Pentacyclodecane Chemistry. XI. Low-Temperature Proton Magnetic Resonance and Other Studies on the Nature of the Secondary and Tertiary Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl (1,3-Bishomocubyl) Cations[1]

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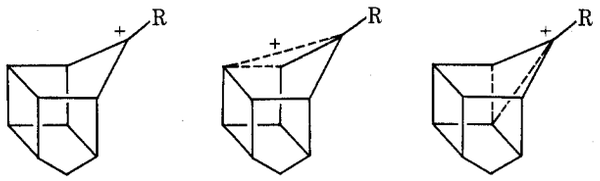
Reaction of 6-methylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-*anti*-6-ol (**10**) with fluorosulfonic acid–sulfur dioxide at −50° gave the ring-opened allylic 3-methyl-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-yl cation (**21**). *anti*-6-Chloropentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (**14**) was synthesized by a photochemical ring closure; attempts to prepare the corresponding secondary cation **1** by the reaction of **14** with antimony pentafluoride or the reaction of the corresponding alcohol **8** with fluorosulfonic acid–antimony pentafluoride gave either decomposition products or the protonated alcohol. Oxymercuration–reduction of 6-methylenepentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (**11**) gave the alcohols, 6-methylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-*syn*-6-ol (**9**) and **10**, in a 50:50 ratio. The acid-catalyzed addition of formic acid to olefin **11** and the acid-catalyzed equilibration of the formate **15** of the syn alcohol **9** at 27° gave the formate **15** and the formate **16** of the anti alcohol **10** in a 61:39 ratio, respectively. The *p*-nitrobenzoates **20** and **19** of alcohol **9** and of 6-phenylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol (**18**), respectively, were prepared, and a brief examination of their hydrolysis reactions was made. The relationship of these reactions to the problem of the nature of 1,3-bishomocubyl cations is discussed.

Previous papers of this series have described our efforts to determine the nature of the 1,3-bishomocubyl cation which is involved in solvolytic and related reactions.[1,2] Stereochemical and kinetic data seem most consistent with bridged ions, **3** and **5**, in the secondary system, but the classical ion **1** has not been ruled out.[1,2]

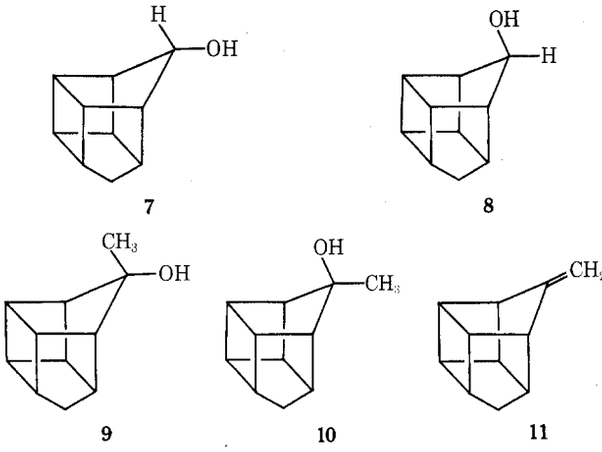


1, R = H; **2**, R = CH_3 — **3**, R = H; **4**, R = CH_3 — **5**, R = H; **6**, R = CH_3

The data on reactions which formally involve the tertiary carbonium ion **2** also are ambiguous with respect to the possible involvement of bridged ions such as **4** and **6**.[1,2d] This paper describes our attempts to observe, by nmr, the secondary and tertiary 1,3-bishomocubyl cations in strong acid media in an effort to gain additional insight into the nature of these carbonium ions. Also reported are several other reactions which relate to the same question.

Results

The stereospecific syntheses of the requisite alcohols **7–9** have been described previously.[1,2a,b,d] The anti tertiary alcohol **10** was obtained only in a 56:44 mixture with the syn isomer **9** by epoxidation of the olefin **11** followed by hydride reduction.[1,2d] The isomer **10** was obtained pure by fractional crystallization.[1]



7 — **8** — **9** — **10** — **11**

Attempts were made to take greater advantage of the slight inherent steric preference for attack on the one-carbon bridge of the 1,3-bishomocubyl skeleton from the anti direction[1,2b] by using the large mercury atom in oxymercuration reactions. Oxymercuration of the olefin **11** followed by sodium borohydride reduction proceeded to give a 50:50 mixture of the alcohols **9** and **10**. The complete lack of stereoselectivity does not necessarily indicate the absence of unbalanced steric effects in **11**, but could indicate a thermodynamic rather than kinetic distribution of products. The equilibrium distribution of alcohols **9** and **10** and of **7** and **8** is 50:50.[1,2b] This thermodynamic distribution probably arises by an equilibration of the initially formed mercurinium ions, a reaction which is well documented.[3] It has been shown, however, that in many cases oxymercuration is highly stereoselective and that the effects of equilibration can be minimized by using very short reaction times.[4] In our work reaction times as short as 1 min failed to alter the ratio of isomeric alcohols. Apparently the equilibration of the mercurinium ions is extremely fast. It was suggested that an equilibration effect can be overcome by carrying out the reaction in acetic acid.[5] This method presumably causes an acetate ligand to be transferred directly from mercury to carbon by an SNi-type process. Application of this technique in our work also failed to alter the isomer ratio.

Treatment of either the syn or anti isomers **9** and **10** with fluorosulfonic acid at −78° gave complex but identical nmr spectra at −30° (see Experimental Section). When a sample of the syn hydroxy isomer **9** was treated with fluorosulfonic acid–sulfur dioxide at −78° the spectrum at −50° was different (Figure 1). At −30° the spectrum was not the same as that obtained at −30° in fluorosulfonic acid alone; all the original absorptions had broadened. Lowering the temperature did not regenerate the original spectrum. When the sample was warmed to −10° the spectrum deteriorated rapidly, finally becoming a broad absorption at 4–1 ppm.

All attempts at preparation of the secondary pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl cation **1** (or a characterizable derived ion) from the alcohol **8** were futile. Dissolution of **8** in fluorosulfonic acid alone or in fluorosulfonic acid–

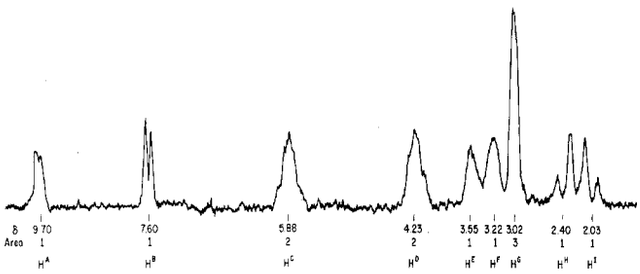
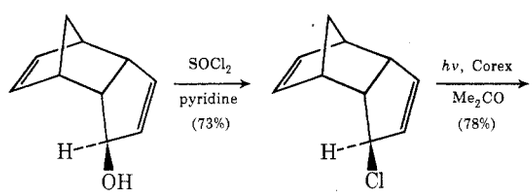


Figure 1. Nmr spectrum of species derived from alcohol **9** in fluorosulfonic acid–sulfur dioxide at −50°.

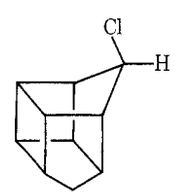
antimony pentafluoride in liquid sulfur dioxide at −78° gave a very dark solution. The nmr spectra of these solutions (−30°) and the alcohol **8** (in $CDCl_3$) were very similar, the main difference being that the proton of the carbinol carbon (C-6) was shifted downfield by about 1.1 ppm in the strong acid solutions. Ice water hydrolysis of the alcohol **8**–acid mixture gave only the starting alcohol **8**; none of the epimeric syn alcohol **7** was detected.

Secondary cations have been generated by reaction of an alkyl fluoride[6] or chloride, etc.,[7] with antimony pentafluoride and observed by nmr spectroscopy. A halogenated derivative of 1,3-bishomocubane was needed in order to attempt the generation of the secondary cation **1** by reaction of the halogenated derivative with antimony pentafluoride. Attempts to replace the hydroxyl group of the alcohol **8** with a chlorine atom were unsuccessful.

The anti chloride **14** was prepared from the anti allylic chloride **13** by photochemical ring closure.[8] The chloride **13** was synthesized by reaction of the anti allylic alcohol **12** with thionyl chloride in pyridine. The stereochemistry of



12 **13**



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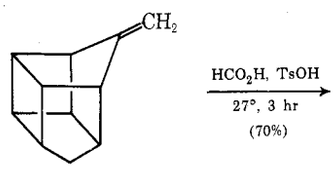
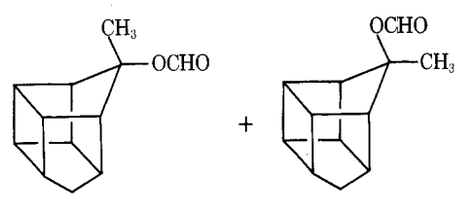
chlorides **13** and **14** was determined readily by nmr spectroscopy: **13** by comparison with **12** and the syn epimer of **12**, and **14** by comparison with the corresponding alcohol **8**, its epimer **7**, and other derivatives.[2b,9]

The product which resulted from the addition of *anti*-pentacyclodecyl chloride (**14**) to antimony pentafluoride in sulfur dioxide at −78° produced an nmr spectrum (at −50°) which showed only a weak, broad, unresolved absorption at 5–1 ppm. Similar results were obtained with **14** in antimony pentafluoride–sulfur dioxide–sulfuryl fluoride at −80°.

The authentic formate esters **15** and **16** were prepared from the corresponding alcohols **9** and **10** by reaction with acetic–formic anhydride. The *p*-toluenesulfonic acid catalyzed addition of formic acid to the olefin **11** produced a 61:39 mixture of syn and anti formates **15** and **16**, respectively. However this product distribution apparently was thermodynamically controlled; subjection of the syn formate **15** to the reaction conditions also gave a 61:39 product (**15**:**16**) distribution. The olefin **11** was insoluble in formic acid, thereby precluding an attempt at the homogeneous uncatalyzed addition. Heating either the syn (**9**) or anti (**10**) tertiary alcohol in refluxing formic acid (~100°) for 4 hr gave the same mixture of product formates (~35%) and decomposition products. None or very little of the unrearranged formates **15** and **16** was formed. The product mixture appeared to consist mainly of rearranged secondary formates, tentatively assigned as 1,4-bishomocubyl[2b] derivatives.

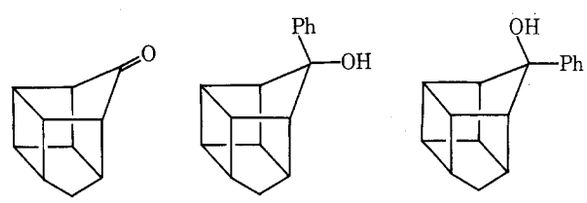


11

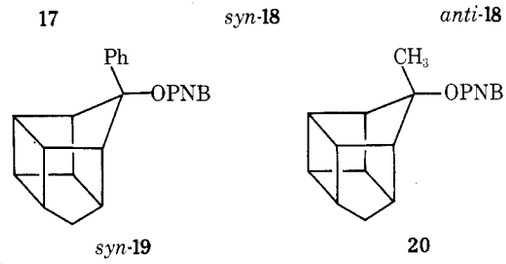


15 **16**
61 39

Phenylmagnesium bromide and the ketone **17** gave a mixture of phenylcarbinols, *syn*-**18** and *anti*-**18**. The exact



17 *syn*-**18** *anti*-**18**



syn-**19** **20**

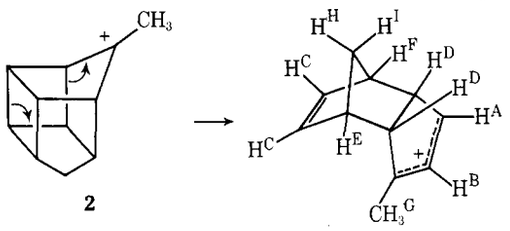
composition of this mixture could not be determined readily. It was apparent that one isomer predominated by at least a 4:1 ratio as determined by comparing infrared and nmr spectra of the crude reaction mixture and the purified major isomer which was isolated easily by recrystallization. The major isomer presumably was the syn hydroxy compound *syn*-**18**; this assignment was based on the analogy of the methyl Grignard reaction, methyllithium addition, and hydride reductions[1,2b] of the ketone **17**.

The *p*-nitrobenzoate ester, presumably *syn*-**19**, of the purified phenyl carbinol was prepared by a standard procedure, as was the methyl-substituted derivative **20**. The phenyl-substituted *p*-nitrobenzoate **19** was relatively unreactive in 60% aqueous dioxane; at 85°, 80% was recovered after 16 hr. At 115°, hydrolysis of **19** was nearly complete in 72 hr. The product (91%) was probably a mixture of the syn and anti isomers of the phenyl carbinol **18** based on spectroscopic data. The spectra indicated a more nearly equal distribution of the syn and anti isomers than was formed in the Grignard reaction with the ketone **17**. However, the exact isomer distribution could not be determined. The methyl-substituted *p*-nitrobenzoate **20** was resistant to sol-

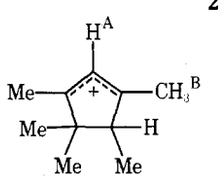
volysis in 60% aqueous dioxane at 100°. After 240 hr, 91% of the starting ester was recovered.

Discussion

The low-temperature (−30 or −50°) pmr spectra which were obtained after dissolving the tertiary alcohols **9** and **10** in fluorosulfonic acid are not consistent with the cation **2**. The low-field absorption at 9.7 ppm (−50°) is consistent with a proton on a carbon atom which bears considerable positive charge, but not a full positive charge.[6] The allylic cation **21** is a possible structure for the species that produced the spectrum in Figure 1. The protons corresponding



2 **21**



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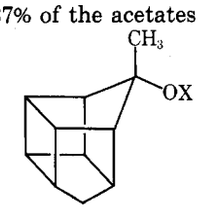
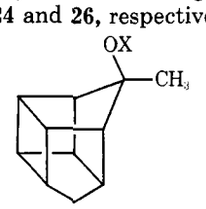
to those listed in Figure 1 are shown on the structure of **21**. For comparison purposes, the cyclopentenyl cation **22** in 96% sulfuric acid exhibited proton resonances at 7.62 ppm for H^A and 2.93 ppm for H^B.[10] Ion **21** must be regarded as a tentative assignment for the species derived from alcohol **9** in fluorosulfonic acid–sulfur dioxide, since attempts to isolate a derived alcohol by hydrolysis with ice in liquid sulfur dioxide[6] gave only a black, carbonaceous material. Ion **21** appears to be the simplest structure which is qualitatively in accord with the nmr spectrum and is easily derivable from the parent ion **2**.

The magnitude of the chemical shift of the proton on the carbinol carbon (C-6) of the secondary alcohol **8** in deuteriochloroform and fluorosulfonic acid is consistent with the formation of a protonated alcohol. The signal for the proton on the hydroxyl-bearing carbon atom of isopropyl alcohol (Me_2CHOH) appeared at 4.00 ppm[11] in deuterated chloroform solution, while in fluorosulfonic acid–antimony pentafluoride–sulfur dioxide at −60° this proton ($Me_2CHOH_2^+$) appeared at 5.5 ppm.[12] Similar results with other alcohols have been observed by Olah and coworkers.[13] In general they found that primary and secondary alcohols reacted with fluorosulfonic acid–antimony pentafluoride to give only the protonated alcohols[12] or monosulfates.[13] The only exceptions to this rule were *exo*-2-norbornanol and benzhydrol, both of which gave well-resolved nmr spectra of the corresponding carbonium ions.[13] In these cases cations are formed presumably because they are stable.

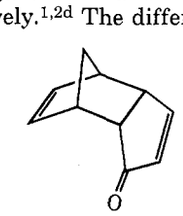
Acetolysis of the tosylates **23** and **25** gave 63–75 and 25–37% of the acetates **24** and **26**, respectively.[1,2d] The difference in behavior of the cationic species generated by the acetolyses of these tosylates at 45° and the reaction of the alcohol **9** in fluorosulfonic acid–sulfur dioxide at −50° is attributed mainly to the much longer lifetime of the ion generated by the latter route. In the solvolyses the ion's lifetime is too short to allow appreciable ring opening to occur. The driving force for the ring opening probably is relief of strain in the pentacyclic ring system (16.4 kcal/mol for the hypothetical **17** → **27** process[14]).



23, X = Ts
24, X = Ac



25, X = Ts
26, X = Ac



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The *p*-toluenesulfonic acid catalyzed addition of acetic acid to the olefin **11** at ~25° gave a 68:32 mixture of acetates **24** and **26**, respectively.[1] The addition of formic acid to the olefin **11** was of interest, since one would predict the intermediate cation's positive charge to be more localized in this more polar medium than in acetic acid. If we assume, for example, that a single cation is involved in the acetic acid addition reaction, and that this cation has structure **4** in which **2** is the major resonance contributor and a localized secondary cation is the minor contributor, then the structure of the cation involved in the formic acid addition reaction should be more nearly like **2** with less contribution from the secondary resonance form. This prediction is based on the higher solvation energy associated with a localized positive charge as in **2** when compared with the more diffuse positive charge in a bridged ion[15] such as **4** (or **6**). Thus one might predict a syn:anti formate ratio (**15**:**16**) that was closer to 20:80 than to the 68:32 ratio observed for the acetates **24** and **26**. The 20:80 ratio was that observed for the syn and anti attack on the ketone **17** by metal hydrides and organometallic reagents.[1,2b] In addition the tosylate anion should have less effect (less ion pairing) in formic acid, which is a more highly ionizing medium than is acetic acid. However, the 61:39 ratio of syn (**15**) to anti (**16**) formates, obtained from the addition of formic acid to the olefin **11** in the presence of *p*-toluenesulfonic acid at 27°, apparently is the equilibrium ratio of the two formates. Treatment of the authentic syn formate **15** under the same reaction conditions gave the same mixture of formates. Since the kinetic product distribution from the formic acid–olefin **11** reaction was not determined, nothing can be said about the character of the presumed cationic intermediate **2**, **4**, or **6** in this reaction. Interestingly the corresponding tertiary acetate esters **24** and **26** were stable at 45° in acetic acid which contained 1 equiv of *p*-toluenesulfonic acid. The mechanism for isomerization of the formates **15** and **16** probably involves protonation followed by the loss of formic acid, and reversal of these processes. The reasons for the isomerization in formic acid and the stability of the acetates **24** and **26** in acetic acid are probably the greater protonating ability of the *p*-toluenesulfonic acid–formic acid mixture and the higher dielectric constant of formic acid compared with acetic acid (58.5 *vs.* 6.15[16]). The formation of charged intermediates, such as **2** and the protonated esters, would be lower energy processes in the higher dielectric medium.

Experimental Section

General. Melting points were taken in capillary tubes and were uncorrected. Boiling points were uncorrected. Infrared spectra were obtained by Mr. F. L. Beman and coworkers with a Perkin-Elmer 337 grating infrared spectrophotometer. Nmr spectra were obtained by Mr. Beman and coworkers with a Varian A-60 analytical spectrometer operating at 60 MHz. All chemical shifts (δ) are relative to internal tetramethylsilane (positive when downfield from the reference). Mass spectral analyses were carried out by Dr. L. A. Shadoff and coworkers with a magnetically scanning 90° sector spectrometer, an electron ionizing voltage of 75 eV, and a sample inlet temperature of 200°. High-resolution mass spectra were obtained with a CEC 21-110B spectrometer that had a variable-temperature direct probe sample introduction system. Gas chro-

matographic analyses were carried out with a F and M 500 temperature-programmed gas chromatograph. Elemental analyses were determined by Mr. R. B. Nunemaker and coworkers.

Oxymercuration of 6-Methylenepentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (11). A. In Water. The olefin 11[1] (18.7 g, 0.13 mol) was added dropwise over a period of 5 min to a stirred solution of mercuric acetate (41.5 g, 0.13 mol) in 130 ml of water and 130 ml of tetrahydrofuran which was cooled in an ice bath. The clear solution was stirred for an additional 5 min, and 130 ml of 3 *M* sodium hydroxide solution followed by 130 ml of a solution 3 *M* in sodium hydroxide and 0.5 *M* in sodium borohydride were added at a rate sufficient to maintain the temperature below 25°. The solution was stirred for another 10 min and saturated with sodium chloride. The organic layer was separated and dried (Na_2SO_4). The tetrahydrofuran was removed under vacuum to give 19.5 g (93%) of a 50:50 mixture (by nmr[1]) of syn and anti alcohols **9** and **10**. Control experiments carried out on a small scale (10 mmol of olefin and 10 mmol of mercuric acetate) utilizing shorter total reaction times (5, 1 min) gave consistently good yields (>90%), but did not change the ratio of isomeric alcohols.

B. In Acetic Acid. To a stirred solution of mercuric acetate (1.75 g, 5.5 mmol) in 15 ml of acetic acid was added the olefin 11 (0.72 g, 5.0 mmol). The mixture was stirred for 5 min and poured into 125 ml of 5.6 *M* sodium hydroxide solution. The temperature rose to 60–70° and was maintained at this temperature for 15 min. Ten milliliters of a solution 3 *M* in sodium hydroxide and 0.5 *M* in sodium borohydride was added. The solution was stirred for an additional 5 min, cooled, extracted with ether, and dried (Na_2SO_4). The solvent was removed under vacuum to give 0.6 g of a waxy solid. Nmr analysis of the product indicated that it consisted of a mixture of syn and anti alcohols (~67%) **9** and **10** (~50:50) and unhydrolyzed syn and anti acetates (~33%) **24** and **26** (~50:50).

Low-Temperature Nmr Spectra of *syn*- (9) and 6-Methylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-*anti*-6-ol (10) in Fluorosulfonic Acid. These spectra were obtained by adding concentrated solutions (~0.1 g/0.1 ml) of the alcohol[1] in chloroform to ~1 ml of fluorosulfonic acid at −7°. The small amount of chloroform was used as an internal reference[12] at 7.27 ppm. Both syn (**9**) and anti (**10**) alcohols gave identical spectra at −30°; a singlet at 9.83 (1 H), a doublet at 8.07 (1 H, J = 5 Hz), a broad absorption at 5.37 (1 H), singlets at 3.67 (1 H), 3.27 (3 H), 2.97 (1 H), and 2.79 (1 H), a broad singlet at 2.28 (2 H), and two doublets centered at 1.48 (1 H) and 0.64 ppm (1 H) (J = 12 Hz). Areas of these peaks could be determined only approximately, since some decomposition caused broad absorption at 4–1 ppm. As the temperature of these solutions was raised to −10° the spectra quickly degenerated into low-lying broad absorption between 4 and 1 ppm. The original spectra were not regenerated as the temperature was lowered again.

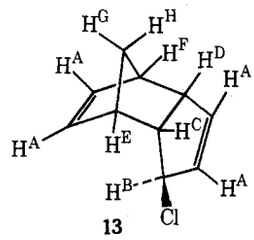
A different spectrum was obtained when the syn alcohol **9** was dissolved in FSO_3H–SO_2 at −78°, and the spectrum was recorded at −50° (Figure 1). The solution was warmed to −30°; the spectrum degenerated, but did not revert to the spectrum obtained originally at −30° in FSO_3H alone. When the solution was warmed to −10°, the spectrum decayed to a broad absorption between 4 and 1 ppm, and did not sharpen when the solution was cooled.

When the acid–cation solution at −50° was hydrolyzed according to the procedure of Olah and coworkers,[6] by pouring the solution into ice–SO_2 at −78°, only an ether-insoluble, carbonaceous tar was formed.

Low-Temperature Nmr Spectra of *anti*-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol (8) in Fluorosulfonic Acid. This spectrum was obtained by adding ~1 ml of fluorosulfonic acid at −78° to 0.1 g of the alcohol 8[2b] at −78°. The solid alcohol dissolved very slowly when the mixture was shaken. A small amount (~10 mg) of tetramethylammonium fluoroborate was added as an internal reference (3.1 ppm[17]). The spectrum was obtained at −30° and consisted of a singlet at 5.4 (1 H), overlapping multiplets at 3.0 and 2.9 (8 H), and two unsymmetrical doublets centered at 1.8 and 1.4 ppm (1 H each, $J \simeq$ 12 Hz). The spectrum quickly degenerated when the sample was warmed to −10°.

A good spectrum was also obtained in antimony pentafluoride–fluorosulfonic acid–sulfur dioxide. In this case a mixture of 1.1 ml (15 mmol) of fluorosulfonic acid and 0.5 ml (7 mmol) of antimony pentafluoride was cooled to −20° with stirring. Approximately 10 ml of sulfur dioxide was condensed into this mixture, which was then cooled to −78°. The alcohol 8 (1.5 g, 10 mmol) was added slowly to the stirred solution as a solid. After the mixture was stirred at −78° for 1 hr, most of the solid had dissolved. The nmr spectra at −50 to −10° were identical with the one obtained above but did not degenerate at −10° in a period of 15 min. The total acid–SbF_5–alcohol solution was poured onto ~200 g of ice. The main product was an ether-insoluble green solid. The soluble portion was taken up in ether, washed with water, and dried. Evaporation of the solvent and sublimation of the residue afforded 0.25 g (17%) of alcohol. Analysis by nmr indicated only the starting isomer 8.

***endo,anti*-5-Chlorotricyclo[5.2.1.0^{2,6}]deca-3,8-diene (13).** Thionyl chloride (15.6 g, 0.13 mol) was added to a stirred solution of *endo,anti*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol (**12**)[18] (16.0 g, 0.11 mol) in 300 ml of dry ether, and the solution was stirred at ~25° for 15 min. No apparent reaction ensued. Pyridine (25 ml, 0.31 mol) was added dropwise to the mixture with immediate formation of the hydrochloride salt. After the mixture was stirred at ~25° for 1 hr, enough water (100 ml) was added to dissolve all the solids, and the ether layer was separated and washed with water. Drying, evaporating, and distilling the residue afforded 13.2 g (73%) of the allylic chloride **13**: bp 60–64° (1 mm); n^{25}D 1.5324; ν_{max} (neat) 3070 (m, =CH), 2970 (s), 2910 (m) and 2875 (m) (CH), 1615 (w, cyclopentenyl C=C), 1580 (w, norbornenyl C=C), 1345 (s), 772 (s), 726 cm^{-1} (s, *cis*-CH=CH–); nmr spectrum (CCl_4) a multiplet at 6.3–5.4 with an intense singlet at 5.90 and another maximum at 5.59 (4.0 H, H^A), a multiplet at 4.33–4.15 with a maximum at 4.25 (H^B, 0.9 H), a multiplet at 3.6–3.2 with maximum intensity at 4.41 (1.0 H, H^C or H^D), a multiplet at 3.3–2.7 with an intense maximum at 3.07 and a weaker maximum at 2.85 (3.1 H, H^D or H^C, H^E, H^F), and two slightly overlapping unsymmetrical doublets of triplets centered at 1.59 (H^G, J_{GH} = 8.2, $J_{EG,FG}$ = 1.6 Hz) and 1.36 ppm (H^H, J_{GH} = 8.1, $J_{EH,FH}$ = 1.2 Hz) (2.0 H total); mass spectrum *m/e* 66 ($C_5H_6^+$), 115 (M$^+$ − HCl, CH_3), 128 (M$^+$ − HCl, H_2), 129 (M$^+$ − HCl, H), 130 (M$^+$ − HCl), 131 (M$^+$ − Cl), 166 and 168 (M$^+$).

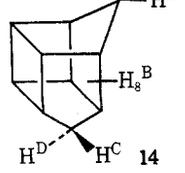


13

Anal. Calcd for $C_{10}H_{11}Cl$: nuclidic mass, 166.0549. Found: nuclidic mass, 166.0531.

The chloro compound **13** was unstable and turned dark in a few days.

***anti*-6-Chloropentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (14).** A solution of 10.0 g (60 mmol) of the allylic chloride **13** in 150 ml of distilled acetone was purged with oxygen-free nitrogen for 2 hr. This solution was irradiated through a Corex filter with a 450-W Hanovia medium-pressure mercury arc lamp in an immersion reactor. The progress of the reaction was followed by gc analysis on a 10 ft × 0.25 in. column packed with 20% Apiezon L on Chromosorb WAW at 225° with a helium flow of 40 ml/min. The product chloride **14** had a retention time of 11.0 min, and the starting material **13** eluted at 9.5 min. After 4 hr there was greater than 99% reaction, and the irradiation was stopped. The solvent was removed under vacuum, leaving ~10 g of a brown oil. Distillation of the residue afforded 7.8 g (78%) of a slightly yellow, partly crystalline oil: bp 58–60° (0.5 mm); n^{20}D 1.5351; ν_{max} (neat) 2980 (s) and 2870 (m) (CH), 1290 (s), 1265 (s), 790 (s), 750 cm^{-1} (s); nmr spectrum (CCl_4) a singlet at 4.20 (0.9 H, H^A), a multiplet at 3.3–2.1 with maxima at 2.80 and 2.62 (8.0 H, H^B), an unsymmetrical doublet at 1.69 (1.0 H, H^C, J_{CD} = 11.1 Hz), and an unsymmetrical doublet centered at 1.27 ppm (1.1 H, H^D, J_{CD} = 10.9 Hz); mass spectrum *m/e* 38 ($C_3H_2^+$), 51 ($C_4H_3^+$), 66 ($C_5H_6^+$), 77 ($C_6H_5^+$), 91 ($C_7H_7^+$), 100 and 102 ($C_5H_5Cl^+$), 115 (M$^+$ − HCl, CH_3), 116 (M$^+$ − HCl, CH_2), 128 (M$^+$ − HCl, H_2), 129 (M$^+$ − HCl, H), 130 (M$^+$ − HCl), 131 (M$^+$ − Cl), 166 and 168 (M$^+$).



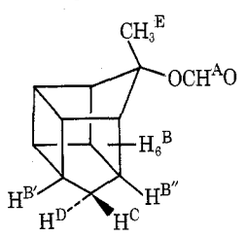
14

Anal. Calcd. for $C_{10}H_{11}Cl$: C, 72.06; H, 6.67; nuclidic mass, 166.0549. Found: C, 72.4; H, 6.94; nuclidic mass, 166.0536.

Low-Temperature Nmr Spectra of Chloride 14 in Antimony Pentafluoride. A solution was made up from 2 ml of sulfur dioxide and 0.2 ml of antimony pentafluoride at −78°. To this stirred solution at −78°, 0.2 ml of chloride **14** was added slowly as a fine spray from a syringe. The dark red solution was stirred at −78° for 15 min and transferred quickly *via* a cold pipette to an nmr tube at −78°. The nmr spectrum was run at −50°; one low-intensity absorption band from ~5 to 1 ppm was observed. Because no reference material was present the position of this band is accurate to no more than 1 ppm.

Essentially the same results were obtained when the spectrum was obtained at −80°. Here the solvent consisted of a ~50:50 mixture of sulfur dioxide and sulfuryl fluoride. Approximately the same quantities of acid, solvent, and halide were used; the same type of spectrum was obtained.

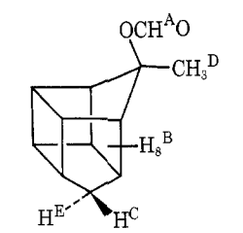
6-Methylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-*syn*-6-yl Formate (15). A solution of acetic–formic anhydride in acetic acid was prepared according to the procedure of Stevens and van Es.[19] The acetic–formic anhydride solution (0.75 ml, 5.6 mmol) was added dropwise to the stirred syn alcohol **9**[1] (94% pure, 6% **10**) (150.5 mg, 0.928 mmol) at 0–5° over a period of ~5 min. The resulting solution was stirred at 0–5° for another 10 min and then at 24–25° for 7 days. The light yellow solution was poured into a solution of 100 ml of water and 50 ml of 5% aqueous sodium bicarbonate solution. The aqueous mixture was extracted with methylene chloride (4 × 15 ml), and the organic extract was washed with water (2 × 30 ml). After being dried ($CaSO_4$), the methylene chloride was evaporated under vacuum to give 136.1 mg (77%) of the syn formate **15** (94% pure by nmr, 6% **16**) as a yellow oil: ν_{max} (neat) 2970 (s) and 2860 (m) (CH), 2740 (w, COH), 1725 (s, C=O), 1450 (m) and 1375 (m) (CH_3), 1172 (s, CO), 825 cm^{-1} (m); nmr spectrum ($CDCl_3$) a singlet at 8.06 (1.0 H, H^A), a multiplet at 3.04–2.54 with maxima at 2.81



15

and 2.71 (7.9 H, H^B), two unsymmetrical doublets of triplets centered at 1.66 (H^C, J_{CD} = 11.3, $J_{B'C,B''C}$ = 1.1 Hz) and 1.35 (H^D, $J_{B'D,B''D}$ = 1.1 Hz) (2.1 H total), and a singlet at 1.27 ppm (3.0 H, H^E); mass spectrum of mixture of formates **15** and **16** given later.

6-Methylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-*anti*-6-yl Formate (16). As described in the preceding experiment, the acetic–formic anhydride solution (0.29 ml, 2.2 mmol) was allowed to react with the anti alcohol **10**[1] (97% pure, 3% **9**) (58.3 mg, 0.359 mmol). Work-up as above gave 38.8 mg (57%) of the anti formate **16** (96% pure by nmr, 4% **15**) as a colorless oil: ν_{max} (neat) 2975 (s) and 2860 (m) (CH), 2740 (w, COH), 1725 (s, C=O), 1450 (m) and 1380 (m) (CH_3), 1172 (s, CO), 942 cm^{-1} (m); nmr spectrum ($CDCl_3$) a singlet at 7.91 (1.0 H, H^A), a multiplet at 3.00–2.50 with maxima at 2.82



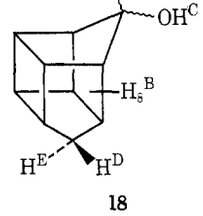
16

and 2.73 (7.7 H, H^B), an unsymmetrical doublet centered at 1.66 (H^C) overlapping a singlet at 1.56 (H^D) (4.3 H total), and an unsymmetrical doublet centered at 1.31 ppm (1.0 H, H^E, J_{CE} = 11.2 Hz).

***p*-Toluenesulfonic Acid Catalyzed Addition of Formic Acid to Olefin 11.** To the olefin **11** (144.1 mg, 0.999 mmol) was added 7.0 ml of formic acid (97+%); the olefin appeared to be largely insoluble. *p*-Toluenesulfonic acid monohydrate (189.5 mg, 0.996 mmol) was added; after the mixture was shaken at ~25° for several minutes the olefin dissolved (0.143 *M* olefin **11**, 0.142 *M* *p*-toluenesulfonic acid). The solution was maintained at 27 ± 1° for 3 hr. The solution turned pale green almost immediately, and became gradually darker as the reaction progressed. At the end of 3 hr the dark blue-green solution was poured into 100 ml of cold water. The aqueous mixture was extracted with methylene chloride (5 × 10 ml), and the combined extracts were washed with 20 ml of 5% aqueous sodium bicarbonate solution and 35 ml of water. After being dried ($CaSO_4$), the methylene chloride was evaporated under vacuum to give 132.2 mg (70%) of a mixture of formates **15** and **16** as a nearly colorless oil. Nmr analysis indicated a composition of 61 ± 1% syn formate **15** and 39 ± 1% anti formate **16** (by electronic integration and planimeter area measurements of the formate proton singlets). The remainder of the nmr spectrum and the infrared spectrum also were consistent with this composition. The mass spectrum showed significant ion peaks at *m/e* (probably structure assignment of ion, and order of intensity, most intense = 1, etc., given): 43, CH_3CO^+, 5; 66, $C_5H_6^+$, 2; 77, $C_6H_5^+$, 11; 78, $C_6H_6^+$, 10; 79, $C_5H_3O^+$ or $C_6H_7^+$, 9; 91, $C_7H_7^+$, 7; 95, $C_5H_4(CH_3)O^+$, 8; 96, $C_5H_4(CH_3)OH^+$, 1; 124, $C_5H_4(CH_3)OCHO^+$, 4; 129, $C_{10}H_9^+$, 3; 144, $M^+ - HCO_2H$, 6; 145, $M^+ - OCHO$, 12; 145, $M^+ - CH_3$, CO, very weak; 162, $M^+ - CO$, very weak; 175, $M^+ - CH_3$, very weak; 190, M^+, ~0.2% of base peak.

***p*-Toluenesulfonic Acid Catalyzed Isomerization of Formate 15.** A 0.147 *M* solution of *p*-toluenesulfonic acid in formic acid was prepared by dissolving *p*-toluenesulfonic acid monohydrate (278.8 mg, 1.466 mmol) in 10.0 ml of 97+% formic acid. A solution of the syn formate **15** (94% pure, 6% **16**) (136.1 mg, 0.715 mmol) in 5.0 ml of the 0.147 *M* *p*-toluenesulfonic acid solution in formic acid (0.143 *M* **15**) turned green within a few minutes, and was maintained at 27 ± 1° for 3 hr. The deep blue-green solution was worked up as in the preceding experiment to give 70.2 mg (52%) of a 61 ± 2:39 ± 2 mixture of formates **15** and **16**, respectively.

6-Phenylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol (18). Phenylmagnesium bromide was prepared by the addition of 10.7 g (68.4 mmol) of bromobenzene in 20 ml of ether to 1.82 g (75 g-atoms) of magnesium turnings under a nitrogen atmosphere. After the reaction started an additional 25 ml of ether was added; the solution refluxed spontaneously for 20 min. To this solution was added a solution of 5.00 g (34.2 mmol) of the ketone **17** in 30 ml of ether, and the solution was refluxed for an additional 2 hr. A few milliliters of water was added, and the mixture was poured into 100 ml of 20% aqueous ammonium chloride solution. The organic layer was separated, washed with water (3 × 100 ml), and dried (Na_2SO_4). The solvent was removed under vacuum to give 7.2 g of crude product. After four recrystallizations from hexane, the white crystals of **18** had constant mp 96–98°; ν_{max} (CCl_4) 3615 (m, free OH), 3450 (m, br, bonded OH), 3070 (m) and 3035 (m) (=CH), 2980 (s) and 2860 (m) (CH), 1505 (m) and 1455 cm^{-1} (m) (C=C); ν_{max} (CS_2) 766 (s), 761 (s), and 695 cm^{-1} (s) (Ph); nmr spectrum ($CDCl_3$) a singlet at 7.30 with minor multiplet bands at 7.5–7.1 (5.0



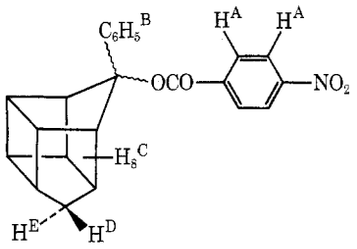
18

H, H^A), a multiplet at 3.4–3.1 with maximum intensity at 3.25 (1.0 H, one of H^B protons), a multiplet at 3.1–2.3 with maxima at 2.91 and 2.58 (6.9 H, seven of H^B protons), a singlet at 1.98 (1.0 H, H^C), an unsymmetrical doublet centered at 1.72 with further ill-defined splitting (1.0 H, H^D, J_{DE} = 11.6 Hz), and an unsymmetrical doublet centered at 1.42 ppm (1.0 H, H^E); mass spectrum *m/e* 66 (weak, $C_5H_6^+$), 91 ($C_7H_7^+$), 105 (base peak, $PhCO^+$), 119 (PhC_2H_2O), 158 ($M^+ - C_5H_6$), 206 ($M^+ - H_2O$), 209 ($M^+ - CH_3$), 224 (M^+).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.67; H, 7.19; mol wt, 224. Found: C, 85.73; H, 7.24; mol wt, 224 (mass spectrometry).

Comparison of the nmr and infrared spectra of the crude reaction mixture with those of the purified material **18** indicated the crude product to contain at least 80% of the isomer which was isolated in purified form (presumably the syn OH); the remainder may have been the epimer.

6-Phenylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl *p*-Nitrobenzoate (19). To a solution of 1.50 g (6.7 mmol) of the alcohol 18 in 40 ml of pyridine was added 1.37 g (7.4 mmol) of *p*-nitrobenzoyl chloride. The solution was stirred at ~25° for 48 hr. The solution was poured into 200 ml of water and extracted with methylene chloride (4 × 25 ml). The combined extracts were washed with water (2 × 10 ml), 0.1 *N* hydrochloric acid (100 ml), and again with water. The solution was dried (Na_2SO_4), and the solvent was evaporated to yield 2.4 g of yellow solid. Recrystallization from methanol–ethanol afforded 2.2 g (88%) of crystals of **19**: mp 139.5–141.5°; ν_{max} (CCl_4) 3070 (m) and 3040 (m) (=CH), 2985 (s) and 2870 (m) (CH), 1730 (s, C=O), 1620 (m, C=C), 1535 (s, NO_2), 1505 (m) and 1455 (m) (C=C), 1360 cm^{-1} (m, NO_2); ν_{max} (CS_2) 1275 (s, CO), 720 (s), 698 cm^{-1} (s, Ph); nmr spectrum ($CDCl_3$) a singlet at 8.20 (4.0 H, H^A), a multiplet at 7.6–7.1 with maximum intensity at 7.33 (5.0

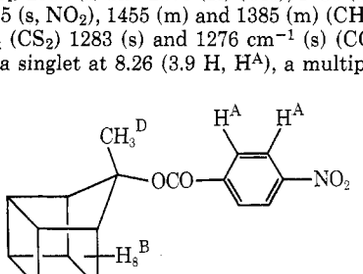


19

H, H^B), a multiplet at 3.8–3.5 with maximum intensity at 3.62 (1.0 H, one of H^C protons), a multiplet at 3.5–3.3 with maximum intensity at 3.40 (1.0 H, one of H^C protons), a multiplet at 3.3–2.4 with maxima at 3.11, 2.84, and 2.63 (6.0 H, six H^C protons), an unsymmetrical doublet centered at 1.78 (1.0 H, H^D, J_{DE} = 11.3 Hz), and an unsymmetrical doublet centered at 1.44 ppm (1.0 H, H^E, J_{DE} = 11.4 Hz); mass spectrum *m/e* 77 ($C_6H_5^+$), 150 ($O_2NC_6H_4CO^+$), 206 ($M^+ - O_2NC_6H_4CO_2H$), 223 ($M^+ - O_2NC_6H_4CO$), 307 ($M^+ - C_5H_6$), 373 (M^+).

Anal. Calcd for $C_{23}H_{19}NO_4$: C, 73.98; H, 5.13; N, 3.75; mol wt, 373. Found: C, 74.06; H, 5.06; N, 3.86; mol wt, 373 (mass spectrometry).

6-Methylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-*syn*-6-yl *p*-Nitrobenzoate (20). To a solution of 1.50 g (9.25 mmol) of the syn alcohol **9**[1,2d] in 10 ml of ether and 1 ml of pyridine was added 1.86 g (10 mmol) of *p*-nitrobenzoyl chloride. The solution was stirred for 48 hr at ~25°. Ether (50 ml) was added and the solution was washed with water (3 × 50 ml). After being dried (Na_2SO_4), evaporation of the solvent afforded 2.75 g of yellow solid. Recrystallization from methonol gave 2.2 g (77%) of pale yellow crystals of **20**: mp 110–112°; ν_{max} (CCl_4) 2980 (s) and 2870 (m) (CH), 1730 (s, C=O), 1620 (m, C=C), 1535 (s, NO_2), 1455 (m) and 1385 (m) (CH_3), 1360 cm^{-1} (m, NO_2); ν_{max} (CS_2) 1283 (s) and 1276 cm^{-1} (s) (CO); nmr spectrum ($CDCl_3$) a singlet at 8.26 (3.9 H, H^A), a multiplet at 3.2–2.6



20

with maximum intensity at 2.81 (8.0 H, H^B), an unsymmetrical doublet centered at 1.69 (1.1 H, H^C, J_{CE} = 11.2 Hz), and an intense singlet at 1.40 (H^D) partially overlapping the stronger low-field branch of an unsymmetrical doublet centered at 1.36 ppm (H^E) (4.0 H total); mass spectrum *m/e* 129 ($M^+ - CH_3$, $O_2NC_6H_4CO_2H$), 144 ($M^+ - O_2NC_6H_4CO_2H$), 150 ($O_2NC_6H_4CO^+$), 161 ($M^+ - O_2NC_6H_4CO$), 245 ($M^+ - C_5H_6$), 311 (M^+).

Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50; mol wt, 311. Found: C, 69.17; H, 5.48; N, 4.62; mol wt, 311 (mass spectrometry).

Hydrolysis of Phenyl *p*-Nitrobenzoate 19. A. At 115°. A solution of 0.748 g (2.0 mmol) of the ester **19** in 80 ml of a 60% dioxane–40% water (by volume) mixture (0.025 *M* **19**) was placed in a glass pressure bottle, heated to reflux, sealed, and heated at 115 ± 5° for 72 hr. The solution was cooled, and the solvent was removed under vacuum. The residual orange solid was dissolved in 50 ml of ether, washed successively with 50 ml of a 5% sodium bicarbonate solution and 50 ml of water, and dried (Na_2SO_4). Evaporation of the ether afforded 0.42 g (91%) of an orange oil. The infrared spectrum was identical with that of the purified alcohol 18 except for some very weak bands in the fingerprint region. The nmr spectrum also was quite similar to that of the alcohol 18 except that the aromatic proton absorption was a multiplet and the methylene region was quite complex. These data indicate that the prod probably is a mixture of syn and anti isomers of 18.

B. At 85°. The reaction in part A was duplicated except that the solution was heated at 85 ± 1° for 16 hr. The solution was cooled, and the solvent was removed under vacuum to give a pale yellow solid. This solid was dissolved in methylene chloride, and the solution was washed successively with water, sodium bicarbonate solution, and water. After being dried, the methylene chloride was evaporated under vacuum to give 0.60 g (80% recovery) of a white solid, which was identified as the starting ester by its infrared and nmr spectra. No significant amount of other products could be detected from the spectra.

Attempted Hydrolysis of Methyl *syn*-*p*-Nitrobenzoate 20. A solution of 0.934 g (3.0 mmol) of the ester **20** in 60 ml of a 60% dioxane–40% water (by volume) mixture (0.05 *M* **20**) was placed in a glass pressure bottle, heated to reflux, sealed, and heated at 100 ± 5°. After 240 hr the reaction mixture was cooled, and the solvent was removed under vacuum. The residual yellow solid was dissolved in 50 ml of ether, washed with 5% sodium bicarbonate solution, and dried (Na_2SO_4). Evaporation of the ether afforded 0.85 g (91%) of yellow crystals. The infrared and nmr spectra were identical with those of the starting material. There was no evidence for the presence of any hydrolysis products.

Acknowledgment. The authors wish to thank Professor D. G. Farnum for helpful discussions.

Registry No.—**8,** 13351-15-0; **9,** 51965-68-5; **10,** 52021-57-5; **11,** 51965-69-6; **12,** 24529-79-1; **13,** 51965-70-9; **14,** 51965-71-0; **15,** 51965-72-1; **16,** 52021-58-6; **17,** 15584-52-8; *syn*-**18,** 51965-73-2; *anti*-**18,** 52021-59-7; *syn*-**19,** 51965-74-3; **20,** 51965-75-4; *p*-nitrobenzoyl chloride, 122-04-3

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