Conformational Equilibria and Rates of Bridgehead Proton Exchange for 3,3-Dimethyl-2-bicyclo[3.3.1]nonanone and 3,3-Dimethyl-7-bicyclo[3.3.1]nonen-2-one[1]

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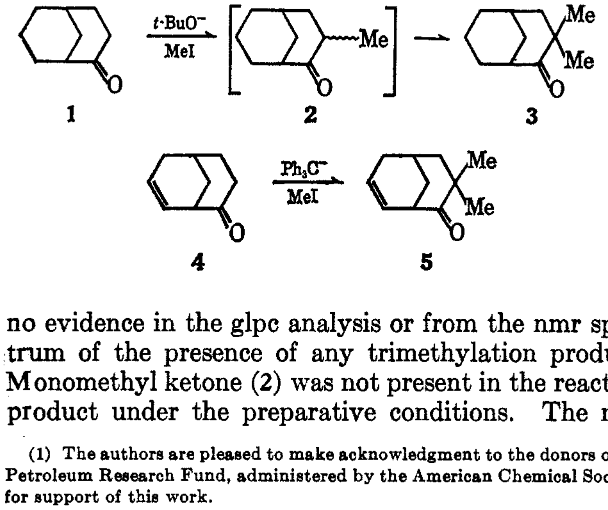
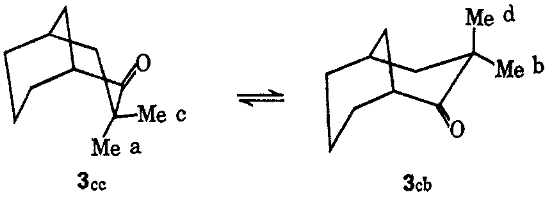
3,3-Dimethyl-2-bicyclo[3.3.1]nonanone (**3**) and 3,3-dimethyl-7-bicyclo[3.3.1]nonen-2-one (**5**) have been obtained by methylation of 2-bicyclo[3.3.1]nonanone (**1**) and 7-bicyclo[3.3.1]nonen-2-one (**4**), respectively. The ease of methylation of **1** and **4** is strikingly different and is attributed to the difficulty of generating the enolate ion from **4**. The nmr spectrum of **3** is temperature dependent and analysis of the spectral data assuming boat $\rightleftharpoons$ chair equilibrium in the ketone ring gives $\Delta H^\circ \approx 1$ kcal/mol. The chair-boat form for **3** was assumed to be the more stable conformer, and some modified Wiberg-type calculations support this assumption. Rate of the bridgehead proton exchange for **3** in deuteriomethanol at 100.8° is 0.67×10^{-4} l./mol sec, and that of **5** is *ca.* 30 times *slower*. The difference is attributed partly to conformational influences. The chair conformation assigned the ketone ring of **5** is supported by spectral evidence.

Early in this century Rabe[2] utilized the bicyclo[3.3.1]nonane ring system in studying questions of interest to theoretical organic chemists. Since that time this bridged ring system has figured quite heavily in studies of bridgehead reactivity[3] and of Bredt's rule.[4] It seems proper to return to a new consideration of the geometric questions relating to bridgehead reactivity and, in particular, of Bredt's rule at a time when the geometry of the bicyclo[3.3.1]nonane ring is known,[5] and the importance of conformations is better appreciated. As an initial step toward gaining more precise data about the energetics of bridgehead substitution, we have examined the rates of bridgehead deuteration of 3,3-dimethyl-2-bicyclo[3.3.1]nonanone (**3**) and 3,3-dimethyl-7-bicyclo[3.3.1]nonen-2-one (**5**).

Preparation and Properties of the Dimethyl Ketones.—The desired dimethyl ketone (**3**) was prepared by methylation of 2-bicyclo[3.3.1]nonanone[6] (**1**) with *t*-butoxide and methyl iodide[7] (Scheme I). There was no evidence in the glpc analysis or from the nmr spectrum of the presence of any trimethylation product. Monomethyl ketone (**2**) was not present in the reaction product under the preparative conditions. The nmr spectrum of **3** shows, as expected, two singlet methyl bands. The chemical shift between these is temperature dependent. We assume that this is due to the conformational equilibrium $3_{cc} \rightleftharpoons 3_{cb}$. If the chemical shifts of the methyl groups are represented by a, b, c, d, as shown and the concentration of $3_{cc} = x$, then the observed chemical shift $\Delta\delta = \mathrm{a}x + \mathrm{b}(1 - x)] - [\mathrm{c}x + \mathrm{d}(1 - x)]$. Substituting $(\mathrm{a} - \mathrm{c}) = n(\mathrm{b} - \mathrm{d})$ we find $\Delta\delta = [1 + x(n - 1)](\mathrm{b} - \mathrm{d})$. This equation cannot be solved for x, n, and (b − d) on the basis of the nmr data alone. Since both 3_{cc} and 3_{cb} are relatively rigid isomers, the rather reasonable assumption is made that $\Delta S^\circ \approx 0$, and, over the temperature range involved, ΔH° is a constant.[8] Using $y = \Delta\delta/(\mathrm{b} - \mathrm{d})$ and equating ΔH° at two different temperatures, $T_1 \log (y_1 - n) - T_2 \log (y_2 - n) = T_1 \log (1 - y_1) - T_2 \log (1 - y_2)$. With this equation the nmr data can be used to calculate n as a function of (b − d). Fortunately most values of either n or (b − d) turn out to be unrealistic, and the most satisfactory interpretation of the data gives $n \approx -1$ and (b − d) $\approx$ 7 cps. When this interpretation was made, we were unable to find any nmr spectra of conformationally uniform and undistorted α,α-dimethylcyclohexanones to check this value of (b − d). Recently Professor M. J. T. Robinson[10] has kindly informed us that *cis*-2,2,6-trimethyl-4-*t*-butylcyclohexanone exhibits methyl frequencies for the geminal dimethyl group separated by 8.2 cps. The agreement with our assumed value for (b − d) is quite gratifying.

SCHEME I





The equilibrium constant for the conformational change derived from the nmr data is $K = 5$ at 18° and $\Delta H^\circ = 1.0$ kcal/mol. No answer as to whether 3_{cc} or 3_{cb} is the more stable conformer is available from these

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[1] The authors are pleased to make acknowledgment to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

[2] P. Rabe, R. Ehrenstein, and M. Jahn, *Ann.*, **360**, 265 (1908); P. Rabe, K. Appuhn, and W. Schuler, *Ber.*, **76**, 982 (1943).

[3] See D. E. Applequist and J. D. Roberts, *Chem. Rev.*, **54**, 1065 (1954); R. C. Fort, Jr., and P. von R. Schleyer, "Advances in Alicyclic Chemistry," Vol. I, H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N. Y., 1966, pp 284–370.

[4] F. S. Fawcett, *Chem. Rev.*, 47, 219 (1950).

[5] M. Dobler and J. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965).

[6] E. N. Marvell, D. Sturmer, and C. Rowell, *Tetrahedron*, **22**, 861 (1966).

[7] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 184.

[8] The assumption that ΔH° is constant over a temperature range of about 80° is not unreasonable. It has been pointed out[9] that over temperature ranges of 100°, ΔH° is generally nearly constant.

[9] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 43.

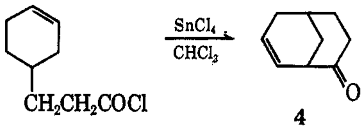
[10] M. J. T. Robinson, Oxford University, private communication, 1966.

data. Clearly it would be of value to establish this point. In many cases with saturated bicyclo[3.3.1]nonanes the appearance of high-frequency stretching bands near 2990 and bending vibrations near 1490 cm^{-1} has been used as a means of identification of the double chair conformation.[11] Unfortunately, the presence of bands at 2981 and 1475 cm^{-1} in the spectrum of **3** is not definitive as to conformation. Similarly, their absence in the spectrum of **1**, though it may suggest that the chair–boat conformation is preferred, does not provide definitive evidence.

Methylation of **4** could not be achieved under conditions which led to rapid methylation of **1**. Sodium hydride and methyl sulfate also failed to bring about methylation. We attribute the problem to an unfavorable equilibrium constant for formation of the enolate with these bases. This would imply that the presence of a double bond in one ring makes it more difficult to form a double bond in the other ring. There is some evidence which appears to support that supposition. Meerwein[12] reported that 2,6-bicyclo[3.3.1]nonadiol could be dehydrated to the monoene but not to the diene. Musso[13] has repeated the experiment and has found a significant difference in the ease of removal of the first compared with the second hydroxyl, but he was able to prepare the diene. By way of contrast Meerwein[12] also reported that the 2,6-dione "smoothly" converts into a double enol acetate when heated with acetic anhydride and sulfuric acid at 145°. Similarly Knoevenagel[14] found that formation of substituted 3,7-bicyclo[3.3.1]nonadiene-2,6-diones occurs with ease. Thus the evidence does not provide unambiguous support for this idea.

Whatever the reason for the lack of success with the methods above, a relatively slow but successful reaction was achieved with triphenylmethide ion and methyl iodide. Reaction leads to a rather complex mixture from which the desired **5** was separated with difficulty by preparative glpc. The prolonged exposure of **4** and **5** to strong base could lead to a product with a rearranged double bond. That this has not occurred in the major product isolated here and used in our studies is clearly indicated by ultraviolet spectral data. The ultraviolet spectrum of **4** showed a band at λ_{max} 297 mμ (ϵ 181) and that for **5** had a band at λ_{max} 301 mμ (ϵ 198). The ultraviolet spectrum for 6-bicyclo[3.3.1]nonen-2-one had a band at λ_{max} 293 mμ (ϵ 15).[15] Thus both **4** and **5** showed the bathochromic and hyperchromic effects associated with a β,γ-unsaturated ketone of proper geometry.[16] The great similarity between the spectra of **4** and **5** point to a similar geometry for the two ring systems. Not only does this indicate that both have the 7-ene structure, but it suggests also that the keto ring has a chair conformation in both molecules. MacKenzie[17] has developed a method for correlating the molar extinction coefficient at 290 mμ with the geometry of the β,γ-unsaturated ketones. Using his procedure we calculate ϵ_{290} 135 for the conformation with the chair cyclohexanone ring and ϵ_{290} 3049 for the conformation with a boat cyclohexanone. Clearly the spectral data support the assignment of a chair conformation to the ketone ring in both **4** and **5**.

The **4** needed for the preparation of **5** was synthesized from β-(3-cyclohexen-1-yl)propionyl chloride *via* a Friedel–Crafts reaction. A mixture of three products was obtained, from which the desired **4** was separated by distillation. Compound **4** is readily reduced to the known 2-bicyclo[3.3.1]nonanone,[12] which serves as a proof of structure. It is easily differentiated from the known 6-bicyclo[3.2.2]nonen-2-one,[18] a possible product of this reaction, by its spectral properties and melting point.



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Bridgehead Proton Exchange.—A number of observations point to the conclusion that the bridgehead position in the bicyclo[3.3.1]nonane system is surprisingly reactive in anionic,[19] radical,[20] cationic,[20] and concerted enol-producing[21-23] reactions. However, there have been few accurate rate studies reported which would help delineate the resistance, or lack of it, of this system to bridgehead reactivity. We have measured the rate of exchange of the bridgehead proton of **3** in deuteriomethanol containing methoxide ion as catalyst. At 100.8° exchange proceeds at a rate equal to 0.67×10^{-4} l./mol sec. The single proton which undergoes exchange in this reaction must be the bridgehead proton since the multiplet at 2.38 ppm (furthest downfield proton) is the one which undergoes exchange. A similar observation is cited by Schaefer and Lark[19a] to support their assumption of the exchange of a bridgehead proton in **1**. The conditions of this study are much less drastic than those required to bring about homoenolization with camphenilone.[24] The only proton except the one at the bridgehead that could be considered as a potential candidate for exchange is the 7 (e) hydrogen. However this proton is not present in **5** which also exchanges only one proton under comparable conditions. Thus, the evidence clearly supports the contention that a normal enolization at the bridgehead is involved in the exchange process.

It is possible to use this data to derive a rough approximation of the energy required to place a double

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(11) G. Eglinton, J. Martin, and W. Parker, *J. Chem. Soc.*, 1243 (1965).

(12) H. Meerwein, F. Kiel, G. Klösgen, and E. Schoch, *J. Prakt. Chem.*, **104**, 161 (1922).

(13) H. Musso, Ruhr-Universität Bochum, private communication, 1966.

(14) E. Knoevenagel, *Ann.*, **281**, 25 (1894).

(15) Dr. N. A. J. Rogers, University of Lancaster, private communication, 1966.

(16) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959); C. F. Wilcox, S. Winstein, and W. G. McMillan, *J. Amer. Chem. Soc.*, **82**, 5450 (1960).

(17) S. MacKenzie, S. B. Saila, and R. A. Shappy, *J. Org. Chem.*, **28**, 548 (1963).

(18) J. A. Berson and M. Jones, Jr., *J. Amer. Chem. Soc.*, **86**, 5019 (1964).

(19) (a) J. P. Schaefer and J. C. Lark, *J. Org. Chem.*, **30**, 1337 (1965); (b) A. C. Cope, D. L. Nealy, P. Schreiner, and G. Wood, *J. Amer. Chem. Soc.*, **87**, 3130 (1965).

(20) P. von R. Schleyer and P. R. Isele, private communication.

(21) J. P. Ferris and N. C. Miller, *J. Amer. Chem. Soc.*, **85**, 1325 (1963).

(22) Ferris and Miller consider that the decarboxylation of 2-oxobicyclo-[3.3.1]nonanecarboxylic acid leads directly to a carbanion. However, the best evidence now available[23] strongly supports the concerted nature of β-keto acid decarboxylations.

(23) D. B. Bigby and J. C. Thurman, *Tetrahedron Lett.*, 2377 (1967); K. MacKenzie in "Chemistry of Alkanes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 457–459.

(24) A. Nickon and J. L. Lambert, *J. Amer. Chem. Soc.*, **84**, 4604 (1962). The conditions reported indicate 48 hr at 185° in *t*-butoxide/*t*-butyl alcohol is required to bring about 88% racemization.

bond at the bridgehead in a bicyclo[3.3.1]nonane ring. There are no rate measurements made with cyclic ketones of an unstrained sort to which the above rate can be directly related. However, Shechter[25] has measured the rate of exchange of cyclohexanone in a mixture of deuterium oxide and dimethylformamide using triethylamine as a catalyst. This work showed that the effective base was deuterioxide ion. The rate for cyclohexanone would be 1500-fold faster at 100° than is the rate for **3**, a difference in rate corresponding to $\Delta E_a = 5.5$ kcal/mol. A rough estimate of the ground-state energy difference between the two molecules can be obtained by adding the 2.7-kcal/mol difference between the chair and boat forms of cyclohexanone[26] to the flagpole methyl to bridge methylene interaction. We have assumed that this latter value is slightly larger, *i.e.*, 2.0 kcal/mol, than is the similar interaction in 1-*cis*-3-pentadiene (1.66 kcal/mol).[27] This gives a very crude estimate of *ca.* 0.8 kcal/mol for the transition-state energy difference. Since Swain[28] has suggested that the bond between carbon and hydrogen is nearly completely broken in the transition state for base-catalyzed enolization, the energy difference between the transition states may give a good approximation to that between the enolate ions of cyclohexanone and **3**. Owing to the crudeness of the present approximation, it is only possible to conclude that this energy difference is not very large.

This conclusion is amply verified by the results of Schaefer and Lark[19a] on the exchange of **1**. After 6 days at 95° in D_2O–dioxane–0.1 *M* NaOD, **1** was found to contain 8.1% d_1, 32.0% d_2, and 58.4% d_3 species. Quite clearly the rates of exchange of the protons at C-3 and at C-1 are comparable. Originally we viewed these results as providing an excellent prognosis for the isolation of a 1-bicyclo[3.3.1]nonene. This expectation has been borne out by the recent reports[29] of isolation of 1-enes by two different sets of investigators.

The bridgehead proton in **5** undergoes exchange ($k = 1.96 \times 10^{-4}$ l./mol sec) 30 times more slowly than does the equivalent one in **3** under the same conditions. At the first glance this seems to be a surprising result. It is generally accepted that removal of a proton from the α carbon of a β,γ-unsaturated ketone is more rapid than from a saturated ketone,[30] though quantitative data are difficult to find. Heap and Whitham[31] recently showed that 3-cyclooctenone undergoes exchange at C-2 1.2 times faster than at C-8. Against this expected electronic effect must be balanced the possible increased strain induced in the ring by the second double bond.

A second rationalization of the slower rate of exchange for **5** compared with **3** has a conformational origin. Schaefer[19a] has emphasized the importance of the boat conformation of the ketone-bearing ring to stabilization of a bridgehead carbanion. We have shown that for **5** the spectral evidence favors a chair form for that ring. Although these data do not provide much information *vis-a-vis* the conformation of **3**, it would not be unreasonable to assign the ketone ring a boat conformation. Then a portion of the *ca.* 2.2-kcal/mol difference in activation energy between reactions of **3** and **5** could be attributed to the necessity for a conformational change in **5** which would be absent in **3**. The remainder would be due to the increased strain in the bridgehead enolate caused by the added double bond. To provide some additional support for this suggestion of a conformational origin for the rate difference, we have carried out calculations of the Henrickson–Wiberg type to determine the relative energies of the various conformations of the relevant molecules.

Calculations of Preferred Conformation.—Calculations of the energy differences between conformations have attained recently a measure of success. Most of these have, however, been applied to saturated hydrocarbon molecules.[32] Recently Gleicher and Schleyer[33] have modified the program of Wiberg[32] to handle molecules having a single trigonal atom in place of a tetrahedral carbon. Their parameters were defined for a carbonium ion rather than a carbonyl group as the trigonal atom. In view first of the considerable difficulties in defining adequately a number of the parameters associated with the carbonyl group, and second of our interest in qualitative rather than accurately quantitative data, a secondary carbonium ion was used to simulate the carbonyl group. This procedure has been used previously by Allinger[26] and amounts to a reversal of the Schleyer–Foote approach.[34] Before considering the problems associated with this simulation process, let us consider the results of the calculations. Bicyclo[3.3.1]nonane itself was calculated to be 3.7 kcal/mol more stable in the double chair conformation than in the chair–boat. Although the order of stabilities is correct,[5] the calculated $\Delta H°$ is probably too high since we have found a value of $\Delta G° = 2.5$ kcal/mol (362°K).[35] For the 3,3-dimethyl derivative the chair–boat conformer (methyl groups in the boat ring) was calculated to be 3.9 kcal/mol more stable than the double chair.[36] This is not an unexpected result.

For the 2-bicyclo[3.3.1]nonyl cation, which is representative here of **1**, the double chair is calculated as 2.7 kcal/mol more stable than the chair–boat conformer (sp^2 carbon in the boat ring). That the energy difference between the conformers is smaller for the cation than for the saturated hydrocarbon is to be expected by analogy with cyclohexanone.[26] However, the difficulties associated with finding proper parameters for energy terms associated with the sp^2 carbon and the uncertainties involved with simulating a carbonyl group by a trigonal cation suggest that this energy value be examined more critically. The energy relation be-

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[25] H. Shechter, M. J. Collis, R. Dessy, Y. Okuzumi, and A. Chen, *J. Amer. Chem. Soc.*, **84**, 2905 (1962).

[26] N. L. Allinger, *ibid.*, **81**, 5727 (1959).

[27] F. M. Fraser and E. J. Prosen, *J. Res. Natl. Bur. Stand.*, **54**, 143 (1955).

[28] C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, **80**, 5885 (1958).

[29] J. A. Marshall and H. Faubl, *ibid.*, **89**, 5965 (1967); J. R. Wiseman, *ibid.*, **89**, 5966 (1967).

[30] H. J. Ringold and S. K. Malhotra, *ibid.*, **84**, 3402 (1962).

[31] N. Heap and G. H. Whitham, *J. Chem. Soc., B*, 164 (1966).

[32] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961); K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

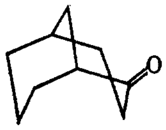
[33] G. J. Gleicher and P. von R. Schleyer, *ibid.*, **89**, 582 (1967).

[34] C. S. Foote, *ibid.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

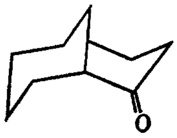
[35] R. S. Knutson, Oregon State University, unpublished data.

[36] Calculation of the relative energy of the interesting second possible chair–boat conformer with the methyl groups on the chair ring was not carried out for economic reasons.

tween 1_{cc} and 1_{cb} can be estimated in another way.



1_{cc}



1_{cb}

All of the present evidence[37] indicates that 1,4-cyclohexanedione exists largely in the twist boat form. Assuming that the conformational equilibrium is tipped toward the boat form by a small $-\Delta H°$ as well as the expected positive $\Delta S°$, this supports in a rough quantitative way the relatively simple analysis of Allinger.[26] According to his procedure, the energy difference between the chair and the boat form should be reduced by 2.4 kcal/mol by the introduction of a carbonyl group. The experimental evidence relative to cyclohexanedione suggests that this value is too low and should be nearer 3.0–3.2 kcal/mol. Taken in conjunction with our experimental value of $\Delta G° = 2.5$ kcal/mol for the double chair to chair–boat conformational equilibrium in the saturated molecule, these data suggest that the energy difference between the double chair and chair–boat forms for the ketone must be very small and may well favor the 1_{cb} conformer. In any event, the difference does not seem likely to be estimated effectively by the calculations involving a cation carried out in this study.

A difference of 4.4 kcal/mol is calculated between the chair–boat and double chair forms of the 3,3-dimethyl 2 cation. In this case the chair–boat conformation is favored. The reasonableness of this as an approximation for **3** needs examination. The most important difference between the parameters of the Gleicher and Schleyer calculation and those which might be expected to pertain to a cyclic ketone is in the "torsional barrier" to rotation about the sp^2–sp^3 carbon–carbon bond.[38] For reasons quoted in their paper Gleicher and Schleyer[33] have justified the use of a negligibly small barrier. For aliphatic aldehydes and ketones the microwave measurements give a value of 0.8–1.2 kcal/mol for the barrier.[38,39] The minimum value for this rotation occurs in acetaldehyde when a hydrogen is eclipsed with the carbonyl oxygen, or in propionaldehyde where either a hydrogen or a methyl group eclipsed the oxygen.[40] Both chemical and thermochemical evidence with respect to cyclohexanone,[41] as well as the data[37] relating to 1,4-cyclohexanedione, shows that the direct application of this information to cyclic ketones would lead to conclusions in direct conflict with chemical experience. Since all the evidence thus supports the theory that replacement of a methylene by a carbonyl unit favors the boat form, we feel that, since the calculations favor the chair–boat conformation for both the dimethyl derivatives of the saturated ring and the cation, the conclusions derived from the cation can indeed be considered significant for the ketone. Thus the calculations do give some reasonable support for the assignment of a chair–boat conformation to **3**.

Experimental Section

3,3-Dimethyl-2-bicyclo[3.3.1]nonanone (3).—Sublimed 2-bicyclo[3.3.1]nonanone[6] (1.43 g, 10.4 mmol) was stirred for 20 min at room temperature with a solution of 4.4 g (40 mmol) of potassium *t*-butoxide in 125 ml of *t*-butyl alcohol. Excess methyl iodide (11.0 g, 77 mmol) was added quickly, and the mixture was stirred at room temperature for 5 hr. Water was added, and most of the solvent was removed under reduced pressure. The residue was acidified, and the organic materials were taken up in hexane. Removal of the hexane followed by distillation, bp *ca.* 80° (0.05 mm), gave 1.23 g (73%) of **3**: $n^{20}{}_D$ 1.4869; mol wt (*via* mass spectrum) 166. The infrared spectrum shows bands at 2981, 1475, 1385, 1363, and 1720 cm^{-1}. The nmr spectrum exhibited a complex band between 1.25 and 2.5 and two singlets (3 H each) at 1.16 and 1.08 ppm.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.27; H, 10.70.

An oxime was prepared by heating **3** with a mixture of hydroxylamine hydrochloride, absolute ethanol, and pyridine at 70° for 24 hr. The oxime was recrystallized from methanol–water: mp 152–153.

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.56. Found: C, 72.79; H, 10.37.

The chemical shift between the two methyl singlets was found to be temperature variable. Spectra taken in tetrachloroethane showed the following changes in δ with temperature: δ_{147} 3.5, δ_{73} 4.1, δ_{18} 4.7, δ_{-5} 5.0, δ_{-25} 5.1. Using the equation (derived above) $T_1 \log (y_1 - n) - T_2 \log (y_2 - n) = T_1 \log (1 - y_1) - T_2 \log (1 - y_2)$ and the data for 147 and 73° one assumes a value for (b − d) and calculates n. This gives the series $n = -4$, (b − d) = 5; $n = -1.1$, (b − d) = 7; $n = -1.0$, (b − d) = 10. Using the data at 147 and 18° the values are $n = -0.8$, (b − d) = 7; $n = -0.9$, (b − d) = 10. If the differences (a − c) and (b − d) are assumed to be largely the result of the spatial relation between the two methyl groups and the carbonyl group, inspection of models indicates that n should be approximately −1. Thus the value for (b − d) is between 7 and 10 for the calculations tabulated above. Over the whole range for the data (b − d) ≈ 7 gave the best agreement.

7-Bicyclo[3.3.1]nonen-2-one.—To a solution of 18.5 g (0.12 mol) of 3-(3-cyclohexen-1-yl)propionic acid[42] and a few drops of pyridine in 350 ml of anhydrous benzene was added 20 ml (0.238 mol) of oxalyl chloride over a 2-hr period. The reaction mixture was maintained at 10° during addition and for 5 hr afterward. The solvent was removed *in vacuo* and the acid chloride was used directly in the next step.

To a well-stirred solution containing 8.16 g (0.048 mol) of 3-(3-cyclohexen-1-yl)propionyl chloride in 300 ml of chloroform was added 11.7 ml (0.10 mol) of anhydrous stannic chloride over a 1-hr period. The reaction mixture was stirred 5 hr at room temperature. The mixture was shaken with cold 10% hydrochloric acid and the organic layer separated. The acid layer was extracted with hexane; the organic solutions were combined. The combined solutions were washed with saturated sodium carbonate solution and then with water. After the solution had been dried over magnesium sulfate, the solvent was removed *in vacuo*. The crude residue was distilled through a column packed with glass helices, bp 60° (0.05 mm). The product, mp 66–68°, was 96–97% pure by glpc (Ucon Polar column at 190°): $\tilde{\nu}$ 3030, 2850, 2750, 1700, 1650, 1270, 1220, 900, 670 cm^{-1}; λ_{max} 297 mμ (ϵ 181), 202 (2090).

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(37) P. Groth and O. Hassel, *Proc. Chem. Soc.*, 218 (1963); A. Mossel, C. Romers, and E. Havinga, *Tetrahedron Lett.*, 1247 (1963); N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, **83**, 5028 (1961); C. W. N. Cumper, G. B. Leton, and A. I. Vogel, *J. Chem. Soc.*, 2067 (1965); M. V. Bhatt, G. Srinivasan, and P. Neelakantan, *Tetrahedron*, **21**, 291 (1965).

(38) Gleicher and Schleyer[33] separate the calculation of torsional strain energy and nonbonded interaction energy. Thus they assume the torsional barrier to be independent of the groups attached to the two atoms about whose bond the rotation is to occur. The barrier obtained from microwave spectroscopy is an experimental quantity which includes all contributions, *i.e.*, the intrinsic torsional barrier due to bonding electrons, nonbonded interactions, and electrostatic effects. Thus the measured value can be equated to the calculation parameter only when reasonable evidence can be presented to show that other energy terms aside from the "intrinsic torsional barrier" can be neglected.

(39) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1966, p 140.

(40) See ref 39, pp 19, 20.

(41) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Amer. Chem. Soc.*, **76**, 467 (1954).

(42) H. L. Finkbeiner and G. D. Cooper, *J. Org. Chem.*, **27**, 3395 (1962).

TABLE I

Substrate **3** (0.61 *M*)[a]	Methoxide ion (1.25 *M*)	
Time, sec	Deuterium, %	$k_1 \times 10^5$, sec^{-1}
1800	13.4	7.7
5700	40.0	8.8
7200	43.8	8.0
	Av	8.2

[a] Temperature was 100.8°; $k_2 = 6.6 \times 10^{-5}$ l./mol sec

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.17; H, 8.87.

A semicarbazone, prepared according to the procedure of Shriner, Fuson, and Curtin,[43] melted at 197.5–198.8°.

Anal. Calcd for $C_{10}H_{15}ON_3$: C, 62.16; H, 7.82. Found: C, 62.35; H, 7.84.

3,3-Dimethyl-7-bicyclo[3.3.1]nonen-2-one (5).—A solution of potassium triphenylmethide in glyme was prepared by heating 12.2 g (0.05 mol) of triphenylmethane and 1.84 g (0.047 g-atom) of potassium in 25 ml of glyme under nitrogen for 12 hr.[44] To the cooled solution was added 1.88 g (0.014 mol) of 7-bicyclo-[3.3.1]nonen-2-one, and, after the solution had been stirred for 20 min, 20.5 g (0.145 mol) of methyl iodide was added dropwise over a 10-min period. The solution was stirred for 10 hr at room temperature. After the reaction mixture had been filtered, the solvent was removed *in vacuo*, and the desired product was isolated (49%) by preparative glpc on a 5 ft × 0.25 in silicone column. The infrared spectrum showed bands at 3030, 2850, 1700, 1650, 1380, 1360, and 1260 cm^{-1}. The nmr spectrum exhibited multiplets at 5.8 (2 H), 2.9 (1 H), 2.2 (2 H), and 1.9 (4 H), and singlets at 1.1 and 1.05 ppm.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.24; H, 9.68.

Kinetic Measurements.—A solution of sodium methoxide in deuteriomethanol (1.5 *M*) was prepared in a dry nitrogen atmosphere. This solution was made up to *ca.* 0.6 *M* in the proper ketone and sealed in carefully baked-out ampoules under nitrogen. The ampoules were placed in a constant-temperature bath at 100.8° and withdrawn at appropriate intervals. Each sample was immediately placed in a Dry Ice bath to quench the reaction. The sample tube was opened, an excess of water was added, and the ketone was extracted with pentane. Analysis of the deuterium content of the samples was made by mass spectrometry. Early runs were made using infrared spectrometry as an analytical instrument and the rate constants generally agreed within 10% with those using the mass spectrometer. Typical data are shown in Tables I and II.

TABLE II

Substrate **5** (2.5 *M*)[a]	Methoxide ion (1.65 *M*)	
Time, sec × 10^{-5}	Deuterium, %	$k_1 \times 10^5$, sec^{-1}
1.00	31.0	0.37
1.44	34.3	0.29
2.59	51.5	0.29
3.46	60.5	0.37
	Av	0.33

[a] Temperature was 100.7°; $k_2 = 2.0 \times 10^{-6}$ l./mol sec.

Spectral Measurements.—Infrared spectral measurements were made on carbon tetrachloride solutions on a Beckman IR-7 grating spectrometer. The ultraviolet spectra were obtained with a Cary Model 15 ultraviolet spectrophotometer. All nmr spectra were made on carbon tetrachloride solutions using a Varian A-60 nmr spectrometer,[45] equipped with a Varian variable-temperature probe. The mass spectra were obtained with an Atlas CH_4 mass spectrometer operated under conditions developed to give a maximum molecular ion peak.

Calculations.—All calculations were performed on the CDC-3300 computer at the Oregon State University computer center.[46] The parameters used in these calculations were the same as those employed by Gleicher and Schleyer,[33] except that an in-plane $H-C^+-C$ bending force constant of 158 kcal/mol rad^2 was introduced. This value is four times the H–C–C bending force constant, a value in keeping with the $C-C^+-C$ bending constant obtained empirically by Gleicher and Schleyer.[47-49]

Registry No.—**3,** 16957-74-7; **3** (oxime), 16969-35-0; **4,** 16957-72-5; **4** (semicarbazone), 16957-71-4; **5,** 16957-73-6.

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[43] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 253.

[44] H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

[45] Acknowledgment is made to the National Science Foundation for financial assistance in the purchase of this instrument.

[46] G. J. G. is indebted to the Oregon State University computer center for financial assistance which paid for part of the calculations made in this study.

[47] Though this value is larger than those used for H—C═C in-plane bending constants by Garbisch[48] and Allinger, *et al.*,[49] the influence of this parameter on the calculated energy differences is small since little distortion of bond angles occurs at the sp^2 center.

[48] E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *J. Amer. Chem. Soc.*, **87**, 2932 (1965).

[49] N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford, and J. C. Graham, *ibid.*, **87**, 3430 (1965).