Studies on Reactions of Isoprenoids. XIV.[1] Facile Lactone Formations from 2-*endo*-Cyano-, 2-*endo*-Cyanomethyl-, and 2-*endo*-Carboxymethyl-5-norbornenes

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(Received October 29, 1970)

Treatment of 2-*endo*-cyano-5-norbornene (I) with polyphospholic acid (PPA) at 60°C afforded 6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (V) in 40—46% yields, while 2-*endo*-cyanomethyl-5-norbornene (IV) prepared from 2-*endo*-methoxycarbonyl-5-norbornene (II) *via* the corresponding alcohol (III) gave 3-*exo*-hydroxybicyclo[2.2.1]heptane-2-*exo*-acetic acid lactone (VIII) in 25% yield by a similar treatment with PPA. With sulfuric acid, IV gave only intractable polymeric materials. However, under milder conditions using a sulfuric acid-acetic acid mixture, IV afforded 2-*exo*-cyanomethyl- (VI) and 2-*exo*-carbamoylmethyl-6-*exo*-acetoxynorbornane (VII) in 69 and 2% yields, respectively. On the other hand, iodolactonization of the carboxylic acid (IX) derived from IV afforded 5-*exo*-iodo-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-acetic acid lactone (X) in 68% yield. The formation of VIII from IV was explained by the successive Wagner-Meerwein rearrangement, 3,2- and 6,2-hydride shifts, followed by cyclization.

Although a number of cyclizations in the 2-*endo*-substituted 5-norbornene (*i.e.*, bicyclo[2.2.1]hept-5-ene) system have been extensively studied recently,[2] no reports seem to have been given on the cyclization reactions under the Ritter reaction conditions. Only a limited number of intramolecular Ritter reactions of acyclic-, monocyclic-, and bicyclic unsaturated nitriles[3] have been reported in contrast to numerous examples of intermolecular reactions.[4] From an interest in the synthesis of cage compounds like adamantane,[5] we investigated the chemical behaviors of 2-*endo*-cyano-5-norbornene (I) and 2-*endo*-cyanomethyl-5-norbornene (IV) under several Ritter reaction conditions,[6] and the iodolactonization of bicyclo[2.2.1]hept-5-enyl-2-*endo*-acetic acid (IX).

Preparation of Starting Materials

Starting nitriles, I and IV, and carboxylic acid IX were prepared by a sequence of reactions summarized in Scheme 1. The Dieles-Alder reaction of acrylonitrile with cyclopentadiene at 160°C produced only a 1:1 mixture of 2-*exo*- and -*endo*-cyano-5-norbornene. The reaction was carried out by mixing acrylonitrile cooled to 0°C with freshly prepared cyclopentadiene trapped at −73°C. The 1:1 adduct thus obtained was confirmed to be the desired 2-*endo*-cyano-5-norbornene (I) on the basis of IR and NMR spectral data, though vpc analysis revealed some (*ca.* 10%) contamination with *exo*-isomer.

The Diels-Alder reaction of methyl acrylate with cyclopentadiene proceeded more stereospecifically under similar conditions and afforded 2-*endo*-methoxycarbonyl-5-norbornene (II) in 79% yield, the vpc analysis of which showed *ca.* 3% contamination of the *exo*-isomer. II could be converted to the corresponding alcohol III by means of lithium aluminum hydride reduction. The tosylate of III was treated with sodium cyanide in dimethyl sulfoxide at 90—95°C to afford 2-*endo*-cyanomethyl-5-norbornene (IV) in 33% overall yield from II. The structure of IV was confirmed by analytical and spectral data. Vpc analysis showed only one peak.

Alkaline hydrolysis of IV afforded the corresponding carboxylic acid IX in 86% yield, and the structure was confirmed by analytical and spectral data.

Results and Discussion

Treatment of I with concd. sulfuric acid (98%, sp. gr., 1.84) under common Ritter reaction conditions[3,6] produced a solid material which was purified by sublimation to give colorless crystals (V), mp 155—157°C, in 41% yield. The IR spectrum (KBr) exhibited a strong absorption band at 1770 cm^{-1} (γ-lactone) but no amide bands. The NMR spectrum ($CDCl_3$) gave signals at τ 5.32 (1H, d, d, J=6.0 and 4.5 Hz, C_{6x}–H),[7] 6.85 (1H, broad t, J=*ca.* 5 Hz, C_{2x}-H), 7.30—7.70 (2H, broad s, C_1–H and C_4–H), 7.90—8.50 (6 H, m, other ring protons), suggesting

1) Part XIII: T. Sasaki, S. Eguchi, and H. Yamada, *J. Org. Chem.*, **36**, No. 6 (1971), in press.

2) a) For halolactonizations, see G. I. Oxer and D. Wege, *Tetrahedron Lett.*, **1969**, 3513 and references cited therein; b) For oxymercurations, see A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968) and references cited therein; c) For intramolecular photocycloadditions, see R. R. Sauers and K. W. Kelly, *ibid.*, **35**, 498 (1970); d) For photocyclizations, see P. J. Kroop and H. J. Krauss, *J. Amer. Chem. Soc.*, **91**, 7466 (1969); e) For carbene and nitrene additions, see A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *ibid.*, **87**, 1615 (1965); I. Brown, O. E. Edwards, J. M. McIntosh, and D. Vocelle, *Can. J. Chem.*, **47**, 2751 (1969).

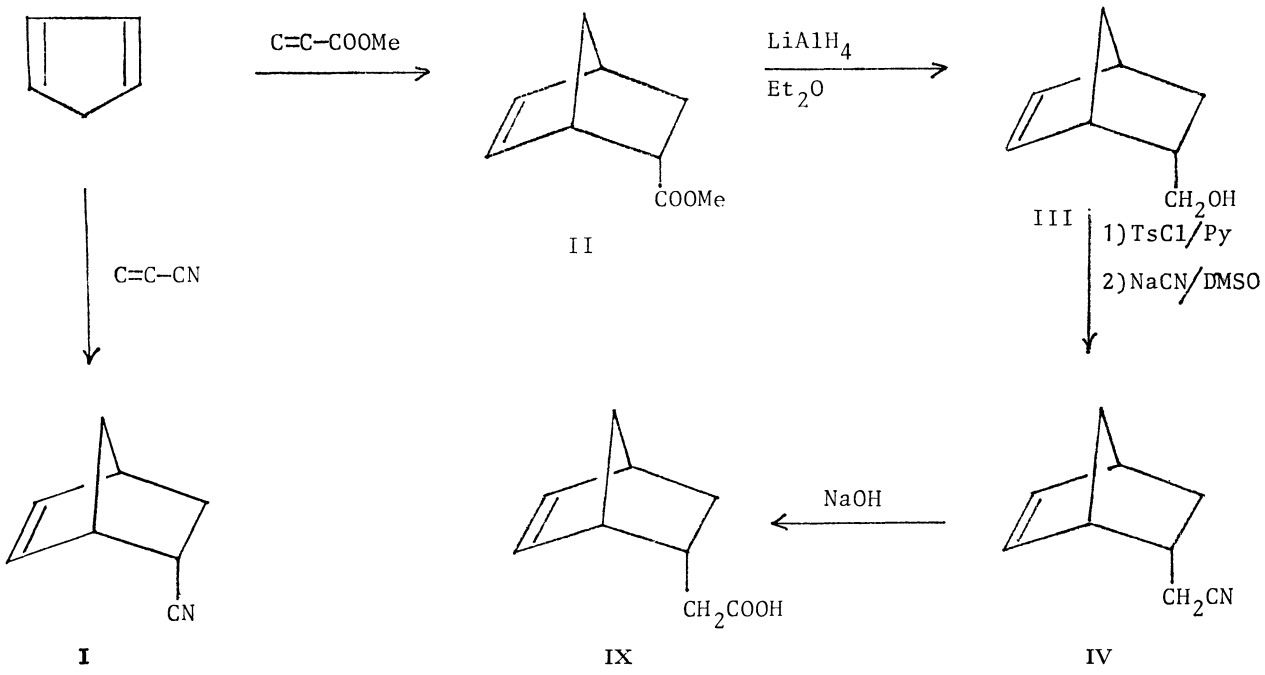
3) For the Ritter reaction of bicyclo[3.3.1]non-6-ene-3-carbonitrile, see J. G. Korsloot and V. G. Keizer, *Tetrahedron Lett.*, **1969**, 3517.

4) For a recent review, *cf.* L. I. Krimen and D. J. Cota, "Organic Reactions," Vol. 17, John Wiley and Sons, Inc., New York, N. Y. (1969), pp. 213—325.

5) For example, T. Sasaki, S. Eguchi, and T. Toru, *Chem. Commun.*, **1970**, 1239, and preceeding papers.

6) For the Ritter reaction of camphene which afforded the corresponding products after the Wagner-Meerwein rearrangement of the ring system, *cf.* T. Sasaki, S. Eguchi, and T. Oyobe, This Bulletin, **43**, 1252 (1970).

7) The subscripts x and n refer to *exo*-and *endo*-configurations, respectively.

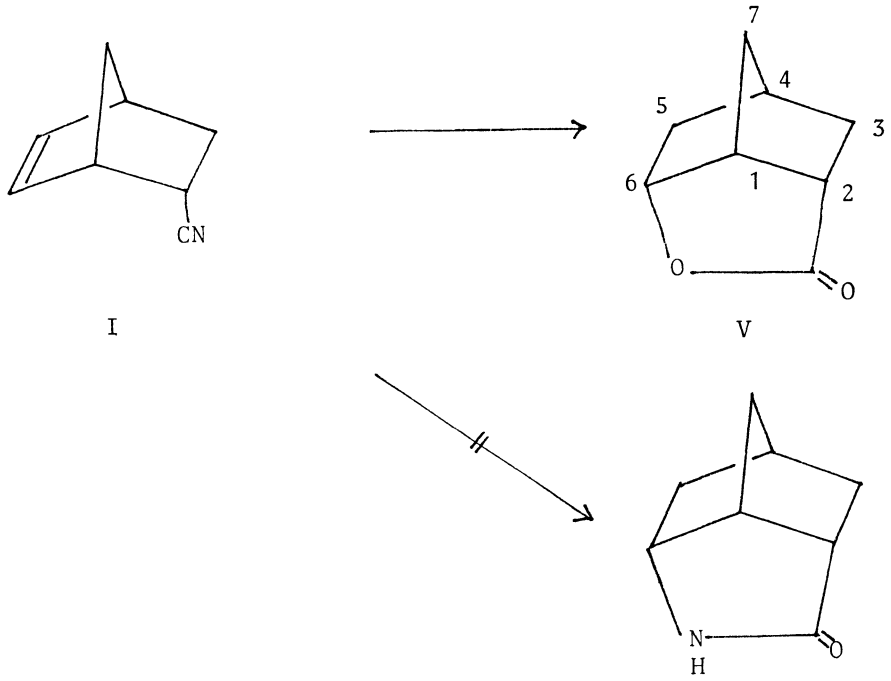


Scheme 1

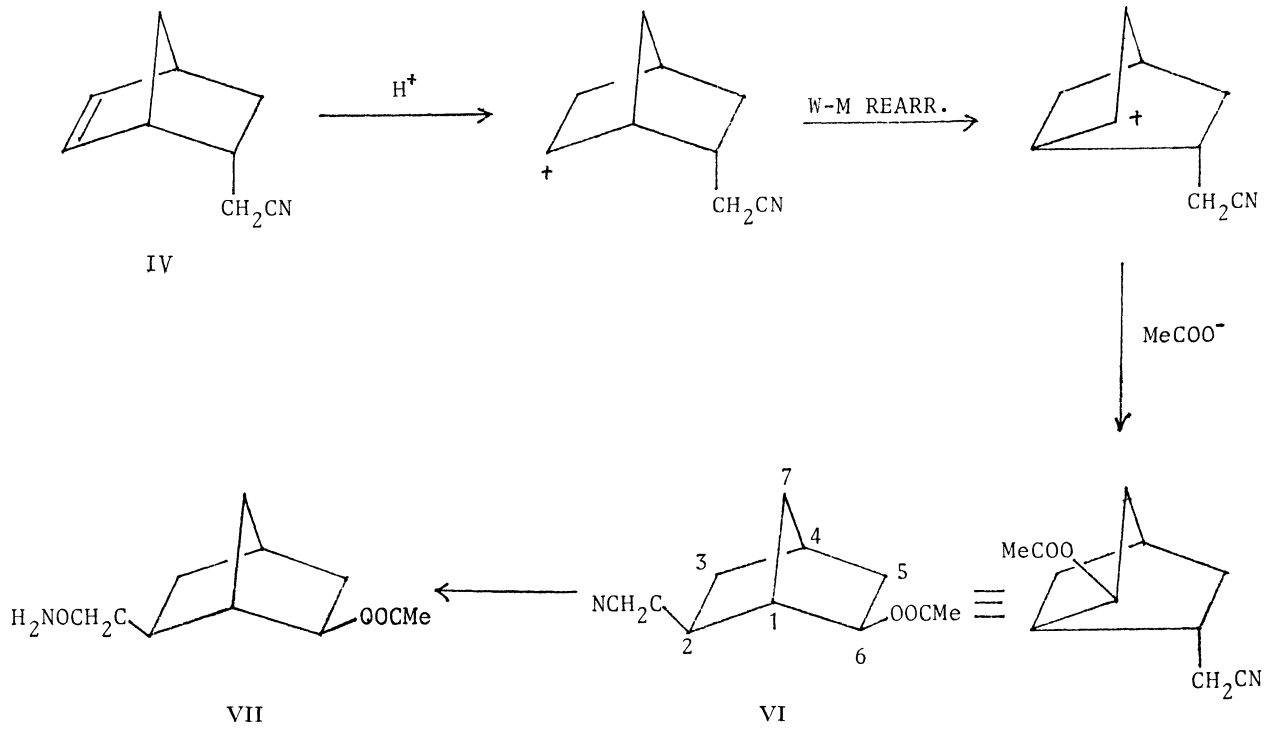
V to be 6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone. The assignment was confirmed by means of mixed melting point determination and complete superimposable IR spectrum with an authentic sample.[8]

Since no intramolecular Ritter reaction products were obtained under the above conditions, PPA was used instead of sulfuric acid. When I was stirred into about 5 times excess PPA (*ca.* 85%), an exothermic reaction took place and the mixture raised the temperature up to *ca.* 60°C, at which temperature the stirring was continued for a day. The product was taken up in chloroform after dilution with water. Chromatography on a silica gel column afforded a semisolid which was purified by sublimation to give the γ-lactone V in 46% yield, together with oily products in *ca.* 10% yield which was still a mixture of at least two compounds as confirmed by tlc and IR (neat) spectrum (γ_{max} 1730 and 1705 cm^{-1}). Further purification of the oily products was unsuccessful.

The results indicate that the normal intramolecular Ritter reaction of I is not favored and cyclization to C_6-position is preceded by the solvolytic reactions of nitrile. This might be ascribed to the steric remoteness



8) S. Beckmann and H. Geiger, *Chem. Ber.*, **94**, 48 (1961).



Scheme 2

of the nitrogen atom from C_6-position.

Treatment of 2-*endo*-cyanomethyl-5-norbornene (IV) with concd. sulfuric acid afforded very insoluble polymeric materials, but treatment of IV with a sulfuric acid-acetic acid mixture (1:10 vol/vol) at room temperature gave an oily acetate VI in 69% yield together with a crystalline acetate VII, mp 122—125°C in 2% yield after chromatography on a silica gel column. In the same reaction at 55—60°C, VI and VII were obtained in 13.8 and 44.2% yields, respectively. However, their structures turned out to be 2-*exo*-cyanomethyl- and 2-*exo*-carbamoylmethyl-6-*exo*-acetoxybicyclo[2.2.1]heptane, respectively, on the basis of analytical and spectral data and mechanistic considerations:[9] VI exhibited IR absorption bands (neat) at 2260 ($\nu_{C\equiv N}$), 1720 ($\nu_{C=O}$), 1245, and 1025 (ν_{C-O}) cm^{-1}, and NMR signals ($CDCl_3$) at τ 5.45 (1H, d, d, d, J=6.7, 3.0, and 2.3 Hz, C_{6n}–H), 7.48—7.90 (4H, m, CH_2CN and C_1–H and C_4–H), 8.00 (3 H, s, $OCOCH_3$), and 8.10—9.60 (7 H, m, other ring protons). VII had IR absorption bands (KBr) at 3320, 3180 (ν_{NH}), 1720 ($\nu_{C=O}$), 1245 and 1020 (ν_{C-O}) cm^{-1}, and NMR signals ($CDCl_3$) at τ 3.50—4.35 (2 H, s, disappeared on deuteration, NH_2), 5.20—5.50 (1 H, m, C_{6n}–H), 7.20—8.12 (7 H, m, other ring protons). Although the stereochemistry of both VI and VII was not conclusive from NMR data, we were led to assign their structures as given in Scheme 2 from the well-established Wagner-Meerwein rearrangement proclivity of the system under the employed conditions[9] and from the fact that no lactone or lactam was produced in the above reaction.

When IV was stirred into PPA in about 5 times excess amount, exothermic reaction (temperature rise to *ca.* 60°C) took place. After being kept at 60°C for a day, the mixture was worked up as above to give an oily product which was purified by chromatography. The major product VIII was obtained as an oil in *ca.* 25% yield. VIII exhibited a strong IR absorption band (neat) at 1770 (δ-lactone) cm^{-1}, indicating that VIII is a γ-lactone derivative but not amide or lactam. Microanalysis indicated a molecular formula of $C_9H_{12}O_2$ and the NMR spectrum ($CDCl_3$) gave signals at τ 5.50 (1 H, d, d, d, J=5.5, 2.0 and 1.0 Hz, C_{3n}–H), 6.80—8.06 (5 H, m, other ring protons); appearance of a signal at τ 5.50 excluded the possibility of 1-hydroxybicyclo[2.2.1]heptane-2-*exo*- or -*endo*-acetic acid lactone for VIII. Finally VIII was confirmed to be 3-*exo*-hydroxybicyclo[2.2.1]heptane-2-*exo*-acetic acid lactone. Possibility of the existence of its *endo*-isomer was excluded since the observed coupling constant 5.5 Hz for the signal due to C_3–H was in the range of the generally accepted value[10] for $J_{3n,2n}$ but not for $J_{3x,2x}$ (9—10 Hz) as shown in Fig. 1. The observed signal pattern was also compatible with the expected one from the dihedral angles.

Several other minor products were also produced in the reaction of IV with PPA. However, their purification by chromatography on a silica gel column was unsuccessful.

9) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).

10) However, the value should be considered as a guide, since it varies according to substituents as well as to the presence of another ring. For example, V exhibited 6 Hz as $J_{6x,5x}$ which is apparently affected by γ-lactone, *cf.* L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd Ed., in "International Series of Monographs in Organic Chemistry," ed. by D. H. R. Barton and W. Doering, Pergamon Press, New York, N. Y. (1969), p. 289, and references cited therein.

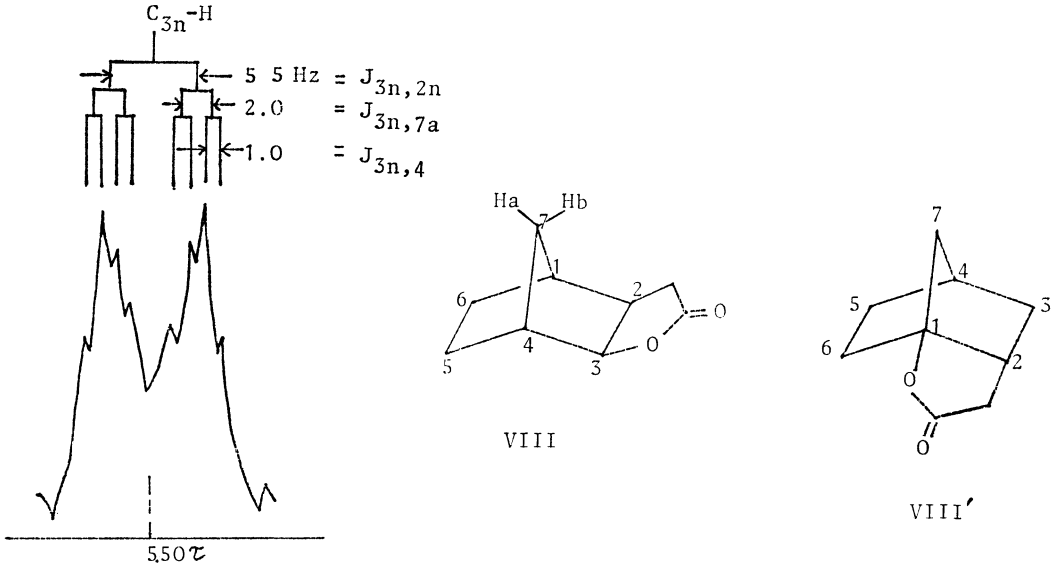
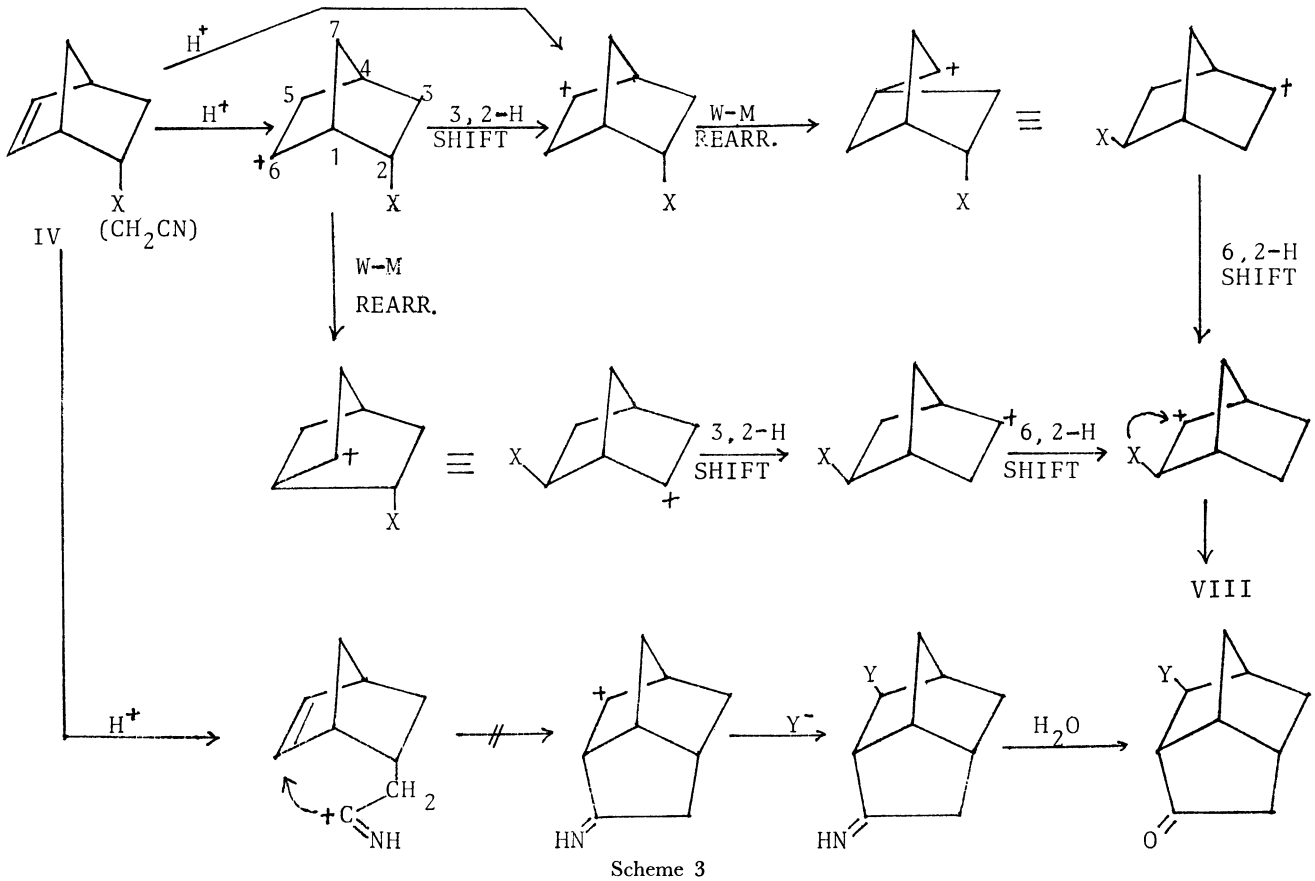


Fig. 1

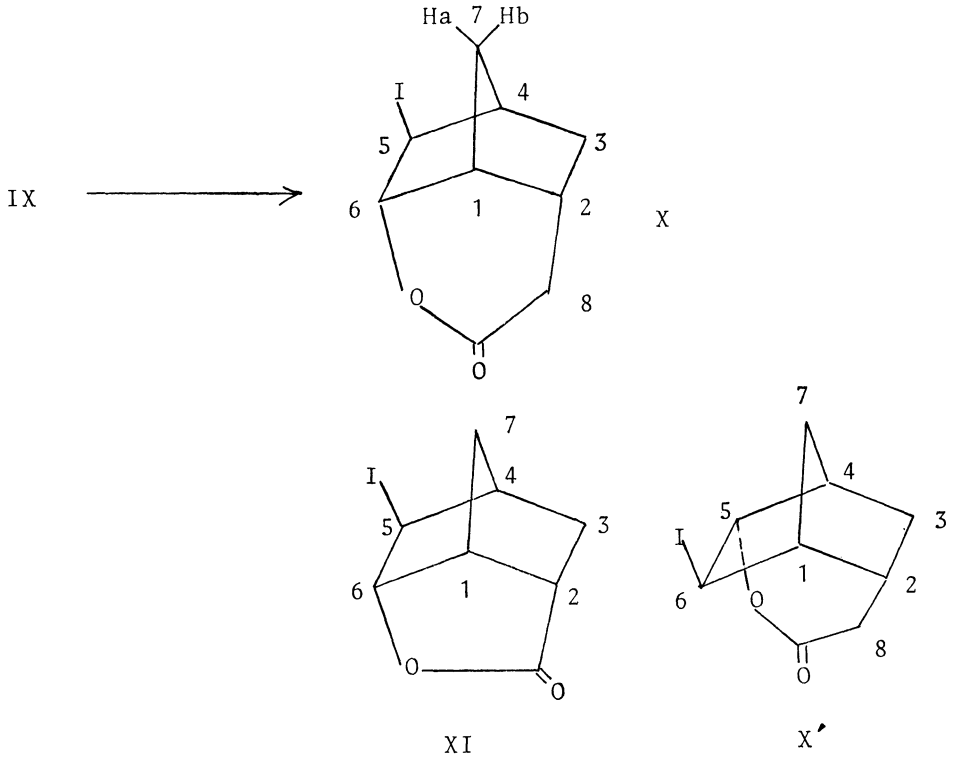


Scheme 3

Formation of VIII from IV could be explained by assuming the reaction paths involving a protonation at C_6 followed by the Wagner-Meerwein rearrangement and a 6,2-H shift, and/or a protonation at C_5 followed by a 3,2-H shift, the Wagner-Meerwein rearrangement and a 6,2-H shift, and/or followed by the Wagner-Meerwein rearrangement, a 3,2-H shift and a 6,2-H shift as explained in Scheme 3. The rearrangement might provide another example of the 6,2-H shift and also the 3,2-H shift in the norbornene ring system in addition to recently reported data.[11]

Iodolactonization of bicyclo[2.2.1]hept-5-ene-2-*endo*-acetic acid (IX), a derived carboxylic acid from IV,

11) *Cf.* C. C. Lee, B-S. Hahn, and L. K. M. Lam, *Tetrahedron Lett.*, **1969**, 3049 and references cited therein, and R. D. Hughes and J. K. Stille, Abst. Paper, The 159th Amer. Chem. Soc. National Meeting (Houston, Texas, Feb., 1970), ORGN 125.



was examined since IV did not produce the corresponding δ-lactone cyclized at C_6-position but afforded a novel γ-lactone (VIII) on treatment with PPA, while I gave a γ-lactone (V) under the same conditions. IX gave crystalline iodolactone X, mp 93—95°C in 68% yield by the standard iodolactonization procedure.[2a] X gave a strong IR absorption band (KBr) at 1737 (δ-lactone) cm^{-1} and NMR signals ($CDCl_3$) at τ 4.75 (1 H, d, m, J=4.5 and *ca.* 1 Hz, C_{6x}–H), 6.22 (1 H, d, d, J=3.0 and 1.5 Hz, C_{5n}–H), 7.20—7.93 (7 H, m, other protons), 8.23 (1 H, d, d, J=10.5 and 3.0 Hz, each peak was further split into m with J=*ca.* 1 Hz, C_{7b}–H), and 8.85 (1 H, d, d, J=11.5 and 2.3 Hz each peak was further split with J=*ca.* 1 Hz, C_{3n}–H). On irradiation of the signal at τ 8.23, the signal at τ 6.22 changed into a doublet with J=1.5 Hz, while the signal at τ 4.75 remained unchanged. Irradiation of the signal at τ 4.75 caused a simplification of the signal at τ 6.22 to a doublet with J=3.0 Hz. From the above spectral data and the analogy of the iodolactonization of bicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid,[2a] the structure of X was assigned to 5-*exo*-iodo-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-acetic acid lactone.[12] The chemical shifts and the coupling were very similar to those reported for 5-*exo*-iodo-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (XI). Only a slight difference is observed between X and XI; X had a larger $J_{5n,6x}$ (1.5 Hz) than XI ($J_{5n,6x}$=*ca.* 0.3 Hz) as was demonstrated by the double resonance experiments.

It should be mentioned that the formation of VIII from IV is the result of the extensive Wagner-Meerwein rearrangement and hydride shifts. No trace of 5-membered ketonic product expected from the Houben-Hoesch type cyclization[4] was found in the reaction of IV (Scheme 3). This also indicates the preference of the above rearrangement and the hydride shifts in this system.

Experimental[13]

2-endo-Cyano-5-norbornene (I). Freshly prepared cyclopentadiene collected at *ca.* −73°C was added to an equimolar amount of cooled acrylonitrile (*ca.* 0°C) with stirring. Stirring was continued for one day, keeping the temperature below 0°C for the first several hours, and then at an ambident temperature. The product was distilled under reduced pressure to give I as a colorless oil in 73.6% yield: bp 98—101°C/37 mmHg; n_D^{20} 1.4910 (lit,[14] bp 84—89°C/13 mmHg; n_D^{25} 1.4934); IR (neat) 2260 ($\nu_{C\equiv N}$) cm^{-1}; NMR ($CDCl_3$) τ 3.63 (1, H, d, d, J=6.5 and 3.0 Hz, C_5-H), 3.85 (1 H, d, d, J=6.5 and 3.0 Hz, C_6–H), 6.72 and 6.91 (each 1 H, broad s, C_1–H and C_4–H), 7.15 (1 H, d, d, J=9.0 and 3.0 Hz, each signal was further split with J=*ca.* 0.5 Hz, C_{2x}–H), 7.55—8.20 (2 H, m, C_3-protons), and 8.24—8.82 (2 H, m, C_7-protons).

Found: C, 80.69; H, 7.62; N, 11.69%. Calcd for C_8H_9N: C, 80.63; H, 7.61; N, 11.76%.

Vpc revealed two peaks in *ca.* 9:1 ratio.

2-endo-Cyanomethyl-5-norbornene (IV). The Diels-Alder reaction of cyclopentadiene with methyl acrylate under similar

12) Further chemical studies would be necessary for the absolute exclusion of an alternative structure X′, though there seem to be no reasons for IX producing the electronically and sterically unfavored product (X′) preferentially.

13) All melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Microanalyses were carried out on a Perkin-Elmer 240 Elemental Analyzer. Infrared spectra were recorded on a JASCO Model IR-S infrared spectrometer and NMR spectra were obtained with a JEOL Model JMN-C-60HL NMR spectrometer using TMS as an internal standard. Vpc analyses were performed on a K-23 Hitachi gas chromatograph.

14) K. Alder, H. Krieger, and H. Weiss, *Ber.*, **88**, 144 (1955).

conditions afforded *ca.* 97% pure 2-*endo*-methoxycarbonyl-5-norbornene (II) in 79% yield as a colorless oil: bp 96—99°C/36 mmHg; n_D^{19} 1.4750 (lit,[14] bp 63.5°C/5.2 mmHg; n_D^{25} 1.4718); the structure was confirmed by IR and NMR data.

Lithium aluminum hydride reduction of II afforded 2-*endo*-hydroxymethyl-5-norbornene (III) in 74.5% yield as an oil: n_D^{19} 1.4988 (lit,[16] n_D^{20} 1.5028).

III was treated with a small excess amount of *p*-toluenesulfonyl chloride in pyridine at room temperature for 1 day. Work-up in the usual way afforded the corresponding tosylate as an oil, n_D^{19} 1.5340, which was treated with an equimolar amount of sodium cyanide in dry dimethyl sulfoxide at 90—95°C for 2 hr. The product was taken in benzene after dilution with water. Removal of the solvent and distillation afforded 2-*endo*-cyanomethyl-5-norbornene (IV) in 33% overall yield from II as a colorless oil: bp 80—82°C/12 mmHg; n_D^{19} 1.4868; IR (neat) 2240 ($\nu_{C\equiv N}$) cm^{-1}; NMR ($CDCl_3$) τ 3.70—4.18 (2 H, complex m, C_5–H and C_6–H), 7.12 (2 H, broad and unsymmetrical s, C_1–H and C_4–H), 7.40—8.85 (6 H, m, other protons), and 9.40 (1 H, d split to m, $J=13.5$ Hz, C_{3n}–H).

Found: C, 81.55; H, 8.24; N, 10.20%. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.33; N, 10.52%.

Vpc showed a single peak.

Treatment of I with Sulfuric Acid. To ice-cooled concd. sulfuric acid (40 m*l*) was added slowly I (14.0 g) with stirring which was continued for 1 day at room temperature. The mixture was poured onto ice-water (*ca.* 400 m*l*) and then extracted with chloroform after neutralization with 10% aq. sodium hydroxide. The combined chloroform extracts were dried (Na_2SO_4) and the solvent was removed to give a yellowish residue which on sublimation at 60—80°C/30 mmHg afforded a colorless solid (6.63 g, 40.7%) of 6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (V), mp 150—153°C. Recrystallization from aq. ethanol raised mp to 155—157°C (lit,[7] 157—158°C).

Treatment of I with PPA. To PPA (*ca.* 25 g) was added I (4.8 g) with stirring. Stirring was continued for several minutes to produce a homogeneous viscous solution (temperature rise to *ca.* 60°C due to heat generation), which was kept at the same temperature for 1 day with occasional stirring. The product was taken in chloroform by extraction after dilution with water and the crude product was purified on a silica gel column eluting with dichloromethane-methanol system. The major product was γ-lactone V (45.8%) and the minor product was a mixture of unidentified amides (*ca.* 10%)

Treatment of IV with Acetic Acid-Sulfuric Acid Mixture. To an ice-cooled mixture of concd. sulfuric acid (0.5 m*l*) and glacial acetic acid (5 m*l*) was added slowly IV (0.5 g) with stirring which was continued for 12 hr at room temperature. The product was taken in chloroform by extraction after dilution of the mixture with water and neutralization with 10% aq. sodium hydroxide. The combined chloroform extracts were dried (Na_2SO_4) and the solvent was removed to give an oily residue (0.76 g) which was chromatographed on a silica gel column eluting with dichloromethane-methanol system. The first fraction afforded 0.51 g (68.9%) of 6-*exo*-acetoxy-2-*exo*-cyanomethylbicyclo[2.2.1]heptane (VI) as an oil, n_D^{17} 1.4816.

Found: C, 68.76; H, 7.81; N, 7.18%. Calcd for $C_{11}H_{15}O_2N$: C, 68.37; H, 7.87; N, 7.25%.

The second fraction gave 0.15 g (2.0%) of 6-*exo*-acetoxy-2-*exo*-carbamoylmethylbicyclo[2.2.1]heptane (VII) as colorless crystals, mp 122—125°C.

Found: C, 62.76; H, 8.13; N, 6.39%. Calcd for $C_{11}H_{17}O_3N$: C, 62.54; H, 8.11; 6.63%.

A similar treatment of IV at 55—60°C for 12 hr and work-up as above gave VI and VII in 13.1 and 44.2% yield, respectively.

Treatment of IV with PPA. A mixture of PPA (*ca.* 7 g) and IV (1.4 g) was stirred manually to give a homogeneous viscous solution (temperature rise to *ca.* 60°C) which was kept at 60°C for 1 day with occasional stirring. The product was taken up in chloroform by extraction after dilution with water. The chloroform extract was dried and evaporated to give an oily residue (1.1 g) which was chromatographed on a silica gel column eluting with dichloromethane-methanol system. The first fraction afforded 0.35 g (25%) of 3-*exo*-hydroxybicyclo[2.2.1]heptane-2-*exo*-acetic acid lactone (VIII) as an oil, n_D^{17} 1.5032.

Found: C, 71.24; H, 7.90%. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95%.

The second fraction was an oil (*ca.* 0.3 g) which was still a mixture of several unidentified products.

*Bicyclo[2.2.1]hept-5-ene-2-*endo*-acetic Acid (IX).* A mixture of IV (1.5 g) and 20% aq. sodium hydroxide was stirred at room temperature for 1 day to afford a clear solution. The solution was washed once with benzene and neutralized with 10% sulfuric acid, and extracted with benzene (20 m*l*×5). The combined extracts were dried (Na_2SO_4) and evaporated to dryness affording a colorless oil (1.47 g, 85.7%) of IX: n_D^{21} 1.4958; IR (neat) 3000—2500 (ν_{OH}), 1710 ($\nu_{C=O}$), and 1410 (ν_{C-O}, δ_{OH}) cm^{-1}.

Found: C, 71.31; H, 7.86%. Calcd for $C_9H_{12}O_2$: C, 71.62; H, 7.95%.

Iodolactonization of IX. To a solution of IX (0.5 g, 3.3 mmol) in aq. sodium carbonate (*ca.* 3%, 100 m*l*) was added slowly a mixture of iodine (1.3 g, 4.9 mmol) and potassium iodide (1.2 g, 6.9 mmol) in water (50 m*l*) with stirring. After stirring was continued for 5 hr, sodium hydrogen sulfite was added until the decolorization was complete. The mixture was then extracted with chloroform (20 m*l*×5). The combined extracts were washed with 3% aq. sodium bicarbonate and dried (Na_2SO_4). Removal of the solvent and work-up with *n*-hexane gave colorless crystals (0.6 g, 68%) of 5-*exo*-iodo-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-acetic acid lactone (X), mp 93—95°C.

Found: C, 38.93; H, 3.93%. Calcd for $C_9H_{11}O_2I$: C, 38.87; H, 3.99%.

The Beilstein test was positive.

The authors wish to thank Miss T. Ikushima for NMR measurements and Mr. M. Okada for elemental analyses.

15) J. D. Roberts, F. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, **72**, 3116 (1950).

16) K. Alder and E. Windermuth, *Ber.*, **71**, 1939 (1938).