Oxygen Participation Induced by Increased Electron Demand

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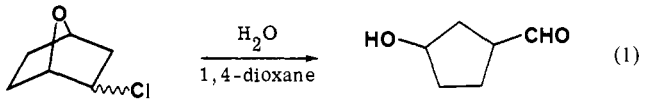
Abstract: *cis,endo*-7-Oxabicyclo[2.2.1]hepta-2,3-diyl dibrosylate (**6**) acetolyzes faster than its diexo isomer (exo/endo ratio of 0.68 at 25 °C). In the corresponding monobrosylate series, the exo isomer acetolyzes more rapidly than the endo isomer (exo/endo ratio of 590 at 25 °C). These kinetic results, together with product studies, indicate that the 7-oxygen does not participate in departure of the endo leaving group in the monobrosylate. Increased electron demand in the diendo dibrosylate, however, brings about the first example of 7-oxygen participation in the norbornyl framework. Positive charge that is developing as the first brosyloxy group departs is destabilized by the presence of the second brosyloxy group. Consequently, participation by the 7-oxygen is induced in order to move positive charge away from the remaining electron-withdrawing brosyloxy group. This observation comprises the first example of inductive enhancement of participation by a heteroatom, oxygen in this case.

Neighboring group participation by ether oxygen is weaker than that of corresponding sulfur or nitrogen systems but should be optimized when the C–O bond is antiperiplanar with respect to the C–X bond to the leaving group.[2] When the oxygen atom is constrained within a polycyclic system, the optimal stereoelectronic arrangement may not be attainable, with resulting diminution in anchimeric assistance. Thus, Martin and Bartlett[3] found no evidence for participation in *endo*-7-oxanorborn-2-yl chloride (*endo*-**1**). In this exo/endo pair, the endo chloride is antiperiplanar to the 7-oxygen atom. The lack of acceleration in the endo form is indicated by a relatively normal exo/endo ratio of 310 at 25 °C. The product for both exo and endo isomers, 3-formylcyclopentanol (eq 1), could be explained in terms of unbridged



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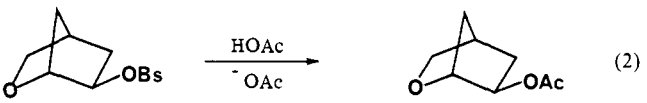
carbocations. The imperfect antiperiplanar relationship, along with the low inherent ability of oxygen to participation because of its electron-withdrawing nature and its low polarizability, prevents any significant amount of participation.

In contrast, oxygen at the 6-position of the norbornyl framework does provide anchimeric assistance to departure of an exo ester (**2**).[4] The *exo-p*-bromobenzenesulfonate solvolyzes about 10^8 times faster than the endo isomer and proceeds to the retained exo acetate almost exclusively (eq 2). The improved neighboring



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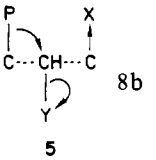
group ability of oxygen at the 6-position may be attributed to an antiperiplanar relationship with the leaving group that is closer to 180° than that in **1**.

In the more flexible oxabicyclo[4.2.1]nonyl and oxabicyclo[3.2.1]octyl systems (**3** and **4**), solvolysis occurs with neighboring group participation when the leaving group is endo, as indicated by kinetic and product studies.[5] The improved ability of oxygen

3 **4**

to participate in **3** and **4**, compared with **1**, may be attributed to the better geometry between the oxygen and the leaving group permitted by the more flexible skeleton.

Because oxygen can range from very weak to strong as a participator within a series of only slightly variable geometries (**1**–**4**), it appeared to be a suitable subject for examination in a series with constant geometry but variable electron demand.[6] We have found that an increase in electron demand at the reactive site can enhance the amount of neighboring group participation.[7] Structure **5** illustrates the requirements for bringing about this inductive enhancement of participation. The group P is sterically



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and electronically capable of participation, Y is an appropriate leaving group, and X is a strongly electron-withdrawing group. The perturbing group X must not be capable of participation itself, for either steric or electronic reasons. We have used this technique to enhance double bond[8] and phenyl[9] participation, and others have used it to enhance σ participation.[10] Before the present study,[11] inductive enhancement had not been observed for participation by the lone pairs of heteroatoms. We report herein that an increase in electron demand can result in participation by the 7-oxygen in 7-oxabicyclonorbornyl systems, contrary to the observation by Martin and Bartlett in the unperturbed system **1**.

Results

We have used the norbornyl framework to embody the elements of structure **5**, in which the participator P is the 7-oxygen, the leaving group Y is 2-*p*-bromobenzenesulfonate (brosylate), and the electron-withdrawing group X is an additional brosyloxy group at the 3-position. Participation should be strongest when the leaving group Y is endo, as in **6**. For comparison, the exo isomer **7** was prepared. This molecule has both leaving group and inductive enhancer (the second brosylate), but the leaving group is in an inappropriate steric position (exo) to permit participation.

(1) This work was supported by the National Science Foundation, Grant CHE83-12285.

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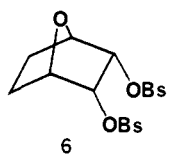
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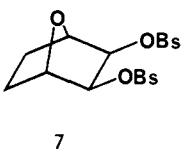
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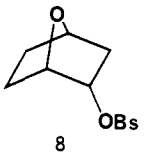
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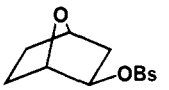
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Compound **8** serves as an additional control, since it contains the stereoelectronically favored endo leaving group but lacks the inductive enhancer. Finally, **9** has the leaving group in the inappropriate exo position and lacks the inductive enhancer.

The key diendo substrate **6** and its diexo isomer **7** were synthesized by the procedure of Scheme I. The Diels–Alder reaction of furan and vinylene carbonate[12] gave a mixture of endo and exo epimers, which were separated by column chromatography. Separate hydrogenation, hydrolysis, and brosylation[13] gave the diendo and diexo isomers, **6** and **7**, respectively.

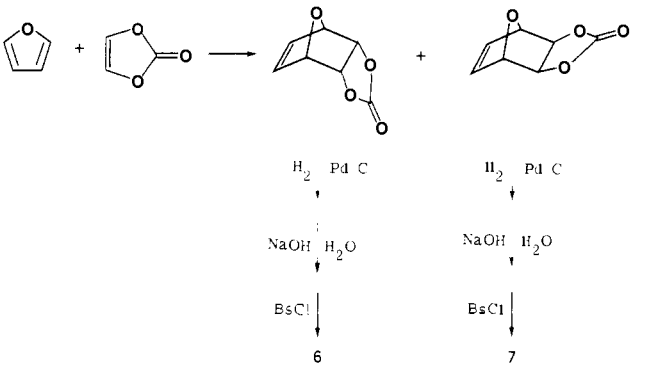
The endo system lacking the inductive enhancer (**8**) was prepared by the procedure of Scheme II. The Diels–Alder adduct of furan and 2-chloroacrylonitrile[14] was hydrogenated and hydrolyzed to give the α-chloro acid as a mixture of epimers. Conversion via the acid chloride to the acyl azide provided a substrate for the Curtius rearrangement. Hydrolysis of the product isocyanate gave the ketone,[15] which was reduced with sodium borohydride exclusively to the endo alcohol. Overall yield from the Diels–Alder adduct to the alcohol was 40–50%. Treatment of the alcohol with brosyl chloride gave **8**.

The exo alcohol **9** lacking the inductive enhancer was prepared by the procedure of Scheme III. The Diels–Alder adduct of furan and methyl acrylate was hydrogenated and saponified to produce the carboxylic acid as a mixture of exo and endo isomers. The acid was converted to the methyl ketone,[16] and Baeyer-Villiger oxidation of the ketone produced only the desired exo acetate. Hydrolysis and brosylation of the acetate gave **9**. The acetates corresponding to **6–8** were prepared for product studies by standard procedures.[17]

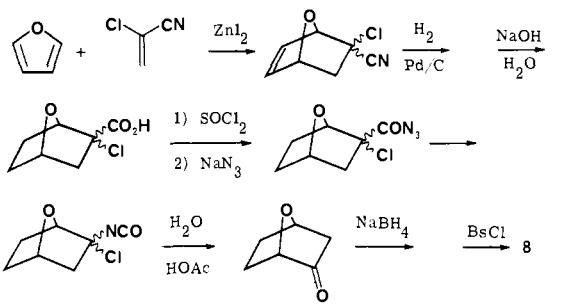
Solvolysis kinetics of brosylates **6–9** were studied in buffered (KOAc) acetic acid by standard titrimetric procedures.[18] Substrates **6**, **8**, and **9** gave extremely good first-order kinetics up to 6–10 half-lives, $\ln (Y - Y_\infty) = -kt + \ln (Y_0 - Y_\infty)$, in which Y is the volume of perchloric acid used in the titration. The rate for **7** was first order up to about 3 half-lives but increased slightly after that. Consequently, initial rates were calculated for **7**. Each compound was solvolyzed at three temperatures. The rate constants are given in Table I and the activation parameters in Table II. Rate constants were calculated at 25, 100, and 200 °C for all substrates.

For product determinations, samples were solvolyzed in buffered acetic acid for 6–10 half-lives. Percentages were obtained by gas chromatography and are uncorrected for thermal conductivity differences. Each component was isolated by preparative GC and identified by comparison of spectral properties with those of authentic materials. The endo monobrosylate (**8**) gave 64% of the endo acetate, 11% of the exo acetate, 9% of 3-formylcyclopentyl acetate, and 15% of a material isolated in too small an amount

Scheme I



Scheme II



Scheme III

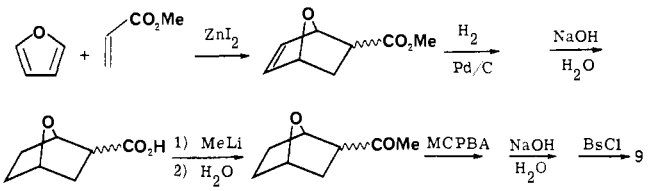


Table I. Acetolysis Rates

compd	temp, °C	k, s^{-1}	corr coeff
6	193.2	1.60×10^{-5}	1.000
	206.0	5.45×10^{-5}	0.999
	220.0	1.59×10^{-4}	0.998
	25.0	$(8.10 \times 10^{-16})^a$	
	100.0	$(4.52 \times 10^{-10})^a$	
7	197.2	1.20×10^{-5} [b]	0.999
	210.0	3.30×10^{-5} [b]	0.998
	220.0	8.23×10^{-5} [b]	0.999
	25.0	$(5.51 \times 10^{-16})^a$	
	100.0	$(2.58 \times 10^{-10})^a$	
8	136.4	2.92×10^{-5}	1.000
	148.2	8.23×10^{-5}	1.000
	163.4	3.03×10^{-4}	1.000
	25.0	$(2.26 \times 10^{-11})^a$	
	100.0	$(7.40 \times 10^{-7})^a$	
9	89.8	1.11×10^{-4}	1.000
	100.0	3.07×10^{-4}	1.000
	110.8	1.05×10^{-3}	1.000
	25.0	$(1.34 \times 10^{-8})^a$	
	100.0	$(3.30 \times 10^{-4})^a$	

[a] Calculated from activation parameters. [b] Initial rate; after 2–3 half-lives, the rate was found to increase with time.

Table II. Activation Parameters

compd	E_a, kcal mol^{-1}	log A	ΔH^*(100 °C), kcal mol^{-1}	ΔS^*(100 °C), eu
6	39.0	13.5	38.2	0.7
7	38.5	12.9	37.7	−1.8
8	30.6	11.8	29.9	−7.0
9	29.8	14.0	29.0	2.8

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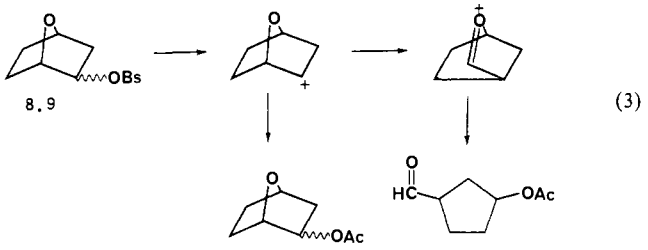
for structure determination. The exo monobrosylate **9** gave 94% of the exo acetate and 6% of the endo acetate. The diendo dibrosylate **6** gave 87% of the retained diendo diacetate, 7% of the diexo diacetate, and 5% of an unidentified material. Products from the diexo dibrosylate **7** at 180–200 °C were black and insoluble. No organic materials could be purified or analyzed by GC. For **6**, **8**, and **9**, the isolated products were found to be stable to reaction conditions. Thus, none of these products, in particular the diexo and diendo diacetates, could be formed from **7**.

Discussion

The primary measure of participation in these systems is the exo/endo rate ratio. Participation by remote double bonds in the norbornyl framework, or possibly by single bonds, can occur more readily when the leaving group is exo,[8] resulting in an enhanced exo/endo ratio over that in control systems lacking the participating functionality. In the 7-oxanorbornyl system, however, it is the endo isomer that has the better stereoelectronic arrangement for participation. Nonetheless, the exo/endo ratio is relatively normal in the chloride pair studied by Martin and Bartlett[3] (318 at 25°C) and in the monobrosylate pair (**9**/**8**) in the present study (590 at 25 °C, 450 at 100 °C, and 350 at 200 °C). These numbers compare to a ratio of 300 at 25 °C for the 2-norbornyl tosylates.[19] In these hetero systems, there seems to be no special effect in the endo isomer that is the result of oxygen participation. By contrast, the much more highly polarizable sulfur atom in the same 7-position gives rise to anchimeric assistance in the endo isomer and a vastly reduced exo/endo ratio.[20]

The products from the *exo*- and *endo*-7-oxanorborn-2-yl brosylates may be explained in terms of eq 3. The first carbocation can lead to the exo and endo 2-acetates, and Wagner-Meerwein rearrangement to the oxonium cation, followed by ring opening, can lead to 3-formylcyclopentyl acetate. The preponderance



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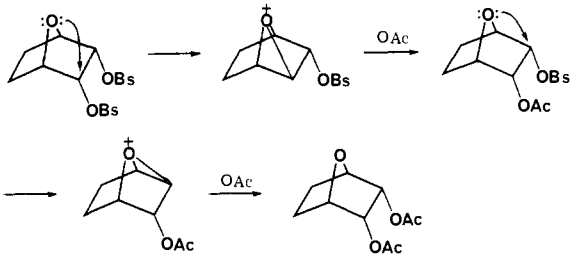
(94/6) of exo acetate from the exo brosylate **9**, in which oxygen participation (k_Δ) is not possible, suggests that the open carbocation of eq 3 (k_C pathway) leads mainly to an exo product, as expected on steric grounds. The modest excess (64/11) of endo over exo acetate from the endo brosylate **8** suggests that a k_Δ pathway may be competitive with the k_C path that should have given a similar exo/endo rate ratio to that from **9**. As this k_Δ path is only weakly competitive with the k_C path, it is not manifested kinetically. This point could not be affirmed definitively by these experiments.[21]

Introduction of the second brosyloxy group causes considerable diminution in the overall rate (Table I). The open carbocation analogous to that in eq 3 would be much destabilized by the increased electron demand of the remaining 3-brosyloxy group. When the leaving group is exo (**7**), the oxygen atom is stereoelectronically prohibited from participation, so that the open carbocation pathway analogous to eq 3 is compulsory. In the diendo isomer **6**, the oxygen atom is available for participation. Increased electron demand at the 2-position, where positive charge is developing, caused by the presence of the remaining 3-brosyloxy group brings about a higher degree of oxygen participation. As a result, the endo isomer actually acetolyzes at a faster rate than the exo isomer (exo/endo ratio for **7**/**6** 0.68 at 25 °C, 0.57 at 100 °C, and 0.49 at 200 °C). This observation comprises one of the few examples of an inverse (<1.0) exo/endo ratio in norbornyl chemistry. Thus, participation by oxygen can be inductively enhanced by the presence of an electron-withdrawing group close to the leaving group, as in arrangement **5**.

The products from the diendo dibrosylate are consistent with a participation pathway. Thus, none of the cyclopentane product analogous to that in eq 3 was observed. The major product (87%) is the doubly retained diendo diacetate of the structure analogous to that of the starting material **6**. Oxygen participation to a bridged oxirane intermediate in each of two steps, followed by backside opening of the oxirane ring each time, would lead to the observed product, as in eq 4. There are two possible modes of



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ring opening of each of the oxirane rings in eq 4, to give the [2.2.1] system as indicated or to give a [3.1.1] system, which is presumably disfavored because of the strained four-membered ring. A third formal mode of attack, at the 1-position to retain the epoxide functionality within a cyclohexene oxide, is not observed. Leakage of the first oxirane cation of eq 4 to an open carbocation analogous to that in eq 3 would lead to exo attack by acetate, eventually giving rise to the minor product (7%), the diexo diacetate. Alternatively, the minor product could arise via a solvent-transfer mechanism, analogous to that proposed by Spurlock and Fayter.[4]

The high temperatures required to solvolyze the diexo dibrosylate, in which participation is not possible, led to destruction of the products, so that we cannot discuss their structures.

This work provides the first example of inductively enhanced participation by a lone pair on a heteroatom. Previous examples of enhanced participation involved double bond,[8] phenyl,[9] and single bond.[10] The total magnitude of the enhancement can be estimated by comparison of the exo/endo rate ratio in the monobrosylates (590 at 25 °C) with that in the dibrosylates (0.68): 590/0.68, or about 900. Participation of the type in eq 4 reduces the destabilization that would have occurred in the open carbocation analogous to that in eq 3. Thus, greater need causes greater participation.

Experimental Section

Nuclear magnetic resonance spectra were obtained at 60 MHz on a Varian EM360 or a Perkin-Elmer R20B spectrometer, at 90 MHz on a Varian EM390 spectrometer, or at 270 MHz on a JEOL FX270 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) downfield from Me_4Si (δ 0.00). Elemental analyses were performed by Micro-Tech Laboratories Inc., Skokie, IL. Melting points were determined on a Hershberg apparatus. All melting points and boiling points are uncorrected. Vapor-phase chromatograms were obtained on Varian Vista 6000 and Hewlett-Packard Series 700 gas chromatographs with $^1/_8$ and $^1/_4$ in. packed columns for analytical and preparative purposes, respectively. A Haake NB-22 constant temperature bath and a Metrohm Hersiau type E-415 automatic titrator were used for the kinetic measurements.

Kinetic Studies. Rate constants were determined by standard titrimetric procedures.[18] A known quantity of substrate was dissolved in anhydrous acetic acid (HOAc), and a sufficient quantity of base was added to give a solution containing a 10% equivalent excess of base. Aliquots (2 mL) of this solution were transferred via a pipet to Pyrex tubes, which were then sealed. Twelve tubes were selected for each rate determination. The tubes were placed in a constant temperature bath (±0.2 °C). After 10 min for equilibration, tubes were withdrawn at appropriate intervals and quenched by cooling. The contents of each tube were titrated with standard $HClO_4$ solution with 1 drop of 0.5% solution of crystal violet as the indicator. The first tube titrated was called the zero tube, and the reaction was followed from that point. One unheated tube also was titrated to verify the initial base concentration. Infinity tubes were allowed to react for 6–10 half-lives.

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(21) We thank a referee for suggestions regarding the product ratios of **8** and **9**.

Solvent. Anhydrous HOAc containing 1% acetic anhydride (Ac_2O) was prepared by refluxing reagent grade HOAc (99.7%) with enough Ac_2O to react with any water present and with 0.6 g of CrO_3 per liter of acid. The mixture was heated under reflux overnight and distilled through a Vigreaux column. Enough Ac_2O was then added to make the distilled acid 1% by weight in anhydride.

Standard Acid. A solution approximately 6.0×10^{-3} M in $HClO_4$ was prepared by diluting 70% $HClO_4$ with reagent grade HOAc and adding enough Ac_2O to remove all the water from the solution and leave it 1% in anhydride. The solution was allowed to stand for 2 days so the Ac_2O could react completely with the water present. The $HClO_4$ solution was then titrated against potassium acid phthalate in purified HOAc, with crystal violet as the indicator, to determine the molarity of $HClO_4$.

Preparation of Standard KOAc. An approximately 1 M solution of KOAc in HOAc was prepared by the reaction of K_2CO_3 and HOAc. Purified HOAc was treated with 17.33 g (0.125 mol) of K_2CO_3 and 12.80 g (0.125 mol) of Ac_2O and then diluted to 250 mL in a volumetric flask. One milliliter of this standard base solution was diluted to 50 mL in a volumetric flask. Aliquots (2 mL) of this solution were then titrated with the standard $HClO_4$ with crystal violet as the indicator to give the concentration of the original KOAc solution.

Brosylate Preparation. All brosylates and dibrosylates were prepared by a modification of the standard method of Winstein.[13] A solution of the purified alcohol or diol in dry pyridine was treated with a 10% equivalent excess of *p*-bromobenzenesulfonyl chloride (Aldrich). This solution was kept at 0 °C until precipitation of pyridinium chloride indicated that the reaction was complete (24–48 h for brosylates; 1 week for dibrosylates). The reaction mixture was poured slowly into a mixture of ice and dilute HCl. The impure brosylate product was collected by suction filtration and recrystallized twice from CH_2Cl_2/pentane. The yield and characterization of individual brosylates are given below for each individual case.

Product Studies. Acetolysis products of all the mono- and dibrosylates in this study were obtained by solvolysis in buffered solutions as for the kinetic runs. The solutions were solvolyzed for 6–10 half-lives, cooled, and diluted with water. The HOAc was neutralized with an equivalent of Na_2CO_3. The organics were extracted into ether and dried over $MgSO_4$, and the solvent was removed by distillation. The products were then analyzed by VPC on a $^1/_8$ in. × 1 m column packed with 10% diethylene glycol succinate on Chromosorb W. Comparison of VPC retention times and NMR chemical shifts with known compounds was made whenever these compounds were available. Acetates were prepared from the corresponding alcohols by treatment with an excess of Ac_2O containing 1 drop of concentrated H_2SO_4.[17]

2-Chloro-2-cyano-7-oxabicyclo[2.2.1]hept-5-ene was prepared by the general procedure of Brion[14] in 55–70% yield: ^{1}H NMR ($CDCl_3$) δ 6.7–6.3 (m, 2, vinyl), 5.3–5.05 (m, 2, bridgehead), 2.82 and 1.80 (AB of ABX, $J_{3\text{-endo},3\text{-exo}} = 1.25$, $J_{3\text{-exo},4} = 4.5$ Hz, H3-endo and H3-exo of one isomer), 2.45–2.2 (m, H3-endo and H3-exo of the other isomer).

2-Chloro-2-cyano-7-oxabicyclo[2.2.1]heptane was prepared by dissolving the alkene (7 g) in ethyl acetate (20 mL) containing 10% Pd on C (0.5 g). The reaction mixture was stirred in an atmosphere of H_2 until the theoretical volume of gas had been taken up. The mixture was filtered, and the volatiles were removed. The residue was distilled under reduced pressure to give 6.73 g (95%) of the desired chloronitrile as a colorless liquid: bp 48–50 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 4.9–4.6 (m, 2, bridgehead), 3.0–1.7 (br m, 6, methylene).

2-Chloro-7-oxabicyclo[2.2.1]heptane-2-carboxylic Acid. The procedure of Moursounidis and Wege[22] gave the acid as a mixture of isomers in 80% yield: ^{1}H NMR ($CDCl_3$) δ 11.2 (s, 1, CO_2H), 4.90 (m, 1, bridgehead), 4.6 (m, 1, bridgehead), 3.0–1.5 (m, 6, methylene).

7-Oxabicyclo[2.2.1]heptan-2-one. Preparation followed closely the procedure of Moursounidis and Wege:[22] yield 55% from the acid, bp 83–85 °C (25 mm); ^{1}H NMR ($CDCl_3$) δ 4.9 (m, 1, H1), 4.35 (m, 1 H4), 2.8–1.5 (br m, 6, methylene).

***endo*-7-Oxabicyclo[2.2.1]heptan-2-ol.** To a solution of the ketone (1.0 g, 8.9×10^{-3} mol) in CH_3OH (20 mL) cooled to 0 °C in an ice–salt bath was added $NaBH_4$ (0.6 g) in small portions and with stirring. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Water (10 mL) was added, and most of the CH_3OH was removed under reduced pressure. The aqueous residue was extracted with ether (4 × 50 mL). The combined ether layers were dried ($MgSO_4$) and concentrated to give 1.04 g of the endo alcohol as a clear oil: ^{1}H NMR ($CDCl_3$) δ 4.6–4.3 (m, 2, H1 and H4), 4.3–4.15 (m, 1, H2), 1.9 (s, 1, OH), 2.4–1.4 (br m, 5, methylene), 1.1 (B of ABX, $J_{3\text{-endo},3\text{-exo}} = 13$, $J_{3\text{-endo},2} = 3.5$ Hz, 1, H3-endo).

***endo*-7-Oxabicyclo[2.2.1]heptyl Brosylate (8).** The alcohol was treated with brosyl chloride by the above procedure to give a 58% yield of the desired brosylate: mp 63–65 °C [lit.[21] 64–65 °C]; ^{1}H NMR ($CDCl_3$) δ 7.75 (m, 4, aromatic), 4.85–4.4 (m, 3, bridgehead and H2), 2.3–1.4 (m, 5, methylene), 1.3 (B of ABX, $J_{3\text{-endo},3\text{-exo}} = 13.5$, $J_{3\text{-endo},2} = 3.0$ Hz, 1, H3-endo).

***endo*-7-Oxabicyclo[2.2.1]heptyl Acetate.**[21] The alcohol was treated with Ac_2O by the above procedure to give an analytical sample of the desired acetate as a clear liquid: ^{1}H NMR ($CDCl_3$) δ 5.05–4.45 (m, 3, bridgehead and H2), 2.05 (s, 3, CH_3), 2.45–1.40 (m, 5, methylene), 1.3 (B of ABX, $J_{3\text{-endo},3\text{-exo}} = 13$, $J_{3\text{-endo},2} = 3.5$ Hz, 1, H3-endo).

Methyl *endo*- and *exo*-7-Oxabicyclo[2.2.1]hept-5-ene-2-carboxylate. Diels–Alder reaction of furan and methyl acrylate by the procedure of Brion[14] gave the desired compound in 60% yield: ^{1}H NMR ($CDCl_3$) δ 6.6–6.2 (m, 2, vinyl), 5.2–5.0 (m, 2, bridgehead), 3.7 (s, 3, CH_3), 3.3–1.6 (br m, 3, methylene).

Methyl *endo*- and *exo*-7-Oxabicyclo[2.2.1]heptane-2-carboxylate. A solution of the adduct (18 g, crude) in 150 mL of ethanol with 1 g of 10% Pd on C was stirred under a H_2 atmosphere until no more H_2 was taken up. The reaction mixture was filtered, and the volatiles were removed, leaving 16.13 g of the desired ester (89%), which was not purified further: ^{1}H NMR ($CDCl_3$) δ 4.9–4.5 (m, 2, bridgehead), 3.7 (s, 3, CH_3), 3.0 (m, 1, H2-exo), 2.6 (m), 2.3–1.4 (br m, 6, methylene).

***endo*- and *exo*-7-Oxabicyclo[2.2.1]heptane-2-carboxylic Acid.** The above methyl ester (16.13 g, 0.10 mol) was treated with 150 mL of 5% NaOH and stirred for 2.5 h. The reaction mixture was then acidified with concentrated HCl and extracted with $CHCl_3$ (4 × 90 mL). The combined organic extracts were dried ($MgSO_4$), and the volatiles were removed at reduced pressure. The residue was distilled to give 11.44 g (81%) of the desired acid as a mixture of isomers: bp 106–111 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 11.4 (s, 1, CO_2H), 4.95–4.6 (m, 2, bridgehead), 3.1 (m, 1, H2-exo), 2.65 (m, 1, H2-endo), 2.3–1.4 (br m, 6, methylene).

***endo*- and *exo*-2-Acetyl-7-oxabicyclo[2.2.1]heptane.** To a cold (0 °C), vigorously stirred solution of the acid (5.16 g, 0.036 mol) in 100 mL of anhydrous THF was added 60 mL of an ethereal solution containing 76 mmol of CH_3Li dropwise during 1 h. The reaction mixture was then stirred for 4 h at room temperature. Aliquots (50 mL) were removed from the reaction mixture by syringe and added dropwise with stirring to fresh portions of ice and dilute HCl. The combined ether layers were washed with saturated Na_2CO_3 and with brine and were dried ($MgSO_4$) and concentrated. The residue was distilled under reduced pressure to give the ketone (3 g, 0.0214 mol, 59%) as a mixture of isomers: bp 41–49 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 4.9–4.55 (m, 2, bridgehead), 3.24 (m, 1, H2-exo), 2.7 (m, 1, H2-endo), 2.2 (s, 3, CH_3), 2.1–1.1 (m, 6, methylene).

***exo*-7-Oxabicyclo[2.2.1]heptyl Acetate.** To a stirred suspension of *m*-chloroperoxybenzoic acid (5.2 g, 0.024 mol) and $NaHCO_3$ (8.4 g, 0.10 mol) in dry CH_2Cl_2 (100 mL) was added dropwise a solution of the methyl ketone (3 g, 0.021 mol) in 15 mL of CH_2Cl_2. After addition was complete, the reaction mixture was heated under gentle reflux for 48 h. The solid was removed by filtration, and the filtrate was washed with 10% Na_2SO_3 (2 × 50 mL), saturated $NaHCO_3$ (3 × 50 mL), and brine (50 mL). The organic layer was dried ($MgSO_4$) and concentrated to a residue of 2.22 g. Analysis by NMR and VPC showed that the residue was a mixture of the desired acetate (85%) and the endo methyl ketone (15%). Preparative VPC gave an analytical sample of the acetate, with a $^1/_4$ in. × 8 ft 10% diethylene glycol succinate (DEGS) column: ^{1}H NMR ($CDCl_3$) δ 4.83–4.45 (m, 3, bridgehead and H2), 2.05 (s, 3, CH_3), 2.0–1.2 (br m, 6, methylene).

***exo*-7-Oxabicyclo[2.2.1]heptan-2-ol.** The crude exo acetate (2 g) was treated with 20% NaOH (25 mL) and THF (20 mL). The mixture was stirred for 4.5 h at room temperature and then extracted with ether. The ether extracts were dried ($MgSO_4$) and concentrated to give a 1.5-g residue. Analysis by NMR and VPC indicated that the residue was a mixture of the desired alcohol (90%) and the exo methyl ketone (10%). An analytical sample of the pure alcohol was obtained by preparative VPC with a $^1/_4$ in. × 8 ft 10% DEGS column: ^{1}H NMR ($CDCl_3$) δ 4.7–4.3 (m, 3, bridgehead and OH), 4.02–3.78 (m, 1, H2), 2.05–1.2 (br m, 6, methylene).

***exo*-7-Oxabicyclo[2.2.1]heptyl Brosylate (9).** The crude alcohol was treated with brosyl chloride by the above procedure to give a 40% yield of the desired brosylate: mp 81–82 °C; ^{1}H NMR ($CDCl_3$) δ 7.75 (ABq, 4, aromatic), 4.8–4.55 (m, 3, bridgehead and H2), 1.9–1.25 (m, 6, methylene). Anal. Calcd for $C_{12}H_{13}BrSO_4$: C, 43.26; H, 3.93. Found: C, 43.11; H, 3.91.

***cis*,*endo*-7-Oxabicyclo[2.2.1]hept-5-en-2,3-diyl carbonate** was prepared and separated from the exo isomer as described by Newman:[12] mp 146–149 °C [lit.[12] 148.8–149.6 °C]; ^{1}H NMR ($CDCl_3$) δ 6.5 (m, 2, vinyl), 5.15 (m, 2, bridgehead), 4.95 (m, 2, H2 and H3).

***cis*,*exo*-7-Oxabicyclo[2.2.1]hept-5-en-2,3-diyl carbonate** was prepared and separated from the endo isomer as described by Newman:[12] mp

(22) Moursounidis, J.; Wege, D. *Aust. J. Chem.* **1983**, *36*, 2473–2482.

133-135 °C [lit.[12] 137-137.7 °C]; ^{1}H NMR ($CDCl_3$) δ 6.4 (m, 2, vinyl), 5.02 (m, 2, bridgehead), 4.65 (s, 2, H2 and H3).

***cis,endo*-7-Oxabicyclo[2.2.1]heptane-2,3-diol.** A mixture of the cis,-endo carbonate (1.8 g, 0.012 mol), 0.4 g of 10% Pd on C, and 100 mL of ethanol was stirred in a H_2 atmosphere until the theoretical amount of H_2 was taken up. The catalyst was removed by filtration, and the filtrate was concentrated. The residue was treated with 50 mL of 5% NaOH, and the mixture was shaken until all the solid had dissolved. The solution was then neutralized with concentrated HCl. Continuous ether extraction for 4 days gave the crude diol, which was recrystallized from benzene/hexane to give 1.23 g (81%) of the desired diol: mp 148-150 °C; ^{1}H NMR ($CDCl_3$) δ 4.47 (br s, 2, bridgehead), 3.94 (br s, 2, H2 and H3), 2.8 (very br s, 2, OH), 2.05-1.23 (m, 4, methylene). Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 54.88; H, 7.73.

***cis,endo*-7-Oxabicyclo[2.2.1]hepta-2,3-diyl Dibrosylate (6).** The cis,endo diol was treated with brosyl chloride by the above procedure to give a 60% yield of the desired dibrosylate: mp 179-181 °C; ^{1}H NMR ($CDCl_3$) δ 7.8 (narrow ABq, 8, aromatic), 4.6-4.45 (m, 4, bridgehead, H2, and H3), 2.1-1.5 (m, 4, methylene). Anal. Calcd for $C_{18}H_{16}Br_2S_2O_7$: C, 38.05; H, 2.84. Found: C, 37.83; H, 2.72.

***cis,endo*-7-Oxabicyclo[2.2.1]hepta-2,3-diyl Diacetate.** The cis,endo diol was treated with Ac_2O by the above procedure to give an analytical sample of the diacetate as a clear liquid: ^{1}H NMR ($CDCl_3$) δ 4.85 (m, 2, H2 and H3), 4.65 (m, 2, bridgehead), 2.05 (s, 6, CH_3), 2.0-1.55 (m, 4, methylene).

***cis,exo*-7-Oxabicyclo[2.2.1]heptane-2,3-diol** was prepared from the cis,exo carbonate by the same procedure used to prepare the cis,endo isomer, except that the cis,exo diol could not be recovered by ether extraction. Instead, after neutralization, the H_2O was removed by rotary evaporation at reduced pressure, and the residue was treated with warm CH_2Cl_2. The crude diol was obtained by filtration and concentration of the filtrate in nearly quantitative yield. Recrystallization from benzene afforded the diol as a white solid: mp 77-79 °C; ^{1}H NMR ($CDCl_3$) δ 4.35 (m, 2, bridgehead), 3.84 (s, 2, H2 and H3), 3.4 (s, 2, OH), 1.85-1.2 (m, 4, methylene). Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.29; H, 7.57.

***cis,exo*-7-Oxabicyclo[2.2.1]hepta-2,3-diyl Dibrosylate (7).** The diol was treated with brosyl chloride by the above procedure to give the desired dibrosylate in 82% yield: mp 169-170 °C; ^{1}H NMR ($CDCl_3$) δ 7.8 (narrow ABq, 8, aromatic), 4.75 (s, 2, H2 and H3), 4.60 (m, 2, bridgehead), 1.85-1.40 (m, 4, methylene). Anal. Calcd for $C_{18}H_{16}Br_2S_2O_7$: C, 38.05; H, 2.84. Found: C, 37.89; H, 2.77.

***cis,exo*-7-Oxabicyclo[2.2.1]hepta-2,3-diyl Diacetate.** Treatment of the cis,exo diol with excess Ac_2O by the above procedure produced an analytical sample of the desired diacetate as a clear liquid: ^{1}H NMR ($CDCl_3$) δ 4.88 (s, 2, H2 and H3), 4.51 (m, 2, bridgehead), 2.08 (s, 6, CH_3), 1.80-1.45 (m, 4, methylene).

3-Formylcyclopentyl acetate was isolated by preparative GC from the product mixture of the endo brosylate **6** and the exo brosylate **7**: ^{1}H NMR ($CDCl_3$) δ 9.75 (s, 1), 5.22 (m, 1), 2.2-1.3 (m, 7), 2.04 (s, 3).

Photochemistry of Iron Atoms and Dimers with Ethylene in Cryogenic Matrices. The FTIR Spectrum of Ethenyliron Hydride

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Abstract: Evidence from infrared studies shows that atomic and molecular iron interact with ethylene in two distinct ways. One type of interaction leads to the formation of the classical π-complex known for many transition metal/ethylene systems. In this context we have isolated $Fe(C_2H_4)_n$, where $n \geq 2$, as well as $Fe_2(C_2H_4)_m$, where $m = 1, 2$ in solid inert gas matrices. Another type of interaction deduced from the present study takes place between one or more of the hydrogen atoms of ethylene and atomic iron. Two forms of a hydrogen-bonded complex exhibit a slightly perturbed ethylene-like infrared spectrum. Perturbations on all the ethylene infrared active modes have been measured. A photoreversible oxidative-addition/reductive-elimination reaction of the form

$$Fe(C_2H_4) \underset{\lambda \geq 400\ nm}{\overset{280-360\ nm}{\rightleftharpoons}} HFeC_2H_3$$

has been observed at 14 K in solid argon and krypton. One of the hydrogen-bonded complexes, $Fe(C_2H_4)$, was found to be the primary precursor for formation of the insertion product, $HFeC_2H_3$. Frequencies of ten fundamental modes of $HFeC_2H_3$, $HFe^{13}C_2H_3$, and $DFeC_2D_3$ have been measured in the 450-4000 cm^{-1} infrared region.

The interactions between transition metals and ethylene have been known since the discovery of Zeise's salt in 1831.[1] Recently many studies[2-18] have concentrated on the interaction between zerovalent transition metals and ethylene in cryogenic matrices. The synthesis of triethylene-nickel[19] has spurred many theoreticians to attempt to understand the type of bonding that exists between zerovalent transition metals and ethylene as well as to predict the geometry of this new class of π-complexes.[20-24] The

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