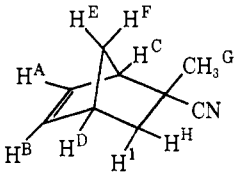
triplet centered at −1.44 ppm ($J_{DJ,EJ \text{ or } DI,EI}$ = 2.6 cps) (4.0 H total H^G, H^H, H^I, H^J) (lit.[29b,30c,81d,83] nmr spectrum).

endo-**5-Cyano-*exo*-5-methyl- (49) and *exo*-5-Cyano-*endo*-5-methylbicyclo[2.2.1]hept-2-ene (50).** The mixture of isomers from Eastman Kodak Co. was separated by preparative gc (column H, 140°, 60 ml of He/min); retention times *exo*-cyano **50**, 11.6 min; *endo*-cyano **49** 13.0 min. The following nmr spectral data (CCl_4) were obtained on the isolated isomers: *endo*-cyano-**49**, an apparent triplet centered at −6.28 (2.0 H, H^A, H^B, line separation 1.9 cps),



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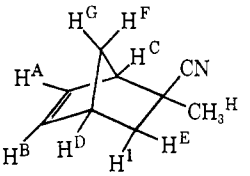
a six-line multiplet centered at −2.95 (1.0 H, H^C or H^D, line separations 1.8 cps), a six-line multiplet centered at −2.79 (1.0 H, H^D or H^C, line separations 1.6 cps), a multiplet centered at −1.7 (2.2 H, two of the four protons, $H^{F,E,H,I}$), and a singlet at −1.52 (CH_3^G) overlapping with a multiplet centered at −1.5 ppm (two remaining protons from $H^{F,E,H,I}$) (4.8 H total); *exo*-cyano-**50**, an unsymmetrical doublet of doublets centered at −6.25 (1.0 H, H^A or H^B, J_{AB} = 5.6 cps, $J_{AC \text{ or } BD}$ = 3.0 cps), an unsymmetrical doublet of doublets centered at −6.00 (0.9 H, H^B or H^A, J_{AB} = 5.7 cps, $J_{BD \text{ or } AC}$ = 3.0 cps), a multiplet at −3.1 to −2.8 with maximum intensity at −3.01 (1.9 H, H^C, H^D), a doublet of doublets



50

centered at −2.28 (H^E, J_{EI} = 12.1 cps, J_{DE} = 3.7 cps), a doublet of an apparent triplet centered at −1.81 (H^F, J_{FG} = 8.8 cps, $J_{CF,DF}$ = 1.3 cps) and a doublet of an apparent quartet centered at −1.63 (H^G, J_{FG} = 9.0 cps, $J_{CG,DG,GI}$ = 2.0 cps) (2.1 H total), and a singlet at −1.20 (CH_3^H) overlapping with a doublet of doublets centered at −1.05 ppm (H^I, J_{EI} = 12.1 cps, J_{GI} = 2.4 cps) (4.0 H total). Irradiation of the multiplet at −3.0 ppm caused the doublet of doublets centered at −2.28 ppm to collapse to a doublet, $J \sim 12.1$ cps. Irradiation at −2.3 ppm caused the doublet of doublets centered at −1.05 ppm to collapse to a narrow multiplet, *ca.* 4 cps wide at half-height.

Acknowledgment. The authors wish to thank Dr. T. Alfrey, Jr., Dr. M. J. Mintz, Dr. V. R. Sandel, and Professor M. Stiles for many helpful discussions.

(83) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

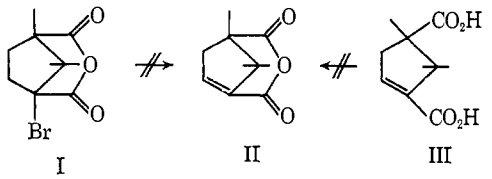
The Synthesis and Chemistry of Bicyclo[3.3.1]non-1-ene

James A. Marshall and Hermann Faubl

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received May 13, 1969*

Abstract: Bicyclo[3.3.1]non-1-ene, a strained bicyclic olefin that violates Bredt's rule, was prepared *via* heterolytic β fragmentation of *endo*-2-methanesulfonoxybicyclo[3.3.1]nonane-1-carboxylic salts in dimethyl sulfoxide. The β-lactone, *exo*-2-hydroxybicyclo[3.3.1]nonane-1-carboxylic acid lactone, resulting from internal displacement of the mesylate grouping, was also isolated from this reaction mixture. Pyrolysis of the β-lactone above 260° constituted a second route to the strained bicyclononene. This olefin exhibited normal spectral properties but showed a high degree of reactivity in addition reactions. Acetic acid and methyllithium added to the double bond with the expected Markovnikov orientation. The epoxide and the 2,5-diphenylisobenzofuran adduct were readily prepared but a stable silver complex could not be isolated.

In 1902 J. Bredt and coworkers postulated that their inability to prepare the camphoric anhydride II either by dehydrobromination of α-bromocamphoric anhydride (I) or through cyclization of the unsaturated diacid III might be attributable to the instability of such unsaturated bicyclic structures.[1] These findings and



I II III

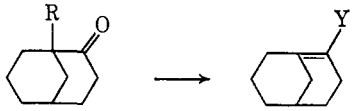
related observations[2] prompted Bredt some 22 years later to suggest that double bonds at the bridgehead atoms of camphenes, pinenes, and similarly constituted bicyclic compounds would impose an unnatural spatial arrangement upon the involved atoms and these compounds would therefore suffer prohibitive strain.[3] Bredt's rule[4] was more precisely defined by the work of Prelog and coworkers[5] who found that bicyclo[*n*.3.1] systems with bridgehead double bonds could be prepared if *n* were greater than 4. In Fawcett's terminology,[4] these findings indicated that for bicyclo[*x*.*y*.*z*] systems in which $x \geq y \geq z$ ($z \neq 0$), Bredt's rule fails to apply when *S*, the sum of *x*, *y*, and *z*, equals or exceeds 9.

Prelog's studies were carried out under conditions where double bond isomerization could be expected and his findings therefore apply only to systems at equilibrium. Conceivably, bridgehead olefins with *S* values less than 9 might be considered as feasible synthetic objectives if their synthesis could be carried out in

(1) J. Bredt, J. Houben, and P. Levy, *Ber.*, **35**, 1286 (1902).
(2) P. Rabe, *Ann.*, **360**, 265 (1908).
(3) J. Bredt, H. Thouet, and J. Schmitz, *ibid.*, **437**, 1 (1924).
(4) For a review, see F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).
(5) V. Prelog, P. Barman, and M. Zimmerman, *Helv. Chim. Acta*, **33**, 356 (1950), and references cited therein.

such a manner as to prevent isomerization of the double bond.

In 1966, when we initiated our work on potential bridgehead olefins, a number of points could be cited to support the idea that bicyclo[3.3.1]non-1-ene ($S = 7$) might be a realistic synthetic objective.[6] Specifically, Ferris and Miller[7] found that the β-keto acid **1a** undergoes decarboxylation at 145°, and Schaefer and Lark[8] noted that the related ketone **1b** exchanges three protons at 95° in alkaline deuterium oxide. Both processes presumably require enolic intermediates (**2a** and **2b**, respectively)[9] related to bicyclo[3.3.1]non-1-ene.

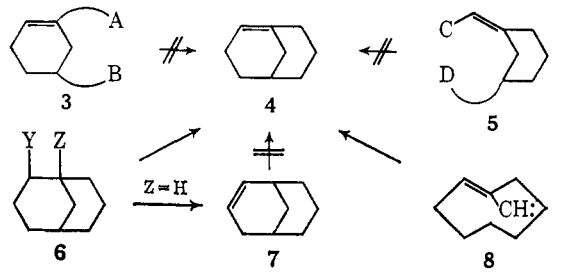


1a, R = CO_2H b, R = H

2a, Y = OH b, Y = O^-

Another point in favor of this objective became apparent from molecular models which depict bicyclo[3.3.1]non-1-ene (**2**, Y = H) as a methylene-bridged *trans*-cyclooctene with a geometry approaching that of *trans*-cyclooctene itself.[10] In this light, the strain energy of the bicyclononene, while undoubtedly appreciable, would not appear prohibitive.

The expectedly strained nature of the bridgehead double bond limited the types of synthetic approaches that could be realistically contemplated for bicyclo[3.3.1]non-1-ene. Geometric considerations precluded ring closures of unsaturated cyclohexane precursors (*e.g.*, **3** → **4** or **5** → **4**). Transannular cyclization of an appropriate *trans*-cyclooctene derivative (*e.g.*, **8** → **4**) appeared hazardous in view of the variety of potential side reactions and the problems associated with a synthesis of the requisite precursor. Unquestionably, the most promising avenue for exploration lay in the direction of elimination reactions of bicyclo[3.3.1]nonane derivatives (*e.g.*, **6** → **4**). In this connection, we rejected intermediates wherein elimination could lead to the 2-ene (**6** → **7**) since this pathway would undoubtedly



predominate, on energetic grounds, over that leading to the 1-ene (**4**). Furthermore, the chances of effecting the isomerization of the 2-ene (**7**) to the 1-ene (**4**) seemed slim.

Several types of elimination reactions based on the bicyclo[3.3.1]nonane system **6** can be envisioned depending on the nature of Y and Z. Most simply a scheme involving the elimination of HZ, where Z is an appropriate leaving group, could suffice.[11] Conceivably, Y and Z could assume some other role compatible with the elimination of YZ [*e.g.*, Y = Z = halogen;[12] Y = $B(OR)_2$, Z = halogen[13]]. Alternatively, Z and Y could be directly bonded in a cyclic system (*e.g.*, Y–Z = –OCSO–;[14] Y–Z = –OCO–[15]).

We felt that the last mentioned alternative offered the maximum opportunity for synthetic control and we therefore set out in this direction. Our initial plan employed the β-lactone **22** as the key intermediate which would be converted to the bridgehead olefin by decarboxylation. Hopefully, this step could be carried out photochemically at low temperature[16] or thermally in a flow system where short contact times could be utilized to minimize decomposition of the olefinic product.

The β-keto ester **9** seemed a logical starting point for our proposed synthesis, especially since the corresponding acid (**1a**) had previously been prepared by Ferris and Miller.[7] After repeated trials we were able to devise procedural modifications which substantially improved the overall yield of their reaction sequence (see the Experimental Section). Reduction of keto ester **9** with aluminum isopropoxide in isopropyl alcohol led to a 1.3:1 mixture of the *exo* and *endo* alcohols **10** and **13** which was separated by preparative gas chromatography. Saponification of each gave the respective hydroxy acids **11** and **14**. The stereochemical assignments, initially made on the basis of the nmr spectra, were later confirmed by chemical transformations. With ethanolic sodium borohydride or hydrogen over platinum as the reducing agents, keto ester **9** yielded the *endo*-hydroxy ester **15** as the sole product. These results are readily accommodated on steric grounds assuming addition preferentially takes place at the less hindered face of the carbonyl grouping.

Attempts to convert the *exo*-hydroxy acid **11** to the β-lactone **22** failed and we therefore turned to an alternative route to this intermediate. To that end, the *endo*-hydroxy ester **14** was converted to the methanesulfonate derivative **20** which yielded the corresponding acid **21** upon saponification under mild conditions. The direct preparation of this acid from the *endo*-hydroxy acid **14** was less satisfactory owing to anhydride formation. Surprisingly, the isomeric *exo*-mesylate acid **19** could not be prepared either from the hydroxy acid **11** (*via* the anhydride) or the hydroxy ester **12**. Basic

(6) (a) For a preliminary report, see J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **89**, 5965 (1967); (b) two $S = 8$ systems have since been synthesized: N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968); J. C. Brial and M. Mousseron-Canet, *Bull. Soc. Chim. Fr.*, 3321 (1968). We later found that W. G. Dauben and F. T. Bond had isolated bicyclo[4.3.1]dec-1-ene ($S = 8$) as a solvolysis product: F. T. Bond, Ph.D. Dissertation, University of California, Berkeley, Calif., 1962.

(7) J. P. Ferris and N. C. Miller, *J. Amer. Chem. Soc.*, **88**, 3552 (1966); **85**, 1325 (1963).

(8) J. P. Schaefer and J. C. Lark, *J. Org. Chem.*, **30**, 1337 (1965).

(9) *Cf.* F. H. Westheimer and W. A. Jones, *J. Amer. Chem. Soc.*, **63**, 3283 (1941); D. B. Bigley and J. C. Thurman, *Tetrahedron Lett.*, 2377 (1967); P. D. Bartlett and C. F. Woods, *J. Amer. Chem. Soc.*, **62**, 2933 (1940).

(10) A. C. Cope, R. A. Pike, and C. F. Spencer, *ibid.*, **75**, 3212 (1953); R. B. Turner and W. R. Meador, *ibid.*, **79**, 4133 (1957).

(11) For an execution of this scheme leading to bicyclo[3.3.1]non-1-ene where Z = $-N(CH_3)_3^+$, see J. R. Wiseman, *ibid.*, **89**, 5966 (1967). An analogous synthesis of bicyclo[4.2.1]non-1-ene and bicyclo[4.2.1]-non-1(8)-ene has recently been reported [J. R. Wiseman, H.-F. Chan, and C. J. Ahola, *ibid.*, **91**, 2812 (1969)].

(12) *Cf.* J. K. Kochi and D. M. Singleton, *ibid.*, **90**, 1582 (1968).

(13) *Cf.* D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773, 2777 (1966).

(14) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, **87**, 934 (1965).

(15) *Cf.* M. U. S. Sultanbawa, *Tetrahedron Lett.*, 4569 (1968).

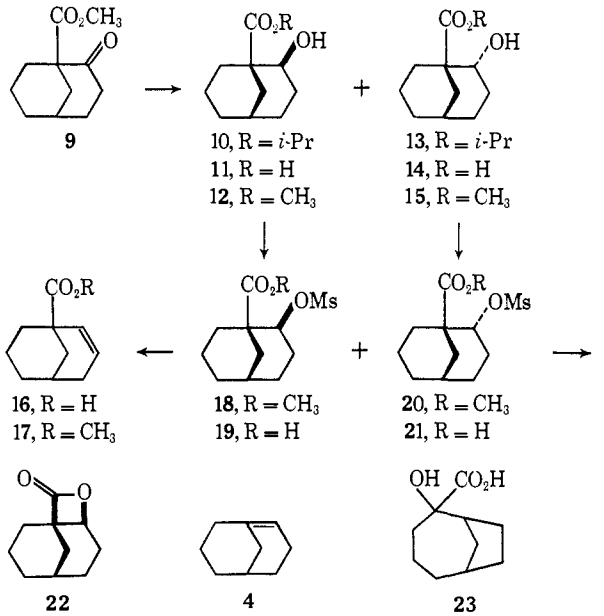
(16) *Cf.* O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **90**, 2333 (1968).

Table I. Products from *endo*-2-Methanesulfonoxybicyclo[3.3.1]nonane-1-carboxylate Salts

Entry	Base[a]	Solvent	Temp, °C	Time, hr	Products (% yield) 4[b]	22[b]	11[c]	14[c]	16[c]	23[c,d]
1	$NaCH_2SOCH_3$	DMSO	60	16.5	20	28	0.7	4.2	37	1.3
2	KO-*t*-Bu	DMSO	60	12	24	28	0.3	2.3	27	0.9
3	KO-*t*-Bu	DMSO	100	1.75	25	29	0.3	1.4	19	0.5
4	NaOH	H_2O	64	2.5	2–3[e]	1[f]	26	13	29	23
5	KO-*t*-Bu	DME[g]	84	5	Trace[e,h]					
6	LiH	DME[g]	84	8	Trace[e,h]					

[a] Slightly less than 1 equiv was employed. [b] Yield of purified product. [c] Yield based on gas chromatographic analysis of the methyl ester. [d] A mixture of epimers. [e] Yield based on evolved CO_2. [f] Yield estimated from the infrared spectrum. [g] 1,2-Dimethoxyethane. [h] Mostly recovered starting material.

hydrolysis afforded the unsaturated acid **16** as the only acidic product even when the hydrolysis was terminated short of completion.



The reported enhancement of carboxylate nucleophilicity in dimethyl sulfoxide[17] (DMSO) prompted our choice of this solvent for the conversion of salts of the *endo*-mesylate acid **21** to the β-lactone **22**. We were

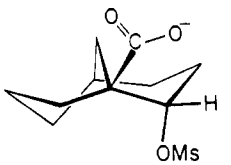


Figure 1. A conformation of the salt derived from acid **21** suitable for the conversion to olefin **4** and β-lactone **22**.

pleased to find that a solution of the sodium salt prepared *in situ* by adding the acid **21** to slightly less than 1 equiv of the DMSO conjugate base in DMSO[18] gave on heating not only the β-lactone **22**, but yielded appreciable quantities of the desired bridgehead olefin **4** as well. Subsequent experiments established that carbon dioxide evolution became substantial at 60° and essentially ceased after 13–16 hr at this temperature.

(17) *Cf.* C. A. Kingsbury, *J. Amer. Chem. Soc.*, **87**, 5409 (1965); A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(18) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962).

Table I summarizes results from a number of experiments. In addition to the neutral products **22** and **4**, the acids **11**, **14**, **16**, and **23** were also obtained. Direct comparison of the corresponding methyl esters **12**, **15**, and **17** with authentic samples established the identity of the first three acids. The fourth, a mixture of stereoisomers, yielded the known ketone, bicyclo[4.3.1]-nonan-2-one,[19] upon oxidation with periodic acid.[20]

As can be seen from Table I, changes in temperature and cation only slightly affected the relative amounts of β-lactone **22** and olefin **4** obtained from salts of the mesylate acid **21** in DMSO. Since the β-lactone **22** afforded none of the olefin **4** upon heating with sodium methanesulfonate in DMSO, the olefin must arise directly from the salt of acid **21**, presumably *via* a β-fragmentation pathway.[21] Figure 1 illustrates a conformation of this salt that meets the geometric requirements of the fragmentation reaction. This conformation would also suffice for the internal SN2 displacement leading to the β-lactone **22**. Evidently, both processes have similar energy profiles in DMSO.[22]

An aqueous solution of the sodium salt of acid **21** yielded mainly the acidic solvolysis products **11**, **14**, **16**, and **23** upon heating (Table I, entry 4). Neither the potassium nor the lithium salt of this acid underwent appreciable reaction in refluxing 1,2-dimethoxyethane (Table I, entries 5 and 6). Two factors may be cited to account for the latter observation. In the first place, the carboxylic salts precipitated from the reaction mixture thereby precluding effective solvation of ionic reaction intermediates. Secondly, the all-chair conformation seems to be the preferred one for crystalline bicyclo-[3.3.1]nonanes,[23] and a high preference for this conformation on the part of the crystalline salts of acid **21** would prevent these salts from attaining the requisite geometry (Figure 1) for fragmentation and internal displacement.

Decarboxylation of the β-lactone **22** could not be effected photochemically either by direct irradiation or through sensitization; the starting material was recovered nearly quantitatively from all attempts. However, thermal decarboxylation of the β-lactone did take

(19) M. Hartman, *Z. Chem.*, **4**, 457 (1964). We are grateful to Professor Hartman for supplying an infrared spectrum of this ketone.

(20) Y. Yanuka, R. Katz, and S. Sorel, *Tetrahedron Lett.*, 1725 (1968).

(21) *Cf.* C. A. Grob and P. W. Schiess, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1 (1967).

(22) Space limitations prevent a more detailed discussion of mechanistic aspects pertinent to the formation of the various side products. Further details are reported in the Ph.D. Thesis of H. Faubl, Northwestern University, June 1969.

(23) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); I. Laszolo, *Rec. Trav. Chim. Pays-Bas*, **84**, 251 (1955); W. A. C. Brown, J. Martin, and G. A. Sims, *J. Chem. Soc.*, 1844 (1965).

place, albeit only above 260°, and the conversion to olefin **4** could be carried out in nearly 40% yield at 290° in a flow system. Simple β-lactones generally decarboxylate between 80 and 150°.[24] The higher temperature required for the bicyclo[3.3.1]-nonane β-lactone **22** no doubt reflects the high degree of strain inherent in the olefinic product **4**.

The most obvious characteristic of the bicyclononene **4** was its extremely penetrating odor, similar in character to cyclooctene but appreciably more intense. Thermal instability presented no problem; the olefin distilled without decomposition and survived gas chromatography on a number of nonacidic columns. The spectral properties entirely supported the assigned structure and showed no striking abnormalities. Characteristic infrared bands attributable to vinyl C–H stretching, C=C stretching, and vinyl C–H bending appeared at 3.33, 6.15, and 12.35 μ, respectively.[25] The nmr spectrum featured a triplet at 5.52 ppm with J = 3.5 Hz attributable to the vinylic proton,[26] and the mass spectrum confirmed the molecular weight.

Hydrogenation of olefin **4** proceeded rapidly over platinum and afforded bicyclo[3.3.1]nonane (**24**). Hydrogenation could likewise be effected with tristriphenylphosphinerhodium chloride in a remarkably short time (2 hr) considering that ordinary trisubstituted double bonds reduce slowly or not at all with this catalyst.[27] Clearly, the strained nature of olefin **4** appreciably enhances its susceptibility to addition reactions.

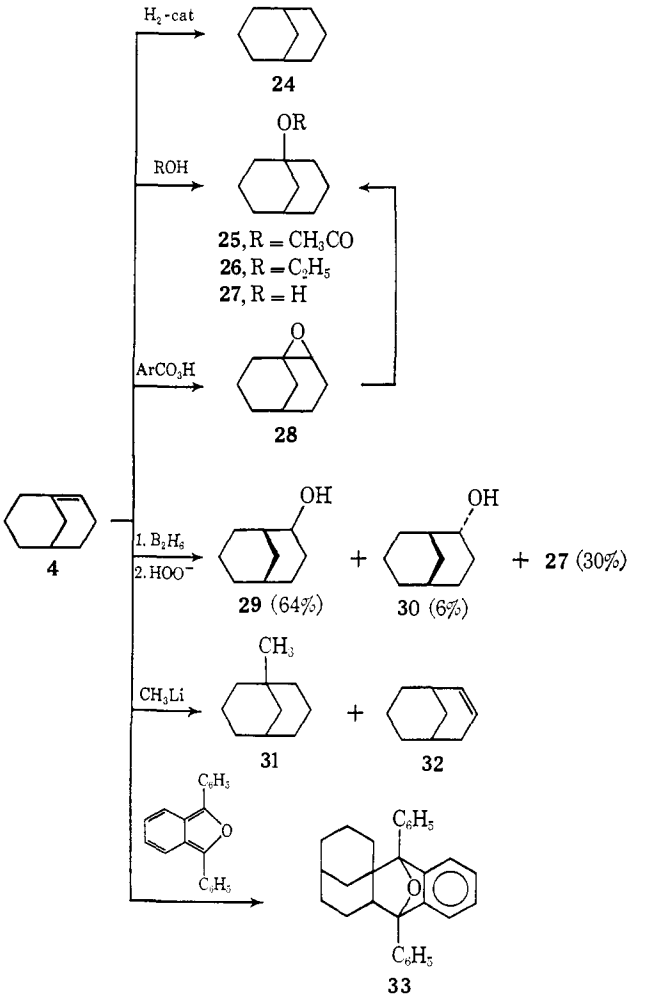
This point was dramatically illustrated by the vigorous reaction of olefin **4** with glacial acetic acid which quantitatively afforded bicyclo[3.3.1]nonyl acetate (**25**) within 25 sec after mixing.[28] In contrast, 1-methylcyclohexene afforded no detectable addition product in 12 days under the same conditions. The olefin **4** was slowly converted to the ether **26** in refluxing absolute ethanol. However, this reaction did not occur in carefully purified ethanol or in ordinary absolute ethanol made slightly alkaline with sodium hydroxide, and therefore trace acidic impurities must have catalyzed the ethanol addition. Indeed, the acid-catalyzed addition of ethanol to olefin **4** proceeded rapidly at room temperature.

Photoinduced hydration of olefin **4** to give the alcohol **27** was readily accomplished[29] under conditions where nonphotochemical hydration did not take place. Hence, olefin **4** resembles 1-methylcyclohexene, insofar as photoexcitation leads to a strained species (possibly the *trans*-cyclohexene) which readily adds acidic reagents in the Markovnikov sense.[29]

A highly exothermic reaction ensued upon the addition of *m*-chloroperoxybenzoic acid to a solution of the bicyclononene **4** with conversion to the epoxide **28** being complete within 2 min. Reduction of this epoxide with lithium aluminum hydride gave the alcohol **27**. Surprisingly, hydroboration–oxidation[30] of olefin **4** yielded a significant proportion (30%) of this tertiary alcohol as well as the expected *exo*-alcohol **29** (64%) and the *endo*-alcohol **30** (6%). The unexpectedly low regiospecificity[31] of this reaction may stem from excessive strain in the olefin which decreases the activation energy of the addition process and thereby makes the transition state more reactant-like and hence less sensitive to steric and polar factors.[32]

We were unable to prepare a crystalline silver complex of olefin **4**. Aqueous silver nitrate led to the hydration product, alcohol **27**, and silver borofluoride afforded no discrete products.

Olefin **4** slowly reacted with methyllithium in ether to give 1-methylbicyclo[3.3.1]nonane (**31**) in 54% yield[33] and the isomerized olefin **32** in 39% yield.



Evidently, allylic proton abstraction competes with addition even though the resulting incipient allylic anion offers no relief of strain. Whereas the addition of methyllithium to olefin **4** proceeded reasonably well,

(24) *Cf.* H. E. Zaugg, *Org. Reactions*, **8**, 305 (1954); D. S. Noyce and E. H. Banitt, *J. Org. Chem.*, **31**, 4043 (1966), and references cited therein.

(25) Ordinary trisubstituted olefins exhibit bands at 3.3, 6.0, and 11.8–12.6 μ for these vibrational modes: K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 24.

(26) This spectrum is reproduced in a preliminary report of this work.[6a]

(27) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 1574 (1967), and references cited therein.

(28) The heat of reaction for this addition has been measured and used to estimate the strain energy of bicyclo[3.3.1]non-1-ene as 12 kcal/mol: P. M. Lesko and R. B. Turner, *J. Amer. Chem. Soc.*, **90**, 6888 (1968).

(29) *Cf.* J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969).

(30) *Cf.* G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 22 (1963).

(31) For a definition of this term, see A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

(32) *Cf.* J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., p 162 ff.

(33) An analogous addition to *trans*-cyclooctene has recently been noted: J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Commun.*, 1593 (1968).

the analogous addition of lithium aluminum hydride could not be realized, even after prolonged reaction times.

Both *trans*-cyclooctene and *trans*-cycloheptene form Diels–Alder adducts with 1,3-diphenylisobenzofuran.[14] The olefin **4**, a bridged *trans*-cyclooctene, likewise gave a 1:1 adduct (**33**) with this reagent within minutes at room temperature.

Finally, it should be noted that olefin **4** readily combines with atmospheric oxygen. A small sample stored at −20° became viscous and lost its characteristic odor after 4 months. The infrared spectrum of this sample showed bands at 2.9, 3.65, and 5.82 μ suggesting hydroxylic, aldehydic, and possibly ketonic functionality. On the other hand, a sample of olefin **4** from which air had been rigorously excluded appeared unchanged after 15 months at −20°.

Experimental Section[34]

2-Oxobicyclo[3.3.1]nonane-1-carboxylic Acid (1a). The following sequence is an improved version of the route employed by Ferris and Miller.[7] A solution of 218.7 g (1.36 mol) of diethyl malonate in 650 ml of dilute ethanolic sodium ethoxide (from 0.5 g of sodium) was maintained at −30 ± 5° while 173 g (3.09 mol) of acrolein in 200 ml of ethanol was added dropwise with efficient stirring over a 6-hr period.[34a] The solution was allowed to reach room temperature, 50 ml of ethanolic sodium ethoxide (from 0.75 g of sodium) was added, and stirring was continued for 16 hr. The solution was acidified with 5 ml of acetic acid, concentrated under reduced pressure, and the product was isolated with ether[34b] and distilled, affording 156.5 g (45.3%) of diethyl 3-formyl-3-cyclohexene-1,1-dicarboxylate, bp 130–140° (1 mm); λ_{max}^{film} 3.69 (aldehyde CH), 5.78 (ester CO), 5.98 (aldehyde CO), 6.08 (C=C), 7.95, 8.85, 9.18, 9.28, and 11.58 μ; $\delta_{TMS}^{CCl_4}$ 9.6 (aldehyde CH), 6.92 (vinyl H), 4.22 ($-CH_2-$, quartet, J = 7 Hz), and 1.26 ppm (CH_3, triplet, J = 7 Hz).

The 2,4-dinitrophenylhydrazone exhibited mp 157–159° (lit. mp 162–163°).

A 51.8-g (0.203 mol) sample of the above aldehyde in 250 ml of 1,2-dimethoxyethane (DME) was added over 10 min to a stirred mixture of 5.29 g (0.22 mol) of sodium hydride and 51.2 g (0.225 mol) of triethylphosphonoacetate in 500 ml of DME.[35] The mixture was stirred at reflux for 2.5 hr,[34a] cooled, treated with dilute sodium chloride solution, and the product was isolated with ether[34b] and distilled affording 54.5 g (83%) of diethyl 3-(2-carbethoxyvinyl)-3-cyclohexene-1,1-dicarboxylate, bp 113–130° (0.01–0.04 mm); λ_{max}^{film} 3.39 (vinyl H), 5.75 (ester CO), 5.80 (conjugate ester CO), 6.11 and 6.15 (C=C), 7.95, 11.66, and 11.90 μ; $\delta_{TMS}^{CCl_4}$ 7.30 (vinyl CH, doublet, J = 16 Hz), 6.16 (vinyl CH), 5.86 (vinyl CH, doublet, J = 16 Hz), 4.21 (OCH_2, quartet, J = 7 Hz), and 1.28 ppm (CH_3, triplet, J = 7 Hz).

A 132.3-g sample of unsaturated ester, prepared as described above, was hydrogenated in 160 ml of ethanol over 1.03 g of platinum oxide in a Parr shaker affording 133.1 g (99%) of diethyl 3-(2-carbethoxyethyl)cyclohexane-1,1-dicarboxylate; λ_{max}^{film} 5.76 (CO), 8.00, 9.64, 10.27, and 11.60 μ.

A 48.0-g (0.146 mol) sample of the above triester in 2 l. of DME was stirred at reflux with 14 g (0.584 mol) of sodium hydride for 7.5 hr.[34a] The cooled mixture was treated with a solution of 34.4 ml of acetic acid in 1 l. of ether and the product was isolated with ether[34b] and distilled affording 32.8 g (80%) of diethyl 2-oxobicyclo[3.3.1]nonane-1,3-dicarboxylate, bp 140° (0.1 mm); λ_{max}^{film} 3.42 (enol OH), 5.74 (CO), 6.01 (CO), 6.19 (C=C), 7.80, 8.10, 9.20, and 9.66 μ; $\delta_{TMS}^{CCl_4}$ 12.3 (enol OH), 4.00–4.45 (OCH_2, quartets, J = 7 H), and 1.28 ppm (CH_3 triplet).

A solution of 110 g (0.39 mol) of keto diester, comparable in quality to that described above, and 200 g (3.57 mol) of potassium hydroxide in 3 l. of methanol and 900 ml of water was heated at reflux for 35 hr.[34a] Most of the methanol was removed under reduced pressure, the solution was diluted with water, acidified with cold concentrated hydrochloric acid, and the product was isolated with ether[34b] affording 67.2 g (94.5%) of solid acid. A sublimed sample (70–80° at 0.01 mm) exhibited mp 105–106° (lit.[7] mp 104–106°); $\lambda_{max}^{CHCl_3}$ 2.9–3.4 (acid OH), 5.85 (CO), 8.0, 8.40, 8.65, 9.30, and 10.50 μ.

Methyl 2-Oxobicyclo[3.3.1]nonane-1-carboxylate (9). The procedure of Clinton and Laskowski[36] was employed. A solution of 22.1 g (0.121 mol) of keto acid **1a**, 20 ml of methanol, and 2.0 ml of sulfuric acid in 600 ml of 1,2-dichloroethane was heated at reflux for 4.5 hr.[34a] The mixture was cooled and the product was isolated with ether[34b] and distilled affording 21.0 g (88%) of keto ester **9**, bp 90–100° (0.05 mm); λ_{max}^{film} 5.75 (ester CO), 5.86 (ketone CO), 8.02, 8.35, 9.30, 10.00, and 11.60 μ.

The analytical sample, mp 70–70.5°, was secured by crystallization from hexane.

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.6; H, 8.1.

Meerwein–Ponndorf Reduction of Keto Ester 9. *exo*- and *endo*-2-Hydroxybicyclo[3.3.1]nonane-1-carboxylic Acids (11 and 14). The procedure of Robinson and Walker[37] was followed. A mixture of 3.00 g of keto ester **9**, 2.98 g of aluminum isopropoxide, and 50 ml of isopropyl alcohol was heated at reflux for 16 hr with slow distillation of acetone through a 25-cm distillation column.[34a] The mixture was treated with 10% aqueous sulfuric acid and the product was isolated with ether[34b] and distilled affording 3.14 g (94%), bp 77–80° (0.05 mm), of the isopropyl esters **10** and **13** as a 40:54 mixture according to the gas chromatogram.[38]

The isomeric hydroxy esters were separated by preparative gas chromatography.[39] From 2.13 g of the mixture was isolated 0.77 g of the shorter retention component identified as the *endo*-isomer **13** [λ_{max}^{film} 2.90 (OH), 5.80 (CO), 7.95, 8.24, 8.97, and 10.32 μ; $\delta_{TMS}^{CCl_4}$ 4.95 (–OCH, septet, J = 6 Hz), 3.93 (H-2, $W_{h/2}$ = 20 Hz), 3.28 (OH), and 1.20 ppm (CH_3, doublet, J = 6 Hz)], and 0.72 g of the longer retention component identified as the *exo*-isomer **11** [λ_{max}^{film} 2.88 (OH), 5.80 (CO), 7.95, 8.95, 9.22, 9.50, 9.72, 10.12, and 10.70 μ; $\delta_{TMS}^{CCl_4}$ 4.95 (–OCH, septet, J = 6 Hz), 4.02 (H-2, $W_{h/2}$ = 6 Hz), 3.11 (OH), and 1.20 ppm (CH_3, doublet, J = 6 Hz)].

Saponification of esters **10** and **13** was effected by stirring each of the above samples with a solution of 1.5 g of potassium hydroxide and 1.5 ml of water in 15 ml of ethanol for 10 hr.[34a] The solution was acidified with cold hydrochloric acid and the product was isolated with ether.[34b] From 0.72 g of the *exo*-hydroxy ester **10** was obtained 0.34 g of recrystallized *exo*-hydroxy acid **11**, mp 140–141.5°: λ_{max}^{KBr} 3.0 (OH), 3.1–3.4 (acid OH), 5.88 (CO), 8.29, 9.21, 9.75, 10.11, 10.80, and 13.60 μ; $\delta_{TMS}^{CDCl_3}$ 7.00 (OH) and 4.10 ppm (H-2, $W_{h/2}$ = 8 Hz). The analytical sample was obtained by sublimation at 135° (0.05 mm).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.4; H, 8.7.

In the same manner 0.77 g of the *endo*-hydroxy ester **13** afforded 0.59 g of solid *endo*-hydroxy acid **14**. Recrystallization from ether–hexane gave 0.38 g, mp 121–121.5°; λ_{max}^{KBr} 2.9 (OH), 3.1–3.4 (acid OH), 5.88 (CO), 8.25, 9.42, 9.58, 10.30, and 11.40 μ; $\delta_{TMS}^{CDCl_3}$ 7.90 (OH) and 4.10 ppm (H-2, $W_{h/2}$ = 20 Hz). The analytical sample was obtained after sublimation at 105° (0.05 mm).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.4; H, 8.6.

Methyl *exo*-2-Hydroxybicyclo[3.3.1]nonane-1-carboxylate (12). A solution of 280 mg of hydroxy acid **11** in 15 ml of ether was treated with excess ethereal diazomethane for 1 hr. Acetic acid was added and the product was isolated with ether[34b] and distilled affording 300 mg [bp 100–110° (bath temperature) at 0.3 mm] of solid. Recrystallization from hexane gave 165 mg (55%) of white needles, mp 46.5–47°: λ_{max}^{film} 2.90 (OH), 5.80 (CO), 8.25, 9.26, 9.52, 9.75, 9.96,

(34) (a) The apparatus described by W. S. Johnson and W. P. Schneider [*Org. Syn.*, 30, 18 (1950)], was used to maintain a nitrogen atmosphere over reaction mixtures. (b) The isolation procedure consisted of thoroughly extracting the reaction mixture with the specified solvent, washing the combined extracts with saturated brine, and drying the extracts over anhydrous magnesium sulfate. Pyridine was removed from the organic phase by washing with water and aqueous 2% sulfuric acid. Acids were removed by washing with saturated aqueous sodium bicarbonate or cold 5% aqueous sodium hydroxide. (c) Melting points were determined on a Fisher-Johns hot stage. (d) Microanalyses were done by Micro-Tech Laboratories, Inc., Skokie, Ill.

(35) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, 83, 1733 (1961).

(36) R. O. Clinton and S. C. Laskowski, *ibid.*, 70, 3135 (1948).

(37) R. Robinson and J. Walker, *J. Chem. Soc.*, 64 (1937).

(38) A 1/8 in. × 20 ft column of Silicone Oil DC-550 on F and M HiPack was employed for this analysis.

(39) A 1/2 in. × 10 ft column of Carbowax 20-M on 60–80 mesh Chromosorb W was used for this separation.

10.20, 10.80, 11.31, and 12.93 μ; $\delta_{TMS}^{CCl_4}$ 4.09 (H-2, $W_{h/2}$ = 7 Hz), 3.65 (OCH_3), and 2.90 ppm (OH).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.6; H, 9.1.

Methyl *endo*-2-Hydroxybicyclo[3.3.1]nonane-1-carboxylate (15). A. Esterification of Hydroxy Acid 14. A solution of 223 mg of hydroxy acid **14** in 15 ml of ether was treated with excess ethereal diazomethane. The product was isolated with ether[34b] and distilled affording 233 mg (97%) of hydroxy ester **15**, bp 60° (bath temperature) at 0.03 mm. The oil was crystallized from pentane affording 190 mg of white solid, mp 39–39.5°; λ_{max}^{KBr} 2.90 (OH), 5.78 (CO), 7.95, 8.25, 9.50, 10.30, 11.40, and 12.82 μ; $\delta_{TMS}^{CCl_4}$ 3.95 (H-2, X of ABX, $J_{AX} + J_{BX}$ = 16 Hz), 3.63 (OCH_3), and 3.2 ppm (OH).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 67.0; H, 9.3.

B. Hydrogenation of Keto Ester 9. A solution of 6.19 g of keto ester **9** in 100 ml of ethanol was hydrogenated at 1 atm over 0.70 g of platinum oxide. The mixture was filtered and concentrated under reduced pressure and the residue was crystallized from pentane affording 5.05 g (81%) of hydroxy ester **15**, mp 39–39.5°. The spectral properties of this material exactly matched those of the substance prepared in part A.

C. Reduction of Keto Ester 9 with Sodium Borohydride. A solution of 1.90 g of keto ester **9** and 0.68 g of sodium borohydride in 40 ml of methanol was stirred at 0° for 30 min.[34a] Aqueous acetic acid was added, the solution was concentrated under reduced pressure, and the product was isolated with ether[34b] affording 1.79 g (94%) of material whose spectral properties matched those of the material prepared above in parts A and B.

Methyl *endo*-2-Methanesulfonoxybicyclo[3.3.1]nonane-1-carboxylate (20). A solution of 12.17 g (61.4 mmol) of hydroxy ester **15** in 70 ml of pyridine was chilled in an ice bath and 5.38 ml (70 mmol) of methanesulfonyl chloride was added with stirring over 5 min.[34a] After 30 min, the ice bath was removed and stirring was continued for 2.5 hr. The mixture was chilled and several chips of ice were added followed by 100 ml of cold water. The product was isolated with ether[34b] (the pyridine was extracted from the ethereal solution with 10% aqueous sulfuric acid) affording 16.93 g (99%) of oily mesylate **20**: λ_{max}^{film} 5.78 (CO), 7.39–7.50 ($-SO_3-$), 8.20, 8.48, 9.30, 9.45, 10.85, 11.32, 11.55, and 11.95 μ; $\delta_{TMS}^{CCl_4}$ 5.10 (H-2, X of ABX, $J_{AX} + J_{BX}$ = 17 Hz), 3.66 (OCH_3), and 2.88 ppm (CH_3SO_3). The oil was freed of solvent *in vacuo* and submitted for analysis.

Anal. Calcd for $C_{12}H_{20}O_5S$: C, 52.16; H, 7.30; S, 11.60. Found: C, 52.1; H, 7.5; S, 11.75.

***endo*-2-Methanesulfonoxybicyclo[3.3.1]nonane-1-carboxylic Acid (21).** A solution of 16.93 g of mesylate ester **20**, 30 g of potassium hydroxide, 40 ml of water, and 1 ml of pyridine in 150 ml of ethanol was stirred at room temperature for 12 hr.[34a] The solution was acidified with cold hydrochloric acid and the product was isolated with ether[34b] affording 15.59 g (97%) of an oil which was crystallized from ether–hexane to give 9.81 g (61%) of solid acid, mp 115.5–116°; λ_{max}^{KBr} 3.1–3.8 (acid OH), 5.85 (CO), 7.4–7.5 ($-SO_3-$), 7.85, 8.5, 9.30, 10.30, 10.65, 10.85, 11.32, 11.58, 12.0, and 14.7 μ; $\delta_{max}^{CDCl_3}$ 11.2 (acid OH), 5.45 (H-2, triplet, X of ABX, $J_{AX} + J_{BX}$ = 18 Hz), and 3.14 ppm (CH_3SO_3).

Anal. Calcd for $C_{11}H_{18}O_5S$: C, 50.45; H, 6.91; S, 12.23. Found: C, 50.5; H, 6.9; S, 12.4.

Methyl *exo*-2-Methanesulfonoxybicyclo[3.3.1]nonane-1-carboxylate (18). The procedure outlined above for the *endo*-mesylate **20** was employed to convert 192 mg of the *exo*-hydroxy ester **12** to 246 mg (95%) of oily mesylate **18**: λ_{max}^{film} 5.78 (CO), 7.4 ($-SO_3-$), 7.95, 8.24, 8.50, 9.25, 9.52, 9.80, 10.39, 10.9–11.3, 11.54, 11.72, 12.60, and 12.92 μ; $\delta_{TMS}^{CCl_4}$ 5.15 (H-2, $W_{h/2}$ = 6 Hz), 3.75 (OCH_3), and 2.95 ppm ($-CH_3SO_3$).

Saponification of Methyl *exo*-2-Methanesulfonoxybicyclo[3.3.1]nonane-1-carboxylate (18). Bicyclo[3.3.1]non-2-enecarboxylic Acid (16). The saponification procedure described for the *endo*-ester **20** was employed on 263 mg of the *exo*-isomer **18**. After 10 hr, 74 mg of starting mesylate **18** was recovered and 129 mg of solid acid **16** was isolated. Recrystallization of the latter material gave 48 mg of solid, mp 96.5–97°; λ_{max}^{KBr} 3.0–3.4 (acid OH), 5.90 (CO), 6.05 (C=C), 8.26, 9.13, 9.27, 10.55, 11.21, 12.51, 12.85, 13.21, and 14.15 μ; $\delta_{TMS}^{CDCl_3}$ 10.8 (acid OH), and 5.92 ppm (vinyl H).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.3; H, 8.6.

No sulfonic ester bands could be detected in the infrared spectrum of the acid mother liquor.

Bicyclo[3.3.1]non-1-ene (4) and *exo*-2-Hydroxybicyclo[3.3.1]nonane-1-carboxylic Acid Lactone (22). A. From the Sodium Salt of Acid 21 in Dimethyl Sulfoxide. The mineral oil was removed from 982 mg (20.5 mmol) of 50% dispersion by thorough washing with benzene. The resulting solid was stirred with 200 ml of dimethyl sulfoxide (DMSO) at 65° until a homogeneous solution resulted and 4.93 g (18.8 mmol) of mesylate acid **21** in 100 ml of DMSO was then added.[34a] The mixture was stirred at 60° for 40 hr, cooled, and diluted with cold water. The neutral material was isolated with cold ether–pentane (1:1).[34b] The extracts were washed with cold aqueous sodium hydroxide and the solvent was removed by careful distillation (water bath) through a Vigreux column affording 3.22 g of neutral material consisting largely of olefin **4** and β-lactone **22**. The combined basic solution and aqueous washes were cooled, acidified with hydrochloric acid, and extracted with ether affording 1.04 g of acidic material, largely unsaturated acid **16** (see below).

The neutral material was chromatographed on silica gel. Elution with pentane gave 325 mg (15%) of olefin **4**, bp 50–60° (bath temperature) at 5–6 mm: λ_{max}^{film} 3.33 (vinyl H), 6.15 (C=C), 8.09, 8.21, 9.06, 9.72, 9.83, 10.03, 10.30, 10.42, 11.57, 12.01, 12.32, 12.60, and 14.00 μ; $\delta_{TMS\ (external)}^{neat}$ 5.52 ppm (H-2, triplet, J = 3.5 Hz);[26] $n^{20}D$ 1.5052; $\lambda_{max}^{cyclohexane}$ 207 (ϵ 7000); mass spectrum, calcd for C_9H_{14}, M^+ = 122; found, M^+ = 122.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.4; H, 11.7.

Trace amounts of this olefin could be readily detected by its powerful, penetrating odor.

Continued elution of the chromatographic column with ether–pentane afforded 800 mg (25%) of β-lactone **22**, mp 128–130°: λ_{max}^{KBr} 5.50 (CO), 8.38, 8.79, 9.45, 10.83, 11.36, and 11.89 μ; $\delta_{TMS}^{CCl_4}$ 4.22 ppm (H-2, X of ABX, $J_{AX} + J_{BX}$ = 16 Hz); λ_{max}^{hexane} 200 mμ (ϵ 390); mass spectrum, calcd for $C_{10}H_{14}O_2$, M^+ = 166; found, M^+ = 166 (the fragmentation pattern below *m/e* 122 strongly resembled that of olefin **4**).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.3; H, 8.4.

Somewhat better results were obtained when the reaction time was decreased to 16.5 hr and the neutral product was chromatographed on Florisil. In this manner olefin **4** was isolated in 20% yield and β-lactone **22** in 28% yield.

B. Using Potassium *t*-Butoxide in Dimethyl Sulfoxide. A solution of 7.80 g (29.8 mmol) of acid **21** in 250 ml of DMSO was treated with 3.35 g (29.8 mmol) of potassium *t*-butoxide.[34a] The mixture was heated at 100° with stirring for 1.75 hr, cooled, and processed as described above to yield 3.02 g of neutral and 1.26 g of acidic material. Chromatography of the neutral material on Florisil afforded 0.91 g (25%) of olefin **4** (after distillation) and 1.40 g (29%) of crystalline β-lactone **22**.

C. Attempts to Convert Mesylate Acid to Olefin 4 under Other Conditions. 1. The Sodium Salt in Water. A solution of 183 mg (0.70 mmol) of acid **21** in 7.0 ml of 0.1 *N* aqueous sodium hydroxide was heated at 60°. A nitrogen sweep leading to a solution of barium hydroxide was employed to measure evolved carbon dioxide. After 2 hr the evolution of carbon dioxide corresponded to 2–3% of theory as judged by gravimetric analysis of precipitated barium carbonate. Extraction with ether–pentane[34b] afforded 3 mg of an oil which possessed the odor of olefin **4** and whose infrared spectrum was substantially that of the β-lactone **22**. Acidification of the aqueous solution and extraction with ether afforded 125 mg of acidic material. A small sample of this material was esterified with diazomethane and analyzed *via* gas chromatography which indicated the following composition for the acidic material: *endo*-hydroxy acid **14**, 28%; *exo*-hydroxy acid **11**, 14%; unsaturated acid **15**, 32%; hydroxy acid **23**, 25%. The remainder of the acidic material was separated by chromatography on silica gel. Acids **16** and **23** were identified by comparison with authentic samples. The characterization of these acids is described below.

2. The Potassium Salt in 1,2-Dimethoxyethane. A solution of 489 mg (1.86 mmol) of acid **21** in 30 ml of DME was treated with 209 mg (1.86 mmol) of potassium *t*-butoxide and the mixture was heated at reflux for 5 hr.[34a] At this point only a trace of carbon dioxide could be detected and isolation of the products afforded only starting material. This recovered acid in 160 ml of DME was resubjected to the reaction conditions for 15 hr. Again only a trace of carbon dioxide was liberated and mainly starting material was recovered. The small amount of neutral material which was isolated possesses a faint odor of the olefin **4** and showed infrared bands of the β-lactone **22**. In both trials the potassium salt of acid **21** appeared to be virtually insoluble in the reaction medium.

3. The Lithium Salt in 1,2-Dimethoxyethane. A solution of 298 mg (1.10 mmol) of acid **21** in 95 ml of DME was treated with 8.8

mg (1.1 mmol) of lithium hydride, whereupon a precipitate formed. The mixture was stirred at reflux for 8 hr[34a] during which time a trace of carbon dioxide was evolved, mainly during the first hour. Work-up afforded 9 mg of neutral material with a faint odor of olefin **4** and containing no β-lactone bands in the infrared spectrum. The acidic material consisted of 274 mg (95%) of starting acid **21**.

Bicyclo[3.3.1]non-2-enecarboxylic Acid (16). The acidic material (1.04 g) from part A of the above experiment was distilled (120° at 0.1 mm) affording 0.97 g of pasty solid. This material was recrystallized twice from ether–hexane to give 0.38 g of microcrystalline solid, mp 96.5–97°, identical with the material prepared as described above.

The structure of this acid was ascertained through its methylation with ethereal diazomethane followed by hydrogenation over platinum in ethanol to give methyl bicyclo[3.3.1]nonane-1-carboxylate, mp 27.5–28°; λ_{max}^{film} 5.78 (CO), 7.96, 8.18, 9.24, and 12.92 μ; $\delta_{TMS}^{CCl_4}$ 3.68 (CH_3O), 1.90, and 1.78 ppm.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.6; H, 10.2.

An authentic sample of this ester was obtained *via* conversion of the keto ester **2** to the thioketal derivative [mp 84.5–85°: λ_{max}^{KBr} 5.79 (CO), 7.98, 8.03, 8.25, 9.11, and 10.18 μ] by the method of Fieser.[40]

Anal. Calcd for $C_{13}H_{20}O_2S_2$: C, 57.32; H, 7.39; S, 23.54. Found: C, 57.5; H, 7.4; S, 23.7.

Desulfurization of this thioketal (0.60 g of thioketal and 2 level teaspoons of W-2 Raney nickel in 30 ml of ethanol at reflux for 4 hr) afforded a sample of methyl bicyclo[3.3.1]carboxylate identical with that prepared from the unsaturated acid **16**.

2-Hydroxybicyclo[4.2.1]nonane-2-carboxylic Acid (23). The acidic material derived from basic hydrolysis of the mesylate acid **21** was chromatographed on silica gel. Elution with 1:1 ether–benzene afforded a solid hydroxy acid [$\lambda_{max}^{CHCl_3}$ 2.9 (OH), 3.1–3.3 (acid OH), 5.85 (CO), 8.00, 8.20, 8.44, 8.89, 9.55, 10.25, 11.10, and 11.40 μ] whose infrared and nmr spectra were compatible with structure **23**.

A 100-mg sample of a mixture of this hydroxy acid and hydroxy acid **14** (~1:1 according to the gas chromatogram of the methyl esters) was oxidized with periodic acid according to the procedure of Yanuka, *et al.*[20] The product was isolated with ether[34b] and separated into neutral and acidic material by basic extraction. The acidic fraction afforded 62 mg of hydroxy acid **14** and the neutral fraction gave 19 mg of bicyclo[4.2.1]nonan-2-one, bp 70° (bath temperature) at 0.2 mm; λ_{max}^{film} 5.90 (CO), 7.90, 8.90, 9.21, 10.25, 10.79, and 11.54 μ. The infrared spectrum of this latter substance exactly matched that of an authentic sample.[41,19]

Conversion of the β-Lactone 22 into the Olefin 4. Preliminary studies showed that a 10% ethereal solution of the β-lactone **22** gave rise to a peak in the gas chromatogram arising from the olefin **4**, as evidenced by its retention time and the odor of the effluent, when the temperature of the injection port was above 260°.

An 11 cm × 4 mm glass tube was heated along the central 7 cm to 290° by means of electrical heating tape. One end of this tube was charged with 38 mg of β-lactone **22**. The charged end was connected to a nitrogen source and heated by means of an infrared lamp while nitrogen (50 ml/min) was passed through the tube. The volatile organic material was collected in a cold trap at −78°. After 2 hr, the β-lactone was completely volatilized and the material in the cold trap was isolated with pentane[34b] affording 27 mg of an oil containing 13% of olefin **4** and 87% of unchanged β-lactone **22** as judged by the gas chromatogram.

Attempts to effect this conversion photochemically[42] in pentane with benzene or xylene as sensitizers or through direct irradiation with the Hanovia lamp[42] or a GE-1395-w UA11 lamp in a quartz apparatus were unsuccessful. Only recovered starting material could be identified in these experiments. Furthermore only trace amounts of carbon dioxide were evolved during these photolyses.

Addition Reactions of Bicyclo[3.3.1]non-1-ene. A. Hydrogenation. 1. Over Platinum. A solution of 108 mg of olefin **4** in 10 ml of ethanol was stirred with 200 mg of platinum dioxide under 1 atm of hydrogen. The uptake of hydrogen was complete within several minutes. The catalyst was removed by filtration and the product was isolated with pentane[34b] and sublimed to give 68 mg of solid bicyclo[3.3.1]nonane (**24**) identified by comparison with an authentic sample.[43]

2. Homogeneous Catalysis.[44] A solution of 9.9 mg of tristriphenylphosphinerhodium chloride[27] in 1.0 ml of ethanol and 2.0 ml of benzene was shaken at 25° under 1 atm of hydrogen by means of an oscillating agitator. A solution of 25.0 mg of olefin **4** in 1.0 ml of benzene was added and the solution was shaken until hydrogen uptake ceased (2 hr). The solution was diluted with saturated brine and the product was isolated with pentane and sublimed affording 18 mg of bicyclo[3.3.1]nonane (**24**).

B. Acetic Acid. A solution of 73 mg of olefin **4** in 10 ml of acetic acid was stirred at room temperature.[34a] A sample taken after 0.4 min contained none of the starting olefin according to gas chromatography. The product was isolated with 1:1 ether pentane affording 110 mg (90%) of acetate **25** judged homogeneous by gas chromatographic analysis. The infrared and nmr spectra were identical with those of an authentic sample prepared as follows.

A solution of 1.14 g (6.8 mmol) of bicyclo[3.3.1]nonane-1-carboxylic acid [mp 91.5–92°; λ_{max}^{film} 3.0–3.6 μ (acid OH), 5.9 (CO), 7.10, 7.17, 7.85, 9.20, 13.5, and 15.1 μ. *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.58. Found: C, 71.3; H, 9.3] prepared *via* disulfurization of the thioketal derivative of keto ester **9** followed by saponification as described above, in 50 ml of ether at 0° was treated dropwise with 16 ml (25 mmol) of 1.62 *M* ethereal methyllithium.[34a] The mixture was stirred at room temperature for 2 hr, ethyl formate (5 ml) was added to destroy the excess methyllithium, and the product was isolated with pentane[34b] and distilled affording 1.03 g of oil, bp 60–70° (bath temperature) at 0.1 mm, which was shown to be an 85:10:5 mixture by gas chromatography. The major product was isolated by preparative gas chromatography and distilled affording 0.56 g of bicyclo[3.3.1]non-1-yl methyl ketone (+99% pure according to gas chromatography): λ_{max}^{film} 5.88 (CO), 6.70, 6.82, 6.88, 7.38, 7.49, 8.01, 8.41, 9.34, and 10.32 μ.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.6; H, 11.0.

A 363-mg sample (2.18 mmol) of the above ketone in 7.5 ml of chloroform was stirred in the dark with 1.00 g (5.00 mmol) of *m*-chloroperoxybenzoic acid (86%) for 50 hr. The product was isolated with ether[34b] and distilled affording 380 mg of crystalline acetate **25**, mp 28–30° (99% pure according to gas chromatography): λ_{max}^{film} 5.78 (CO), 6.70, 6.76, 6.84, 7.96, 8.10, 9.39, 9.50, 9.76, and 11.73 μ.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.7; H, 9.9.

C. Ethanol. A solution of 21 mg of olefin **4**, 0.05 ml of sulfuric acid, and 1.00 ml of ethanol was stirred at room temperature for 20 min[34a] at which point no more olefin remained according to gas chromatography. The product was isolated with ether to give a 70:30 mixture of ether **26** and alcohol **27** (gas chromatographic analysis). This mixture, upon treatment with sodium hydride and ethyl iodide according to the procedure of Dauben and Poulter,[45] afforded the ethyl ether **26** identified by infrared spectral comparison.[45]

No observable addition took place within 7 days between olefin **4** and freshly distilled ethanol. Ethanol likewise failed to add to olefin **4** in basic solution (added NaOH).

D. Photochemical Hydration. A solution containing 165 mg of olefin **4**, 0.10 ml of *p*-xylene, 25 ml of water, and 130 ml of DME was irradiated[29,42] for 1 hr. The product was isolated with pentane[34b] and chromatographed on silica gel. Elution with ether afforded 62 mg (30%) of alcohol **27** identified by spectral and gas chromatographic comparison with an authentic specimen obtained *via* cleavage of the acetate **25**.[45] No addition took place under the above conditions in the dark.

E. Epoxidation. A solution of 155 mg (1.27 mmol) of olefin **4** in 3.0 ml of chloroform was treated with 280 mg (1.40 mmol) of *m*-chloroperoxybenzoic acid (86%) whereupon an exothermic reaction ensued with almost immediate precipitation of *m*-chlorobenzoic acid. An aliquot taken after 2 min showed no peak in the gas chromatogram attributable to the olefin. The product was isolated with ether[34b] and distilled affording 135 mg of white solid. Sublimation (50° at 1.0 mm) yielded 106 mg of crystalline epoxide **28**, mp 106–107.5°: λ_{max}^{KBr} 5.88, 9.88, 11.02, 11.25, 11.60, and 11.82 μ.

Anal. Calcd for $C_9H_{14}O$: C, 78.13; H, 10.21. Found: C, 77.9; H, 10.3.

(40) L. F. Fieser, *J. Amer. Chem. Soc.*, **76**, 1945 (1954).

(41) We are grateful to Professor Hartman for providing this spectrum.

(42) A 450-W Hanovia Mercury Arc, Type L, in a Vycor immersion well was employed as a light source.

(43) We are grateful to Professor R. L. Burwell, Jr., for a sample of this hydrocarbon.

(44) We are indebted to Mr. Y. Takeuchi for performing this experiment.

(45) W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, **33**, 1237 (1968).

A 32-mg sample of epoxide **28** (90% pure) in 3.5 ml of DME was heated at reflux with 30 mg of lithium aluminum hydride for 15 hr. The cooled solution was treated with 5% aqueous sulfuric acid and the product was isolated with ether[34b] affording 29 mg of alcohol **27** (85% pure according to gas chromatography) whose infrared spectrum matched that of an authentic sample.

F. Hydroboration–Oxidation. The procedure of Brown and Zweifel[46] was employed. To 3.0 ml of 0.6 *M* diborane in tetrahydrofuran (THF) at 0° was added a solution of 75 mg of olefin **4** in 4.0 ml of THF.[34a] The solution was stirred at room temperature for 2.5 hr, cooled to 0°, and 0.10 ml of water, 1.0 ml of 10% aqueous sodium hydroxide, and 1.0 ml of 30% aqueous hydrogen peroxide were added successively. The solution was stirred at 0° for 1 hr and at room temperature for 1 hr, then saturated brine was added and the product was isolated with ether.[34b] The resulting waxy solid was sublimed affording 75 mg of material consisting of 30% of the bridgehead alcohol **27**, 64% of the *exo*-alcohol **29**, and 6% of the *endo*-alcohol **30** (gas chromatographic analysis). These alcohols were separated by chromatography on silica gel and identified through comparison with authentic samples.[47]

G. Methyllithium. A solution of 100 mg of olefin **4** in 3.0 ml of ether was treated with 3.0 ml of 1.7 *M* ethereal methyllithium.[24a] After 4 days at room temperature, the product was isolated with pentane[34b] affording 95 mg of material containing 20% starting olefin according to the gas chromatogram. The crude product was therefore treated with ethereal methyllithium (2.5 ml of 1.7 *M*) for an additional 4 days. Isolation as before afforded 82 mg of a mixture containing 54% of 1-methylbicyclo[3.3.1]nonane (**31**), 39% of bicyclo[3.3.1]non-2-ene (**32**), and 7% of an unidentified product. The hydrocarbons were separated by column chromatography on silver nitrate impregnated silica gel. The olefin **32** was identified by comparison with an authentic sample.[47] An authentic sample of the methylbicyclononane **31** was synthesized as follows.

A mixture of 185 mg of bicyclo[3.3.1]nonane-1-carboxylic acid and 100 mg of lithium aluminum hydride in 20 ml of DME was stirred at reflux for 4.5 hr. The cooled mixture was treated with 10% aqueous sulfuric acid and the product was isolated with ether[34b] affording 156 mg of bicyclo[3.3.1]non-1-ylmethanol (98% pure according to gas chromatography), bp 80–85° (bath temperature) at 0.2 mm): λ_{max}^{film} 3.00 (OH), 8.79, 8.90, 9.65, 9.85, 10.32, 10.60, and 10.92 μ. The analytical sample was secured by preparative layer chromatography and short-path distillation.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.7; H, 11.7.

A 170-mg (1.13 mmol) sample of the above alcohol (obtained from a comparable reduction experiment) in 2.0 ml of pyridine at 0° was treated with 0.15 ml (2.0 mmol) of methanesulfonyl chloride. The ice bath was removed and after 2.5 hr the product was isolated with ether[34b] affording 254 mg of the methanesulfonate derivative: λ_{max}^{film} 6.71, 6.81, 6.88, 7.40, 8.50, 10.50, 11.60, 12.00, and 13.30 μ; $\delta_{TMS}^{CDCl_3}$ 3.08 (CH_3SO_2–) and 3.85 ppm (–CH_2OSO_2–).

The above sample of methanesulfonate in 2.0 ml of ethanol was added to a solution of 300 mg of lithium in 25 ml of ammonia at −78°. After 30 min, solid ammonium chloride was added to discharge the color, the mixture was diluted with water, and the product was isolated with pentane.[34b] The crude product was chromatographed on silica gel affording 39 mg (31%) of 1-methylbicyclo[3.3.1]nonane (**31**), bp 80° (bath temperature) at 20 mm; λ_{max}^{film} 3.45, 6.70, 6.85, 7.23, 7.31, 8.80, 8.90, 10.00, 10.31, 10.80, 11.35, 11.65, and 12.26 μ; $\delta_{TMS}^{CDCl_3}$ 0.75 ppm (CH_3); mass spectrum, calcd for $C_{10}H_{18}$, M^+ = 138; found M^+ = 138. The gas chromatogram indicated a purity of 95% for this material.

Elution of the above column with ether–pentane afforded 92 mg (66%) of bicyclo[3.3.1]non-1-ylmethanol.

H. 1,3-Diphenylisobenzofuran. The procedure of Barnett[48] was followed. A solution of 115 mg (0.94 mmol) of olefin **4** in 2.0 ml of ether was treated with a solution of 248 mg (0.92 mmol) of 1,3-diphenylisobenzofuran in 10 ml of ether. The solution rapidly changed in color from yellow to greenish yellow and, after 4 min, none of the starting olefin could be detected by gas chromatography. The solution was centrifuged to remove traces of solid material, the ether was removed under a stream of nitrogen, and the solid residue was recrystallized from ethanol affording 307 mg (86%) of the adduct **33**, mp 80.5–81°; λ_{max}^{KBr} 3.29, 6.22, 6.67, 6.85, 6.89, 7.40, 7.65, 10.0, 10.23, 10.98, 13.40, 13.67, 14.20, 14.73, and 15.10 μ; $\delta_{TMS}^{CCl_4}$ 1.18, 1.44, 1.91, 7.05, 7.10, 7.40, 7.42, and 7.50 ppm. The integral indicated an equal number of aliphatic and aromatic protons.

Anal. Calcd for $C_{29}H_{28}O$: C, 88.73; H, 7.19. Found: C, 88.4; H, 7.2.

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(46) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 2544 (1961).

(47) We are indebted to Professor J. P. Schaefer for a generous sample of the *endo*-alcohol **30** and related bicyclo[3.3.1]nonane derivatives: J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, **32**, 1372 (1967).

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