195°). These additional unidentified decomposition products could readily be detected by nmr and by vpc under the analytical conditions given above.

Anal. Calcd for C_7H_9BrO: C, 44.47; H, 4.80; Br, 42.27. Found: C, 44.69; H, 5.00; Br, 42.32.

Addition of Hydrogen Chloride to 7-Norbornenone (1).—To 7-norbornenone (**1**), 3.0 g (28 mmol), in a test tube was added 40 ml of concentrated (37%) hydrochloric acid. The tube was sealed and shaken vigorously for 48 hr at room temperature. The tube was opened and extracted with two 100-ml portions of ethyl ether. The ethereal extracts were combined and washed well with water and dried over anhydrous magnesium sulfate. The ether was removed under vacuum, and the dark residue was distilled to yield 2.3 g (58%), bp 52–56° (0.4 mm). Partial additions were carried out in 19% hydrochloric acid and shorter reaction times. The addition of deuterium chloride as a 20% solution in deuterium oxide was carried out in 9 days. As with the hydrobromides the major adduct was unstable under autoprep conditions. The retention times on a 5-ft QF-1 fluorosilicon column were 8.5 and 12 min for the minor and major adducts, respectively.

Anal. Calcd for C_7H_9ClO: C, 58.14; H, 6.28; Cl, 24.52. Found: C, 57.94; H, 6.42; Cl, 24.74.

Acknowledgments.—We are indebted to the Research Corporation and the Graduate School of the University of Minnesota for support of this work.

The Stereochemistry of Acyl Halide Addition to Olefins. The Intramolecular Cyclization of Cyclooct-4-*cis*-ene-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-*exo*-chlorobicyclo[3.3.1]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[3.3.1]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[3.3.1]non-2-en-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 *exo* isomer **2** undergoes elimination to bicyclo[3.3.1]non-2-en-9-one (**4**), while the *endo* isomer **3** suffers fragmentation to the potassium salt of cyclooct-4-ene-1-carboxylic acid (**6**).

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.[1] 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.[1] Indeed, stereochemical resolution of the chloro ketone products from the addition of acid chlorides to simple acyclic 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 or epimerization of the chloride function from the initially produced chloro ketone, the stereochemistry of addition could be ascertained at least for this system.

Results

We were able to find reaction conditions for cyclization of **1** which stereoselectively produced either 2-*exo*-chlorobicyclo[3.3.1]nonan-9-one (**2**) (*cis* addition) or 2-*endo*-chlorobicyclo[3.3.1]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 converse 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**[4] in 5% boron trifluoride etherate–diglyme at 100° effected cycloaddition of the acid chloride function but with almost complete loss of hydrogen chloride. Thus, bicyclo[3.3.1]non-2-en-9-one (**4**), the structure of which was verified by comparison with an authentic sample,[5] 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*-ene-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 chlo-

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[1] (a) For a review of acyl halide additions to alkenes, see G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. I, Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y., 1963, pp 129–133; (b) H. Wieland and L. Bettag, *Ber.*, **55**, 2246 (1922); (c) J. R. Catch, D. F. Elliot, D. H. Hey, and E. R. H. Jones, *J. Chem. Soc.*, 278 (1948), and references cited therein; (d) R. H. Carroll and G. B. L. Smith, *J. Amer. Chem. Soc.*, **55**, 370 (1933); (e) E. M. McMahon, J. N. Roper, Jr., W. P. Utermohlen, Jr., R. H. Hasek, R. C. Harris, and J. H. Brant, *ibid.*, **70**, 2971 (1948); (f) J. Colonge and K. Mostafavi, *Bull. Soc. Chim. Fr.*, (5), **6**, 335, 342 (1939).

[2] 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[3.3.1]nonane derivatives are produced almost exclusively from this latter solvolysis reaction.[3] Under more vigorous conditions, the initially produced bicyclo[3.3.1]nonane derivatives are apparently equilibrated to significant quantities of bicyclo[4.2.1]nonane compounds.[3a]

[3] (a) W. Kraus, W. Rothenwöhrer, W. Kaiser, and M. Hanack, *Tetrahedron Lett.*, 1705 (1966); M. Hanack and W. Kaiser, *Angew. Chem.*, **76**, 572 (1964); *Angew. Chem., Intern. Ed. Engl.*, **3**, 583 (1964); (b) A. C. Cope, D. L. Nealy, P. Scheiner, and G. Wood, *J. Amer. Chem. Soc.*, **87**, 3130 (1965); (c) H. Felkin, G. LeNy, C. Lion, W. D. K. Macrosson, J. Martin, and W. Parker, *Tetrahedron Lett.*, 157 (1966); (d) K. H. Baggaley, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 299 (1967).

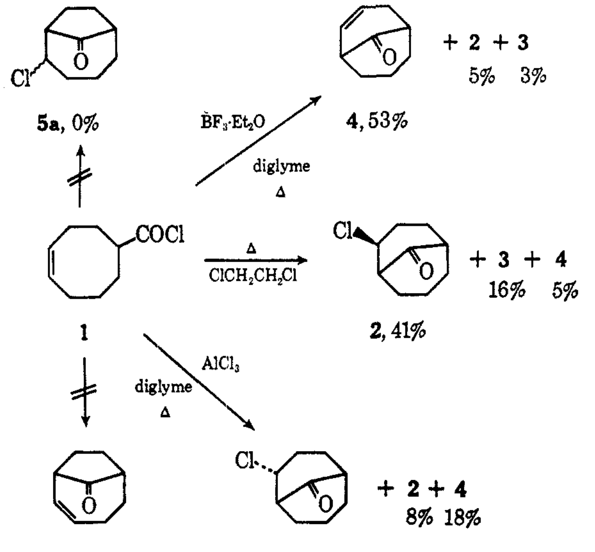
[4] (a) Prepared in 86% yield by treatment of cyclooct-4-*cis*-ene-1-carboxylic acid[4b] with oxalyl chloride; (b) K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

[5] C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

ride was heated at 83–84° in ethylene dichloride solution for 16 hr in the absence of an added catalyst, *exo*-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/*exo* 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 16 hr afforded the *endo* epimer **3** as the principal product (20–26%). The *exo* 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 *exo*-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 $C_9H_{13}OCl$ 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[5] and bicyclo[3.3.1]non-2-en-9-one[5] 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-carboxylate[10] (87%) and potassium cyclooct-3-*cis*-ene-1-carboxylate[10] (4%). 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*-butyl 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 *exo* 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-one[7,8] and the isomeric 7-methylbicyclo[4.2.1]nonan-9-ones[9] display carbonyl absorption at 5.75 μ, the 1-methyl and 1,5-dimethyl derivatives[9] at 5.73 μ, and the 2-methyl derivative[9] at 5.72 μ.

(7) C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960).

(8) G. Opitz and H. Mildenberger, *Ann.*, **650**, 115 (1961).

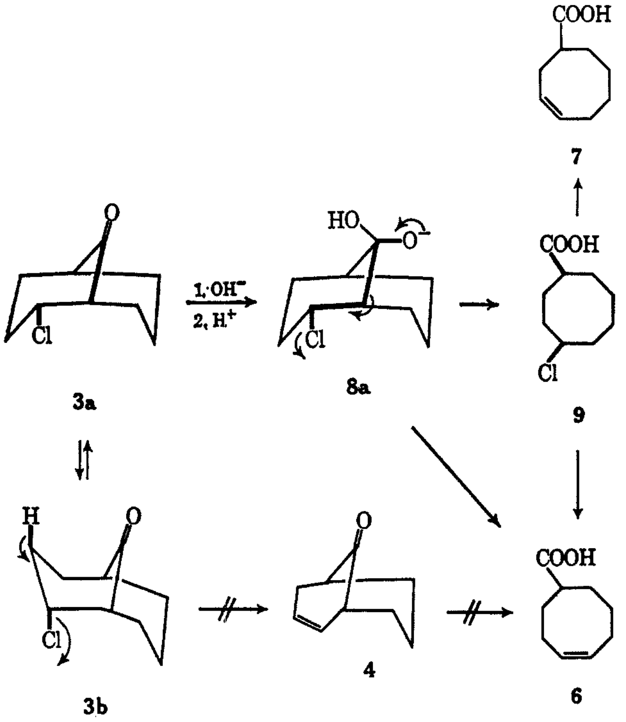
(9) C. D. Gutsche and J. E. Bowers, *J. Org. Chem.*, **32**, 1203 (1967).

(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**, 3842 (1967).

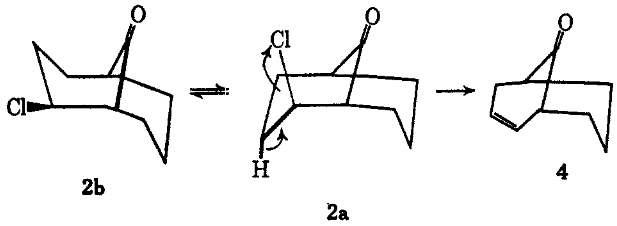
(11) Facile bridge fission seems to be a characteristic property of bicyclo[3.3.1]nonan-9-ones containing an easily eliminated functional group in the 2-*endo* position.[12] In contrast, 2-*exo*-substituted bicyclo[3.3.1]nonan-9-ones undergo elimination to produce the corresponding bicyclo[3.3.1]non-2-en-9-ones apparently at a slower rate than the bridge fission of the corresponding 2-*endo* isomers.[12]

(12) (a) J. Martin, W. Parker, and R. A. Raphael, *J. Chem. Soc.*, 289 (1964); (b) G. L. Buchanan and G. W. McLay, *Tetrahedron*, **22**, 1521 (1966).

being broken are approximately parallel and coplanar.[13] 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-3-*cis*-en-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 conformer **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*-diaxial elimination.[14]



Final confirmation of the structure **2** was made by X-ray diffraction. Webb and Becker[15] have shown that monoclinic needles of this isomer exist in the twin-chair conformation.[16,17] 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.

Fully 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.[3a,17a,b] 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 τ 5.46 as a multiplet of total band width 10.5 Hz, typical of an equatorial proton of a cyclohexane in the chair conformation.[12b,18] 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)[12b,18] and at higher field (τ 5.78)[12b,19] 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.[12b,18,20] 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**.[12b,18,20]

Discussion

The mode of cycloaddition of the acid chloride **1** is reminiscent of the ionic addition of hydrogen bromide to aryl-substituted olefins.[21] Dewar and Fahey[21] have observed that the ionic addition of hydrogen bromide to acenaphthalene 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

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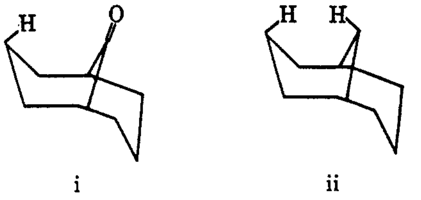
[13] (a) C. A. Grob in "Theoretical Organic Chemistry" (papers presented to the Kèkulé Symposium organized by The Chemical Society, London, Sept 1958), Butterworths Publications Ltd., London, 1959, p 114 ff; (b) C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955); C. A. Grob, *Experientia*, **13**, 126 (1957); (c) R. B. Clayton, H. B. Henbest, and M. Smith, *J. Chem. Soc.*, 1982 (1957), and references cited therein; (d) D. H. Gustafson and W. F. Erman, *J. Org. Chem.*, **30**, 1665 (1965), and references cited therein.

[14] (a) D. H. R. Barton, *Experientia*, **6**, 316 (1950); (b) see also E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 219-234.

[15] N. C. Webb and M. R. Becker, *J. Chem. Soc, Sect. B*, 1317 (1967).

[16] This observation is in accord with previous reports that fully saturated bicyclo[3.3.1]nonane compounds exist in the twin-chair conformation.[17] It is noteworthy that introduction of an sp^2 carbon at the 1-carbon bridge (thereby removing a 1,4-hydrogen-hydrogen interaction in the boat conformation [*i.e.*, i *vs.* ii]) does not alter the conformation of the bicyclo[3.3.1]-nonane structure in the crystal form.



[17] (a) W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 57 (1964); W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965), and references cited therein; (b) G. Eglinton, J. Martin, and W. Parker, *ibid.*, 1243 (1965).

[18] (a) A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 1350 (1964); (b) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 47, 48, 136-138.

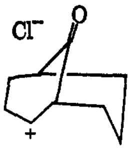
[19] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Ltd., London, 1959, p 116.

[20] It must be emphasized that these are only approximate couplings since the C-2-H and C-3-H resonances are strongly perturbed by mutual coupling and coupling with adjacent protons.[18b]

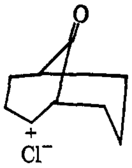
[21] (a) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 3645 (1963); (b) **85**, 2248 (1963); (c) **85**, 2245 (1963); (d) **84**, 2012 (1962).

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.[22,23]

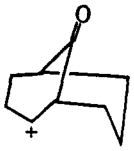
In an analogous manner, then, the acid chloride **1** could interact with the olefin to produce the *exo*-chloro ion pair **10**. The chloride could be associated with hydrogen chloride (formed by partial decomposition of the acid chloride to the corresponding ketene), with solvent, or with aluminum 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.



10, *exo*-Cl



11, *endo*-Cl



12

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 $AlCl_4^-$ of Cl^- from the *endo* side of the molecule.[23] 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**[24] 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 acyl halide additions to olefins.

Finally, the synthetic contribution of this work should be recognized. Of various preparations of bicyclo[3.3.1]nonane derivatives,[5,6,12,17b,c,25] 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 solvolysis 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 corrected; boiling points are uncorrected. Infrared spectra were recorded on a Perkin-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 τ 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-*cis*-ene-1-carboxylic Acid Chloride (**1**).—To 190.4 g (1.235 mol) of cyclooct-4-*cis*-ene-1-carboxylic acid[4b] 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°. 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° (25 mm), and the residue was distilled under vacuum. Cyclooct-4-*cis*-ene-1-carboxylic acid chloride (**1**), 185.5 g (86%), was obtained as a colorless liquid: bp 92° (4.6 mm); infrared (Infracord), λ^{neat} 5.58 μ (C=O), 6.08, 14.2 μ (*cis*-olefin); nmr spectrum (10% in CCl_4), τ 4.38, m, 2 H (C-4 and C-5 protons), τ 7.25, m, 1 H (C-1 proton), τ 7.4–9.0, m, 10 H (C-2, C-3, C-6, C-7, C-8 protons).

Anal. Calcd for $C_9H_{13}OCl$: C, 62.6; H, 7.6; Cl, 20.5. Found: C, 62.9; H, 7.4; Cl, 19.3.

Cycloaddition Reaction of Acid Chloride (**1**). **A. Absence of Catalyst.**—A solution of 10.0 g (0.058 mol) of acid chloride **1** in 15 ml of ethylene dichloride, bp 83–84°, was heated at reflux for 72 hr. The warm reaction mixture was poured into 100 ml of warm water (40–50°) and stirred at this temperature for 1 hr. The mixture was cooled to 27° 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° (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-HMDS at 200° 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-*endo*-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 5.8 min). Samples

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[22] For an analysis of *cis vs. trans* electrophilic additions to other olefin systems, see references cited in footnote 21, ref 15–18, 20, 21, 23; in W. F. Erman, *J. Org. Chem.*, **32**, 765 (1967), footnote 21; and in several articles by Cristol: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2719, 2726, 2733 (1966); S. J. Cristol and R. Caple, *ibid.*, **31**, 2741 (1966).

[23] The question arises as to whether part of the *endo* product is generated by attack of chloride ion on the π complex i (particularly in the presence of $AlCl_3$). Although this possibility cannot be overruled without further experimentation, the π complex i certainly cannot play an *important* role in product formation in the absence of added catalyst since the *cis*-addition product predominates under these conditions. Only *exo* product would be anticipated from an attack of a chloride ion species on the π complex i.

i

[24] In analogy, sodium borohydride reduction of bicyclo[3.3.1]nonan-2-one occurs predominantly from the *exo* side to give 2-*endo*-hydroxybicyclo[3.3.1]nonane.[3b]

[25] S. Brewis and P. R. Hughes, *Chem. Commun.*, 6 (1966).

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. The solvent, temperature, and yield of each product is listed in order for each run. The reaction period (72 hr) and work-up conditions were identical with those described above: (1) benzene, 80°; **2**, 34%; **3**, 13%; **4**, 4%; (2) monoglyme, 83°; **2**, 39%; **3**, 9%; **4**, 4%; methyl cyclooct-4-*cis*-ene-1-carboxylate, 9%; (3) 1,1,2-trichloroethane, 113°; **2**, 41%; **3**, 20%; **4**, 3%; (4) acetic acid, 118°; **2**, 27%; **3**, 15%; **4**, 7%; unidentified acetate, 25%.

B. In Diglyme Using Boron Trifluoride Etherate As Catalyst. Preparation of Bicyclo[3.3.1]non-2-en-9-one (4).—To a solution of 50.0 g (0.29 mol) of acid chloride **1** in 1 l. of anhydrous diglyme was added 50 ml of boron trifluoride etherate. This mixture was heated at 100° under a nitrogen atmosphere for a period of 72 hr. To the cooled solution (26–27°) was added dropwise 100 ml of water. The mixture was further diluted with 2 l. of water and stirred for 1 hr. The precipitated liquid was extracted with four 200-ml portions of ether. The combined ether extracts were washed with two 100-ml portions of water, dried over $MgSO_4$, and evaporated to yield 32.0 g of brown liquid. Gas chromatographic analysis on a 10 ft × $^1/_4$ in. column packed with 20% GE-SF-96 silicon oil on 60–80 mesh Chromosorb W-HMDS at 200° with a flow of 60 cc of helium per min showed the presence of olefin **4** (65%) (relative retention time 3.3 min), methyl cyclooct-4-*cis*-ene-1-carboxylate (17%) (relative retention time 4.0 min, identified by comparison with an authentic sample[10]), chloro ketone **3** (5%) (relative retention time 5.7 min), chloro ketone **2** (7%) (relative retention time 7.0 min) and an unidentified compound (6%) (relative retention time 9.5 min). The liquid was dissolved in 200 ml of 10% methanolic potassium hydroxide solution, and this mixture was heated at reflux for 3 hr. The solution was diluted with 200 ml of water and extracted with three 100-ml portions of ether. The combined ethereal extracts were washed with three 50-ml portions of water, dried, and the ether removed under reduced pressure to afford 21.2 g (53%) of light yellow solid, mp 90–96°. Sublimation of this solid at 70° (25 mm) gave 10.0 g (25%) of **4** as colorless needles, mp 95–98°. The nmr and infrared spectral properties and glpc retention time of this material were identical with an authentic specimen of **4** prepared by the method of Foote and Woodward.[5] The 2,4-dinitrophenylhydrazone derivative, on recrystallization from ethanol–ethyl acetate, had mp 193–194° (lit.[5] mp 194.5–195.5°).

C. Using Aluminum Chloride As Catalyst. Preparation of 2-*endo*-Chlorobicyclo[3.3.1]nonan-9-one (3).—A mixture of 10.0 g (0.058 mol) of cyclooct-4-*cis*-ene-1-carboxylic acid chloride (**1**) and 0.050 g (0.0004 mol) of aluminum chloride in 30 ml of diglyme was heated under a nitrogen atmosphere at 100° for 16 hr. The mixture was cooled to 26–27° and 100 ml of water was added dropwise with stirring over a 10-min period. The mixture was stirred an additional 1 hr and was extracted with three 100-ml portions of ether. The ethereal extract was washed with three 50-ml portions of water, dried, and the ether evaporated to afford 8.502 g of dark brown liquid. The liquid was distilled in a modified Hickman still to yield 6.058 g of colorless liquid, bp 90–105° (0.1 mm). Gas chromatographic analysis on a 10 ft × 0.25 in. column packed with 20% Reoplex-400 on 60–80 mesh Chromosorb W-HMDS at 200° with a flow of 60 cc of helium per min showed the presence of **4** (30%, relative retention time 2.2 min), **2** (14%, relative retention time 8.0 min), **3** (33%, relative retention time 4.5 min). Samples of the olefinic ketone **4** and the *exo*-chloro ketone **2** were collected by preparative glpc, and their identity was established by nmr and infrared spectral comparisons with samples prepared under the respective headings. A sample of the *endo*-chloro ketone **3** was collected by preparative glpc as colorless needles: mp 65–66.5° (20% yield); infrared (Perkin-Elmer 421), ν (5% CS_2) 2985 cm^{-1} (abnormal C–H stretching), 1729 (strong), 1713 (weak) (C=O); nmr (10% CCl_4), τ 5.78, m (total band width 24 Hz), 1 H (C-2-*exo* proton). Irradiation of the C-1 proton indicated J (H-2, H-3-*exo*) = 4.9 Hz; J (H-2, H-3-*endo*) = 12.0 Hz.

Anal. Calcd for $C_9H_{13}OCl$: C, 62.6; H, 7.6; Cl, 20.5. Found: C, 62.7; H, 7.9; Cl, 19.8.

When monoglyme was employed as solvent under the same conditions, the yields of **2**, **3**, and **4** were 33, 14, and 30%, respectively.

Preparation of 2-*exo*-Chlorobicyclo[3.3.1]nonan-9-one (2).—A solution of 8.0 g of the crude product (before distillation) from cyclization of **1** as described in procedure A, above, and 10.0 g of potassium *t*-butoxide in 100 ml of wet *t*-butyl alcohol was stored at 26–27° for a period of 16 hr. The mixture was diluted with 100 ml of water and extracted with three 100-ml portions of petroleum ether (bp 41–45°). The combined petroleum ether extracts were washed with water (50 ml), 5% hydrochloric acid (50 ml), and three 100-ml portions of water and dried over magnesium sulfate. Removal of solvent under reduced pressure afforded 3.0 g of **2** (34% yield based on starting acid chloride **1**) as colorless needles, mp 64–67°. Recrystallization from acetone afforded **2** as colorless needles: mp 70–72°; infrared (Perkin-Elmer 421), ν (10% in CS_2), 2995 cm^{-1} (abnormal C–H stretching), 1732 (weak), 1728 (strong), 1707 (weak) (C=O); nmr (10% CCl_4), τ 5.46, m (total band width 10.5 Hz), 1 H (C-2-*endo* proton).

Anal. Calcd for $C_9H_{13}OCl$: C, 62.6; H, 7.6; Cl, 20.5. Found: C, 62.6; H, 7.6; Cl, 20.3.

Treatment of Bicyclo[3.3.1]non-2-en-9-one (4) with 10% Methanolic Sodium Hydroxide Solution.—A solution of 250 mg (0.0018 mol) of **4**, mp 95–98°, in 30 ml of 10% methanolic sodium hydroxide solution was heated at reflux under a nitrogen atmosphere for a period of 16 hr. The mixture was cooled to 26–27°, diluted with 50 ml of water, and extracted with three 25-ml portions of ether. The combined ethereal layers were washed with three 25-ml portions of water, dried, and the solvent evaporated to afford 187 mg (75%) of starting **4** as colorless prisms, mp 97–99°. The identity was further established by nmr and infrared spectral comparisons with an authentic specimen.[4] A mixture melting point with an authentic specimen (mp 95–98°) showed no depression (94–99°).

Treatment of 2-*exo*-Chlorobicyclo[3.3.1]nonan-9-one (2) with 10% Methanolic Sodium Hydroxide Solution.—A solution of 250 mg (0.0014 mol) of *exo*-chloro ketone **2**, mp 67–69°, in 30 ml of 10% methanolic sodium hydroxide solution was heated at reflux under a nitrogen atmosphere for a period of 16 hr. Work-up as above afforded 183 mg (95%) of keto olefin **4** as colorless prisms, mp 95–98°. The identity was confirmed by spectral comparisons and mixture melting point with an authentic specimen,[5] as above.

Treatment of 2-*endo*-Chlorobicyclo[3.3.1]nonan-9-one (3) with 10% Methanolic Sodium Hydroxide Solution.—A solution of 250 mg (0.0014 mol) of chloro ketone **3** in 30 ml of methanolic sodium hydroxide was heated as above. The cooled mixture was diluted with 50 ml of water and the neutral products extracted with three 25-ml portions of ether. The ethereal layers were combined, washed with three 25-ml portions of water, dried, and the solvent evaporated to afford 15 mg of light yellow liquid. The basic layer was cooled to 0–5° and acidified with concentrated hydrochloric acid. The resulting liquid was extracted with two 50-ml portions of ether. The ethereal solution was washed with three 25-ml portions of water and dried over magnesium sulfate. Evaporation of the ether afforded 203 mg (91%) of light yellow liquid: infrared (Infracord), λ 3–4 μ (carboxyl OH), 5.91 (carboxyl C=O). The liquid was dissolved in 25 ml of ether and treated with 50 ml of 2% ethereal diazomethane at 0° for 3 hr. The excess diazomethane was destroyed by addition of 15 ml of 10% hydrochloric acid; the ethereal layer was washed with 10 ml of 10% hydrochloric acid, two 20-ml portions of water, 25 ml of 10% sodium bicarbonate, and three 20-ml portions of water and dried. Evaporation of ether and short-path distillation afforded 166 mg of colorless liquid: bp 50–60° (0.5 mm); infrared (Infracord), λ 5.75, 8.1–8.6 μ (ester), 6.08, 13.35, 14.0 (*cis*-olefin). Gas chromatographic analysis on a 150-ft capillary column packed with polyphenyl ether and programmed from 100 to 180° with a heating rate of 5° per min with a helium flow of 20 cc per min showed the presence of methyl cyclooct-4-*cis*-ene-1-carboxylate (**6a**, 95%, relative retention time 14.62 min), methyl cyclooct-3-*cis*-ene-1-carboxylate (**7a**, 5%, relative retention time 14.26 min). The infrared and nmr spectra and the glpc retention times of each were identical with authentic samples[10] of the esters **6a** and **7a**.

Treatment of 2-*exo*-Chlorobicyclo[3.3.1]nonan-9-one (2) with Aluminum Chloride in Benzene.—A mixture of 1.00 g (5.8 × 10^{-3} mol) of **2**, mp 67.5–69°, and 0.50 g (3.8 × 10^{-3} mol) of aluminum chloride in 50 ml of benzene was heated at reflux under a nitrogen atmosphere for a period of 16 hr. The cooled mixture (26–27°) was poured into 200 ml of ice–water. The benzene layer was partitioned, washed with three 25-ml portions of water, and dried and solvent removed under reduced pressure to afford 800 mg (80% recovery) of crystalline solid. Glpc analysis on a 10 ft × 0.25 in. column packed with 20% GE-SF-96 silicon 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 glpc showed mp 70–72°. A mixture melting point with an authentic specimen of **2**, mp 67.5–69°, showed no depression, mp 67.5–69.5°.

Treatment of 2 with Aluminum Chloride in Diglyme.—A mixture of 1.00 g (5.8×10^{-3} mol) of **2**, mp 67–69°, and 10 mg (7.5×10^{-5} mol) of aluminum chloride in 3 ml of diglyme was heated under a nitrogen atmosphere at 100° for 16 hr. After work-up as above there was isolated 840 mg (84% recovery) of **2** as colorless crystals, mp 69–71°; there was no depression of melting point on admixture with an authentic specimen of **2**.

Treatment of Olefin 4 with Aluminum Chloride in Diglyme.—A mixture of 1.47 g (1.08×10^{-2} mol) of **4** and 20 mg (1.5×10^{-4} mol) of aluminum chloride in 5 ml of diglyme was heated at 100° for 16 hr. After work-up as above there was isolated 1.37 g (93% recovery) of **4** as colorless crystals, mp 94–98°. A mixture melting point with the starting material **2**, mp 97–99°, showed no depression, mp 94–98°.

Treatment of 4 with Hydrogen Chloride–Aluminum Chloride in Diglyme.—A solution of 1.00 g (7.4×10^{-3} mol) of **4** and 20 mg (1.4×10^{-4} mol) of aluminum chloride in 5 ml of diglyme, saturated with gaseous hydrogen chloride, was heated at 100° for 6 hr. After work-up as above there was isolated 870 mg of soft crystals. Glpc analysis on a 10 ft × $^1/_8$ in. column packed with 20% Reoplex on 60–80 mesh Chromosorb W-DMCS at 200° with a helium flow of 60 cc/min showed **2** (91%, relative retention time 4.3 min), the chloro ketone **3** (2%, relative retention time 10.0 min), four unidentified chloro ketones: relative retention times 11.3 min (2%), 11.7 (2%), 12.8 (1%), 13.0 (0.3%) and **2** (0.4%, relative retention time 18.0 min).

Registry No.—**1**, 15973-61-2; **2**, 16031-45-1; **3**, 16031-46-2; **4**, 4844-11-5; **6a**, 16031-48-4; **7a**, 15973-62-3.

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Iron Carbonyl Catalyzed Isomerization of Unsaturated Ethers and Esters. The Effect of Carbomethoxy and Methoxy Groups on Olefin Equilibria[1]

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Equilibrations of the double bonds in methyl *n*-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 octenoate isomers is 2-octenoate, 18%; 3-octenoate, 8%; 4-octenoate, 21%; 5-octenoate, 24%; 6-octenoate, 29%; and 7-octenoate, 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 destablization effect of the carbomethoxy and methoxy groups and (b) the conjugative stabilization effects of these groups. The net effect of a carbomethoxy group on the stability of an α,β isomer is approximately that of an alkyl group. A methoxy group stabilizes an α,β isomer by a factor of 10 compared to an alkyl group. The relatively low percentages of β,γ isomers found in both series are explained by the inductive destabilization effect of the $-CH_2CO_2CH_3$ and $-CH_2OCH_3$ groups.

Several transition metal compounds have recently been used as extremely efficient isomerization agents of *n*-olefins.[2] For example, Asinger and coworkers[3] have described the double bond isomerization of 1-undecene to an equal distribution of internal isomers by iron pentacarbonyl catalyst at 50° 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[8] 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

$$\underset{\textstyle 1}{\mathrm{RCH_2CH_2CH{=}CHX}} \overset{B^-}{\rightleftharpoons} \underset{\textstyle 2}{\mathrm{RCH_2CH{=}CHCH_2X}} \qquad (1)$$

$R = \text{alkyl}$
$X = CO_2R,\ CO_2H,\ CN,\ COR'$

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.

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(1) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, Abstracts, p O159.

(2) For up-to-date discussions on the mechanism of olefin isomerization by transition metal catalysts, see R. Cramer and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **88**, 3534 (1966), and M. Orchin, *Advan. Catal.*, **16**, 1 (1966).

(3) (a) F. Asinger, B. Fell, and K. Schrage, *Chem. Ber.*, **98**, 372 (1965); (b) *ibid.*, 381 (1965).

(4) M. D. Carr, V. V. Kane, and M. C. Whiting, *Proc. Chem. Soc.*, 408 (1964).

(5) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

(6) G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 4591 (1962).

(7) R. Damico and T. J. Logan, *J. Org. Chem.*, **32**, 2356 (1967).

(8) Recently discussed by D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 201–202.