Stereochemistry of acyl halide addition to olefins. Intramolecular cyclization of cis-4-cyclooctene-1-carboxylic acid chloride

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The intramolecular cyclization of cyclooct-4-cis-ene-1-carboxylic acid chloride (1) proceeds by cis addition to produce 2-cis-chlorobicyclo[3.1.1]nonan-9-one (2) as the principal product in a variety of solvents and in the absence of added Lewis acid catalysts. In the presence of catalytic quantities of aluminum chloride, the addition proceeds predominantly trans to produce 2-endo-chlorobicyclo[3.1.1]nonan-9-one (3) as the major product. Under more polar conditions (e.g., 5% solution of boron trifluoride etherate in diglyme), cyclization occurs with loss of hydrogen chloride to produce principally bicyclo[3.1.1]nonan-2-endo-9-one (4). These results are compared with the course of hydrogen halide addition to olefins. Structure elucidation of the chloro ketones 2 and 3 was based upon spectral analysis, X-ray crystal analysis, and the contrasting behavior of each isomer to base. In refluxing methanolic potassium hydroxide the cis isomer 2 undergoes elimination to bicyclo[3.1.1]nonan-2-endo-9-one (4), while the endo isomer 3 suffers fragmentation to the potassium salt of cyclooct-4-cis-1-carboxylic acid (5).

Although limited examples of the Friedel-Crafts addition of acid chlorides to olefins to produce chloro ketones can be cited, knowledge of the stereochemistry of these additions is completely lacking. In the examples studied, either the stereochemistry of the chloro ketone products was not determined, or the structure of the products was not amenable to stereochemical elucidation. Indeed, stereochemical resolution of the chloro ketone products from the addition of acid chlorides to simple cyclic or cyclic systems may be inconclusive, since the initially formed products would probably undergo rapid enolization and epimerization under the conditions employed for the reaction. For this reason we chose to investigate the intramolecular cyclization of cyclooct-4-cis-ene-1-carboxylic acid chloride (1). Intramolecular addition of the acid chloride function to the olefin function of 1 would produce a bicyclic ketone which could not undergo enolization. If cyclization of 1 could be effected without loss of the chloro compound or prevalent dehydrohalogenation. It is noteworthy that bicyclo[4.2.1]nonane derivatives (i.e., 5a and 5b), which would have been formed by the reverse addition of acid chloride to the olefin moiety, were not produced under these conditions.2,3

In initial experiments, treatment of a 5% solution of 1 in 5% boron trifluoride etherate-diglyme at 100°C effected cyclodaddition of the acid chloride function with almost complete loss of hydrogen chloride. Thus, bicyclo[3.1.1]nonan-2-endo-9-one (4), the structure of which was verified by comparison with an authentic sample, was produced in 53% yield while only small quantities of the chloro compounds 2 (5%) and 3 (3%) were formed under these conditions. An appreciable quantity (10%) of methyl cyclooct-4-cis-1-carboxylate was also produced, undoubtedly by esterification of methanol (generated by acid cleavage of the diglyme) with the acid chloride 1. When the acid chloride 2.(1) In this regard, it is interesting to compare the cyclization of 1 with the solvolysis of cyclooct-4-ene-1-methanol derivatives. Under conditions of kinetic control, bicyclo[3.1.1]nonane derivatives are produced almost exclusively from this latter solvolysis reaction.3 Under more vigorous conditions, the initially produced bicyclo[3.1.1]nonane derivatives are apparently equilibrated to significant quantities of bicyclo[4.2.1]nonane compounds.4,5

We were able to find reaction conditions for cyclization of 1 which stereoselectively produced either 2-cis- or 2-endo-chlorobicyclo[3.1.1]nonan-9-one (2) (cis addition) or 2-endo-chlorobicyclo[3.1.1]nonan-9-one (3) (trans addition) without epimerization of the initially produced chloro compound or prevalent dehydrohalogenation. It is noteworthy that bicyclo[4.2.1]nonane derivatives (i.e., 5a and 5b), which would have been formed by the reverse addition of acid chloride to the olefin moiety, were not produced under these conditions.2,3

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ride was heated at 83–84° in ethylene dichloride solution for 16 hr in the absence of an added catalyst, ezo-2-chlorobicyclo[3.3.1]nonan-9-one (2) was the principal product of the cyclization reaction. The latter ketone, produced in 41% yield, was accompanied by the endo isomer 3 (16%) and a small quantity of the olefinic ketone 4 (5%). When benzene, monoglyme, trichloroethane, or acetic acid was employed as solvent, the yields of products 2, 3, and 4 were decreased, but the ratio of olefin/ezo isomer 2/endo isomer 3 was not altered significantly (see Experimental Section). The remaining products were dimeric or polymeric in nature. An appreciable quantity of methyl cyclooct-4-cis-ene-1-carboxylate also was produced when monoglyme or diglyme was employed as solvent.

On the other hand, treatment of 1 with catalytic quantities of aluminum chloride in monoglyme or diglyme at 88 and 100°, respectively, for 18 hr afforded the endo epimer 3 as the principal product (20–26%). The ezo epimer 2 was produced in 6–8% yield and the olefin 4 in 18–19% yield. Products of intermolecular condensation were increased in the presence of aluminum chloride catalyst.

The following two experiments established that the ketone 3 was produced directly from the acid chloride 1 and not by aluminum chloride catalyzed epimerization of 2 or by addition of hydrogen chloride to the olefin 4. These experiments also indicate that the olefin 4 was produced directly from 1 and not by aluminum chloride catalyzed dehydrohalogenation of 2.

(1) When a solution of the ezo-chloro epimer 2 was heated in benzene or in diglyme with aluminum chloride (see Experimental Section), starting ketone 2 was recovered in 77 and 84% yields, respectively. Only trace amounts of the olefin 4 and no detectable quantities of the epimeric chloro ketone 3 were observed under these conditions. (2) Treatment of the olefin 4 with aluminum chloride under the same conditions in the absence or presence of added hydrogen chloride led to 93 and 91% recoveries of starting olefin, respectively. The chloro ketones 2 and 3 were produced in 0.4 and 2%, respectively, from the latter reaction but were accompanied by at least four other isomeric chloro ketones, produced in 2, 2, 1, and 0.3%, respectively. Since the reaction product from the cyclization of 1 is devoid of these latter chloro ketones, the probability that even a small portion of the endo isomer 3 is produced from the olefin 4 under the conditions described here seems remote.

**Structure Elucidation of Ketones 2 and 3.** Mass spectral data and elemental analyses established the empirical formula C₅H₅OCl for the two cyclization products 2 and 3. The infrared spectra of ketones 2 and 3 displayed carbonyl absorption at 5.79 and 5.78 μ, respectively, in excellent agreement with the values 5.80 and 5.77 μ recorded for the parent bicyclo[3.3.1]nonan-9-one and bicyclo[3.3.1]non-2-en-9-one structures, respectively. In contrast, the 2-chlorobicyclo[4.2.1]nonan-9-one epimers (5a), which might have resulted from reverse addition of the acid chloride to the olefin, should show absorption at no greater than 5.72–5.75 μ for a nonstrained five-membered ring ketone.6-9

The basic ring skeleton and the positions and stereochemistry of the chloro functions in 2 and 3 were implied from the characteristic behavior of each isomer to base. The epimer 3, on treatment with refluxing 2 M methanolic potassium hydroxide, suffered cleavage to potassium cyclooct-4-cis-ene-1-carboxylate10 (77%) and potassium cyclooct-3-cis-ene-1-carboxylate10 (45%). In contrast, under the same conditions, the epimer 2 underwent dehydrochlorination to the olefin 4. The fragmentation of 3 to 6 is apparently rapid compared to the dehydrochlorination of 2 to 4. Thus, a mixture of 2 and 3 on treatment with potassium t-butoxide in wet t-buty alcohol at room temperature led to quantitative fragmentation of 3, while the epimer 2 was recovered unchanged. In fact, the latter treatment represents an excellent procedure for isolation of the ezo epimer free of the endo isomer.

That the fragmentation product 6 was produced directly from 3 and not from the olefin 4 (which might have been formed by initial dehydrochlorination of the conformer 3b) was confirmed by the observed stability of 4 to the same basic conditions. Thus, the olefin 4, after treatment for 16 hr with refluxing 5 M methanolic potassium hydroxide was recovered unchanged.11,12

The remarkable ease with which the endo-chloro ketone undergoes ring scission can be interpreted as an exemplification of the general rule that fragmentation reactions proceed with greatest facility when the bonds

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6] Thus the parent bicyclo[4.2.1]nonan-9-one14 and the isomeric 7-methyldihydrobicyclo[4.2.1]nonan-9-ones15 display carbonyl absorption at 5.73 μ, the 1-methyl and 1,5-dimethyl derivatives at 5.73 μ, and the 2-methyl derivative at 5.72 μ.


10] Isolated after acidification as the free acids 6 and 7, respectively, and identified as the methyl ester derivatives. The esters were compared to authentic specimens, the syntheses of which are described by W. F. Erman and H. C. Kretschmar, J. Amer. Chem. Soc., 89, 3384 (1967).

11] Fasile bridge fission seems to be a characteristic property of bicyclo[3.3.1]nonan-9-ones containing an easily eliminated functional group in the 2-endo position.11 In contrast, 2-endo-substituted bicyclo[3.3.1]nonan-9-ones undergo elimination to produce the corresponding bicyclo[3.3.1]non-2-en-9-ones apparently at a slower rate than the bridge fission of the corresponding 2-endo isomers.13

being broken are approximately parallel and coplanar. In the chair conformation (3a) of the endo-chloro isomer the C-1,9 bond and the equatorial C-Cl bond are perfectly parallel and coplanar. The initially produced intermediate anion 8a, then, would be expected to collapse readily to the acid 6. The production of a small quantity of the cyclooct-5-ene-2,1-carboxylic acid (7) could be explained by a competitive protonation at C-1 concerted with bond scission to produce the intermediate chloro acid 9. This acid could then undergo elimination to 6 and 7. The collapse of 8a to 6 apparently is a lower energy process than elimination of HCl from the boat conformation 3b.

Even when the exo epimer 2 assumes a boat conformation (2b) the equatorial C-Cl bond is not coplanar with the C-1,9 bond, and fragmentation would not be anticipated. On the other hand, when 2 assumes the chair conformation 2a, the axial C-Cl bond is ideally oriented for trans-diabolic elimination.

Final confirmation of the structure 2 was made by X-ray diffraction. Webb and Becker have shown that monoclinic needles of this isomer exist in the twin-chair conformation. That the two epimers 2 and 3 also show preference for the twin-chair conformation in solution was indicated from the infrared C-H stretching frequency and nmr spectrum of each.

Fulr saturated bicyclo[3.3.1]nonane compounds exhibit abnormal C-H stretching frequencies in the region of 2985-2995 cm⁻¹, ascribed to interaction of the C-3 and C-7 endo-hydrogen atoms of the twin-chair conformer of the bicyclo[3.3.1]nonane skeleton. In correspondence, the isomers 2 and 3 show C-H stretching frequencies at 2995 and 2985 cm⁻¹, respectively.

In the nmr spectrum of the exo-chloro ketone 2, the C-2 proton appears at 1.5 4.56 as a multiplet of total band width 10.5 Hz, typical of an equatorial proton of a cyclohexane in the chair conformation. In the nmr spectrum of the endo-chloro ketone 3, the C-2 proton appears as a multiplet of greater total band width (24 Hz) and at higher field (1.5 7.55) as expected for an axial proton of a cyclohexane in the chair conformation. By decoupling the C-1 proton, apparent splittings of 4.9 and 12.0 Hz were determined for J (C-2-H, C-3-exo H) and J (C-2-H, C-3-endo H), respectively, in agreement with the assigned structure. An apparent splitting of 5.2 Hz for J (C-2-H, C-3-exo H) and J (C-2-H, C-3-endo H) was in accord with the equatorial assignment for the C-2 proton in structure 2.

Discussion

The mode of cycloaddition of the acid chloride 1 is reminiscent of the ionic addition of hydrogen bromide to aryl-substituted olefins. have observed that the ionic addition of hydrogen bromide toacenaphthene or 1-phenylpropene proceeds predominantly cis, the ratio of cis to trans product decreasing in going from nonpolar to polar solvents. The trans adduct was shown to be a primary product of ionic addition and was not produced by a secondary isomerization.
of the initially produced cis isomer or by a radical addition. These results were inconsistent with a simple π-complex mechanism, previously proposed for hydrogen bromide additions, or a concerted process involving a four-centered cyclic transition state. The authors proposed instead a mechanism involving a classical carbonium ion formed in the rate-determining step as an ion pair with an acid-complexed halide ion. The ion pair either collapses to cis product or rearranges to a trans ion pair which then produces trans-addition product. Whether rearrangement from cis ion pair to trans ion pair occurs faster than collapse of cis ion pair to cis product depends upon the structure of the olefin involved and the polarity of the solvent system.

In an analogous manner, then, the acid chloride 10 could interact with the olefin to produce the exo-chloro ion pair 10. The chloride could be associated with hydrocarbon chloride (formed by partial decomposition of the acid chloride to the corresponding ketene), with solvent, or with aluminum chloride, when the latter catalyst is employed. The rate of rearrangement to endo-chloro ion pair 11 relative to collapse to 2 would be affected by the degree of association of chloride ion with the species mentioned above, the relative bulk of the associating species, and the relative stability of the carbonium ion.

The production of predominantly endo isomer in the presence of aluminum chloride and predominantly exo isomer in the absence of aluminum chloride is consistent with this mechanistic picture. Complex formation with aluminum chloride should lead to more rapid dissociation and rearrangement of ion pair 10. In fact, dissociation in this instance could be concerted with attack of AlCl₄⁻ or Cl⁻ from the endo side of the molecule. Conversely, in the absence of aluminum chloride, ion pair 10 might be expected to collapse to exo isomer faster than dissociation or rearrangement to 11.

Also consonant with the observed stereochemical course of addition, however, is the proposal that chloride ion adds from the least-hindered side of the completely dissociated ion 12 in the absence of complexing agents to give cis product. Complex formation between the carbonyl function and aluminum chloride might sterically retard attack from the exo side of the molecule and lead to endo product. These and other influencing factors on the course of stereochemical addition to the present model make obvious the necessity for further studies on other systems in order to fully elaborate the mechanism of allyl halide additions to olefins.

Finally, the synthetic contribution of this work should be recognized. Of various preparations of bicyclo[3.3.1]nonane derivatives, the cyclization of the readily prepared acid chloride 1 represents one of the simplest laboratory approaches to these structures. It is the only method, in fact, which produces significant quantities of readily separated 2-exo-substituted isomers of this bicyclic system. The solvolytic of the latter derivative should give us a better insight into the chemistry of carbonium ion intermediates of type 12.

**Experimental Section**

Melting points were determined on a Thomas-Hoover capillary apparatus or on a micro hot stage and are uncorrected; boiling points are uncorrected. Infrared spectra were recorded on a Germain-Elmer 421 spectrophotometer or a Perkin-Elmer Model 137 infrared spectrophotometer as indicated. Nuclear magnetic resonance spectra were run on a Varian HA-100 spectrometer using tetramethylsilane as an internal reference. Chemical shifts are recorded as ppm on the δ scale, with coupling constants as hertz (Hz). Nuclear magnetic resonance data are recorded in the order: chemical shift, multiplicity where s is singlet, d doublet, t triplet, and m multiplet (coupling constant), integration (interpretation). Microanalyses were performed by T. Atanovich and associates of these laboratories and by Spang Microanalytical Laboratories, Ann Arbor, Mich. The monoglyme and diglyme solvents were freshly distilled from calcium hydride before use. Gas chromatography retention times are recorded relative to air.

**Cyclooct-4-exo-ene-1-carboxylic Acid Chloride**

To 190.4 g (1.255 mol) of cyclooct-4-exo-ene-1-carboxylic acid chloride was added dropwise with stirring 200 g (1.576 mol) of oxalyl chloride under a nitrogen atmosphere at such a rate that the temperature was maintained between 26 and 30°C. After the addition was complete, the reaction mixture was stirred an additional 18 hr at room temperature. The excess oxalyl chloride was removed by evaporation at 40°C (25 mm), and the residue was distilled under vacuum. Cyclooct-4-exo-ene-1-carboxylic acid chloride (1), 185.5 g (86%), was obtained as a colorless liquid with 185°C (5%), 174°C (13%), and 170°C (69%) boiling points. Additional characterization.

**Cycloaddition Reaction of Acid Chloride**

—A solution of 10.0 g (0.058 mol) of acid chloride 1 in 15 ml of ethylene dichloride, bp 83-84°C, was heated at reflux for 72 hr. The warm reaction mixture was poured into 100 ml of warm water (40-50°C) and stirred at this temperature for 1 hr. The mixture was cooled to 27°C and extracted with three 35-ml portions of ether. The combined ether layers were washed with a nitrogen atmosphere at such a rate that the temperature was maintained between 26 and 30°C. After the addition was complete, the reaction mixture was stirred an additional 18 hr at room temperature. The excess oxalyl chloride was removed by evaporation at 40°C (25 mm), and the residue was distilled under vacuum. Cyclooct-4-exo-ene-1-carboxylic acid chloride (1), 185.5 g (86%), was obtained as a colorless liquid with 185°C (5%), 174°C (13%), and 170°C (69%) boiling points. Additional characterization.

**Acetalization**

Cyclooct-4-exo-ene-1-carboxylic Acid Chloride (1).—A solution of 10.0 g (0.058 mol) of acid chloride 1 in 15 ml of ethylene dichloride, bp 83-84°C, was heated at reflux for 72 hr. The warm reaction mixture was poured into 100 ml of warm water (40-50°C) and stirred at this temperature for 1 hr. The mixture was cooled to 27°C and extracted with three 35-ml portions of ether. The combined ether layers were washed with three 50-ml portions of water, dried, and solvent evaporated to yield 9.2 g of light brown liquid. The liquid was distilled in a modified Hickman still to afford 6,340 g of colorless liquid, bp 90-110°C (0.1 mm). Gas chromatographic analysis on a 10 ft × 0.25 in. column packed with 20% ethylene glycol succinate polymer on 60-80 mesh Chromosorb W-IHDS at 200°C with a flow of 60 cc of helium per min showed the presence of 2-exo-chlorobicyclo[3.3.1]nonan-9-one (2) (65%), relative retention time 28.9 min; 2-exo-chlorobicyclo[3.3.1]nonan-9-one (3) (24%), relative retention time 14.5 min; bicyclo[3.3.1]non-2-en-9-one (4) (7%), relative retention time 3.8 min. Samples

**References**


(22) The question arises as to whether part of the endo product is generated by attack of chloride ion on the π complex (particularly in the presence of AlCl₃). Although this possibility cannot be overridden without further experimentation, the π complex certainly cannot play an important role in product formation in the absence of added catalyst since the π-addition product predominates under these conditions. Only endo product would be anticipated from an attack of a chloride ion species on the π complex.

(23) In analogy, sodium borohydride reduction of bicyclo[3.3.1]nonan-9-one occurs predominantly from the exo side to give 2-exo-hydroxybicyclo[3.3.1]nonane.
of 2, 3, and 4 were collected by preparative glpc under the conditions described above, and their identities were established by nmr and infrared spectral comparisons with authentic specimens prepared as described under separate headings below.

When other solvents were employed, comparable results were obtained. When monoglyme was employed as solvent under the same conditions, the yields of 3, 3/2, 3, 4 were collected by preparative glpc under the conditions described above, and their identities were established by nmr and infrared spectral comparisons with authentic specimens prepared as described under separate headings below.

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water, and dried and solvent removed under reduced pressure to afford 800 mg (80% recovery) of crystalline solid. Gpce analysis on a 10 ft \( \times \) 0.25 in. column packed with 20% GE-SF-96 silicone oil on 60-80 mesh Chromosorb W-DMCS at 200° and helium flow of 65 cc/min indicated the presence of 2 (96%), trace quantities of 4, and several unidentified peaks. No evidence for the endo-chloro epimer 3 was observed. A sample of 2 collected by preparative gpce showed mp 70-72°. A mixture melting point with an authentic specimen of 2, mp 67.5-69°, showed no depression, mp 67.5-69°.

**Treatments of 2 with Aluminum Chloride in Diglyme.**—A mixture of 1.00 g (5.8 \( \times \) 10^{-4} mol) of 2, mp 67-69°, and 10 mg (7.5 \( \times \) 10^{-4} mol) of aluminum chloride in 3 ml of diglyme was heated at 100° for 16 hr. After work-up as above there was isolated 840 mg (84% recovery) of 4 as colorless crystals, mp 94-96°. A mixture melting point with the starting material 2, mp 97-99°, showed no depression, mp 94-98°.

Iron Carbonyl Catalyzed Isomerization of Unsaturated Ethers and Esters.

**The Effect of Carbomethoxy and Methoxy Groups on Olefin Equilibria**

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Equilibrations of the double bonds in methyl \( \alpha \)-alkenyl- and cyclohexenylcarboxylates and ethers have been studied. Iron pentacarbonyl in hydrocarbon solvents at reflux (125-150°) or with ultraviolet light at 20° was used to catalyze isomerization. Distribution of the double bonds to all possible positions is found with this catalyst system. For example, the equilibrium distribution of methyl octanoate isomers 2-ocetenoate, 18%; 3-octanoate, 8%; 4-octanoate, 21%; 5-octanoate, 24%; 6-octanoate, 29%; and 7-octanoate, 1%. Equilibration of methyl pentenyl isomers gave the distribution 1-pentenyl, 86%; 2-pentenyl, 5%; 3-pentenyl, 8%; and 4-pentenyl, 1%. These data are rationalized on the basis of two main effects: (a) the inductive electron-withdrawal destabilization effect of the carbomethoxy and methoxy groups. The net effect of a carbomethoxy group on the stability of an alkyl group. A methoxy group stabilizes an \( \alpha, \beta \) isomer by a factor of 10 compared to an alkyl group. The relatively low percentages of \( \beta, \gamma \) isomers found in both series are explained by the inductive destabilization effect of the \( \text{CH}_2\text{CO}_2\text{CH}_3 \) and \( \text{CH}_2\text{OCH}_3 \) groups.

Several transition metal compounds have recently been used as extremely efficient isomerization agents of \( \alpha \)-olefins.2 For example, Asinger and coworkers have described the double bond isomerization of 1-undecene to an equal distribution of internal isomers by iron pentacarbonyl catalyst at 30° for 1 hr in the presence of ultraviolet light. Other workers,4,5 have shown that the mixture of isomers from iron carbonyl catalyzed isomerizations closely parallels the theoretical thermodynamic equilibrium values. The use of iron carbonyls to catalyze the isomerization of unsaturated alcohols to aldehydes and ketones has been reported.6,7 Enol alcohols formed in these isomerizations are irreversibly converted into their carbonyl forms, precluding a study of olefin equilibrium in those systems. We wished to use iron carbonyl catalysts for the isomerization of functionally substituted olefins under conditions of reversible equilibrium. By a comparison of the relative percentages of olefin isomers at equilibrium, the effect of the functional group on the relative stability of the various olefin isomers can be ascertained.

Almost four decades ago, Kon and Linstead and collaborators investigated the effects of carbonyl and cyano groups on three carbon atom olefin equilibria as depicted in eq 1. Their results show that the carbonyl

\[
\text{RCH}_2\text{CH}_2\text{CH} = \text{CH}_{2} \xrightleftharpoons{B} \text{RCH}_2\text{CH} = \text{CH}_{2} \text{X}
\]

(1) R = alkyl
X = CO_R, CO_H, CN, COR

or cyano substituents favor isomer 1 over isomer 2 by a factor of 2-11.1. Under the basic isomerization conditions employed, migration of the double bond further down the chain in 2 is extremely slow due to the low acidity of the unactivated allylic hydrogen atoms compared to the hydrogen atoms adjacent to the substituent in 2.


