

leaving a viscous liquid residue which resisted repeated attempts at crystallization. The ir spectrum of this residue showed neither a band at *ca.* 3430 nor at 1575 cm^{-1} , and thus contained neither 1 or 11 in significant amounts.

Attempted Condensation of 11 with Cyclopentadiene.—A solution of 0.6 g (*ca.* 0.002 mol) of 11 and 0.150 g (*ca.* 0.002 mol) of freshly prepared cyclopentadiene in anhydrous ether was maintained at 15–20° for 24 hr under nitrogen with magnetic stirring.³ Upon stripping all volatiles at the water pump up to steam bath temperatures slightly more than 0.6 g of a solid remained which had an ir spectrum nearly identical with that of the starting compound 11.

Mass Spectra.—That of *N,N'*-bis-*p*-toluenesulfonylhydrazine was taken on an Atlas double focus high resolution instrument (Atlas Mess and Analysentechnik GMBH Bremen) through the courtesy of Dr. C. Djerassi at Stanford University, Stanford, California, while one of us (H. K.) was in residence as visiting professor of Chemistry in 1964. Direct introduction of the sample was possible with this instrument and consequently pyrolytic decomposition could be avoided. The spectra of *N,N'*-bisbenzenesulfonylhydrazine and of compound 11 were recorded

under conditions specified in Table II through the courtesy of Dr. W. B. Askew, for which we are most grateful.

Nmr spectra were determined with either a Varian A-60 or Varian HR-100 instruments.

H bonding data were taken with a Perkin-Elmer Model 337 grating infrared spectrometer.

pK_a measurements were obtained by use of a Sargeant Model D recording titrator.

Ebullioscopic determinations of the molecular weight of 11 were carried out in benzene solution with benzyl as a standard and using an instrumental design described in the literature.¹³ Four determinations were made with the results ranging from 298–299, compared to calculated 310.

Registry No.—1, 6272-36-2; 3, 98-10-2; 4, 2618-96-4; 11a, 15815-54-0; 11b, 15815-55-1; *N*-bromodibenzene-sulfonimide, 15815-56-2.

(13) R. V. Bonnar, M. Dimbal, and F. H. Strass, "Number Average Molecular Weight," Interscience Publishers, Inc., New York, N. Y., 1958.

The Hydrohalogenation and Deuteriohalogenation of 7-Norbornenone

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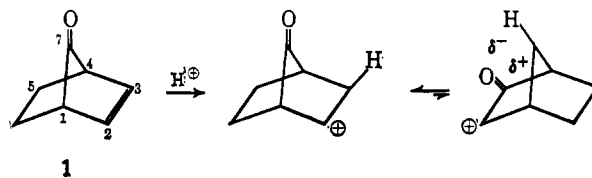
The polar addition of hydrogen bromide, hydrogen chloride, and the corresponding deuterio halides to 7-norbornenone (1) has been carried out. The products cannot be reconciled with an intermediate involving interaction between the protonated carbonyl group and the π electrons of the ethylenic system. The major product is the result of *cis-exo* addition with the rearranged *exo* product occurring to a much smaller extent. The importance of steric, bridging, and torsional effects in controlling the stereochemistry are considered.

The stereochemistry of the electrophilic addition of hydrogen halides to olefins has received considerable attention.^{1–8} It has become apparent that the *trans* addition of a hydrogen halide to an α,β -unsaturated carboxylic acid is the result of a 1,4 addition and is not related mechanistically to the reaction of an isolated olefin.⁹ It has also become apparent that the stereochemical course of addition to an isolated olefin is not a simple function of π complexes and steric effects. The occurrence of ion pairs or complexes leading to a preference for *cis* addition, unless torsional strain effects are unfavorable, is now recognized.^{3,7}

The norbornene system has occupied a place by itself in these investigations owing to the importance, if any, of the delocalized "nonclassical" carbonium ion or the "windshield wiper effect"¹⁰ in determining the stereochemistry of electrophilic additions. Steric effects alone cannot account for all of the *exo* products^{2,4,5} since the hydrochlorination of bornylene and

apobornylene also produces *exo* adducts.⁶ The occurrence of a delocalized structure in the transition state of the proton-addition step also seems unlikely in view of the recent results of Brown⁶ and Schleyer.⁷

We have investigated the hydrohalogenation, and deuteriohalogenation, of 7-norbornenone (1) in the hopes that we would be able to examine the stereochemical course of addition when a classical secondary norbornyl cation was involved. Attack of a proton on the double bond of 7-norbornenone (1) should produce a carbonium ion which is reluctant to rearrange as the rearranged carbonium ion involves a juxtaposition of positive charges. Likewise delocalization of the σ electrons of the C-1, C-6 bond in the transition state of



the proton-addition step would seem less important here as compared to the norbornyl cation. If this is true, then it is possible that neither the nonclassical carbonium ion nor the equilibrating classical ions would be involved in the product-controlling attack of the halide ion.

Results

The polar hydrobromination, and deuteriohalogenation, of 7-norbornenone (1) was carried out in methylene chloride saturated with hydrogen bromide, or deuterium bromide, at 0°. The reaction was complete within

(1) P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, **29**, 1625 (1964).

(2) S. J. Cristol, J. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2719, 2726, 2733, 2738 (1966), and previous papers; S. J. Cristol and R. Caple, *ibid.*, **31**, 2741 (1966).

(3) M. J. S. Dewar and R. C. Fahey, *Angew. Chem., Intern. Ed. Engl.*, **3**, 245 (1964), and references cited therein.

(4) H. Kwart and J. L. Nyce, *J. Amer. Chem. Soc.*, **86**, 2601 (1964).

(5) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, **88**, 4922 (1966).

(6) H. C. Brown and K.-T. Liu, *ibid.*, **89**, 466, 3898, 3900 (1967), and references cited therein.

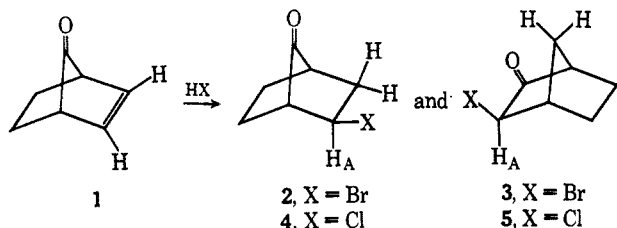
(7) P. von R. Schleyer, *ibid.*, **89**, 3901 (1967).

(8) R. C. Fahey, *Chem. Commun.*, **18**, 936 (1967), and previous papers.

(9) R. Caple, and W. R. Vaughan, *Tetrahedron Lett.*, 4067 (1966), and references cited therein.

(10) H. C. Brown, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 21, 1961, p 2-O; "Non-Classical Intermediates," Organic Reaction Mechanisms Conference, Brookhaven, N. Y., Sept 5, 1962.

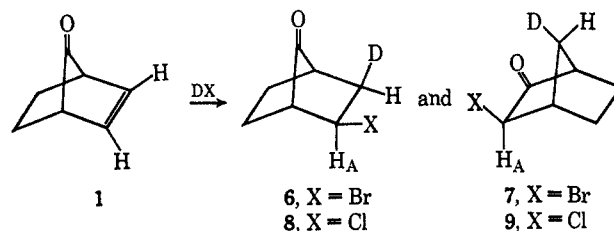
15 hr, and the crude adducts were recovered in 85% yields. The polar hydrochlorination in methylene chloride of this deactivated olefin however was very slow, less than 10% in 7 days at 0°, and the addition was carried out using 37% hydrochloric acid. The aqueous solution for the deuteriochlorination was generated by hydrolyzing dichlorodimethylsilane.¹¹ The mixtures were shaken vigorously for *ca.* 48 hr, and the adducts were recovered by extraction in 55–65% yields. Product analyses were made by nuclear magnetic resonance (nmr) and vapor phase chromatographic (vpc) techniques.



Only two major products in the ratio of 85:15 were observed in the hydrobromination of 7-norbornenone (1). These products are the unrearranged *exo* hydrobromide 2 and the rearranged *exo* adduct 3. No other adducts could be detected by thin layer chromatography, vpc, or by nmr. This product ratio does not change as the reaction time is reduced, the same ratio of 2/3 being observed at 40% reaction. Furthermore, an authentic sample of *exo*-3-bromonorcamphor (3) is stable under the reaction conditions. The presence of hydroquinone also does not alter the product distribution. It is felt, therefore, that kinetically controlled adducts resulting from a polar addition are being observed. Essentially the same product ratio is obtained when the addition is carried out in 48% hydrobromic acid although the per cent recovery was only 50%.

The configurational assignments for 2 and 3 were made by nmr.¹² The signal for H_A in *exo*-2-bromo-7-norbornanone (2) occurs as a triplet, $J = 5.8$ cps, at $\delta 4.3$. This multiplet is consistent with the assigned configuration^{13–15} where $J_{obsd} = \frac{1}{2}(J_{cis} \text{ and } J_{trans})$ and where there is no detectable coupling with the bridgehead hydrogen. This averaging effect for J_{cis} and J_{trans} is confirmed in the nmr analysis of the deuterio bromide discussed shortly. The signal for H_A in *exo*-3-bromonorcamphor (3) occurs as a doublet, $J = 3.0$ cps, at $\delta 3.8$ with finer splitting being less than 0.5 cps. This is in agreement with the reported spectrum for 3¹⁶ and a spectrum obtained by us on an authentic sample.

The addition of deuterium bromide confirms the *cis-exo* nature of the addition to produce 2. The triplet for H_A in 2 collapses to a clean doublet in 6, $J_{cis} = 8.8$ cps. This is the value expected for a *cis-endo* vicinal coupling¹⁷ and confirms the nature of the "decep-

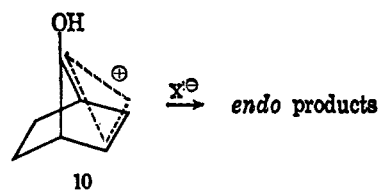


tively simple spectrum" of the *endo* hydrogen H_A in 2 as described by Flautt and Erman.^{13,18} The multiplet for H_A in 7 is unchanged as one would predict for deuterium at the *syn*-C-7 position.

The results from the hydrochlorination are similar. The *exo* hydrochlorides, 4 and 5, are obtained in a ratio of 93:7. The product ratio again does not vary even when the reaction is carried to 13% completion in 19% hydrochloric acid. The multiplet for H_A in 4 is again a "deceptively simple" triplet, $J = 4.6$ cps, at $\delta 4.2$. The triplet collapses to a doublet, $J = 8.5$ cps, in the labeled adduct 8.

Discussion of Results

It was initially hoped that appreciable *endo* products would be observed in the hydrohalogenation of 7-norbornenone (1). An *endo* isomer conceivably could result from the interaction between the protonated carbonyl group and the π electrons of the double bond. It has recently been shown by nmr studies that such an interaction can occur leading to the delocalized structure 10.¹⁹ There is also some indication, LCAO-MO calculations and ultraviolet data,²⁰ for an interaction of the π -carbonyl system of 7-ketonorbornene (1) with the π -ethylenic system although the sodium borohydride reduction of this ketone does not involve delocalization.²¹ Likewise the products observed in this study are not derived from the protonated structure 10.



The hydrohalides are consistent with those derived from *exo* protonation of the carbon-carbon double bond in 1. Attempts to promote interaction between the π systems of 1 by catalyzing the addition with aluminum bromide or aluminum chloride lead to increased polymerization and no detectable change in the product distribution.

The *exo/endo* product ratios observed in this investigation differ from those observed in solvolysis studies.^{22–24} These differences are expected⁶ owing to the presence of intimate ion pairs in the solvolysis work. Thus the acetolysis of the *endo*- and *exo*-7-ketonorbornyl tosylates produces considerable *endo*

(11) W. H. Greive and K. F. Sporek, *J. Chem. Educ.*, **43**, No. 7, 381 (1966).

(12) Chemical shifts are relative to tetramethylsilane on 60-Mc instrument.

(13) T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 3212 (1963).

(14) A. L. Thomas, R. A. Schneider, and J. Meinwald, *ibid.*, **89**, 68 (1967).

(15) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

(16) J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, **85**, 2513 (1963).

(17) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(18) For other examples, see ref 14.

(19) S. Winstein, *Chem. Eng. News*, 54 (April 3, 1967).

(20) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).

(21) H. C. Brown and J. Muzzio, *ibid.*, **88**, 2811 (1966).

(22) P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2822 (1966); *ibid.*, **87**, 4648 (1965).

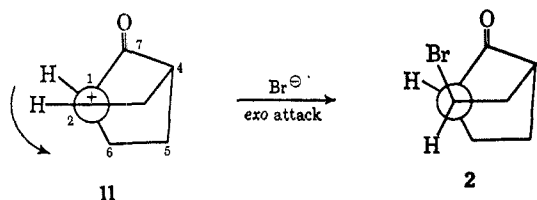
(23) P. G. Gassman and J. L. Marshall, *Tetrahedron Lett.*, No. 46, 4073 (1965).

(24) M. Hanack and J. Dolde, *ibid.*, No. 3, 321 (1966).

acetates but no rearranged acetates^{22,23} owing to the early coordination of acetic acid with the developing ion pair.

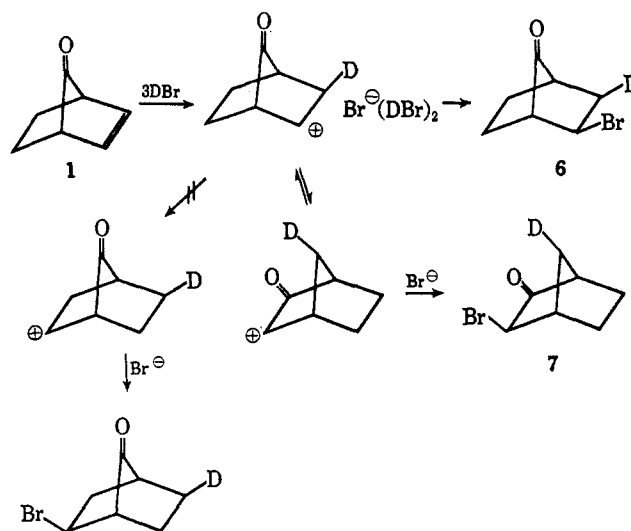
The formation of the unrearranged hydrohalide as the primary product supports the classical character of the 7-ketonorbonyl cation **11**.^{22,23} The extent to which rearrangement does occur would seem to be more consistent with the relief of angle strain involved in placing the trigonal carbonyl carbon in the ethylene bridge than with a nonclassical intermediate involving a partial delocalization of the C-1, C-6 σ electrons. The internal angle at C-7 is about 96.5° compared to about 104° at C-2.²⁵ Although the observed major *cis-exo* adduct can be explained in this system as being derived from a transfer to the least-hindered side of the double bond, it must be emphasized that hydrogen chloride also adds to bornylene and apobornylene to yield *exo* adducts.⁶ Furthermore, the concerted four-centered addition mechanism for the electrophilic addition of hydrogen chloride to certain norbornene systems has recently been considered to be less likely than a mechanism involving a carbonium ion intermediate.⁶ If similar considerations are applicable here, the *exo* approach of the proton and the *exo* approach of the halide ion, as a complex with hydrogen halide, are probably independent steps although the stereochemical control of approach may be governed by a common factor.

An alternate explanation to account for the stereochemistry is the torsional strain factor. Similar interpretations have been used to explain why, although there is preference for *cis* addition of a hydrogen halide,³ in certain olefins the *trans* addition product is the major adduct.²⁶⁻²⁸ Both steps in the addition involve a conversion of a sp^2 -hybridized carbon into a sp^3 -hybridized carbon. Approach from the *exo* side proceeds with relief of torsional strain in the transition state as compared to *endo* approach where eclipsing will occur between the bridgehead carbon-hydrogen bond and the adjacent carbon-hydrogen bond on the ethylene bridge. The importance of torsional effects in controlling the stereochemistry of attack in norbornane derivatives has recently been discussed by Schleyer.²⁹ The effect is indicated by the *exo* attack of bromide ion on the 7-ketonorbonyl cation **11** to produce **2**.



The stepwise addition of deuterium bromide to 7-norbornenone (**1**) is outlined in Scheme I. The mechanism is consistent with the other known facts concerning the electrophilic addition of a hydrogen halide to an olefin.^{3,30-32} It must be pointed out that the clean

SCHEME I
FLOW DIAGRAM FOR THE ELECTROPHILIC ADDITION OF DBr TO 1



collapse of the triplet for the proton on the carbon-bearing bromine upon addition of deuterium bromide means that a 6,2-hydride shift must be occurring to an undetectable extent.

Experimental

Materials.—7-Norbornenone (**1**) was synthesized by the oxidation of bicyclo[2.2.1]hept-2-en-*anti*-7-ol³³ according to the procedure of Bly.³⁴ Deuterium bromide was generated by the addition of deuterium oxide, 99.8% (Columbia Organic Chemicals Co., Inc.) to Eastman phosphorus tribromide. The deuterium bromide was trapped and distilled into reagent methylene chloride from a Dry Ice-acetone trap. An aqueous solution of deuterium chloride was formed by the hydrolysis of dichlorodimethylsilane (Dow Chemical Co.) according to the procedure of Greive and Sporek.³¹ The aqueous solution of approximately 20% deuterium chloride was removed and separated from the polymeric silicone oil layer by means of a syringe.

Analytical.—Nuclear magnetic resonance spectra were obtained using a Varian Associates Model A-60 spectrometer using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on an Aerograph A90-P3 instrument using 20% silicone GE (5 ft \times 0.25 in.), 20% Carbowax 20M (10 ft \times 1/8 in.), and 10% fluorosilicone QF-1 (5 ft \times 0.25 in.) columns. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Addition of Hydrogen Bromide to 7-Norbornenone (1).—7-Norbornenone (**1**), 2.9 g (27 mmol), was dissolved in 200 ml of reagent methylene chloride and saturated with anhydrous hydrogen bromide (Matheson Co., Inc.) at 0° in a bubbler trap. The acid solution was tightly stoppered and allowed to stand for 36 hr at 0° . After the addition, the excess hydrogen bromide and methylene chloride were removed by gentle heating on a hot plate. Fresh methylene chloride was added, and the solution was dried over anhydrous magnesium sulfate. Removal of the solvent under vacuum yielded 4.3 g (85%) of hydrobromides and no starting ketone as indicated by nmr and vpc. The retention times on the fluorosilicone column at 125° were 14 and 18 min for the minor and major hydrobromides, respectively. The retention time of the minor adduct was indistinguishable from a sample of *exo*-3-bromonorcamphor (**3**) obtained by the bromination of norcamphor (Aldrich Chemical Co.). The purified product ratio was essentially identical with the original as indicated by both nmr and vpc. Shorter runs and the addition of deuterium bromide were carried out in a similar fashion. Attempts to separate the adducts by preparative vpc were unsuccessful owing to the thermal instability under autotprep conditions (Aerograph A-700, silicone SE-30 (20 ft \times 1/8 in.),

(25) P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

(26) G. S. Hammond and T. D. Nevitt, *ibid.*, **77**, 1594 (1955).

(27) J. V. Smirnov-Zamkov and G. A. Piskovitina, *Ukr. Khim. Zh.*, **28**, 531 (1962).

(28) R. C. Fahey and R. A. Smith, *J. Amer. Chem. Soc.*, **86**, 5935 (1964).

(29) P. von R. Schleyer, *ibid.*, **89**, 701 (1967).

(30) P. B. D. de la Mare and R. Boulton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966.

(31) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms, 1965," John Wiley and Sons, Ltd., London, 1966, p 104 ff.

(32) K. Fukui, *Bull. Chem. Soc. Jap.*, **39**, 498 (1966).

(33) P. Story, *J. Org. Chem.*, **26**, 289 (1961).

(34) R. K. Bly and R. S. Bly, *ibid.*, **28**, 3165 (1963).

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 auto-prep 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 1⁴ 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-

(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).

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