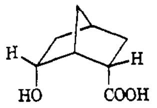
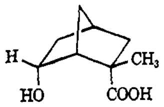
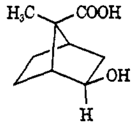
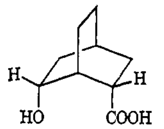
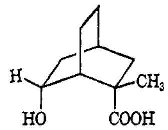
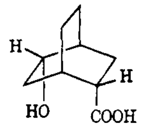
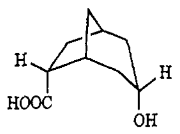
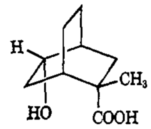
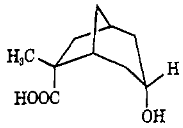
Table I. Rates of Lactonization for Various Bridged Bicyclic Hydroxycarboxylic Acids[a]

Compound	Correct structure	K^{H^+}, M^{-1} min^{-1}
 **1**		1120
 **2**	 **3**	0.30
 **4**		0.950
 **5**		107
 **6**	 **7**	10.0
 **8**	 **9**	522

[a] Taken from ref 12.

Inspection of the rate data in Table I immediately reveals a striking inconsistency. Methyl group substitution in the 2-exo position (compound **2** compared to **1**) *decreases* the rate of lactonization by 3740 while the analogous change in **4** compared to **5** *increases* the rate by a factor of 100. These data led us to suspect an incorrect structure as is in fact the case. Compound **2** is in reality the rearranged hydroxycarboxylic acid **3**. These compounds were originally confused by Meek and Trapp[16] but corrected as early as 1961 by Beckmann and Geiger,[17] and their work has also been confirmed by us.[18]

Hydroxy acids **4**[19] and **5**[20] are correct as drawn and the rate enhancement of 100 is real and also expected. It probably stems from a compression effect of the type originally suggested by Bunnett and Hauser[21] and discussed by Cohen[6-8] in which the methyl group acts to decrease the rotational possibilities for the carboxyl group, leading to an energetically more favorable orientation for lactonization. The rate decrease of 3740 between **1** and **3** is probably due largely to a distance factor[22,23] although other important parameters such as torsional strain, solvation, and angle strain must certainly play a role.

Structures **6** *vs.* **7** and **8** *vs.* **9** are more complicated and could only be sorted out on the basis of complete chemical degradations to known compounds.[20]

It is worth noting that the kinetic effect of methylation in going from **7** to **9** is as expected based upon compression. In a corollary sense one can argue that a favorable orientation of atomic orbitals results from this structural modification. In this sense the present work does not call into question the validity of the *concept* of orbital steering, but rather questions some of the *premises* which derive from incorrect models.

Acknowledgment. The authors wish to thank Professor C. W. Jefford, University of Geneva, for helpful discussions.

[16] J. S. Meek and W. B. Trapp, *J. Amer. Chem. Soc.*, **79**, 3909 (1957).

[17] S. Beckmann and H. Geiger, *Chem. Ber.*, **94**, 48 (1961).

[18] We have repeated the work of Beckmann and Geiger,[17] using different oxidizing conditions, namely, oxidation of **3** with RuO_4 in base to 2-keto-7-*anti*-methylbicyclo[2.2.1]heptane-7-*syn*-carboxylic acid, mp 206–208° (lit.[17] 206–208°) (ir 1735 cm^{-1}), followed by Wolff–Kishner reduction to 7-methylbicyclo[2.2.1]heptanecarboxylic acid, mp 194–195° (lit.[17] 194–195°). 6-*endo*-Hydroxy-2-*exo*-methylbicyclo[2.2.1]-heptane-2-*endo*-carboxylic acid γ-lactone has mp 65–66°. 2-*exo*-Hydroxy-7-*anti*-methylbicyclo[2.2.1]heptane-7-*syn*-carboxylic acid γ-lactone has mp 125–126°. Storm and Koshland[12] used the material of mp 125–126° as the source of **2**.

[19] H. W. Whitlock, *J. Amer. Chem. Soc.*, **87**, 2214 (1965).

[20] Structures **5**, **7**, and **9** are established by work reported in the following communication.

[21] J. F. Bunnett and C. F. Hauser, *J. Amer. Chem. Soc.*, **87**, 2214 (1965).

[22] Inspection of Dreiding models of **3** reveals around a 0.7 Å greater distance between the hydroxyl group and carboxyl carbonyl group relative to **1**. There also exists qualitative information about the difficulty of bridging between the C_2–C_7 positions. Isoborneol does not undergo intramolecular oxidative cyclization between the C_2 hydroxyl and C_7 methyl group upon reaction with lead tetraacetate.[23] Also acidification of a basic solution of the lactone related to **3** does not cause spontaneous lactonization as does occur with 2,6 substituted compounds such as **1** and **4**.

[23] R. E. Partch, *J. Org. Chem.*, **28**, 276 (1963).

[24] Visiting Professor, University of Geneva, Geneva, Switzerland

Robert M. Moriarty*[24]
Department of Chemistry
University of Illinois at Chicago Circle Campus
Chicago, Illinois 60680

Timothy Adams
Department of Chemistry, The Catholic University of America
Washington, D. C. 20017

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Acid-Catalyzed Lactonization of *exo*- and *endo*-Bicyclo[2.2.2]oct-5-enecarboxylic Acids. Structural Clarifications

Sir:

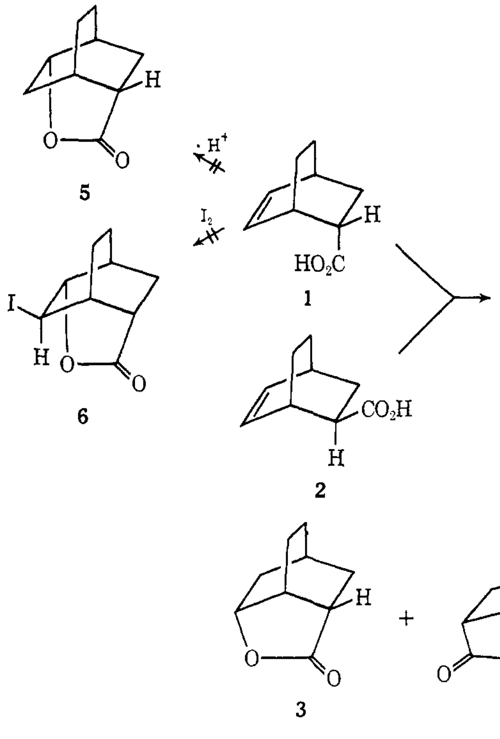
Considerable confusion exists in the literature regarding the structure of the δ-lactone obtained in the intramolecular lactonization of *exo*- and *endo*-bicyclo-[2.2.2]oct-5-enecarboxylic acids, **1** and **2**, respectively. For example, the lactone thought to be **5** has been used as a model compound in the development of the concept of orbital steering,[1] when in fact, the correct structure of the δ-lactone from the acid-catalyzed cyclization of **1** or **2** is **4**, *vide infra*. Similarly, iodo-δ-lactone (**6**) has been claimed,[2] but attempts to repeat this synthesis by us and others[3] has failed to produce any lactone other than the expected 2,6-γ-lactone (Scheme I).

[1] D. R. Storm and D. E. Koshland, Jr., *J. Amer. Chem. Soc.*, **94**, 5815 (1972).

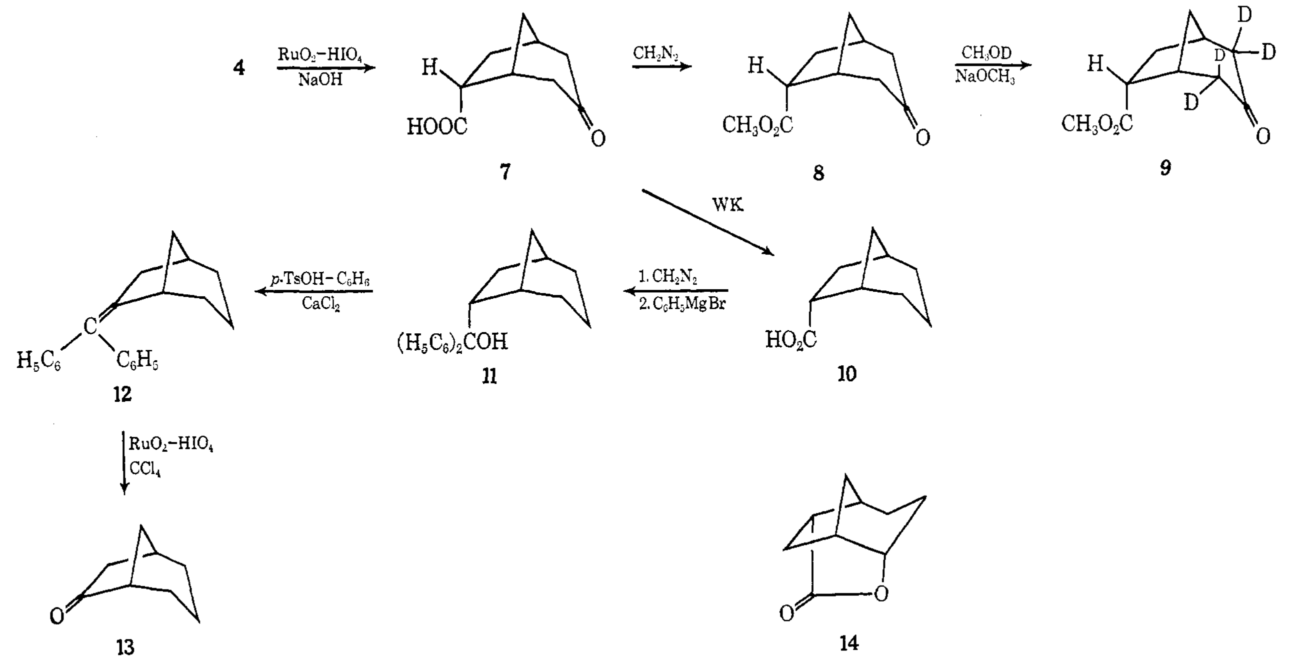
[2] W. R. Boehme, E. Schipper, W. G. Scharpf, and J. Nichols, *ibid.*, **80**, 5488 (1958).

[3] H. W. Whitlock, *ibid.*, **84**, 3412 (1962).

Scheme I



Scheme II



Furthermore, since such bridged lactones are valuable starting materials in organic synthesis, it appeared to us to be of importance to establish rigorously their structures as well as to define conditions for their formation. Table I gives ratios of lactones **3** and **4** formed under various conditions for dehydration.

Under conditions of strong acid each carboxylic acid affords high yields of both lactones. Under milder conditions, where the product of kinetic control **3** is not equilibrated, low conversions to a mixture of the two lactones occurs with **3** predominating.

Table I. Yields and Ratios of Lactones **3** and **4** under Various Dehydration Conditions

Reactants	Conditions	Time, hr	Temp, °C	% conversion	3:4[a,b]
1	99.5% H_2SO_4	0.5	0	88	3:5
2				85	1:3
1	75% H_2SO_4	3.0	0	90	1.1:1
2				93	1:1.1
1	HOAc-cat.	8	Reflux	39	8:1
2	H_2SO_4			35	2.4:1

[a] The lactones could be separated by glc (25% SE-30, 270°) or by column chromatography on silica gel and elution with 10% ether–petroleum ether. [b] No conversion occurred using HCl–Et_2O, 24 hr at 25°, or in acetic acid at reflux for 24 hr.

The structure of **3**, mp 205–206° (lit.[3] 205–206°), was proven by comparison with an authentic sample prepared by Raney-nickel reduction of 5-*exo*-iodo-6-*endo*-hydroxybicyclo[2.2.2]octane-2-*endo*-carboxylic acid γ-lactone.

The structure of **4**, mp 239–241°, 233–235° after 1 week at 25° (lit.[1] 229–230°), ir ($CHCl_3$) 1730 cm^{-1} (lactone C═O), mass spectrum *m/e* 152, was proven by chemical degradation to the known bicyclo[3.2.1]octan-6-one (**13**).[4–7] Using a method developed by us for oxidation of secondary alcohols under basic conditions (RuO_2–HIO_4–NaOH)[8] **4** was converted in 88% yields to bicyclo[3.2.1]octan-3-one-6-*endo*-carboxylic acid (**7**),[9] mp 179–180°, ir (Nujol) 1740 cm^{-1} (ketone C═O) and 1688 cm^{-1} (acid C═O), 2,4-DNP mp 235–236.5°, thioketal mp 150–150.5°. Wolff–Kishner reduction of **7** (Scheme II) yielded bicyclo[3.2.1]octane-6-*endo*-carboxylic acid (**10**) in 88% yield, mp 79.5–82°, ir ($CHCl_3$) 3525 (acid OH) and 1700 cm^{-1} (acid C═O).

Bicyclo[2.2.2]octane-2-carboxylic acid has mp 83–

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(4) V. N. Ipatieff, J. E. Germain, W. W. Thompson, and H. Pines, *J. Org. Chem.*, **17**, 272 (1952).

(5) T. Kubota, T. Matsuura, T. Tsutsui, S. Uyeo, H. Irie, A. Numata, T. Fijita, and T. Suzuki, *Tetrahedron*, **22**, 1654 (1966).

(6) K. B. Wiberg and B. A. Hess, *J. Org. Chem.*, **31**, 2250 (1966).

(7) H. A. House, S. Boots, and V. Jones, *ibid.*, **30**, 2519 (1965).

(8) H. Gopal, T. Adams, and R. M. Moriarty, *Tetrahedron*, **28**, 4259 (1972).

(9) All new compounds had correct microanalyses.

84°[10] but **10** gave a mixture melting point with this substance of 64–68°.

The methyl ester was prepared by treatment of **10** with diazomethane. This in turn was converted to the diphenylcarbinol **11** and dehydrated with *p*-toluenesulfonic acid in benzene to yield 6-diphenylmethylenebicyclo[3.2.1]octane (**12**), mp 105–106°, in 100% yield. Cleavage of **12** with RuO_2–$NaIO_4$ in carbon tetrachloride yielded bicyclo[3.2.1]octan-6-one (**13**) in 40% yield, mp 153–155°, semicarbazone 180–182° (lit.[4] 150–153°), semicarbazone 190–192° (lit.[5] 155–157°), semicarbazone 187–190° (lit.[6] 155–157°), ir (CCl_4) 1745 cm^{-1} (lit.[7] 1745 cm^{-1}), ir ($CHCl_3$) 1725 cm^{-1} (lit.[5] 1726 cm^{-1}), mass spectrum: *m/e* 124, 81, 80, 67, 54, 41 (lit.[7] *m/e* 124, 81, 80, 67, 54, 41). An authentic sample[11] showed the same tlc (10% ether–pentane on silica gel), glc retention time (15% SE-30°, 80°) and ir spectrum as **13**.

These data alone do not rule out **14** as a possible structure; however, ester **8** was found to incorporate four atoms of deuterium.[12] The ketonic carbonyl of ester **8** occurs at 1710 cm^{-1} which is the same frequency as that reported for bicyclo[3.2.1]octan-3-one.[13] The mechanism of the acid-catalyzed lactonization will be discussed in the full paper.[14]

[10] K. D. Gundermann and H. Schulze, *Chem. Ber.*, **94**, 3254 (1961).

[11] We thank Professor H. Goering, University of Wisconsin, Madison, for kindly providing a sample of **13**.

[12] The M + 4 peak at *m/e* 186 of deuterated **8** has intensity 48% of the base peak occurring at *m/e* 98. The parent molecular ion of **8** itself is at *m/e* 182 (44% of the base peak at *m/e* 96). Under the conditions used (CH_3OD, and a catalytic amount of $NaOCH_3$ at room temperature for 24 hr) the proton bond to the carbon bearing the carbomethoxy group does not exchange, as indicated in the nmr by no change in the methyl resonance at δ 3.7.

[13] W. R. Moore, W. R. Moser, and J. E. La Prade, *J. Org. Chem.* **28**, 2200 (1963).

[14] Acid-catalyzed cyclization of *exo*- or *endo*-2-methylbicyclo[2.2.2]oct-5-ene-2-carboxylic acid yielded a γ-lactone, mp 131–132° (lit.[1] 131–132°), ir (γ-lactone C═O) 1770 cm^{-1} and a δ-lactone, mp 128–129° (lit.[1] 123–123°), ir (δ-lactone C═O) 1735 cm^{-1}. Raney-nickel reduction of 5-*exo*-iodo-6-*endo*-hydroxy-2-*exo*-methylbicyclo[2.2.2]octane-2-*endo*-carboxylic acid γ-lactone yielded the γ-lactone mp 131–132°. A complete chemical degradation of the δ-lactone was not carried out but the keto acid (RuO_2–HIO_4–NaOH) showed a carbonyl stretching frequency at 1730 cm^{-1} (six-membered ketone.) By analogy with results in the present system it appears likely that the above δ-lactone possesses the [3.2.1]octyl structure.

[15] Visiting Professor, University of Geneva, Geneva, Switzerland.

Timothy Adams
Department of Chemistry, The Catholic University of America
Washington, D. C. 60680

Robert M. Moriarty*[15]
Department of Chemistry
The University of Illinois at Chicago Circle Campus
Chicago, Illinois 60680

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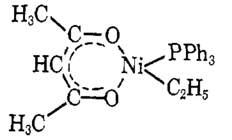
Preparation and Properties of a Nonrigid Ethyl Nickel Complex, $NiC_2H_5(acac)(PPh_3)$, and Its Methyl Analog, $NiCH_3(acac)(PPh_3)_2$

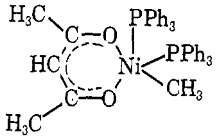
Sir:

Processes involving an olefin insertion into a metal–hydrogen bond and a reverse β-hydrogen elimination from the transition metal alkyl have been widely assumed as a mechanism explaining the hydrogen exchange and isomerization reactions of olefins catalyzed by transition metals and their compounds.[1] However, the examples of appropriate model compounds which show the interconversion are quite limited.[2–4] We wish to report here the syntheses and properties of ethyl(acetylacetonato)(triphenylphosphine)nickel(II), $NiEt(acac)(PPh_3)$ (**1**), whose nmr shows the rapid hydrogen interchange in the ethyl group and of a related methyl complex, methyl(acetylacetonato)bis(triphenylphosphine)nickel(II), $NiCH_3(acac)(PPh_3)_2$ (**2**).

These nickel complexes with alkyl, acetylacetonato, and triphenylphosphine ligands[5,6] have been isolated as intermediates in the alkylation reactions of nickel acetylacetonate in the presence of triphenylphosphine to give unstable dialkyl nickel complexes and their dealkylated zerovalent nickel complexes.[7,8] **1** and **2**



1



2

have been obtained as yellow crystals in good yields by the reactions of nickel acetylacetonate with dimethyl- and diethylaluminum monoethoxide in the presence of triphenylphosphine in toluene below −30° for 40 hr. The complexes can be recrystallized from toluene, benzene, acetone or ether. *Anal.* Calcd for **1**: C, 66.9; H, 6.0; mol wt, 449. Found: C, 66.9; H, 6.1; mol wt (cryoscopic in benzene), 450. Calcd for **2**: C, 72.3; H, 5.8. Found: C, 72.5; H, 6.0.

The ir spectra of **1** and **2** indicate the presence of the alkyl, acetylacetonato, and triphenylphosphine ligands. Acid hydrolysis of the methyl and ethyl complexes gave methane and ethane quantitatively, and deuteriolysis afforded CH_3D and C_2H_5D, respectively. Thermolysis of **1** (mp 93°) at 100° released ethylene, hydrogen, and a small amount of ethane, whereas from **2** (mp 102–103°) methane and ethane were liberated at 120° in a ratio of 1:2.

The proton and ^{31}P nmr spectra of **1** and **2** in various solvents and at various temperatures reveal complicated fluxional behaviors of these complexes in solutions. Table I summarizes the proton nmr data of the ethyl and methyl complexes. The two methyl groups in the acetylacetonato ligand in **2** are magnetically nonequivalent in benzene whereas they are equivalent in pyridine. The methyl groups of the acetylacetonato ligand in **1** also behave similarly; they are nonequivalent in acetone, benzene, and toluene while equivalent in pyridine at room temperature and nonequivalent

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[1] C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967; M. L. H. Green, "Organometallic Compounds," Vol. 2, Methuen, London, 1968.

[2] H. Bönneman, Ch. Grard, W. Kopp, and G. Wilke, I.U.P.A.C. XXIIIrd Congress, Special Lectures, Vol. 6, Boston 1971, p 265.

[3] T. Hosokawa and P. M. Maitlis, *J. Amer. Chem. Soc.*, **94**, 3238 (1972).

[4] F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971).

[5] Jolly, *et al.*,[6] have recently isolated the similar complexes with tricyclohexylphosphine ligand, $NiCH_3(acac)[P(C_6H_{11})_3]$ and NiC_2H_5-$(acac)[P(C_6H_{11})_3]$, without mentioning the fluxional behavior of the ethyl complex.

[6] P. W. Jolly, K. Jonas, C. Krüger, and Y-H. Tsay, *J. Organometal. Chem.*, 33, 109 (1971).

[7] G. Wilke and G. Hermann, *Angew. Chem.*, **74**, 693 (1962).

[8] A. Yamamoto, T. Yamamoto, and M. Takamatsu, unpublished.