GLC. Fully decomposed samples of azocumene in chlorobenzene without thiophenol but containing toluene as an internal standard were analyzed by GLC using an F&M Model 700 dual-column thermal conductivity gas chromatograph containing a pair of matched 6 ft × $^1/_8$ in., 10% UC-W98, stainless-steel columns. Operating conditions were as follows: injection port, 215 °C; detector, 250 °C; oven, isothermal at 70 °C for 7 min and then programmed at 10 °C/min to 220 °C; helium flow rate, 31.1 mL/min. Samples of 2 μL were injected with a Hamilton automatic syringe. Appropriate calibration curves relating concentrations to peak areas were prepared and utilized to analyze the samples.

Rates of Thermal Decomposition of an Intermediate. Partially decomposed high-pressure samples of **1a** or **1b** in cumene with no scavenger showed a moderate absorption at 330 nm and an intense absorption below 310 nm. The loss of the longer wavelength band was monitored at 320 nm in a Cary UV spectrometer at ambient cell compartment temperature (ca. 28 °C). Corrections were necessary for end azo absorption at that wavelength.

In a separate study the effect of pressure on the decomposition rate of the intermediate absorbing at 315 nm from decomposition of **1a** in cyclohexane was monitored by UV spectroscopy using a high-pressure optical cell previously described.[33] A 1×10^{-2} M master solution of **1a** in cyclohexane (Mallinckrodt, spectrophotometric grade) was prepared, carefully deoxygenated by utilizing procedures described above, and stored in a refrigerator, in the dark, under a nitrogen atmosphere. Samples of this solution were placed in the high-pressure optical cell under an inert atmosphere and photolyzed at various pressures for periods from 30 to 90 min by using a Hanovia 100-W high-pressure quartz mercury-vapor lamp in conjunction with a Corning 737 filter to provide light primarily at 366 nm. The cell was thermostated at 20 °C, and UV spectra were repeatedly scanned from 450 to 300 nm as a function of time. Disappearance of the intermediate was monitored at 316 nm. Decomposition was usually followed for 2 or 3 half-lives, and an "infinite time" trace was obtained after at least 20 h of decomposition.

(33) G. D. Lockyer, Jr., Ph.D. Dissertation, University of California, Riverside, CA, 1971.

Acknowledgment. The authors are grateful for support from the National Science Foundation and also wish to thank Professors J. M. Bride and E. G. Janzen for helpful discussions.

Registry No. **1a**, 5676-79-9; **1b**, 18344-79-1; **2**, 1889-67-4; **3**, 98-82-8; **4**, 98-83-9; **8**, 62545-70-4; 2-nitro-2-methylpropane, 75-64-9; di-*tert*-butyl nitroxide, 2406-25-9; cumylamine, 585-32-0; benzyl cyanide, 140-29-4; iodomethane, 74-88-4; azobis(isobutyronitrile), 78-67-1; di-*tert*-butyl hyponitrite, 14976-54-6; 3,4,5,6-tetrahydro-3,6-diphenylpyridazine, 66090-52-6; 4,5,6,7-tetrahydro-3,7-diphenyl-3*H*-1,2-diazepine, 7433-52-5; [(*p*-nitrophenyl)azo]triphenylmethane, 16186-97-3.

Generation of 2-Chloronaphthalene-1,3-diyl

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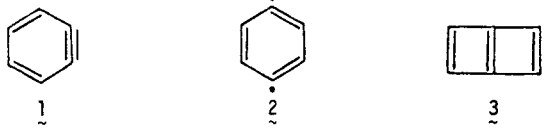
Reaction of 1-bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane with potassium *tert*-butoxide in tetrahydrofuran yields 2-chloronaphthalene along with nine other naphthalenes which result from solvent incorporation or reaction with nucleophile (Br^-, Cl^-, t-BuO^-). Use of tetrahydrofuran-d_8 as the solvent leads to the incorporation of two deuterium atoms into the chloronaphthalene. This result is interpreted in terms of a 1,3-dehydronaphthalene opening to the diradical, followed by abstraction of deuterium atoms from the solvent. The products which result from incorporation of solvent would then arise by dimerization of radical pairs. The remaining products are thought to arise from nucleophilic addition to the closed form of the dehydronaphthalene.

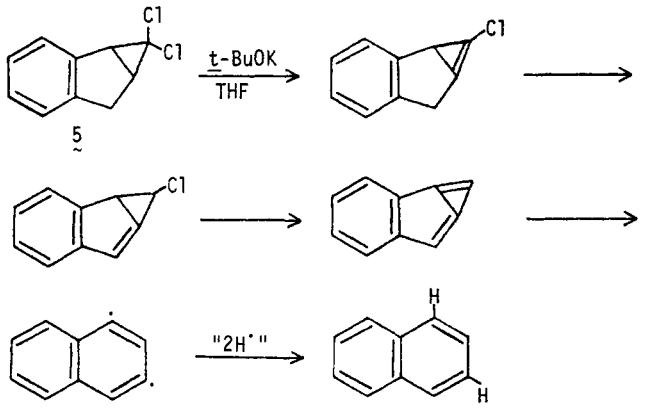
Although *o*-benzyne has been generated, trapped, and characterized spectroscopically as **1**,[12] evidence for the para



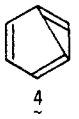
1 **2** **3**

and meta isomers rests primarily on trapping experiments. Two different approaches to *p*-benzyne led to reactive intermediates possessing quite different properties. Pyrolysis of *cis*-1,2-diethynylethylene yielded products derived from diradical **2**,[3] whereas treatment of 1-chlorobicyclo[2.2.0]hexadiene with lithium diethylamide gave polyene **3**,[4] which was trapped in situ by addition of the base across the central bond. The vigorous conditions required to generate **3** suggest that this intermediate does not experience significant resonance stabilization.

Scheme I



Washburn and his co-workers used *exo,exo*-4,6-dibromobicyclo[3.1.0]hexane as a precursor to *m*-benzyne (**4**).[5] When the bicyclic dibromide was treated with several



4

(1) R. W. Hoffman, Ed., "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967.
(2) O. L. Chapman, K. Mattes, C. L. McIntosh, J. Pacansky, G. V. Calder, and G. Orr, *J. Am. Chem. Soc.*, **95**, 6134 (1973).
(3) R. R. Jones and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 660 (1972).
(4) R. Breslow, J. Napierski, and T. C. Clarke, *J. Am. Chem. Soc.*, **97**, 6275 (1975).

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Scheme II

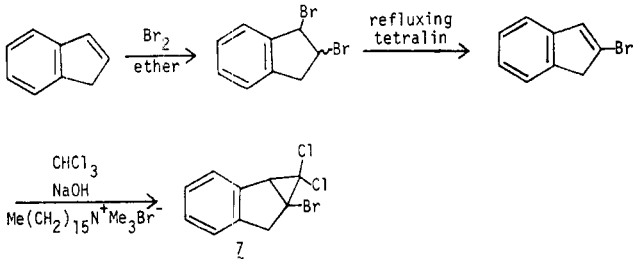
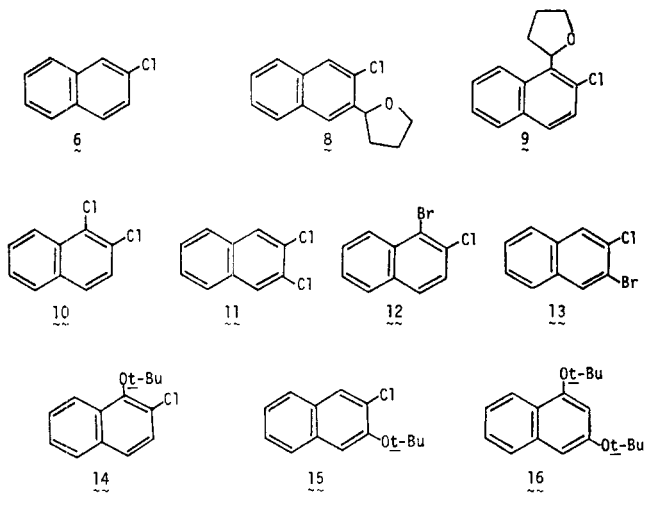


Chart I



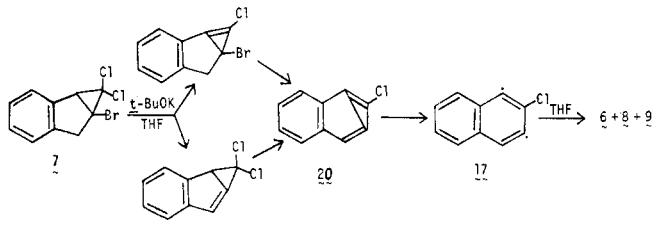
bases, successive HBr eliminations resulted, leading to 6-substituted fulvenes. Extensive labeling studies suggest that the fulvenes are derived from **4** via nucleophilic addition to the cyclopropenyl double bond. No evidence in support of a diradical intermediate was found. In this paper we report our results which show that 1,3-dehydronaphthalenes can be generated and trapped as the diradicals.[6]

Our initial studies were carried out with the adduct of dichlorocarbene and 1*H*-indene, compound **5**.[7] Treatment of **5** with potassium *tert*-butoxide in tetrahydrofuran yielded 2-chloronaphthalene (**6**) in >99% yield along with a trace of naphthalene. Although the isolation of naphthalene can be rationalized in terms of the sequence of steps illustrated in Scheme I, it is clear that the well-known base-induced ring opening of *gem*-dichlorocyclopropanes reported previously by Parham and co-workers[7] accounts for **6**.

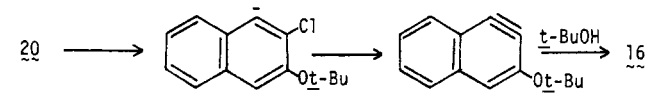
In order to minimize the process leading to **6**, we synthesized precursor **7**, which incorporates a leaving group (bromide) at the bridging carbon, via the straightforward procedure illustrated in Scheme II.

Treatment of **7** with a solution of potassium *tert*-butoxide in tetrahydrofuran at 0 °C or at −78 °C yielded the complex mixture of naphthalenes illustrated in Chart I. Any mechanistic scheme which explains the origin of these products must account not only for the incorporation of

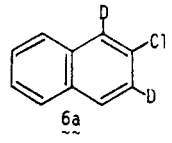
Scheme III



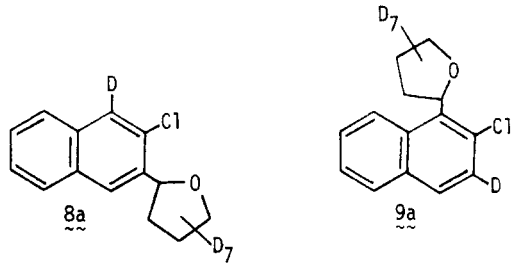
Scheme IV



solvent and nucleophiles but also for **6**, which has gained two hydrogen atoms from the reaction medium. Fortunately, the use of labeled solvent helped to elucidate the origin of **6**. Thus when tetrahydrofuran-d_8 is the solvent, the 2-chloronaphthalene is 79% d_2, 13% d_1, and 8% undeuterated. The ^{13}C NMR spectrum was used to establish the position of the deuterium atoms as in **6a**.[8]



The introduction of deuterium into **6** and the isolation of products from reaction with solvent implicate the diyl **17** as a reactive intermediate. The formation of **6**, **8**, and **9** can then be rationalized by assuming one (or both) of the paths of Scheme III. Both **8** and **9** were mainly d_8, suggesting structures **8a** and **9a**.[10]



The origin of **10**–**16** is not easily explained. If one discounts zwitterions **18** and **19** as viable intermediates, then

the nonregiospecific addition of the nucleophile (t-BuO$^-$, Cl$^-$, or Br$^-$) across the bridging bond in **20** (see Scheme III) would seem to be the most reasonable route to these products. 1,3-Di-*tert*-butoxynaphthalene (**16**) could then arise via Scheme IV.

The thermal production of ions **21** and **22** might also

account for some of the products; however, the starting

(5) W. N. Washburn, *J. Am. Chem. Soc.*, **97**, 1615 (1975); W. N. Washburn and R. Zahler, *ibid.*, **98**, 7827, 7828 (1976); **99**, 2012 (1977); W. N. Washburn, R. Zahler, and I. Chan. *ibid.*, **100**, 5863 (1978). For earlier references, see: R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, 1011 (1965); R. B. McGriff, *Diss. Abstr. B*, **28**, 844 (1967); H. E. Bertorello, R. H. Rossi, and R. H. de Rossi, *J. Org. Chem.*, **35**, 3332 (1970).

(6) For a preliminary account, see W. E. Billups, J. D. Buynak, and D. Butler, *J. Org. Chem.*, **44**, 4218 (1979). See also G. C. Johnson, J. J. Stofko, Jr., T. P. Lockhart, D. W. Brown, and R. G. Bergman, *J. Org. Chem.*, **44**, 4215 (1979).

(7) W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Am. Chem. Soc.* **78**, 1437 (1956).

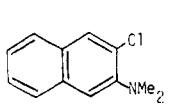
(8) The studies of monosubstituted naphthalenes by Kitching, Bulpitt, Doddrell, and Adcock[9] provided a reference for the effects observed on deuteration of naphthalenes.

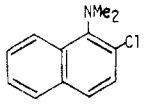
(9) W. Kitching, M. Bulpitt, D. Doddrell, and W. Adcock, *Org. Magn. Reson.*, **6**, 289 (1974).

(10) These products probably arise by collapse of a caged radical pair.

material 7 was shown to be stable in tetrahydrofuran at the reaction temperature. Furthermore, thermolysis of 7 in tetrahydrofuran at 60 °C or in dimethyl sulfoxide at 40 °C produces a 19:1 mixture of 13 and 11, respectively. Products 10 and 12 were not detected.

The reaction of 7 with potassium *tert*-butoxide in tetrahydrofuran in the presence of dimethylamine (conditions of Washburn)[5] yielded 13 and 23–25. Since it is difficult


23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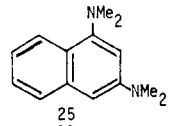
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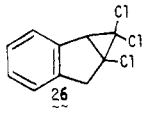
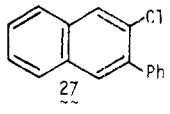
to imagine how these products could be derived from diyl 17, one is forced to conclude that they arise from nucleophilic addition to some intermediate which is generated prior to formation of the diyl. Addition to 20 as suggested in Schemes III and IV accounts for 23–25. The greater nucleophilicity of the amide (vs. *tert*-butoxide and the halides would account for the trapping of 20 before it opens to the diyl.[11] The isolation of 13 (and not 12) might result from the proximity of the incipient bromide to the end of the bridging bond in 19 which leads to 13. Formation of 12 would, of course, require that the bromide diffuse to the other side of 20. *However, the origin of these products is not unambigous, and intermediates other than 20 might be precursors to the nucleophilic addition products.*

The trichloride 26, which was synthesized as a precursor


26

to authentic 11, was also treated with potassium *tert*-butoxide in tetrahydrofuran. As expected, this reaction yielded the naphthalenes 6, 8–11, and 14–16 in strict analogy to the observations made above when 7 was the starting material.

For the sake of economy, 1,4-cyclohexadiene[12] (rather than tetrahydrofuran-d_8) was used to trap the diyl generated from the trichloride. Thus, reaction of 26 under the usual conditions and in the presence of 1,3-cyclohexadiene led to several new products in addition to the naphthalenes described above. Two of these were isolated by preparative thin-layer chromatography and identified as 27 and 28. Other minor products detected by GC/MS,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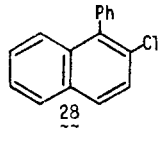
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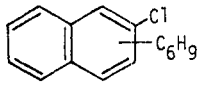
but not isolated, had parent molecular ions and fragmentation patterns corresponding to 29 (two isomers) and 30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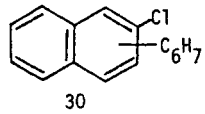
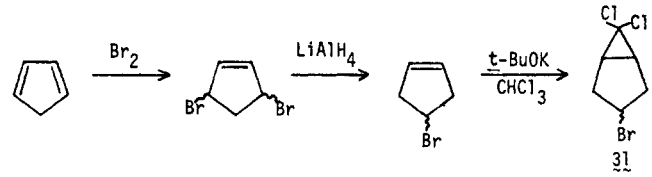

30

(two isomers). Some phenylnaphthalene was also detected. It is interesting that the yield of chloronaphthalene nearly doubled (37% vs. 20% in the absence of 1,3-cyclohexadiene), reflecting the good atom donor quality of the diene. This result further suggests that the open and closed forms of the dehydronaphthalene might be in equilibrium. Additional work will be required to confirm this hypothesis.

Scheme V



Finally, we have also attempted to generate 1,3-dehydrobenzene itself[5] from the readily available precursor 31 (Scheme V). Unfortunately, treatment of 31 with potassium *tert*-butoxide in tetrahydrofuran yielded mainly chlorobenzene (>95% yield). Traces of other products were also detected by gas chromatography, although none of them had the retention time of benzene.

Experimental Section

General Methods. Proton magnetic resonance spectra were recorded, using a Varian Model EM-390 (90 MHz), XL-100 (100 MHz), or A 56/60 (60 MHz) spectrometer. Chemical shifts (δ) are expressed in parts per million downfield from internal Me_4Si. Infrared spectra were recorded by using a Beckman IR spectrometer. High-resolution mass spectra were recorded on a double-focusing CEC 21-110 mass spectrometer operated at 70 eV. A Finnigan Model 3300 gas chromatograph–mass spectrometer equipped with a 6 ft × $^1/_2$ in. column packed with 10% SE-30 on Chromosorb WAW was used for the GC/MS work.

Tetrahydrofuran was distilled from sodium–benzophenone ketyl immediately before use. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure and stored over 4A molecular sieves. Column chromatography was performed on Baker reagent grade silica gel (60–200 mesh). Merck precoated silica gel plates were used for analytical (100 × 50 × 0.25 mm) and preparative (200 × 200 × 2 mm) thin-layer chromatography.

Synthesis of 2,3-Benzo-6,6-dichlorobicyclo[3.1.0]hexane (5). Hexadecyltrimethylammonium bromide (0.528 g, 1.4 mmol), freshly distilled indene (23.2 g, 0.2 mmol), and alcohol-free chloroform (50 mL, 0.63 mol) were added to a 500-mL three-necked flask fitted with a reflux condenser, a mechanical stirrer, and an addition funnel. With external cooling (ice bath), sodium hydroxide (61.4 g, 1.53 mol) dissolved in 122 mL of water was added dropwise over approximately 30 min. The ice bath was then allowed to warm to room temperature and the reaction mixture stirred overnight. After the reaction mixture was acidified with 10% sulfuric acid, the product was extracted into ether and washed several times with water. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo. The product was then dissolved in petroleum ether and filtered through a pad of alumina. Recrystallization from petroleum ether afforded 13.2 g (57% yield) of 5, mp 74–76 °C (lit.[7] mp 75–76 °C).

Reaction of 2,3-Benzo-6,6-dichlorobicyclo[3.1.0]hexane (5) with Potassium *tert*-Butoxide in Tetrahydrofuran. A solution of potassium *tert*-butoxide (2.24 g, 20 mmol) in tetrahydrofuran (15 mL) was added to a 50-mL three-necked flask fitted with a condenser, a mechanical stirrer, and an addition funnel. A solution of 5 (0.995 g, 5 mmol) in tetrahydrofuran (10 mL) was then added dropwise under nitrogen while the temperature was maintained between 15 and 20 °C. The reaction mixture was stirred 30 min, poured into ice–water, and extracted with ether. The extract was washed with water and dried over sodium sulfate, and the solvent was removed in vacuo. The products were separated from tars by TLC (silica gel, cyclohexane) and then purified by gas chromatography using a 6 ft × $^1/_2$ in. column packed with 20% SE-30 on Chromosorb P. The major product, 2-chloronaphthalene, was isolated in >98% yield. A trace of naphthalene (<0.1% yield) was isolated.

1,2-Dibromoindan. 1,2-Dibromoindan was prepared as described by Winstein and Roberts.[13] Bromine (73 mL, 1.34 mmol)

(11) For a recent theoretical study, see J. O. Noell and M. D. Newton, *J. Am. Chem. Soc.*, 101, 51 (1979).

(12) We thank Professor R. G. Bergman for sugggesting this experiment.

(13) S. Winstein and R. M. Roberts, *J. Am. Chem. Soc.*, 75, 2297 (1953).

was added dropwise to a stirred solution of freshly distilled 1*H*-indene (150 g, 1.29 mol) in 650 mL of ether while the temperature was maintained between 0 and −5 °C. The reaction mixture was then extracted twice with a saturated solution of sodium thiosulfate, twice with water, and with brine and dried over $MgSO_4$. Removal of the solvent in vacuo followed by vacuum distillation afforded 310 g (87% yield) of product, bp 115–120 °C (1.5 mmHg).

2-Bromo-1*H*-indene.[14] A solution of crude 1,2-dibromoindan (400 g) in 500 mL of freshly distilled tetralin was refluxed for 8 h. Evolution of HBr was observed. Fractional distillation of the reaction mixture afforded 2-bromoindene [bp 77 °C (1.5 mmHg)] which was recrystallized from anhydrous methanol to yield 33 g (13% yield from 1*H*-indene) of the 1*H*-indene as a white solid, mp 38 °C.

Preparation of 1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (7). A solution of sodium hydroxide (37.0 g, 0.925 mol) in 75 mL of water was added to a chilled mixture of 2-bromo-1*H*-indene (11.9 g, 61.0 mmol), hexadecyltrimethylammonium bromide (0.226 g, 0.620 mmol), and alcohol-free chloroform (61 mL, 0.76 mol). The reaction mixture was stirred vigorously at room temperature for approximately 8 h. The chloroform layer was then washed several times with ice–water and dried over Na_2SO_4. Evaporation of the chloroform at 0 °C in vacuo yielded a brown sludge which was dissolved in cold petroleum ether and filtered through a pad of Florisil. Evaporation of the petroleum ether at 0 °C in vacuo yielded 5.2 g (30% yield) of **7**, mp 80–82 °C dec. On being allowed to stand at room temperature, **7** decomposes slowly to a 19:1 mixture of 2-bromo-3-chloronaphthalene (**13**) and 2,3-dichloronaphthalene (**11**). The low-resolution mass spectrum showed no parent molecular ion at *m/e* 276. However, the base peaks at *m/e* 162.0227 (calcd for $C_{10}H_7Cl$, *m/e* 162.0236), 196.9910 (calcd for $C_{10}H_7Cl_2$, 196.9924), and 239.9334 (calcd for $C_{10}H_7Cl$, 239.9340) establish the presence of two chlorine atoms and one bromine atom. The NMR spectrum exhibits narrow multiplets at δ 3.20 (1 H) and 3.71 (2 H) and a four-proton complex multiplet centered at δ 7.02. In the decoupled ^{13}C NMR spectrum resonances, two at 46.2 and 68.3 ppm and two aromatic at 138.1 and 142.6 ppm, could be detected easily. Of the remaining six signals two were at 45.9 and 50.0 ppm and the four remaining aromatic ones at 123.6, 125.1, 126.7, and 128.0 ppm. The signals at 45.9 and 50.0 ppm split into a triplet ($J \simeq$ 2.2 ppm) and a doublet ($J \approx$ 2.2 ppm), respectively.

As a final confirmation of the carbon skeleton **7** was submitted to reduction with sodium in ammonia. A quantitative yield of two hydrocarbons identified as 2,3-benzobicyclo[3.1.0]hexane (16.6% yield), identical with an authentic sample prepared from reduction of **5**, and 1,4-dihydronaphthalene[15] (83.4% yield) was obtained.

Reaction of 1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (7) with Potassium *tert*-Butoxide in Tetrahydrofuran. A solution of **7** (1.0 g, 3.60 mmol) in tetrahydrofuran (5 mL) was added at 0 °C to a slurry of potassium *tert*-butoxide (1.63 g, 14.7 mmol) in tetrahydrofuran (15 mL). The reaction mixture was stirred at 0 °C for 30 min, diluted with water, and extracted into ether. The extract was washed several times with water and dried over Na_2SO_4. The solution was then concentrated in vacuo to yield 0.7 g of brown solid. From this solid, products **6** and **8–16** were isolated by a combination of preparative and thin-layer chromatography (silica gel, several solvents) and preparative gas chromatography (6 ft × $^1/_4$ in. column packed with 10% SE-30 on Chromosorb WAW). The GC (uncorrected) percentages (80–85% material balance) of compounds **6** and **8–16** are as follows: **6**, 7%; **8** + **9**, 6%; **10** + **11**, 16%; **12** + **13**, 17%; **14**, 27%; **15**, 13%; **16**, 14%.

Structures were assigned on the basis of the following data: **6** was identified by comparison of its spectral properties and GC retention time with an authentic sample (Aldrich Chemical Co., Inc.); **8** and **9** were obtained as a 56:44 mixture as determined by GC using a 250-ft SF-96 capillary column. It is not known which isomer corresponds to which peak. The mixture exhibits NMR signals at δ 1.0–2.8 (m, 8 H), 3.70–4.12 (m, 2 H), 4.14–4.5 (m, 2 H), 5.2–5.4 (t, 1 H, J = 6 Hz), 5.6–5.8 (m, 1 H), 6.7–8.0 (m, 11 H), and 8.25–8.5 (m, 1 H) and IR (neat) signals at 3060 (w), 2980 (s), 2870 (m), 1620 (w), 1590 (m), 1505 (m), 1460 (m), 1365 (m), 1325 (m), 1185 (m), 1165 (m), 1130 (m), 1070 (s), 1050 (s), 805 (m), and 745 (s) cm^{-1}. Elemental composition was determined by high-resolution mass spectroscopy; *m/e* 232.0666 (m^+), calcd for $C_{14}H_{13}{}^{35}ClO$ *m/e* 232.0655. Authentic samples of **10** and **12** were prepared as described in the literature[16] (experimental outlined below). NMR and IR spectra and GC retention times were identical with those exhibited by the materials isolated in this study. Compounds **11** and **13** (1:19 mixture) were prepared by heating **7** (half life 48 min) in Me_2SO at 40 °C. Compound **11** has NMR signals at δ 7.34–7.5 (dd, 2 H, J = 6, 3 Hz), 7.56–7.7 (dd, J = 6, 3 Hz), and 7.86 (s, 2 H), whereas **12** has signals δ 7.3–7.65 (AB q, 4 H, J = 9 Hz), 7.80 (s, 1 H), and 7.98 (s, 1 H). An authentic sample of **14** was prepared from the corresponding chloronaphthol (see experimental procedure below): NMR δ 1.47 (s, 9 H), 7.3–7.9 (m, 5 H), 8.0–8.3 (m, 1 H). Compound **15** has NMR signals at δ 1.47 (s, 9 H), 7.25–7.4 (m, 4 H), and 7.45 (s, 2 H) and an exact mass of *m/e* 234.0803 (calcd *m/e* 234.0811). Compound **16** exhibits the following spectral data: NMR δ 1.40 (s, 9 H), 1.48 (s, 9 H), 6.80–6.86 (d, 1 H, J = 3 Hz), 7.10–7.17 (d, 1 H, J = 3 Hz), 7.25–7.50 (m, 2 H), 7.55–7.75 (m, 1 H), 8.05–8.23 (m, 1 H); IR (neat) 3060 (w), 2970 (s), 2940 (sh), 1622 (m), 1595 (m), 1575 (m), 1500 (m), 1390 (s), 1362 (s), 1280 (w), 1260 (w), 1230 (w), 1180 (s), 1160 (s), 1130 (s), 1080 (m), 995 (m), 905 (w), 880 (w), 840 (w), 750 (m). Cleavage of this compound with 40% HBr in HOAc provided 1,3-naphthalenediol, identified by comparison of its NMR spectral data with those published.[19] Anal. Calcd for $C_{14}H_{15}ClO$ (**14**): C, 71.64; H, 6.44. Found: C, 70.06; H, 6.38 (isobutylene lost during purification). Calcd for $C_{14}H_{15}ClO$ (**15**): C, 71.64; H, 6.44. Found: C, 71.77; H, 6.53.

Reaction of 1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (7) with Potassium *tert*-Butoxide in Tetrahydrofuran at −78 °C. A solution of **7** (0.1 g, 0.36 mmol) in tetrahydrofuran (1 mL) was added to a slurry of potassium *tert*-butoxide (0.2 g, 1.78 mmol) in tetrahydrofuran (1 mL) at −78 °C. The reaction mixture was then worked up as described above and shown by gas chromatography to be nearly identical in composition with the product mixture obtained from the reaction run at 0 °C.

Synthesis of 1,2-Dichloronaphthalene (10). Ice–water (20 mL) was added to a stirred solution of 2-amino-1-nitronaphthalene (1.0 g, 5.31 mmol) in concentrated HCl (5 mL). After being stirred for 1 h, the mixture was filtered and the filtrate added to a solution of CuCl (3.0 g, 30.3 mmol) in HCl (8 mL). The mixture was then allowed to stand overnight, diluted with water, and extracted into ether. Removal of the solvent in vacuo and purification of the solid residue by TLC (silica gel, petroleum ether) yielded 0.4 g (38% yield) of **10**, mp 35 °C (lit.[16] mp 35 °C).

Synthesis of 1-Bromo-2-chloronaphthalene (12). Compound **12** was prepared from 1-bromo-2-aminonaphthalene as described in the literature.[16] Solid sodium nitrite (0.345 g, 5.0 mmol) was added to a suspension of 1-bromo-2-aminonaphthalene (1.0 g, 4.5 mmol) in HCl (8.0 mL) and the resulting solution added to CuCl (3.0 g, 30.3 mmol) in HCl (8 mL). The solution was allowed to stir overnight and then poured into water. The product was extracted into ether, dried over Na_2SO_4, and concentrated in vacuo. Purification of the resulting yellow solid by preparative TLC (silica gel, pentane) yielded 0.43 g (40% yield) of **12**, mp 46 °C (lit.[16] mp 46 °C).

1-*tert*-Butoxy-2-chloronaphthalene (14). 2-Chloro-1-naphthol[17] (1.24 g, 6.94 mmol) was added to a solution of sulfuric acid (0.04 mL, 0.72 mmol) in isobutylene (5 mL, 53.0 mmol) at −78 °C in a Diels–Alder tube. The tube was capped and the solution allowed to stir at 25 °C overnight. The mixture was then cooled to −78 °C and poured into 10% NaOH. The product was extracted into ether, washed with 10% NaOH and water, and dried over $MgSO_4$. After removal of the ether in vacuo, the product was purified by preparative TLC (silica gel, 4:20 acetone–pentane) to yield 0.163 g (9% yield) of pure (gas chromatography) **14**: mass spectrum, *m/e* 234.0814 (m^+), calcd for $C_{14}H_{15}ClO$ *m/e* 234.0811.

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Reaction of 1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (7) with Potassium *tert*-Butoxide in Tetrahydrofuran-d_8. A solution of **7** (7.7 mg, 0.0277 mmol) in tetrahydrofuran-d_8 (0.5 mL) was added dropwise at 0 °C to a slurry of potassium *tert*-butoxide (1.25 mg, 0.0111 mmol) in tetrahydrofuran-d_8 (1.5 g). The reaction mixture was then stirred at 0 °C for 30 min, diluted with water, and extracted into ether. The extract was then washed several times with water and dried over Na_2SO_4. The solvent was moved in vacuo to yield 4.0 mg of brown solid (83% material recovery). Analysis by GC/MS revealed that products **6** and **8**–**16** were produced in the following percentages: **6**, 2.4%; **8** + **9**, 2.9%; **10** + **11**, 17.8%; **12** + **13**, 21.5%; **14**, 17%; **15**, 29.5%; **16**, 8.8%.

The 2-chloronaphthalene was shown by mass spectroscopy to be 79% d_2, 13% d_1, and 8% undeuterated. Products **8** and **9** were >85% d_8. The remaining products were not deuterated.

Blank Reaction of 2-Chloronaphthalene (6), 1,2-Dichloronaphthalene (10), and 1-Bromo-2-chloronaphthalene (12) with Potassium *tert*-Butoxide in Tetrahydrofuran-d_8. A mixture (0.08 g) of **6**, **10**, and **12** (81:3:6) was added to a cold (0 °C) slurry of potassium *tert*-butoxide (0.125 g, 1.1 mmol) in tetrahydrofuran-d_8 (1.0 g). The mixture was allowed to warm to room temperature over 1 h, diluted with water, and extracted into ether. Workup afforded a quantitative recovery of the naphthalenes, in their original composition and free of label.

Reaction of 1-Bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (7) with Potassium *tert*-Butoxide in Tetrahydrofuran in the Presence of Dimethylamine. Dimethylamine (2.7 mL, 40.8 mmol) was added at −78 °C to a slurry of potassium *tert*-butoxide (2.0 g, 18 mmol) in tetrahydrofuran (15 mL). A solution of **7** (1.0 g, 3.6 mmol) in tetrahydrofuran (5 mL) was then added over 10 min at −78 °C. After being stirred at −78 °C for 1 h, the reaction mixture was diluted with water, extracted several times with ether, and dried over Na_2SO_4. Concentration of the solution in vacuo yielded 0.7 g of product (brown solid) which was found by GC/MS spectroscopy to contain four major products. Further purification (93% material balance) by preparative TLC (silica gel, several solvents) yielded **13** (6%), **23** (32%), **24** (44%), and **25** (13%). Compound **23** exhibits the following: NMR δ 2.87 (s, 6 H), 6.8–7.5 (m, 5 H), 7.9–8.2 (m, 1 H); IR (neat) 3060 (m), 2980 (m), 2940 (m), 2800 (m), 1590 (m), 1570 (m), 1505 (m), 1485 (m), 1455 (m), 1390 (s), 1120 (s), 1055 (s), 940 (m), 860 (m), 805 (s), 790 (m), 750 (m) cm^{-1}. The elemental composition was determined by high-resolution mass spectroscopy, m/e 205.0657 (m$^+$), calcd for $C_{12}H_{12}ClN$ m/e 205.0658. For **24**: NMR δ 2.7 (s, 3 H), 7.1 (s, 1 H), 7.05–7.5 (m, 4 H), 7.55 (s, 1 H); IR (neat) 3060 (m), 2950 (m), 2860 (m), 2830 (m), 2790 (m), 1625 (w), 1590 (m), 1495 (m), 1480 (m), 1450 (s), 1435 (s), 1360 (m), 1330 (m), 1200 (m), 1180 (m), 1135 (s), 1120 (s), 1005 (s), 940 (m), 870 (m), 850 (m), 745 (s), 680 (m) cm^{-1}; mass spectrum, m/e 205.0646 (m$^+$), calcd for $C_{12}H_{12}ClN$ m/e 205.0658. For **25**: NMR δ 2.75 (s, 3 H), 2.88 (s, 3 H), 6.45 (AB q, J = 3 Hz, 1 H), 6.55 (AB q, J = 3 Hz, 1 H), 6.9–7.2 (m, 2 H), 7.32–7.5 (m, 1 H), 7.75–7.9 (m, 1 H); IR 3060 (w), 2980 (m), 2950 (m), 2840 (m), 1620 (s), 1600 (s), 1580 (m), 1460 (m), 1450 (m), 1440 (m), 1400 (m), 1365 (m), 1325 (m), 1300 (m), 1200 (m) 1160 (m), 1140 (m), 1120 (m), 1055 (m), 1045 (m), 1000 (m), 940 (m), 815 (m), 780 (m), 550 (m) cm^{-1}; mass spectrum, m/e 214.1480 (m$^+$), calcd for $C_{14}H_{18}N_2$ m/e 214.1470. Anal. Calcd for $C_{12}H_{12}ClN$ (**23**): C, 70.07; H, 5.88; N, 6.81. Found: C, 69.97; H, 6.00; N, 6.77. Calcd for $C_{12}H_{12}ClN$ (**24**): C, 70.07; H, 5.88; N, 6.81. Found: C, 69.92; H, 5.65; N, 7.02. Calcd for $C_{12}H_{12}ClN$ (**25**): C, 78.46; H, 8.47; N, 13.07. Found: C, 78.35; H, 8.39; N, 12.93.

2-Chloro-1*H*-indene. Crude 1,2-dichloroindan[18] (185 g, 0.99 mol) was heated for 5 h at 225–235 °C. The resulting solution was fractionally distilled at reduced pressure to yield 2-chloro-1*H*-indene: 100 g (67% yield); bp 110–116 °C (113 mmHg); NMR δ 3.45 (dd, 2 H, J = 2, 0.5 Hz), 6.62 (td, 1 H, J = 2, 0.5 Hz), 7.1–7.4 (m, 4 H); IR (neat) 3070 (m), 3050 (m), 3020 (m), 2900 (w), 1610 (m), 1590 (m), 1560 (m), 1455 (s), 1390 (s), 1275 (s), 1205 (m), 1190 (w), 1165 (w), 1110 (w), 1090 (w), 1040 (m), 1015 (m), 905 (m), 870 (m), 860 (m), 840 (m), 745 (s), 705 (s) cm^{-1}; mass spectrum, m/e (relative intensity) 152 (7.9, m$^+$), 150 (26, m$^+$), 115 (100), 89 (11), 75 (8.5), 63 (20), 57 (17), 50 (7.9), 49 (14).

Synthesis of 1-Chloro-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (26). A solution of sodium hydroxide (40 g in 80 mL water) was added dropwise to a solution of chloro-1*H*-indene (10 g, 0.66 mol) and hexadecyltrimethylammonium bromide (0.672 g, 0.71 mmol) in chloroform (66 mL) at 0 °C. The reaction was warmed to 15 °C and allowed to stir vigorously at this temperature for 8 h. The reaction mixture was then washed several times with ice–water and dried over Na_2SO_4. The resulting solution was concentrated in vacuo at 0 °C, and the residue dissolved in cold petroleum ether and filtered through a pad of Florisil. The filtrate was concentrated in vacuo to yield 3.33 g (21.5% yield) of **26**: mp 74 °C; NMR δ 3.30 (s, 1 H), 3.67 (s, 2 H), 7.0–7.4 (m, 4 H); IR (CCl_4 for 4000–1400 cm^{-1} and CS_2 for 1400–600 cm^{-1}) 3080 (m), 3050 (m), 2930 (m), 2870 (w), 2840 (w), 1955 (w), 1920 (w), 1880 (w), 1840 (w), 1800 (w), 1480 (s), 1465 (m), 1430 (m), 1340 (w), 1330 (w), 1310 (w), 1290 (m), 1220 (w), 1190 (w), 1170 (w), 1150 (w), 1105 (m), 1095 (m), 1025 (w), 990 (m), 975 (m), 940 (s), 930 (s), 905 (w), 850 (s), 755 (s), 725 (s), 695 (w), 615 (m) cm^{-1}; mass spectrum, m/e 231.9604 (m$^+$), calcd for $C_{10}H_7Cl_3$ m/e 231.9613.

Reaction of 1-Chloro-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane (26) with Potassium *tert*-Butoxide in Tetrahydrofuran. A solution of **26** (0.5 g, 2.08 mmol) in tetrahydrofuran (3 mL) was added to a slurry of potasstium *tert*-butoxide (1.17 g, 10.4 mmol) in tetrahydrofuran (14 mL) at 0 °C. The reaction was allowed to stir for 30 min, diluted with water, and extracted several times with ether. The combined extracts were washed with water and dried over Na_2SO_4. Concentration in vacuo yielded 0.36 g (84% recovery) of brown solid which was analyzed by GC/MS and by comparison with authentic samples and shown to be **6** (20%), **8** + **9** (9%), **10** (5%), **11** (40%), **14** (4%), **15** (12%), and **16** (4%).

Reaction of 3,4-Benzo-1,6,6-trichlorobicyclo[3.1.0]hexane (26) with Potassium *tert*-Butoxide in Tetrahydrofuran in the Presence of 1,4-Cyclohexadiene. 1,4-Cyclohexadiene (2 mL) was added to a slurry of potassium *tert*-butoxide (1.17 g, 10.4 mmol) in tetrahydrofuran (15 mL). The resulting mixture was cooled to 0 °C, and a solution of **26** (0.5 g, 2.08 mmol) in tetrahydrofuran (2 mL) was added dropwise. The reaction mixture was then allowed to warm to room temperature over 1 h, diluted with water, and extracted with ether. The extracts were washed several times with water and dried over Na_2SO_4. Removal of the solvent in vacuo yielded 0.44 g (86% recovery) of crude material which was analyzed by GC/MS and shown to be **6** (37%), **10** + **11** (51%), **14** (2%), **15** (3%), **16** (1%), **27** + **28** (4%), **29** (1%), **30** (<1%), and phenylnaphthalene (1%). The mixture of **27** and **28** exhibits the following: NMR δ 7.3–7.4 (m, 3 H), 7.4 (s, 5 H), 7.7–7.9 (m, 3 H); IR (neat) 3070 (m), 1625 (w), 1590 (s), 1500 (m), 1450 (w), 1420 (m), 1380 (m), 1340 (w), 1290 (w), 1120 (w), 1095 (w), 1035 (w), 975 (m), 880 (m), 860 (s), 840 (m), 785 (s), 770 (m), 750 (s), 730 (m), 705 (s), 630 (m), 610 (m) cm^{-1}; mass spectrum, m/e 238.0549, calcd for $C_{16}H_{11}Cl$ m/e 238.0549. Anal. Calcd for $C_{16}H_{11}Cl$ (**27** + **28**): C, 80.50; H, 4.64. Found: C, 80.39; H, 4.79.

Synthesis of 3-Bromo-6,6-dichlorobicyclo[3.1.0]hexane (31). Alcohol-free chloroform (35 mL, 0.44 mol), 4-bromocyclopentene (18.2 g, 0.124 mol), and hexadecyltrimethylammonium bromide (0.33 g, 0.9 mmol) were added to a 500-mL three-necked flask fitted with a mechanical stirrer, a reflux condenser, and an addition funnel. A solution of sodium hydroxide (46 g, 2 mol) in water (77 mL) was then added dropwise, and the resulting mixture was stirred overnight at room temperature, poured over ice, and acidified with 10% sulfuric acid. The product was extracted into ether, washed with water and saturated sodium chloride solutions, and dried over sodium sulfate. After removal of the ether, vacuum distillation afforded 2.03 g (7% yield) of **31**: bp 47 °C (0.6 mmHg); NMR δ 2.0–2.8 (m, 6 H), 4.1–4.6 (m, 1 H).

Reaction of 3-Bromo-6,6-dichlorobicyclo[3.1.0]hexane (31) with Potassium *tert*-Butoxide in Dimethyl Sulfoxide. Compound **31** (0.806 g, 3.52 mmol) was added dropwise within 10 min to a solution of potassium *tert*-butoxide (0.97 g, 8.7 mmol) in dimethyl sulfoxide (15 mL) while the temperature was maintained at 15–20 °C. After the mixture was stirred at room temperature an additional 0.5 h, the reaction was quenched with 20 mL of water. The products were extracted into pentane and dried over sodium sulfate. Gas chromatography of the pentane solution

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of the products showed one major product (98.4%) identified as chlorobenzene. Two minor products were not identified, although neither had the retention time of benzene.

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Registry No. **5**, 56485-66-6; **6**, 91-58-7; **7**, 71436-63-0; **8**, 71436-64-1; **9**, 71436-65-2; **10**, 2050-69-3; **11**, 2050-75-1; **12**, 71436-66-3; **13**, 71436-67-4; **14**, 71436-68-5; **15**, 71436-69-6; **16**, 71436-70-9; **23**, 74925-43-2; **24**, 74925-44-3; **25**, 51526-36-4; **26**, 74925-45-4; **27**, 74925-46-5; **28**, 66768-81-8; **31**, 74925-47-6; indene, 95-13-6; 1,2-dibromoindan, 20357-79-3; 2-bromoindene, 10485-09-3; 2,3-benzobicyclo[3.1.0]hexane, 15677-15-3; 1,4-dihydronaphthalene, 612-17-9; 1,3-naphthalenediol, 132-86-5; chlorobenzene, 108-90-7; 1-bromo-2-aminonaphthalene, 20191-75-7; 2-chloro-1-naphthol, 606-40-6; 2-chloroindene, 18427-72-0; 1,2-dichloroindan, 74925-48-7; 4-bromocyclopentene, 1781-66-4; 2-chloronaphthalene-1,3-diyl, 74925-49-8.

Models for Glycoside Hydrolysis. Synthesis and Hydrolytic Studies of the Anomers of a Conformationally Rigid Acetal

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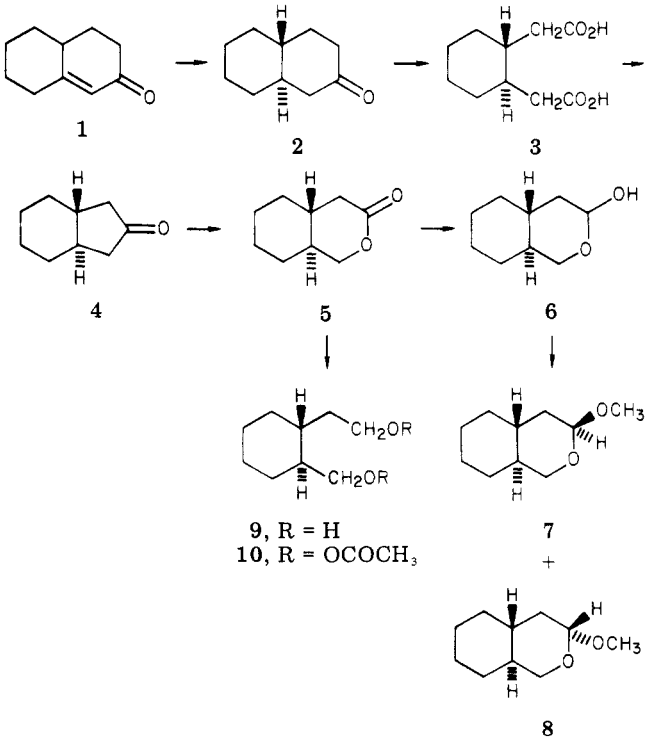
The methyl acetals of 2-hydroxy-3-oxa-*trans*-decalin were synthesized as models for conformationally rigid methyl glycosides. The compounds were prepared by Baeyer–Villiger oxidation of *trans*-hexahydrohydrindan-2-one followed by reduction of the resulting lactone with diisobutylaluminum hydride. Treatment of the hemiacetal with methanol and an acid catalyst afforded a mixture of acetals which were separated by chromatography and identified by NMR. Hydrolytic studies were carried out under a range of acid concentrations and temperatures. The mechanistic implications of the relative hydrolysis rates (axial/equatorial ratio of 1.51 ± 0.22) and activation parameters are discussed.

Due to the biological and commercial importance of the reaction, the acid-catalyzed hydrolysis of glycosides has been the object of extensive research as well as the subject of several reviews.[1,2] In spite of abundant data on glycoside hydrolysis, an in-depth understanding of the factors that affect the rate remains obscure. One of the factors which affects the rate of hydrolysis of glycosides is the configuration about the anomeric center. In an extensive study comparing the rates of hydrolysis of the anomers of methyl glycosides, Feather and Harris[3] found that the β anomers containing the equatorial methoxy group hydrolyzed more rapidly than the α anomers containing the axial methoxy group. Ten anomeric pairs were selected such that the major conformation of both members of the pair is the same. The hydrolysis ratio (axial to equatorial) was 0.52 ± 0.12. Since the equatorial isomer is more stable than the axial as a result of the anomeric effect,[4] the conformations of the initial state determined the relative rates of hydrolysis. This general conclusion appears to be contradicted by the observation that the β anomers of *O*-aryl glycosides frequently hydrolyze more slowly than the corresponding α anomer.[3] The contradiction may be resolved by proposing that the stable conformation of the α anomer of *O*-aryl glycosides contains the leaving group in the equatorial position. Hence, it becomes apparent that the interpretation of the relative rates of anomer hydrolysis rests on one's ability to determine the most stable conformation. Furthermore, although the assigned conformation is more stable than other possible conformations, the molecule is not compelled to react in that conformation. To overcome these difficulties, we synthesized the conformationally rigid methyl acetals **7** and **8** as models for a study of the hydrolysis of axial and equatorial methyl glycosides.

Scheme I



1 2 3 4 5 6

9, R = H
10, R = OCOCH3

7 + 8

Results and Discussion

The conformationally rigid acetals **7** and **8** were synthesized by the routes outlined in Scheme I. The starting material, $\Delta^{1,9}$-3-octalone (**1**), was prepared by a literature

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