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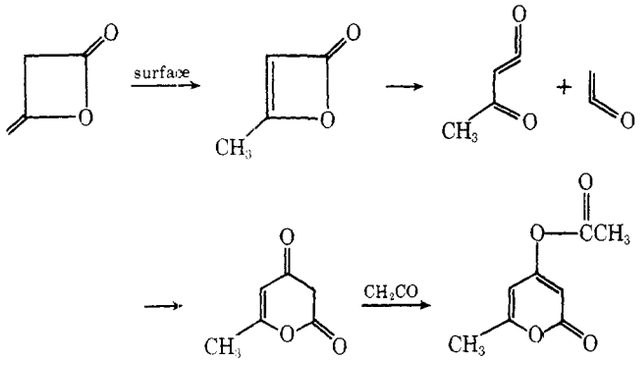

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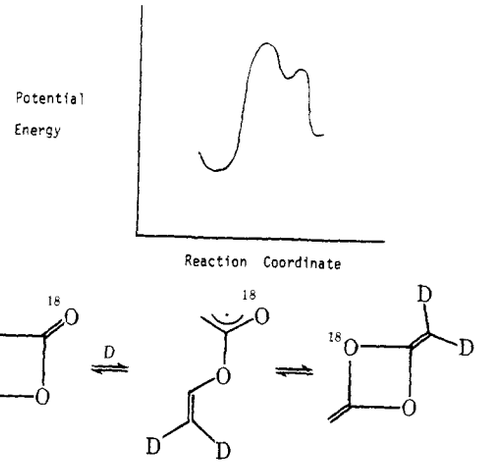

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Bridged Polycyclic Compounds. 86. Multiple Mechanisms in the Reactions of Some Bridged Alcohols with Triphenylphosphine and Carbon Tetrachloride[1]

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Reactions of several isomeric benzobicyclooctadienyl alcohols and dibenzobicyclononatrienyl alcohols with triphenylphosphine–carbon tetrachloride reagent demonstrate that these alcohol to chloride transformations are much more complex than originally proposed. Products from these and from deuterium-labeled alcohols show that direct displacements, Wagner–Meerwein rearrangement displacements, and allylic rearrangement displacements all occur. The reactions are rationalized as involving competitions between S_N2, S_N1, and S_Ni' or S_N2' processes.

Since the discovery[2] of the use of triarylphosphine dihalides in the ready conversion of alcohols to alkyl halides without rearrangement,[2,3b] and with clean inversion of configuration in the reaction of menthol to give neomenthyl halides, there has been considerable use of these reagents.[3] A mixture of triphenylphosphine and carbon tetrachloride was found[4] to cause transformations analogous to triphenylphosphine dichloride, under rather mild conditions. Although the initial papers[2] describing the use of the dichloride reported clean stereochemistry and thus the intervention of a direct displacement mechanism in the attack of chloride ion on the $ROPPh_3Cl$ intermediate,[2,3c] later work suggested alternative mechanistic possibilities. Thus, the lack of inversion (and loss of optical activity) in treatment[3e] of (+)-*exo*-norborneol with

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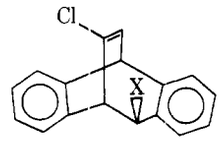
triphenylphosphine dibromide makes clear the possibility of intervention of carbenium ion processes in some cases. Similarly, while it has been found[5] that treatment of alcohols with triphenylphosphine–carbon tetrachloride generally leads to reaction with inversion, in certain cases[5] evidence for carbenium ion intermediates was again noted.

Snyder[5d] showed that the triphenylphosphine–carbon tetrachloride reagent could be utilized with allylic alcohols and that crotyl alcohol was converted cleanly (without allylic rearrangement) to crotyl chloride. α-Methylallyl alcohol did not lead to as clean a product, giving 89% α-methylallyl chloride (allylic retention) and 11% crotyl chloride (allylic inversion).

Our interest in the chemistry and photochemistry of organic halides[6] and our associated need to prepare isotopically labeled compounds of known structure and/or stereochemistry prompted us to investigate this reagent in a number of systems prone to give mixtures and/or rearrangements, in the hope that carbenium ion processes could be avoided. The results and our rationalization of these results are reported in this paper.

Complete reaction of the exo alcohol **1**-OH with triphenylphosphine–carbon tetrachloride required 36 h at 65 °C and gave a product that, by ^{1}H NMR analysis, contained about 20% exo chloride **1**-Cl, but was principally the endo chloride **2**-Cl. Thus inversion of configuration was the principal stereochemical outcome. When the reaction was carried out in 50:50 (by volume) carbon tetrachloride–acetonitrile, the rate, as anticipated,[4c] increased markedly, and the reaction was complete in 2 h at room temperature. The reaction similarly gave mostly (ca. 80%) inverted chloride **2**-Cl. When the endo alcohol (**2**-OH) was used, the product mixture comprised 75% exo chloride **1**-Cl and 25% endo chloride **2**-Cl in CCl_4–acetonitrile. In none of these cases was the Wagner–Meerwein product **3**-Cl or the cyclopropylcarbinyl chloride **4**-Cl observed



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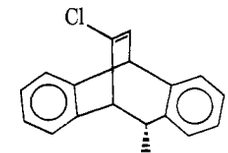

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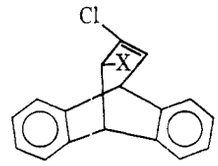

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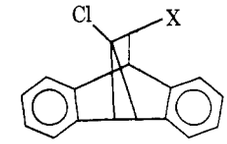
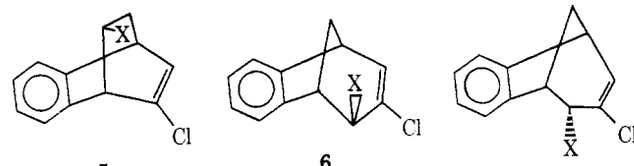


4

(these are thermodynamically more stable than **1**-Cl and **2**-Cl[7]).

When the allylic alcohol **3**-OH, which is related by a Wagner–Meerwein shift to **1** and to **2**, was treated with the reagent, the principal product (55–75%) was the allylic chloride **3**-Cl, but substantial amounts of the rearranged isomer **2**-Cl (and lesser amounts of **1**-Cl) were found. It has been noted[7] that kinetically controlled capture of the cationic manifold produced from species related to **1**, **2**, **3** (and **4**, as well) gives mixtures of the benzylic species **1** and **2**. This is consistent with the results we now report, if we assume that the allylic product **3**-Cl comes from some direct displacement process or processes, while the benzylic products are the result of some cationic-intermediate process (see below for further elaboration).

We have also studied the system represented by the isomers **5**, **6**, and **7**. In this system,[8] carbenium ions produced from **5**, **6**, or **7** are captured predominantly as **6** species, thermodynamic control leads predominantly to **5** species, and mixing of this system with **8** and **9** species is not observed in cationic processes. When **5**-OH was treated with the reagent in 50:50 carbon tetrachloride–acetonitrile at room temperature, we observed (^{1}H NMR) the alkoxychlorotriphenylphosphorane,[9] **5**-$OPPh_3Cl$, that is, the intermediate with unrearranged carbon skeleton.[10] Warming to 70 °C gave clean conversion to **6**-Cl, the result of anti bond migration and exo capture of chloride ion. When **6**-OH was treated with triphenylphosphine in carbon tetrachloride at reflux, the reaction similarly gave only **6**-Cl, no epimeric **7**-Cl (or **5**-Cl) being formed. With **7**-OH at room temperature only **6**-Cl was formed, as was the case when the reaction was carried out at 70 °C. Again no **5**-Cl or **7**-Cl was found.



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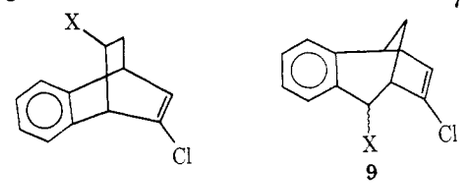
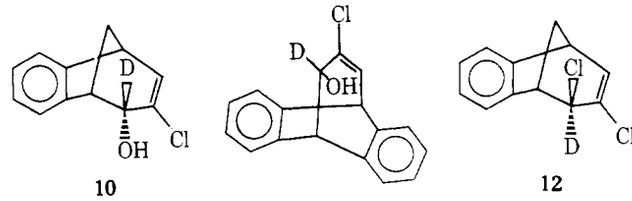
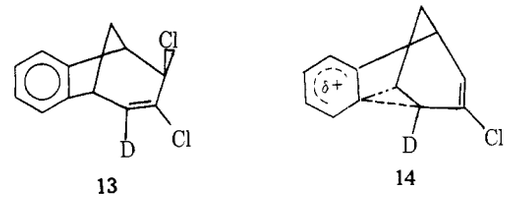


8 9

In order to develop our knowledge of these reactions further, and in the hope of preparing labeled compounds for our other work, we investigated the reactions of the deuterated alcohols **10** and **11**. **10** was prepared by reaction of the corresponding ketone with lithium aluminum deuteride; the deuterium transfer was completely from the exo side; no exo alcohol was produced.



10 11 12

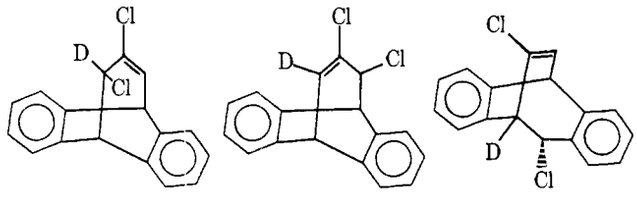


13 14

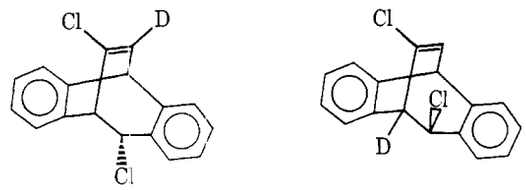
When **10** was treated with triphenylphosphine in carbon tetrachloride, as with the undeuterated alcohol **7**-OH, only the exo chloride resulted. It was a mixture comprising about 80% of **12** and 20% of **13**. The reaction thus does not exhibit either the clean inversion without allylic rearrangement anticipated for an S_N2 reaction or the relatively complete scrambling of deuterium anticipated for a free allylic cationic intermediate. The absence of endo chloride rules out any S_Ni' process.[12] We conclude therefore that the reaction involves a combination of S_N2 and S_N1 processes or perhaps includes some process involving a delocalized ion such as **14**, to rationalize the preponderance of **12** over **13**.

Use of **11** as substrate offers the advantage over **10** that carbenium ion reactions lead to Wagner–Meerwein rearrangement products, but has the drawback that the two faces

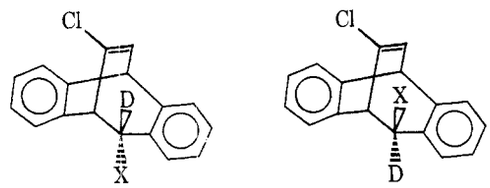
of the allylic cation are indistinguishable. When **11** was treated with triphenylphosphine in carbon tetrachloride at reflux, the product mixture was largely allylic chloride, with some replacement at the initial carbinol carbon atom, but principally with replacement by allylic rearrangement (i.e., about 3:1 of **16**:**15**). Little deuterium scrambling was seen in the benzylic chlorides, as well, where bond migration to the initial carbinol carbon atom to give **17** rather than to the other end of the allylic system to give **18** predominated by a large factor. Just as with **3**-OH, the endo chloride **17** was produced in greater amount than the exo chloride **19.**



15 **16** **17**

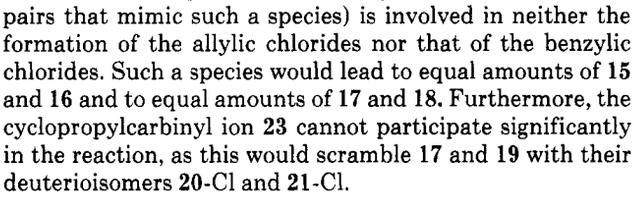


18 **19**



20 **21**

Lack of stereochemical information on the reactions of **11**, that is, whether the formations of **15** and **16** proceed with stereochemical retention or inversion, precludes precise definition of reaction mechanisms. Nevertheless, certain aspects are clear. First, a symmetrical free allylic ion **22** (or a set of ion pairs that mimic such a species) is involved in neither the formation of the allylic chlorides nor that of the benzylic chlorides. Such a species would lead to equal amounts of **15** and **16** and to equal amounts of **17** and **18.** Furthermore, the cyclopropylcarbinyl ion **23** cannot participate significantly in the reaction, as this would scramble **17** and **19** with their deuterioisomers **20**-Cl and **21**-Cl.

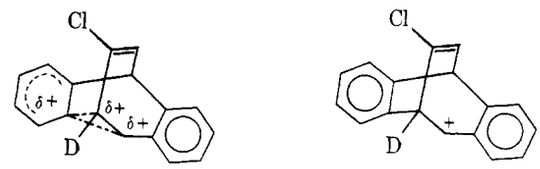


22 **23** **24**

When **20**-OH was treated with the reagent in acetonitrile, it was converted to a 1:3 mixture of **20**-Cl and **21**-Cl. Again the deuterium label was retained at C-4 (within experimental error, **17** and **19** were absent), so that ion **23** was not involved in these transformations either.

It would appear to us most conservative to assume that **15** is produced via an S_N2 reaction on the phosphorane from **11** (and that it probably has a configuration opposite to that shown) and that **16** results from an S_Ni' reaction (and that the configuration shown is correct). When the S_Ni' reaction, which has been noted earlier with allylic alcohols and thionyl chloride, was first discussed,[12] the question was raised about whether the reaction was concerned, with a six-membered transition state, or involved a carbocationic intermediate. We favor the former (**24**) in our example, since, as mentioned above, we assume that the cationic intermediate would lead almost exclusively to benzylic isomers. Clearly we cannot distinguish this mechanism from an S_N2' process[13] in which the phosphorus–chlorine bond is ionized prior to carbon–chlorine bond formation.[14]

We suggest ion **25** as the intermediate leading from the phosphorane of **11**, either as a real species or as the incipient carbocationic portion of the transition state leading to ion **26.** The formation of much more **17** than **19** indicates that **26** is the principal product-forming intermediate in the benzylic system. Again, it would be useful to have stereochemical information to corroborate the assumed migration of the anti bond in **11** in the transformations to **17** and **19.**



25 **26**

Experimental Section

^1H NMR spectra were taken with either a Varian Associates A-60A, T-60, EM-390, or HA-100 spectrometer. ^2D NMR spectra were obtained with a JEOL JNM-PS-100 spectrometer. HPLC separations were carried out on a Waters Associates Model 6000A pump with a Beckamn Model 25 ultraviolet spectrometer detector using two Waters Associates μ-porasil columns connected in series. The mobile phase was 0.25% tetrahydrofuran–hexane. The hexane was obtained from Burdick and Jackson Laboratories, Inc. Melting points were determined on a Thomas-Hoover Unimelt apparatus. Triphenylphosphine was obtained from Eastman Kodak Co. and used without further purification.

In the reactions described below, we were able to obtain reaction product ratios from ^1H NMR by using the benzo ring(s) protons as internal standards. Thus, we obtained product ratios by integrating a unique resonance for each product and comparing it to the integration for the benzo ring(s) protons.

Preparation of *exo*-4,6-Dichloro-2,3:8,9-dibenzo-2,6,8-bicyclo[3.2.2]nonatriene (1-Cl). A solution of 1-OH[7] (1.0 g, 3.7 mmol), in 30 mL of anhydrous ethyl ether, was cooled to 0 °C. Three milliliters of thionyl chloride was added and the stirred solution was slowly warmed to room temperature. After the solution had been stirred for 3 h, it was poured into 50 mL of cold water and extracted with three 30-mL portions of ethyl ether. The combined ether extracts were washed with saturated aqueous sodium bicarbonate and water and then dried ($MgSO_4$). Evaporation to dryness left a pale yellow oil (900 mg, 85%). ^1H NMR analysis of this oil indicated 53% **2** and 47% **1.** These two isomers were separated by low-pressure liquid chromatography (2.5 cm × 100 cm glass column packed with 0.032–0.063-mm silica gel supplied by ICN Pharmaceuticals. The mobile phase was hexane pumped at 9.0 mL/min). A fraction was cut between 1090 and 1280 mL of elution volume which was evaporated to dryness and crystallized from ethanol to produce 170 mg (16%) of white crystals (1-Cl): mp 131–132.5 °C; ^1H NMR ($CDCl_3$) δ 7.10–7.65 (m, 8, aromatic), 6.96 (dd, 1, H-7, $J_{7,1}$ = 7.2 Hz, $J_{7,5}$ = 2 Hz), 5.33 (d, 1, H-4, $J_{4,5}$ = 4 Hz), 4.40 (d, 1, H-1, $J_{1,7}$ = 7.2 Hz), 4.27 (dd, 1, H-5, $J_{5,4}$ = 4 Hz, $J_{5,7}$ = 2 Hz). Anal. Calcd for $C_{17}H_{12}Cl_2$: C, 71.12; H, 4.18. Found: C, 71.02; H, 4.25.

Preparation of 3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-2-one. A solution of the exo alcohol **6**-OH[16] (2.10 g, 10.2 mmol) in 40 mL of acetone was titrated with 2.67 N Jones reagent[17] (~3 mL) until a red tint remained. Excess Jones reagent was destroyed with isopropyl alcohol. The reaction mixture was then diluted with brine and extracted with three 30-mL portions of ethyl ether. The combined ether extracts were washed with saturated aqueous sodium bicarbonate and brine. The solution was then dried ($MgSO_4$), filtered, and evaporated to dryness. The ketone product (1.87 g of white solid, 90%) could be used without further purification. ^1H NMR ($CDCl_3$) δ 7.0

(m, 5, aromatic and H-4), 3.8 (m, 1, H-1), 3.5 (m, 1, H-5), 2.5 (m, 2, H-8 syn + H-8 anti). Sublimation (85 °C, 1 Torr) afforded pure ketone: mp 102.5–104 °C. Anal. Calcd for $C_{12}H_9ClO$: C, 70.43; H, 4.43. Found: C, 70.46; H, 4.33.

Preparation of 3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*exo*-2-ol Acetate (6-OAc). A solution of 6-Cl[16] (1.00 g, 4.44 mmol) in 10 mL of glacial acetic acid was placed in a round-bottom flask equipped with a reflux condenser and magnetic stirring bar. Silver acetate (1.5 g, 9.0 mmol) was added, and the solution was heated at reflux for 2 h. The silver chloride precipitate was filtered off, and the clear solution was diluted with 200 mL of water. The mixture was extracted with three 30-mL portions of ethyl ether. The combined ether extracts were washed with water, saturated aqueous sodium bicarbonate, and brine. The solution was dried ($MgSO_4$), filtered, and evaporated to dryness. The product, 6-OAc, could be used without further purification: yield, 1.1 g (99%); ^1H NMR ($CDCl_3$) δ 7.3 (m, 4, aromatic H), 6.55 (d, 1, H-4, $J_{4,5}$ = 7 Hz), 5.2 (d, 1, H-2, $J_{2,1}$ = 2 Hz), 3.4 (m, 2, H-1 and H-5), 2.2 (m, 2, H-8 syn and H-8 anti), 2.1 (s, 3, CH_3). Crystallization from hexane afforded pure product: mp 92–93 °C. Anal. Calcd for $C_{14}H_{13}ClO_2$: C, 67.61; H, 5.27. Found: C, 67.71; H, 5.25.

Preparation of 6-Chloro-7,8-benzobicyclo[2.2.2]octa-5,7-dien-*anti*-2-ol (5-OH). 6-OAc (1.1 g, 4.2 mmol) was dissolved in 16.5 mL of 0.1 M perchloric acid–acetic acid and placed in a round-bottom flask equipped with a reflux condenser and magnetic stirring bar. The deep red solution was heated at reflux for 1 h, followed by dilution with water and extraction with three 30-mL portions of ethyl ether. The ether extracts were combined and washed with water, aqueous sodium bicarbonate, brine, and then dried ($MgSO_4$). Evaporation to dryness left a pale yellow oil (0.9 g, 82%). ^1H NMR analysis indicated that the acetate mixture contained at least 70% 5-OAc. The mixture was then methanolyzed in 0.1 M sodium methoxide–methanol followed by separation using preparative TLC (silica gel–15% ethyl ether–hexane). The slowest band was collected. Alternatively, the mixture could be dried over P_2O_5 and recrystallized to purity from CCl_4. The ^1H NMR spectrum was consistent with that expected for 5-OH: ($CDCl_3$) δ 7.1 (m, 4, aromatic H), 6.55 (dd, 1, H-5, $J_{5,4}$ = 7 Hz, $J_{5,1}$ = 2 Hz), 4.1 (m, 2, H-1 and H-2), 3.85 (dt, 1, H-4, $J_{4,5}$ = 7 Hz, $J_{4,3syn}$ = 3 Hz, $J_{4,3anti}$ = 3 Hz), 2.0 (ddd, 1, H-3 syn, $J_{3anti,3syn}$ = 13.5 Hz, $J_{3syn,2}$ = 8 Hz, $J_{3syn,4}$ = 3 Hz), 1.4 (dt, 1, H-3 anti, $J_{3syn,3anti}$ = 13.5 Hz, $J_{3anti,2}$ = 3 Hz, $J_{3anti,4}$ = 3 Hz). Spin–spin couplings for H-2 and H-1 were obtained from the methanesulfonate ester[8b] (5-OMs): δ 5.0 (dt, 1, H-2 anti, $J_{2,3anti}$ = 3 Hz, $J_{2,3syn}$ = 8 Hz, $J_{2,1}$ = 3 Hz), 4.35 (dd, 1, H-1, $J_{1,2}$ = 3 Hz, $J_{1,5}$ = 2 Hz). Recrystallization of 5-OH from carbon tetrachloride afforded small white needles: mp 130–131 °C. Anal. Calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.36. Found: C, 69.55; H, 5.45. That the stereochemistry of the hydroxyl in 5-OH is anti to the benzene ring was demonstrated by the fact that acetolysis of 5-OMs gave only 6-OAc and acetolysis of 8-OMs gave only 9-OAc.[8b]

Preparation of 3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*endo*-2-ol (7-OH) and the Corresponding Deuterium-Labeled Alcohol (*10*). A predried round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and calcium chloride drying tube was charged with lithium aluminum hydride (or lithium aluminum deuteride) (0.22 g, 5.8 mmol) in 15 mL of anhydrous ethyl ether. The ketone 3-chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-2-one (1.58 g, 7.72 mmol) dissolved in 25 mL of ether was slowly added by syringe. After the addition was complete (10 min), the reaction mixture was stirred for 2 h at room temperature. Excess lithium aluminum hydride was destroyed with a saturated aqueous solution of sodium potassium tartrate. The reaction mixture was then filtered and dried ($MgSO_4$). Evaporation to dryness yielded 1.54 g (96%) of white crystals whose ^1H NMR spectrum was consistent with that expected for 7-OH: ($CDCl_3$) δ 7.2 (m, 4, aromatic H), 6.4 (dd, 1, H-4, $J_{4,5}$ = 7 Hz, $J_{4,2}$ = 1 Hz), 4.4 (dd, 1, H-2, $J_{2,1}$ = 5 Hz, $J_{2,4}$ = 1 Hz), 3.5 (m, 2, H-1 and H-5), 2.3 (m, 2, H-8 syn and H-8 anti), 1.8 (s, 1, hydroxyl). The stereochemistry at C-2 was determined to be *endo*-OH by comparison of $J_{2,1}$ to the analogous benzobicyclo[3.2.1]octadiene derivatives.[8a] Very pure 7-OH was obtained by recrystallization from carbon tetrachloride: mp 104–105 °C. Anal. Calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.36. Found: C, 69.75; H, 5.25.

Treatment of 3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*exo*-2-ol (6-OH) with Triphenylphosphine–Carbon Tetrachloride. The exo alcohol 6-OH (43.2 mg, 0.209 mmol), prepared using Goldschmidt's procedure,[16] was dissolved in 0.5 mL of carbon tetrachloride and placed in a 5-mm NMR tube. Triphenylphosphine (78 mg, 0.300 mmol) was added and the tube was sealed and left to stand at room temperature for 24 h. A ^1H NMR spectrum indicated only the presence of starting material. The solution was heated at reflux for 3 h to give a mixture whose ^1H NMR spectrum indicated a composition of 70% 6-Cl and 20% starting material. The remaining product(s) could not be identified; however, neither 5-Cl nor 7-Cl was detected.

Treatment of 3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*endo*-2-ol (7-OH) with Triphenylphosphine–Carbon Tetrachloride at Room Temperature. 7-OH (83.2 mg, 0.486 mmol) was dissolved in 1.5 mL of carbon tetrachloride and placed in a 5-mm NMR tube. Triphenylphosphine (131 mg, 0.500 mmol) was added; the tube was sealed and allowed to stand at room temperature for 5 days. At that time, a ^1H NMR spectrum indicated the presence of 20% 7-Cl with the remaining 80% being 7-OH.

Treatment of 3-Chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-*endo*-2-ol (7-OH) with Triphenylphosphine–Carbon Tetrachloride at 70 °C. 7-OH (24.8 mg, 0.120 mmol) was dissolved in 0.25 mL of carbon tetrachloride and placed in a 5-mm NMR tube. Triphenylphosphine (49.4 mg, 0.188 mmol) was added; the tube was sealed and heated for 25.5 h at 70 °C. The contents were eluted through a short silica gel column with hexane. Evaporation of solvent left 18.4 mg (68%) of colorless oil which crystallized upon standing. The ^1H NMR spectrum was consistent with that reported[16] for 6-Cl.

Treatment of 3-Chloro-*exo*-2-deuterio-6,7-benzobicyclo-[3.2.1]octa-3,6-dien-*endo*-2-ol (10) with Triphenylphosphine–Carbon Tetrachloride. The endo alcohol (**10**) (32.2 mg, 0.155 mmol) was dissolved in 0.3 mL of carbon tetrachloride and placed in a 5-mm NMR tube. Triphenylphosphine (64.1 mg, 0.245 mmol) was added; the tube was sealed and heated to 70 °C for 25 h. The resulting yellow oil was eluted through a short silica gel column with hexane. Evaporation of the solvent left 29 mg (80%) of colorless oil. The ^1H NMR spectrum was consistent with that of a mixture of 80% **12** and 20% **13**.

Treatment of 6-Chloro-7,8-benzobicyclo[2.2.2]octa-5,7-dien-*anti*-2-ol (5-OH) with Triphenylphosphine–Carbon Tetrachloride–Acetonitrile. 5-OH (100 mg, 0.48 mmol) was dissolved in carbon tetrachloride–acetonitrile (1:1 v/v) and placed in a 5-mm NMR tube. Triphenylphosphine (120 mg, 0.46 mmol) was added and the tube was sealed. After 1 h at room temperature, analysis by NMR indicated that some starting material still remained. Additional triphenylphosphine was added (30.0 mg, 0.114 mmol) and the reaction mixture was allowed to stand at room temperature for an additional 1.75 h. A TLC (silica gel–hexane) of the reaction mixture demonstrated that neither 6-Cl nor starting material was present. A ^1H NMR spectrum of the product indicated a new ethylenic proton (H-5) whose absorption resonance was about 0.4 ppm downfield from that of H-5 in 5-OH. The carbinol proton (H-2) resonance had also shifted about 1 ppm downfield from its location in 5-OH. The ^1H NMR and TLC evidence leads us to believe that the product of the reaction is the alkoxychlorotriphenylphosphorane (5-OPPh_3Cl). The reaction mixture was then heated to 70 °C for 1 h. The ^1H NMR spectrum then obtained showed that the phosphorane had been completely converted to the exo chloride (6-Cl).

Treatment of 3-Chloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-4-ol (3-OH) with Triphenylphosphine–Carbon Tetrachloride. 3-OH[7] (48 mg, 0.18 mmol) was dissolved in 0.33 mL of carbon tetrachloride and placed in a 5-mm NMR tube. Triphenylphosphine (71 mg, 0.27 mmol) was added and the tube was sealed. After 19 h of heating at 45–50 °C, the following ratio of products was observed (^1H NMR): 75% 3-Cl, 20% 2-Cl, and 5% 1-Cl.

Treatment of 3-Chloro-4-deuterio-6,7:8,9-dibenzobicyclo-[3.2.2]nona-2,6,8-trien-4-ol (11) with Triphenylphosphine–Carbon Tetrachloride. 11[7] (51 mg, 0.19 mmol) was dissolved in 0.5 mL of carbon tetrachloride and placed in a 5-mm NMR tube. Triphenylphosphine (65 mg, 0.25 mmol) was added and the tube was heated at 65 °C for 17 h. The contents of the tube were eluted with hexane through a short silica gel column. Evaporation of solvent left 41 mg (80%) of colorless oil. HPLC analysis of the resulting oil indicated the following ratio: 68% 3-Cl-d_1, 27% 2-Cl-d_1, and 5% 1-Cl-d_1. ^1H NMR analysis of the allylic chloride (3-Cl-d_1) indicated that the ratio of **16**:**15** was about 3:1, while ^2H NMR analysis of 2-Cl-d_1 indicated about 93% **17** and about 7% **18**. **18** was measured by the peak intensity 0.3 ppm upfield from deuteriochloroform and **17** by a peak 3.2 ppm upfield from deuteriochloroform.

Treatment of 6-Chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ol (1-OH) with Triphenylphosphine–Carbon Tetrachloride–Acetonitrile. 1-OH[7] (1.4 g, 5.2 mmol) was dissolved in 16 mL of carbon tetrachloride–acetonitrile (1:1 v/v) and placed in a round-bottom flask equipped with a magnetic stirring bar. Triphenylphosphine (1.4 g, 5.3 mmol) was added and the mixture was stirred at room temperature for 3 h.

The reaction mixture was eluted through a silica gel column with

hexane. A ^1H NMR spectrum of the resulting pale yellow oil (1.75 g) indicated the presence of 2-Cl and 1-Cl in a ratio of 4:1.

Treatment of 6-Chloro-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*exo*-4-ol (1-OH) with Triphenylphosphine–Carbon Tetrachloride. 1-OH[7] (1.08 g, 4.00 mmol) was dissolved in 7 mL of carbon tetrachloride and 1.06 g (4.0 mmol) of triphenylphosphine was added. The solution was heated at 65–70 °C for 36 h. The reaction mixture was cooled and filtered. The yellow solution was chromatographed over a silica gel column and eluted with hexane. The solution was evaporated to dryness and crystallized from 95% ethanol, producing 0.80 g (70%) of a white crystalline solid (2-Cl): mp 113 °C; ^1H NMR ($CDCl_3$) δ 7.13–7.67 (m, 8, aromatic), 6.96 (dd, 1, H-7, $J_{7,1}$ = 7.3 Hz, $J_{7,5}$ = 2 Hz), 5.60 (d, 1, H-4, $J_{4,5}$ = 4 Hz), 4.38 (d, 1, H-1, $J_{1,7}$ = 7.3 Hz), 4.13 (dd, 1, H-5, $J_{5,4}$ = 4 Hz, $J_{5,7}$ = 2 Hz). Anal. Calcd for $C_{17}H_{12}Cl_2$: C, 71.12; H, 4.18. Found: C, 71.06; H, 4.18.

In a similar experiment, the crude reaction mixture was analyzed (^1H NMR) and found to contain 80% 2-Cl and 20% 1-Cl.

Treatment of 6-Chloro-4-deuterio-2,3:8,9-dibenzobicyclo[3.2.2]nona-2,6,8-trien-*endo*-4-ol with Triphenylphosphine–Carbon Tetrachloride–Acetonitrile. The alcohol[7] (20-OH) (500 mg, 1.9 mmol) was dissolved in 8 mL of carbon tetrachloride–acetonitrile (1:1 v/v) and triphenylphosphine (655 mg, 2.50 mmol) was added. The solution was stirred for 2 h at room temperature. A preparative scale TLC was run (silica gel–10% tetrahydrofuran–hexane) on the product to remove triphenylphosphine oxide. Evaporation of solvent gave 410 mg (82%) of a yellow oil which by ^1H NMR integration of resonances at δ 4.13 and δ 4.27 contained 25% 20-Cl and 75% 21-Cl. The oil was crystallized from carbon tetrachloride to produce 250 mg (50%) of a white solid (21): mp 130–132 °C; ^1H NMR ($CDCl_3$) δ 7.10–7.65 (m, 8, aromatic), 6.96 (dd, 1, H-7, $J_{7,1}$ = 7.2 Hz, $J_{7,5}$ = 2 Hz), 4.40 (d, 1, H-1, $J_{1,7}$ = 7.2 Hz), 4.27 (d, 1, H-5, $J_{5,1}$ = 2 Hz).

Mixture melting point and spectral comparison with the nondeuterated chloride (1-Cl) proved this compound to be 21-Cl.

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Registry No.—1-OH, 20887-64-3; 1-Cl, 64600-09-5; 2-Cl, 64626-00-2; 3-OH, 20851-76-7; 5-OH, 64600-10-8; 5-OAc, 64600-11-9; 6-OH, 54647-01-7; 6-Cl, 54647-00-6; 6-OAc, 64600-12-0; 7-OH, 64626-01-3; 10, 64600-13-1; 11, 64600-14-2; 20-OH, 64600-15-3; 21-Cl, 64600-16-4; thionyl chloride, 7719-09-7; 3-chloro-6,7-benzobicyclo[3.2.1]octa-3,6-dien-2-one, 57020-95-8; silver acetate, 563-63-3; carbon tetrachloride, 56-23-5; triphenylphosphine, 603-35-0.

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Prostanoid Endoperoxide Model Compounds: Preparation of 1,2-Dioxolanes from Cyclopropanes[1]

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A synthesis of 1,2-dioxolanes from cyclopropanes, which potentially could be adapted to prepare prostanoid endoperoxide model compounds, is reported. Cyclopropanes with 1-aryl, 1,1-diaryl, and 1-alkyl-1-aryl substituents, readily prepared by 1,1-dichlorocyclopropanation of the corresponding olefins with chloroform and sodium hydroxide under tetraalkylammonium chloride phase-transfer catalysis and subsequent sodium metal/*tert*-butyl alcohol in THF reduction, were hydroperoxybrominated with *N*-bromosuccinimide or 1,3-dibromo-5,5-dimethylhydantoin. The labile γ-hydroperoxy bromides were subsequently cyclized into their respective 1,2-dioxolanes with silver oxide. The substitution pattern of the original olefin in this sequence dictates the substitution pattern of the resulting 1,2-dioxolane.

Prostaglandin endoperoxides (PEP) serve as biosynthetic precursors to the physiologically potent prostaglandins PGF and PGE,[4] thromboxane A_2,[5] and prostacyclin.[6] So far these biologically important intermediates have been accessible through natural sources, but isolation and purification have been tedious and limiting in view of the labile nature of the endoperoxides and their scarce abundance.[7] In fact, until recently even the basic endoperoxide skeleton, i.e., the 2,3-dioxobicyclo[2.2.1]heptane ring system, was unknown. We prepared[8] this novel bicyclic peroxide by in situ, selective

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