together with at least 7 minor ones. The 2 major products were isolated by prep glpc (Column *A* at 130°) and identified as *trans*-7,8-dibromodispiro[2.0.2.2]octane[6] and *cis*-4,6-dibromo-4,5-ethanospiro[2.3]hexane **10a**; the respective yields, estimated by glpc, were40% and 30%. The yield of *cis*-7,8-dibromodispiro[2.0.2.2]octane was estimated as <3%.

A reaction was also carried out by the portionwise addition of 150 μl (*ca.* 0.9 equiv) of Br_2 in 2 ml CCl_4 to 0.316 g (3.0 mmole) of **1** in 10 ml of CCl_4 at 0°. Glpc analysis of the concentrated CCl_4 soln indicated that the product composition was very similar to that obtained in pentane at −75°.

cis-*4,6-Dibromo-4,5-ethanospiro*[2.3]*hexane* **10a**. NMR δ 4.33 (s, 1H), 3.30–3.65 (m, 1H), 1.90–3.00 (m, 4H), 1.15 ppm (broad s, 4H); ms, *m/e* (rel intensity) 268 (0.1), 266 (0.2), 264 (0.1), 187 (3.6), 186 (2.0), 185 (3.8), 184 (1.7), 105 (100), 91 (29), 79 (27), 78 (22), 77 (32), 51 (38), 39 (28), 27 (27). An elemental analysis was not obtained.

(E) *Addition of chlorine. At 0°*. A *ca.* 1:1 mixture of Cl_2 and O_2[10] was passed slowly into a stirred soln of 0.316 g (3.0 mmole) of **1** in 12 ml of dry CCl_4 at below 0° and in the dark. The extent of reaction was monitored by glpc analysis (Column *D* at 145°) of removed aliquots, and the addition of Cl_2 and O_2 was stopped when about 25% of the original dispiroöctene remained unreacted. Most of the CCl_4 was removed by distillation. Glpc analysis of the residue indicated the presence of at least 10 products, all of which had retention times similar to or identical with those of *cis*- and *trans*-**3b**.[6] Of these products, each of 4 appeared to make up 10–15% of the product mixture, and the major product, subsequently isolated by prep glpc (Column *D* at 140°) and identified (NMR) as *cis*-**3b** appeared to make up 30% of the product mixture. A minor product with the same retention time as *trans*-**3b** made up about 4% of the product mixture. The yields of *cis*- and *trans*-**3b**, as estimated by NMR examination of the concentrated reaction mixture, were 20% and 3%, respectively.

At −75°. A similar reaction of 0.316 g of **1** was carried out at −75° in a mixture of 6 ml of $CHCl_3$ and 6 ml of CCl_4. The extent of the reaction was closely monitored by glpc analysis of aliquots, and addition of Cl_2 and O_2 was stopped when only a very small amount (<5%) of **1** remained unreacted. Comparison of the product compositions during the course of the reaction with those for the reaction at 0° showed that they were very similar at similar conversions of **1**. The relative amounts of 6 of the products, including *cis*- and *trans*-**3b**, remained reasonably constant throughout the reaction, but the relative amounts of 4 others, including 2 of the 4 important minor products observed at 0°, decreased substantially during the last stages of the reaction. The yields of *cis*- and *trans*-**3b** were estimated by NMR analysis of the concentrated reaction mixture as 15% and 2%, respectively.

(F) *Hydroboration-oxidation at 25°*. To a stirred soln of 0.233 g (2.22 mmole) of **1** in 2 ml of THF at room temp. was added dropwise 0.33 ml (2.22 mmole B-H, 1 equiv) of a 1.95 M soln of borane in THF. Addition of the borane soln caused a slight foaming of the mixture. The mixture was stirred for an additional hr, and 0.27 ml of 3N NaOH and 0.27 ml of 30% H_2O_2 were added in succession. The addition of the peroxide caused a slight foaming and the formation of a white ppt. After the mixture was stirred for an hr, it was added to 15 ml of ether. The ether soln was extracted with satd NaCl soln (6 × 10 ml) and dried ($MgSO_4$). Most of the ether was removed by distillation, and glpc analysis (Column *A* at 150°) of the residue showed the presence of a small amount of unreacted dispirooctene together with 2 major products in nearly equal amounts. The products were isolated by prep glpc and identified as **2c** and **14**. The 2 major products made up >97% of the product mixture, as estimated by glpc, and their combined yield, estimated by glpc and NMR, was *ca.* 90%. A repetition of the reaction, but with an interval of 24 hr between the hydroboration and oxidation steps, gave essentially the same results.

7-Hydroxydispiro[2.0.2.2]*octane* **2c**. NMR δ 4.31 (app t, $J \approx$ 6.5 Hz, 1 H), 2.8 var (s, 1 H), 2.02–2.58 (AB part of ABM pattern, δ_A 2.39, δ_B 2.21 ppm, J_{AB} = 11.0 Hz, J_{AM} = 6.5 Hz, J_{BM} = 6.0 Hz), and −0.25–0.90 ppm (m, 8 H); ms, *m/e* (rel intensity) 124 (2.4), 123 (4.2), 109 (23), 107 (2.7), 96 (61), 95 (50), 91 (49), 81 (42), 79 (61), 77 (44), 67 (51), 65 (27), 55 (44), 53 (52), 52 (29), 51 (43), 41 (66), 29 (36), 27 (72); C, 77.36; H, 9.63 ($C_8H_{12}O$ requires C, 77.37; H, 9.74).

4-(2-Hydroxyethyl)spiro[2.3]*hex-4-ene* **14**. NMR δ 5.70–5.80 (m, 1 H), 3.56 (t, J = 6.6 Hz, 2H), 2.7 var (s, 1 H), 2.40–2.55 (m, 2 H), 2.00 (t, $J \approx$ 6.6 Hz, with fine structure, $J \approx$ 1.8 Hz), and 0.68 ppm (broad s, 4H); ms, *m/e* (rel intensity) 124 (6.3), 123 (2.8), 93 (41), 91 (100), 79 (71), 78 (53), 77 (78), 65 (34), 55 (30), 54 (25), 53 (44), 51 (42), 50 (25), 41 (42), 39 (82), 31 (40), 29 (28), 27 (63). An elemental analysis was not obtained.

At −10°. A similar reaction sequence was carried out at −10 to −5° with 0.17 g (1.58 mmole) of **1** in 1.5 ml of THF, 0.262 ml of a 2.01 M borane in THF soln (1.58 mmole B-H, 1 equiv), 0.30 ml of 3 N NaOH, and 0.30 ml of 30% H_2O_2. Glpc and NMR analysis of the concentrated ether soln indicated that the **2c**:**14** ratio was *ca.* 20:1, and that the yield of **2c** was 90%.

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