$\Delta E^\circ_{\mathrm{elect}}$ obtained by the linear SEE relationship. In the meanwhile, the linear SEE relationship appears to provide an extremely valuable approximate relationship as discussed above.

Acknowledgment. We are pleased to acknowledge the helpful assistance of Professor Arnett, Dr. C. Douty, and Mr. T. Murty in obtaining preliminary results with their calorimeter.

Analysis of the Nuclear Magnetic Resonance Spectra of Some 2,6-Bridged Bicyclo[2.2.1]heptane Derivatives

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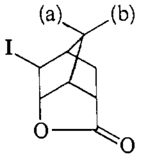
Contribution from the Research and Development Department of the ARCO Chemical Company, a Division of Atlantic Richfield Company, Glenolden, Pennsylvania, and the Department of Chemistry, The Catholic University of America, Washington, D. C. Received December 15, 1966

Abstract: The 60- and 100-Mc/sec nuclear magnetic resonance spectra of several bridged bicyclo[2.2.1]heptane derivatives have been analyzed in detail. These compounds possess the common structural feature of a 2,6 oxygenated bridge which may be either a lactone as in 5-*exo*-iodo-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (**1**) and the 5-*exo*-bromo (**2**), 5-*exo*-acetoxy (**3**), 5-*exo*-tosyloxy (**4**), 2-*exo*-methyl-5-*exo*-iodo (**5**), 2-*exo*-methyl-5-*exo*-bromo (**6**) derivatives; or the 2,6 bridge may be an oxido unit as in 4-*exo*-tosyloxy-6-oxatricyclo[3.2.1.$1^{3,8}$]nonane (**7**) and 4-*exo*-acetoxy-6-oxatricyclo[3.2.1.$1^{3,8}$]nonane (**8**). Chemical shifts for all the protons in these structures have been assigned, and the geminal and vicinal couplings measured. Aromatic solvent shifts observed for compounds **1**, **5**, and **7** are discussed in terms of solvent–solute collisional complexes of defined stereochemistry. Long-range couplings for the proton pairs: 1–4, 3-*endo*–7(a), 5-*endo*–7(b), 2-*exo*–6-*exo*, 1–3-*exo*, 2-*exo*–4, and 6-*exo*–4 in compound **1** were observed and most of these were confirmed using spin-decoupling techniques. For the C_5-*endo* proton doublet in the lactone derivatives it is noteworthy that the principal coupling is with the $C_{7(b)}$ proton; this amounts to about 2.5 cps while the C_5-*endo*–C_6-*exo* vicinal coupling is negligibly small (0.3 cps) and the C_5-*endo*–C_4-vicinal ranges from 0.5 to 1.0 cps. The nmr spectra of the 5-keto and 7-keto derivatives in the 2,6 lactone series are discussed in relationship to the changes in chemical shifts relative to the precursor secondary alcohols. The alcohol–ketone pairs are 5-*exo*,6-*endo*-dihydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (**9**) and 5-keto,6-*endo*-hydroxybicyclo[2.2.1]heptane 2-*endo*-carboxylic acid lactone (**10**); 6-*endo*,7(b)-dihydroxybicyclo[2.2.1]-heptane-2-*endo* carboxylic acid lactone (**11**) and 7-keto,6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (**12**).

The norbornyl system has served as a substrate for the generation and evaluation of numerous mechanistic hypotheses in modern organic chemistry. Mechanistic conclusions originating from studies in the norbornyl series frequently have been based upon the structures of rearranged products. Detailed nuclear magnetic resonance spectral analyses in this series obviously are of importance in facilitating the elucidation of rearrangement products. Moreover, due to the conformational rigidity of these systems, long-range couplings which are often of an unexpectedly large magnitude may be detected. This paper presents detailed analyses of the spectra of compounds **1–8**. The compounds included in this study are of current and particular interest because of uncertainties of interpretation[2a] and previous erroneous assignments.[2b]



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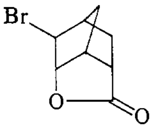

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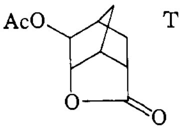

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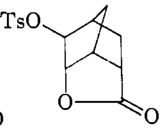

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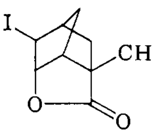

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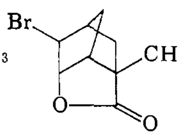

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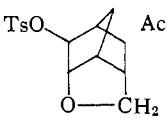

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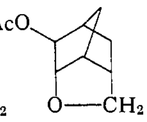

8

Chemical Shifts

In a preliminary communication of a portion of this work,[3] we pointed out that the chemical shifts of the C_1- and C_2-*exo* protons in compound **1** were anomalous in the sense that the C_1 proton appeared at a lower field position relative to the C_2-*exo* proton which is attached to the carbon atom bearing the carbonyl group of the lactone. This assignment was required to explain the magnitude of the couplings associated with the C_6-*exo* proton. An earlier interpretation of the spectrum of **2** used the reverse assignment of the chemical shift of the C_1- and C_2-*exo* protons.[2b] This incorrect assignment was used recently by Jensen and Miller[2a] who corrected stereochemical assignments of Traylor and Factor for the structure of the oxymercuration product derived from 5-norbornene-2-*endo*-car-

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(1) (a) The ARCO Chemical Co., Glenolden, Pa.; (b) The Catholic University of America, Washington, D. C.

(2) (a) F. R. Jensen and J. J. Miller, *Tetrahedron Letters*, **40**, 4861 (1966); (b) E. Crundwell and W. Templeton, *J. Chem. Soc.*, 1400 (1964).

(3) R. M. Moriarty, H. Gopal, H. G. Walsh, K. C. Ramey, and D. C. Lini, *Tetrahedron Letters*, **38**, 4555 (1966).

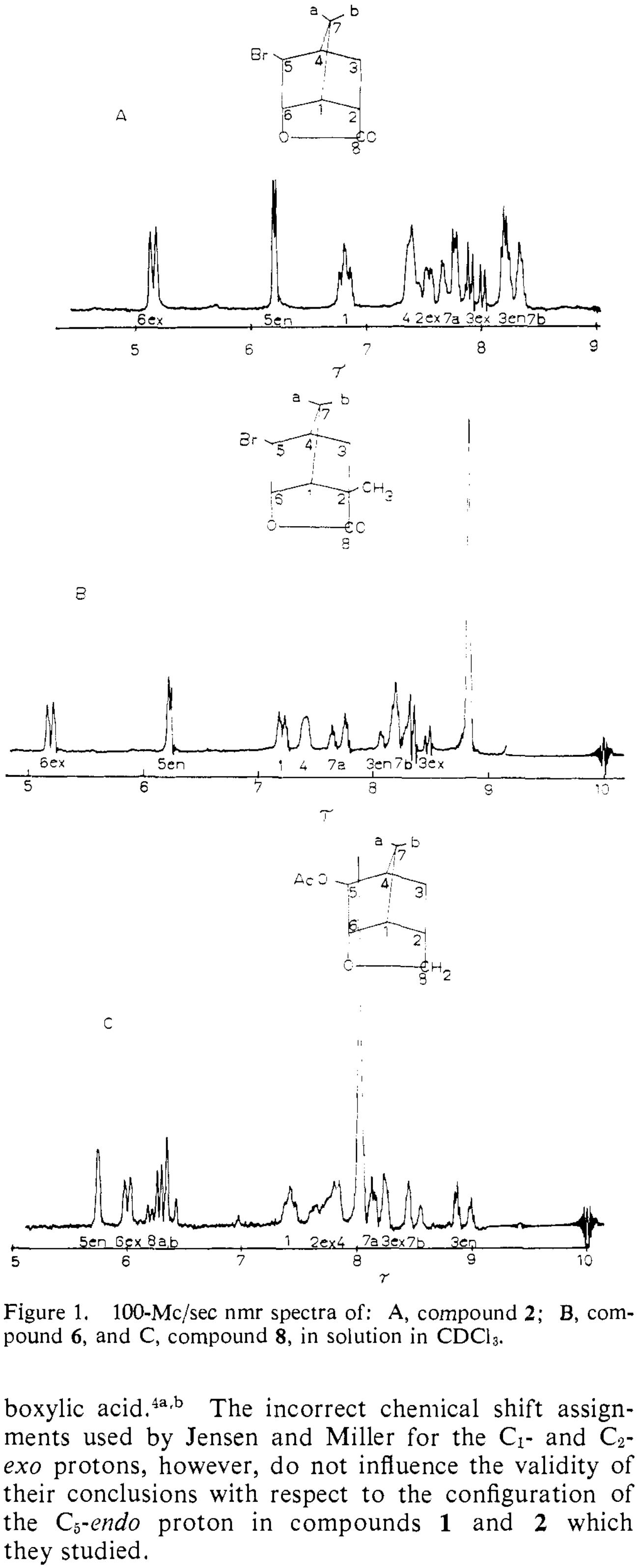

Figure 1. 100-Mc/sec nmr spectra of: A, compound **2**; B, compound **6**, and C, compound **8**, in solution in $CDCl_3$.

boxylic acid.[4a,b] The incorrect chemical shift assignments used by Jensen and Miller for the C_1- and C_2-*exo* protons, however, do not influence the validity of their conclusions with respect to the configuration of the C_5-*endo* proton in compounds **1** and **2** which they studied.

Figure 1A-C presents the 100-Mc/sec nmr spectra of compounds **2**, **6**, and **8**, respectively (Table I presents chemical shifts). For lactones **2** and **6** one may immediately discern a similarity; namely, three resonances equivalent to one proton each appear at downfield positions and these resonances are clearly separated from the complex upfield absorption. The absorptions around τ 5.1 and 6.1 are logically assigned to the C_6-*exo* and C_5-*endo* protons, respectively. The resonance at τ 6.75 in **2** might be due to the C_2-*exo* proton but this assignment leads to a number of unreasonable interactions. For example, spin-decoupling experiments revealed that the proton in **2** at τ 6.75 was coupled with the C_6-*exo* proton to the extent of 5 cps. This would be an unprecedentedly large long-range coupling for such protons. This coupling was clearly better accommodated by a vicinal rather than a 1,3 arrangement of these interacting protons. The spectrum of **6** clarifies this point in that a methyl group occupies the site in this derivative of the C_2-*exo* proton present in **1** and **2**, yet a resonance still occurs at τ 7.20. Accepting this alternative assignment, *i.e.*, that C_1 proton gives rise to the absorption at τ 7.2, appearance of this proton in **6** as principally a doublet is due to the absence of a proton at C_2 for coupling. Furthermore, any reasonable analysis of spectra in this series, as will be shown below, demands these relative assignments of the C_1- and C_2-*exo* protons.

The reason for this unexpected reversal in the chemical shifts of the C_1- and C_2-*exo* protons is based upon a model in which the C_1 proton is axial with respect to the lactone ring and is located in the region of maximum deshielding resulting from the ring current associated with the lactone carbonyl group. This interpretation is also consistent with the results obtained for compounds **5** and **6**. The upfield shifts of about 0.4 ppm for the C_1 proton in compounds **5** and **6** is probably due to the anisotropy of the carbon–carbon σ bond of the methyl group at C_2.[5] Accordingly, the C_3-*exo* proton in **1** should also experience extra shielding, and reference to the data in Table I bears out this prediction. The difference in magnitude of the upfield shift is associated with the dihedral angle between the C_2–CH_3 bond and the C_1–H, C_3-*exo*–H, and C_3-*endo*–H bonds. The maximum upfield shift is experienced by the C_3-*exo* proton, $\Delta\delta$ C_3-*exo*(**1**)–C_3-*exo*(**5**) = +0.54. The dihedral angle here is close to 0°. The C_2–CH_3 and C_1–H dihedral angle is about 40° and $\Delta\delta$ C_1(**1**)–C_1(**5**) = + 0.44. The dihedral angle for the C_2–CH_3–C_3-*endo*–H is about 120° and $\Delta\delta$ C_3-*endo*(**1**)–C_3-*endo*(**5**) = −0.42. Thus, this proton suffers a large deshielding effect due to the anisotropy of the C–CH_3 bond. The effect upon the C_6-*exo* and $C_{7(b)}$ protons is very small. Replacement of the carbonyl group of the lactone by a methylene group, as in compounds **7** and **8**, causes a further upfield shift of the C_1 protons relative to the position in the lactones.

The spectrum of **8**, Figure 1C, exhibits a typical AB part of an ABX pattern for protons 8(a) and 8(b). Inspection of models reveals that only one of the C_8 methylene protons has the correct geometry for spin–spin coupling with the C_2-*exo* proton.

In most cases the assignment of resonances corresponding to the C_3-*exo*, C_3-*endo*, and 7(a), 7(b) proton pairs was straightforward. The expected larger value of $J_{3\text{-}exo\text{-}3\text{-}endo}$ over $J_{7(a)\text{-}7(b)}$ as found by Laszlo and Schleyer was of diagnostic value here.[6] Differentiation of the chemical shifts of the individual protons of these

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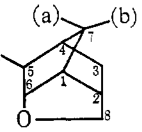
[4] (a) T. G. Traylor and A. Factor, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 36N. (b) Professor Traylor informed us of his revision of the stereochemistry originally proposed by him and Factor[4a] for the oxymercuration product of 5-norbornene-2-*endo*-carboxylic acid on Nov 20, 1964, in a seminar in this department.

[5] J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Chem. Commun.*, 359 (1966).

[6] P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, 86, 1171 (1964).

Table I. Chemical Shifts for Some Bicyclo[2.2.1]heptane Derivatives

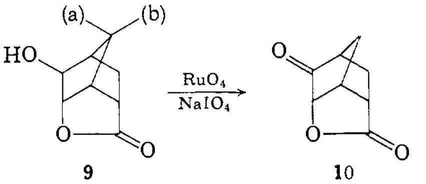


Compd	Chemical shifts, τ								
	1	6_{ex}	5_{en}	4	3_{ex}	3_{en}	2_{ex}	7(a)	7(b)
1	6.78	4.88	6.08	7.30	7.94	8.48	7.46	7.68	8.18
2	6.75	5.06	6.13	7.35	7.89	8.25	7.48	7.72	8.26
3	6.80	5.51	5.45	7.50	7.97	8.28	7.45	8.01	8.38
4	6.87	5.52	5.75	7.51	8.04	8.43	7.60	8.02	8.43
5	7.22	4.93	6.15	7.34	8.48	8.06	8.83 (CH_3)	7.64	8.12
6	7.20	5.15	6.21	7.41	8.41	8.19	8.84 (CH_3)	7.71	8.24
7[a,b]	7.48	5.95	5.91	7.76	8.21	9.10	7.76	8.15	8.53
8[a,b]	7.38	5.94	5.68	7.78	8.17	8.90	7.70	8.10	8.48

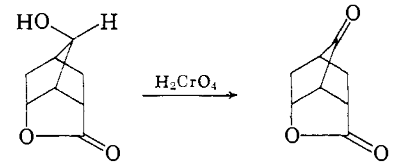
[a] The chemical shifts for the protons in the 8 positions are τ 6.53, and 6.47 for compound **7** and 6.19 and 6.34 for compound **8**. [b] Note that the numbering of the oxido methylene group as C_8 is not correct as far as nomenclature is concerned; *i.e.*, compounds **7** and **8** are tricyclo[3.2.1.1^{3,8}]nonane derivatives. However, we use the above incorrect nomenclature in order to focus on the relationship of these compounds to their norbornyl analogs.

geminal pairs was accomplished by analysis of stereospecific long-range coupling using decoupling techniques; *vide infra*. The assignments of the C_2-*exo*, C_3-*exo*, and C_4 protons were implied from previous studies which showed that the spin–spin coupling of the C_2-*exo* and C_3-*exo* protons should be relatively large, *i.e.*, 7.5–11.5 cps, while the coupling of the C_4 proton with the C_3-*exo*, C_3-*endo*, C_5-*endo*, $C_{7(a)}$, and $C_{7(b)}$ protons should be comparatively smaller.[7a,b]

Further confirmation of the above chemical shift assignments derive from the nmr spectra of compounds **9**, **10**, **11**, and **12**.



9 **10**



11 **12**

In the case of alcohol **9** the C_5-*endo* proton at 60 Mc/sec appears as a singlet peak at τ 6.30. The peak width at half-height is 2.8 cps. The C_6-*exo* proton appears as a doublet at τ 5.5. The principal coupling of the C_5-*endo* proton is with the $C_{7(b)}$ proton, while the principal coupling, 5.0 cps, for the C_6-*exo* proton is with the C_1 proton. Oxidation of **9** to **10** removes the C_5-*endo* proton absorption. The C_6-*exo* proton is shifted by +0.55 ppm. Similarly, for **11**, the $C_{7(b)}$ proton appears as a singlet with peak width at a half-height of 4 cps. The C_1 proton appears as a doublet of doublets with further small splitting ($J_{6\text{-}exo\text{-}1} \sim 5$ cps, $J_{2\text{-}exo\text{-}1} \sim 5$ cps, $J_{7(b)\text{-}1} \sim 1.5$ cps, $J_{1\text{-}4} \sim 1$ cps). Oxidation of **11** to **12** removes the $C_{7(b)}$ resonance and the C_1 resonance is essentially unshifted. The small $C_{7(b)}$-1 coupling also vanishes as expected.

Further points of interest with respect to chemical shifts as presented in Table I are (a) the $C_{7(b)}$ proton resonates at higher field than its $C_{7(a)}$ counterpart; (b) the C_3-*endo* proton occurs at higher field position than the C_3-*exo* except in the case of the C_2 methyl derivatives. Again this may be explained in terms of the anisotropy of the carbon–carbon σ bond of the methyl group; (c) reasonable consistency prevails for the relative chemical shifts of structurally related protons. Finally, since these assigned chemical shifts are largely based on spin–spin decoupling this aspect of the work will be discussed next.

Spin–Spin Decoupling. Figures 2 and 3 show expanded sweeps at 100 Mc/sec of the upfield and downfield portions of the spectrum of compound **2** in benzene solution. Relative to the spectrum of this compound shown in Figure 1, a considerable simplification of the overlapping resonances is immediately apparent. Advantage was taken of this solvent-induced separation of proton chemical shifts, and spin-decoupling experiments were performed using benzene solutions.

Based upon the discussion presented above, the chemical shifts of the C_5-*endo* and C_6-*exo* protons can be assigned with strong certainty. These two resonances were used as probes for assigning other protons in the more complicated high-field portion of the spectrum. While the chemical shift of the C_1 proton also appeared secure on the basis of arguments presented above, we nonetheless attempted an analysis based upon the assignments of Crundwell and Templeton;[2b] *i.e.*, the three downfield resonances would correspond to protons C_6-*exo*, C_5-*endo*, and C_2-*exo* with increasing field strength, respectively. This set of assignments together with the assignments of protons C_1 and C_4 to the resonances at τ 7.35 and 7.48 for **2** used in conjunction with the other assignments as listed in Table I yielded a number of unreasonable interactions such as $J_{4\text{-}3\text{-}exo} = 10.5$ cps, $J_{2\text{-}exo\text{-}4}$ and $J_{2\text{-}exo\text{-}6\text{-}exo} \cong 5$ cps. These results, which indicate that the three downfield resonances are correctly assigned (Table I), were used with spin decoupling to assign the upfield components of the spectra.

The expanded spectrum of the C_6-*exo* and C_5-*endo* protons of **2** is shown in Figure 4. Part a depicts the normal C_6-*exo* proton with coupling constants of 5

(7) (a) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963). (b) These values also agree with theoretically derived ones: J. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

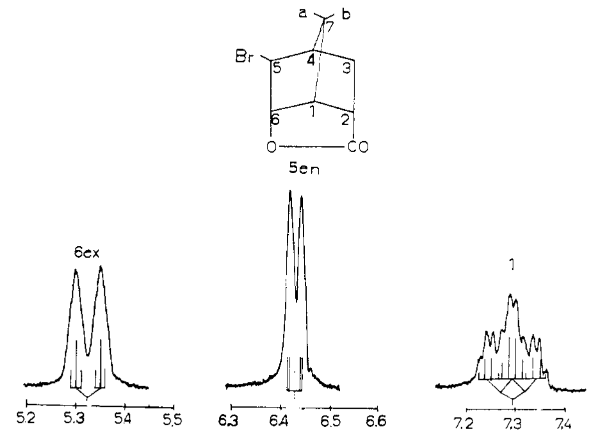


Figure 2. Downfield portion of the nmr spectrum of compound **2** in solution in $\mathrm{C_6H_6}$.

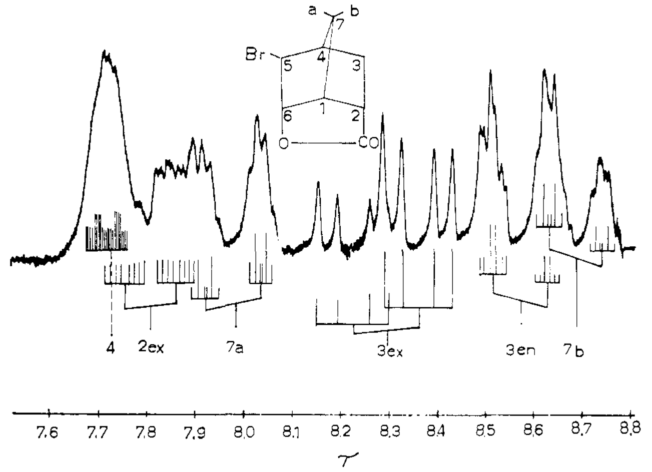


Figure 3. Upfield portion of the nmr spectrum of compound **2** in solution in $\mathrm{C_6H_6}$.

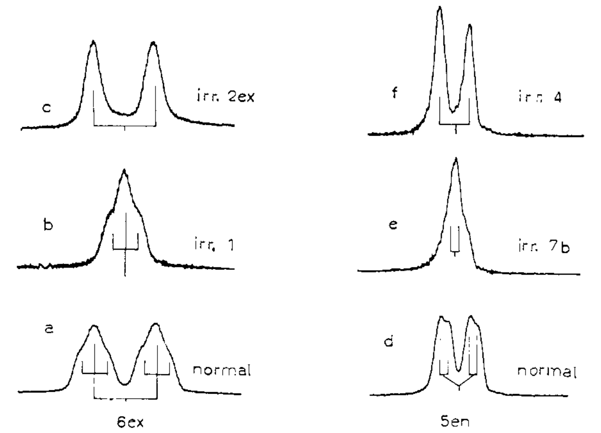


Figure 4. Expanded sweep of $\mathrm{C}_{6\text{-}exo}$ resonance of compound **2**: a, normal; b, decoupled from proton 1; c, decoupled from proton 2-*exo*; and d, normal resonance of $\mathrm{C}_{5\text{-}endo}$ of compound **2**; e, decoupled from proton 7(b); and f, decoupled from proton 4.

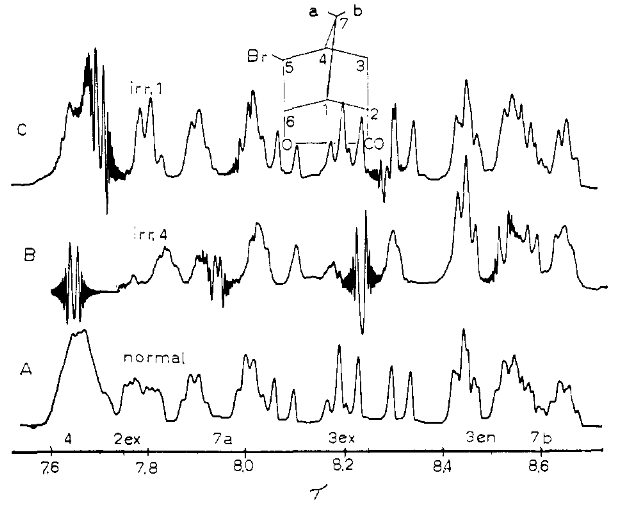


Figure 5. Upfield portion of the spectrum of compound **2** in solution in $\mathrm{C_6H_6}$: A, normal; B, decoupled from proton 4; and C, decoupled from proton 1.

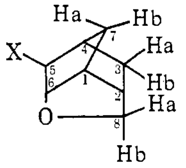
and 1 cps. Part b shows the C_6-*exo* proton absorption upon irradiation of the C_1 proton at τ 7.29. Thus, the 5-cps coupling between the C_1- and C_6-*exo* proton is established clearly. Irradiation of the C_2-*exo* proton at 7.83 cps (part c) eliminates the long-range 1.0-cps $J_{6\text{-}exo\text{-}2\text{-}exo}$, as well as $J_{6\text{-}exo\text{-}4}$. Irradiation of the C_5-*endo* proton at τ 6.43 does not alter the resonance of the C_6-*exo* proton. Hence $J_{6\text{-}exo\text{-}5\text{-}endo}$ is less than 0.3 cps. Turning to the C_5-*endo*, Figure 4, part d, shows the unperturbed resonance of the C_5-*endo* proton; it exhibits a 2.4- and a 0.5-cps coupling. Surprisingly irradiation of the C_4 proton (part b) did not remove the 2.4-cps, but rather only the 0.5-cps coupling. Assuming a zigzag geometric requirement for long-range coupling over four bonds, only the C_1 and $\mathrm{C}_{7(\mathrm{b})}$ protons bear such a relationship to the C_5-*endo* proton.

Irradiation at τ 8.69 removes the 2.4-cps coupling, as shown in part e of Figure 4. Since the chemical shift of the C_1 proton is known, and the resonance in the τ 8.7 region possesses the appearance of a member of an AB pattern, the $\mathrm{C}_{7(\mathrm{b})}$ proton is fixed. Furthermore, the chemical shift of the $\mathrm{C}_{7(\mathrm{a})}$ proton is revealed as the other part of the C_7 AB pattern. In Figure 5, are shown typical decoupled spectra obtained using the frequency sweep technique. Part A shows the upfield part of the normal spectrum of **2** in benzene solution; part B shows the spectrum obtained upon irradiation of the C_4 proton at τ 7.65. First to be noted in going from left to right is the beat note at τ 7.65 which is recorded at reduced amplitude. This indicates the position of irradiation. It is followed by a distorted region extending about 30 cps in both directions from the point of irradiation. Secondly, the appearance of the 7(a) resonance, particularly the upfield part, confirms the interaction $J_{7(\mathrm{a})\text{-}4} = 1.4$ cps. Next and more clearly, despite the beat note in the region, $J_{3\text{-}exo\text{-}4} = 3.8$ cps is confirmed. Lastly, in the upfield region both $J_{3\text{-}endo\text{-}4} = 0.8$ cps and $J_{7(\mathrm{b})\text{-}4} = 1.5$ cps are confirmed. Part C shows the spectrum resulting from irradiation of the C_1 proton at τ 7.3. The overlap of the best note and the resonance of the C_4 complicates the interpretation, but nevertheless protons C_1 and C_2 obviously interact. The resonance of the C_2-*exo* proton confirms the 4.9-cps interaction with the C_1 proton, and also a 1.4-cps coupling of proton C_1 with proton $\mathrm{C}_{7(\mathrm{a})}$.

The spectra shown in Figure 5 are meant to be representative. In order to confirm the various interactions indicated, the individual resonance under study was expanded to 50 cps and decoupled.

Geminal and vicinal coupling constants for the series of compounds are collected in Tables II and III, respectively. The omissions in Table III correspond to cases in which accurate values could not be obtained due to unresolvable overlap.

Table II. Geminal C_3, C_7, and C_8 Coupling Constants for Bicyclo[2.2.1]heptane Derivatives

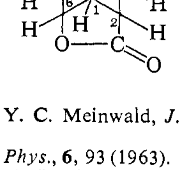


Compd	*J*, cps 3-*exo*–3-*endo*	7(a)–7(b)	8(a)–8(b)
1	13.4	11.2	. . .
2	13.2	11.4	. . .
3	13.0	11.0	. . .
4	13.4	11.0	. . .
5	13.6	11.1	. . .
6	13.6	11.1	. . .
7	13.0	10.6	8.2
8	13.2	10.6	8.2

Table III. Vicinal Coupling Constants for Some Bicyclo[2.2.1]heptane Derivatives

Compd	Coupling constant, *J*, cps 1–6-*exo*	1–2-exo	5-*endo*–4	3-*exo*–4	3-*endo*–4	3-*endo*–2-*exo*	3-*exo*–2-*exo*	7(a)–1	7(a)–4	7(b)–1	7(b)–4	8(a)–2-*exo*
1	5.4	5.0	0.5	3.6	0.5	3.0	10.2	1.6	1.8	0.6	1.5	. . .
2	5.0	4.9	0.5	3.8	0.8	2.0	10.6	1.4	1.4	1.5	1.5	. . .
3	4.6	4.6	0.8	3.8	. . .	. . .	10.5	1.5	. . .	1.6	. . .	. . .
4	4.8	5.0	1.1	4.0	. . .	. . .	10.3	1.8	. . .	1.8	. . .	. . .
5	5.1	. . .	1.0	4.7	0.7	. . .	. . .	1.4	1.6	1.6	1.6	. . .
6	5.0	. . .	0.6	4.1	0.8	. . .	. . .	1.4	1.6	1.3	1.3	. . .
7	. . .	. . .	. . .	4.7	. . .	2.6	10.8	. . .	. . .	. . .	. . .	3.6
8	5.2	4.0	1.1	. . .	. . .	2.2	10.0	1.7	1.7	1.4	1.4	3.6

Long-Range Couplings. Long-range interactions of appreciable magnitude across four saturated bonds have been observed for a number of bicycloheptane[8,9] and bicyclohexane[10,11] derivatives. These long-range interactions appear to depend primarily upon the spatial arrangements of the interacting protons, although other factors such as electronegativity and steric effects of substituents appear also to be of importance. Recent reports have shown, both theoretically and experimentally, that a near-planar zigzag arrangement of the protons is necessary for detectable interactions. With currently available techniques this amounts to about 0.3 cps. On this basis, for the structure below, proton pairs, 1–4, 1–3-*exo*, 2-*exo*–4, 6-*exo*–4, 5-*endo*–7(b), 3-*endo*–7(a), and 2-*exo*–6-*exo* are expected to exhibit long-range couplings. For similar systems, couplings of 3–4 cps[8] have been reported between protons of the C_3-*endo*–7(a), and C_5-*endo*–7(b) type, 0.7–1.8 cps for protons of the C_2-*exo*–C_6-*exo* variety,[12] and 0.8–1.4 cps for protons of the 1–4 type.[12] A weak coupling between protons C_3-*exo*–C_1 and C_6-*exo*–C_4 has been postulated,[13] but no values were reported.



In the present work values of $J_{7(a)\text{-}3\text{-}endo}$ and $J_{7(b)\text{-}5\text{-}endo}$ ranging from 1.3 to 3.2 and 1.7 to 2.6 cps, respectively, were observed. These results are similar to those reported by Musher,[9] but smaller than the values found by Meinwald and Meinwald[8] for related compounds. The published data[8,9] seem to indicate that there is a fairly large substituent effect upon these interactions particularly for compounds of the type **1–4**. However, in the system under investigation in this study, the substitution of a methyl group in the C_2-*exo* position (**5–6**) appears to increase $J_{7(a)\text{-}3\text{-}endo}$ while decreasing $J_{7(b)\text{-}5\text{-}endo}$. Furthermore, a change in the oxygenated bridge spanning the 2–6 positions produces a smaller value of $J_{7(b)\text{-}5\text{-}endo}$ than that of $J_{7(a)\text{-}3\text{-}endo}$. This seems to indicate that the long-range couplings are sensitive to changes in the planarity of the zigzag arrangement of the interacting atoms. The relatively small values of $J_{1\text{-}4}$ and $J_{2\text{-}exo}$–$J_{6\text{-}exo}$ for which the interacting protons conform to a more strictly planar arrangement than other cases, as judged by inspection of scale models, indicate that planarity of the systems may not be the dominant factor in determining the magnitude of coupling over four bonds. Furthermore, a direct relationship does not appear to exist between the size of the coupling constant and the 1,3 proton internuclear distance. Thus, inspection of scale models reveals that the C_1–C_3-*exo* proton distance in **2** is 4 A while the $C_{5\text{-}endo}$–$C_{7(b)}$ and $C_{2\text{-}exo}$–$C_{6\text{-}exo}$ distances are 4.4 A. Yet, the latter gives rise to considerably larger long-range couplings.

As shown in Table IV, a number of small long-range couplings were observed involving $C_{6\text{-}exo\text{-}4}$, $C_{1\text{-}3\text{-}exo}$, and $C_{2\text{-}exo\text{-}4}$ for compounds **1–8**. These interactions were usually less than 1 cps and were generally difficult to detect in normal spectra. Under the condition of our decoupling experiments at 60 and 100 Mc/sec, it was possible to detect long-range couplings as small as 0.5 cps.

Solvent Effects

The effect of solvent upon proton chemical shifts is well documented.[14,15] Solvent–solute interactions be-

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(8) J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

(9) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

(10) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961).

(11) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

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(13) K. Tori, K. Ano, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 9 (1966).

(14) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846

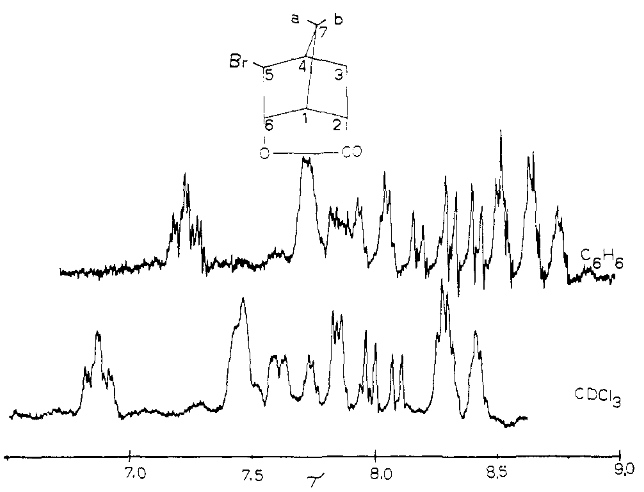
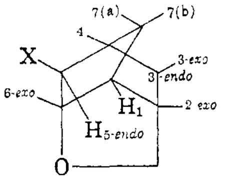


Figure 6. Upfield portion of the spectrum of compound **2** in solution in $CDCl_3$ and C_6H_6.

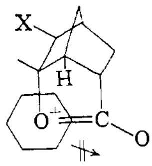
tween aromatic solvents and polar solutes have been used widely to identify conformational isomers of N-methyl amides[16] and N-methyl lactams.[17]

Table IV. Long-Range Coupling Constants for Bicyclo[2.2.1]heptane Derivatives **1–8**



	Coupling constants, *J*, cps						
Compd	6-*exo*–4	3-*exo*–1	7(b)–5-*endo*	7(a)–3-*endo*	2–6-*exo*	2–4	1–4
1	1.0	0.5	2.6	1.3	1.2	0.6	1.4
2	1.0	0.3	2.4	2.0	1.0	...	1.6
3	1.2	0.3	1.7	...	1.2	...	1.2
4	1.1	...	1.7	...	1.1	...	1.0
5		0.8	2.1	2.1	...	...	1.4
6	1.0		2.1	1.9	...	...	1.4
7				2.2			
8			1.8	2.2	1.0		

Structural information from these studies derives from the formation of a weakly associated solvent–solute collisional complex of definite stereochemical composition.[18] A consequence of the nonrandom orientation of the aromatic ring with respect to the polar solute is that nuclei near the disk-like ring are shielded relative to nuclei either remote from the aromatic ring or coplanar with it. The structure of the collisional complex is governed by a weak polar attraction of the aromatic ring for the partially positively charged amide or lactam nitrogen. A comparable interaction is conceivable for *cis* lactones of the type under study.



Connolly and McCrindle[19] have studied benzene-induced chemical shifts for a series of lactones. Table V lists dilution shifts for compounds **1**, **5**, and **7**. The shifts observed for the two lactones **1** and **5** are large, while those for the oxido compound **7** are small. Based upon the model for the benzene–lactone complex proposed above, one might predict that the C_1 proton would experience the largest upfield shift and the C_2-*exo* proton should experience a relatively smaller upfield shift. These predictions are realized and they may be further rationalized on the basis of the tendency of the benzene molecule to avoid the partially negatively charged carbonyl oxygen atom and residue closer to C_1. On the average, the C_1 proton is the more highly shielded. Also, in the assumed model, the benzene ring and the front face of the molecule, which contains the lactone ring, lie in parallel planes. The C_1 proton, therefore, is axial and lies closer to the shield portion of the aromatic. This last point offers additional proof for the correctness of the C_1 proton assignment. The simplified cation of the spectrum observed in benzene solution for compound **2** (Figure 6) relative to the *d*-chloroform solution enables a more definitive analysis of the $C_{3\text{-}endo}$–$C_{7(b)}$, $C_{3\text{-}exo}$–$C_{7(a)}$, and $C_{2\text{-}exo}$–C_4 protons. Finally, note should be made of the advantage of combining spin–spin decoupling with dilution shifts observed for solutions of polar solutes such as *cis* lactones with aromatic solvents such as benzene.

Experimental Section

The spectra were obtained using Varian HA-100 and A-60 spectrometers. Samples were run as 10% (w/v) solutions in $CDCl_3$ and C_6H_6 with tetramethylsilane as an internal refefence. Decoupling was carried out with the HA-100 spectrometer utilizing the frequency sweep technique and the V-6058-1 spin decoupler at 60 Mc/sec, which utilizes the field-sweep technique. A Hewlett-Packard audiofrequency oscillator 201C in conjunction with a Hewlett-Packard audiofrequency counter 5512A was used for frequency sweep decoupling and for the calibration of both instruments.

5-*exo*-Iodo-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (1) was prepared according to the method of Ver Nooy, *et al.*,[20] and had mp 59–60° (lit.[20] 58–59°), $\nu_{C=O}$ 1783 cm^{-1}.

5-*exo*-Bromo-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (2) was prepared according to the method of Roberts, *et al.*,[21] and had mp 65–66° (lit.[21] 64.8–65.9°), $\nu_{C=O}$ 1779 cm^{-1}.

5-*exo*-Acetoxy-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (3) was prepared according to the method of Henbest and Nichols[22] and had mp 95–96° (lit.[22] 95–96°), $\lambda^{\mathrm{CHCl_3}}$ (C=O) 5.60 and 5.75 μ (1786 and 1739 cm^{-1}).

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Table V. Solvent Shifts for Bicyclo [2.2.1] Derivatives upon Dilution with Benzene

	$\Delta(\delta C_6H_6 - \delta CDCl_3)$, ppm[a,b]										
Compd	1	2-*exo*	3-*exo*	3-*endo*	4	5-*endo*	6-*exo*	7(a)	7(b)	8(a)	8(b)
1	0.47	0.30	0.49	0.12	0.38	0.25	0.22	0.27	0.30	...	...
5	0.59	0.28(CH_3)	0.51	0.44	0.46	0.36	0.32	0.32	0.51	...	...
7	0.18	0.29	0.19	0.11	0.10	0.04	0.02	0.17	0.18	0.11	0.08

[a] 5% (w/v) solutions with TMS internal reference. [b] The changes are taken as positive when the resonances move upfield in going from $CDCl_3$ to C_6H_6

5-*exo*-Tosyloxy-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic Acid Lactone (4). To a solution of 1.2 g of alcohol **9** dissolved in the minimum amount of dry pyridine, 2.0 g of *p*-toluenesulfonyl chloride was added. The mixture was warmed on the steam bath until solution was complete, and then the reaction mixture was allowed to stand at room temperature overnight. Ice and water were added, and the mixture was extracted thoroughly with ether. The ether solution was washed with water, a dilute solution of hydrochloric acid, and then with a saturated solution of sodium bicarbonate. The solution was dried with magnesium sulfate and then concentrated to dryness *in vacuo*. The residue was recrystallized from ether–pentane to yield 2.07 g (87.5%), mp 94–95°. *Anal.* Calcd for $C_{15}H_{18}O_4S$: C, 58.58; H, 5.21. Found: C, 58.72; H, 5.21.

5-*exo*,6-*endo*-Dihydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (9) was prepared according to the method of Henbest and Nichols and had mp 155–157° (lit.[22] 160°).

5-Keto-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic Acid Lactone (10). A solution of 400 mg of ruthenium dioxide in carbon tetrachloride was prepared according to the procedure of Nakata.[23] This solution was added dropwise to a suspension in carbon tetrachloride of 5-*exo*,6-*endo*-dihydroxybicyclo[2.2.1]-heptane-2-*endo*-carboxylic acid lactone (9), 5 g, 0.033 mole, with stirring and cooling. Then, 7.0 g (0.033 mole) of sodium metaperiodate solution was added dropwise over a 1-hr period. The two-phase system was stirred at ice temperature for 4 hr, then at room temperature for 18 hr. The excess oxidizing agent was decomposed by addition of isopropyl alcohol. The layers were then separated and the aqueous layer was thoroughly extracted with chloroform. The chloroform and carbon tetrachloride solutions were combined, dried over magnesium sulfate, and concentrated to dryness *in vacuo*. The resulting thick oil, 1.5 g, was sublimed at 70–75° (0.5 mm). The resulting sublimate, 1.2 g, showed five spots on tlc. The sublimate was chromatographed upon silica gel using a column (35 × 3.5 cm) of 100 g of silica gel prepared with benzene. The column was first eluted with benzene–chloroform (1:1), then with chloroform, and finally with chloroform–methanol (97:3). The first eight fractions were oils and were put aside. Fraction 9 gave five spots in thin layer chromatography and infrared spectrum showed a strong carbonyl absorption at 1790, 1755 cm^{-1}, doublet with a weak absorption band at 1705 cm^{-1}. Fractions 10–14, the eluates of chloroform, showed mainly one spot in thin layer chromatography and the infrared spectrum of each showed strong carbonyl absorption at 1800, 1770 cm^{-1}, doublet, and a very weak absorption band at 1705 cm^{-1}. Fractions 15–17, eluates of chloroform–methanol (97:3), showed strong carbonyl absorption at 1705 cm^{-1} and relatively weak absorption in the above-mentioned doublet region. Fractions 18 and 19, chloroform–methanol (97:3) eluates, were identified as unreacted starting material by infrared comparison of authentic sample.

Fraction 11 (100 mg) deposited some crystalline material on keeping the chloroform solution for a few days. Filtration of crystals and washing with ether afforded 30 mg of compound. Recrystallization with chloroform gave quite pure crystalline sample, mp 192–196°, showing strong carbonyl absorption in the infrared at 1800, 1770 cm^{-1}, doublet with no hydroxyl absorption band. This also showed a single spot in thin layer chromatogram using a chloroform–methanol (97:3) system as given before. The molecular weight of 152 was confirmed by a high-resolution mass spectrum.

5-*exo*-Iodo-6-*endo*,2-*exo*-methylbicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (5) was prepared according to the method of Meek and Trapp[24] and had mp 85–86° (lit.[24] 83–86°), $\nu_{C=O}$ 1780 cm^{-1}.

5-*exo*-Bromo-6-*endo*,2-*exo*-methylbicyclo[2.2.1]heptane-2-*endo*-carboxylic acid lactone (6) was prepared according to the method of Meek and Trapp[24] and had mp 74–75° (lit.[24] 74–75°), $\nu_{C=O}$ 1790 cm^{-1}.

4-*exo*-Tosyloxy-6-oxatricyclo[3.2.1.1^{3,8}]nonane (7). A solution of 4.5 g of 4-*exo*-hydroxy-6-oxatricyclo[3.2.1.1^{3,8}]nonane and 9 g of *p*-toluenesulfonyl chloride in 12 ml of very dry pyridine was stored overnight at room temperature. After processing the reaction mixture in the usual way, the crude product was recrystallized from ether–pentane giving 7.6 g (77%), mp 86–87°. *Anal.* Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16. Found: C, 61.50; H, 6.27.

4-*exo*-Acetoxy-6-oxatricyclo[3.2.1.1^{3,8}]nonane (8) was prepared according to the method of Henbest and Nichols[22] and had mp 52–53° (lit.[22] 50–52°).

7(a),6-*endo*-Dihydroxybicyclo[2.2.1]-2-*endo*-carboxylic Acid Lactone (11). A three-necked, 300-ml, round-bottomed flask was equipped with an efficient stirrer and a condenser to which was attached a calcium chloride drying tube. Dried lead tetraacetate (20 g, 0.044 mole), dry $CaCO_3$ (12 g), and 200 ml of dry benzene were introduced into the flask, and the mixture was stirred at reflux for approximately 30 min. *exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid[25] (3 g, 0.022 mole) was then added after which refluxing was maintained for an additional 48 hr.

The solution was allowed to cool to room temperature and was then filtered through Celite. The filtrate was diluted with ether, washed with a small amount of saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated *in vacuo*. Chromatography of the resulting yellow oil (2.5 g) on 100 g of silica gel (Baker) [elution with ether–benzene (1:4)] afforded 1.5 g (35%) of 7(a)-acetoxy-6-*endo*-hydroxybicyclo[2.2.1]-2-*endo*-carboxylic acid lactone. Two recrystallizations from acetone–pentane gave an analytical sample, mp 113–114°, $\nu_{C=O}$ 1735 and 1775 cm^{-1}. *Anal.* Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.07; H, 6.17.

The acetoxy lactone (2.09 g) and 4.5 g of potassium carbonate were refluxed in a mixture of 40 ml of water and 60 ml of methanol for 4 hr. At the end of this time, the water and methanol were removed using a rotary evaporator. The residue was dissolved in 30 ml of water and extracted twice with ethyl acetate to remove any of the unreacted acetate. The aqueous layer was acidified by dropwise addition of 50% H_2SO_4, after which the solution was continuously extracted with ethyl acetate for 36 hr.

The ethyl acetate solution was washed with three portions of saturated aqueous $NaHCO_3$ solution, dried over $MgSO_4$, and concentrated to yield 0.914 g of crude 9(a),6-*endo*-dihydroxybicyclo-[2.2.1]-2-*endo*-carboxylic acid lactone. Continuous extraction of the $NaHCO_3$ combined washings for 24 hr afforded an additional 0.30 g of crude product, total yield 74%. Two recrystallizations from acetone–ligroin gave an analytical sample, mp 203–204°, ν_{O-H} 3600 and 3440 cm^{-1}; $\nu_{C=O}$ 1775 cm^{-1}. *Anal.* Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54. Found: C, 62.13; H, 6.60.

7-Keto-6-*endo*-hydroxybicyclo[2.2.1]-2-*endo*-carboxylic Acid Lactone (12). A solution of 2.4 g of 7(a),6-*endo*-dihydroxybicyclo-[2.2.1]-2-*endo*-carboxylic acid lactone in 8.2 ml of water was maintained at 20° for a period of 45 min while 7.4 ml of 6 *N* chromic acid was added dropwise with stirring. After an additional 10 hr of stirring, 0.3 ml of 2-propanol was introduced to decompose any excess chromic acid and the solution was extracted several times with ethyl acetate. The combined extracts were dried over magnesium sulfate and concentrated at room temperature on a rotary evaporator. Elution chromatography of the crude product mixture (2.4 g) on 140 g of silica gel (Baker) with ether–benzene (1:4) afforded initially 0.67 g (27%) of crude 7-keto-6-*endo*-hydroxybicyclo[2.2.1]-2-*endo*-carboxylic acid lactone followed immediately by approximately 0.5 g of unreacted starting alcohol. A pure

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sample of the ketone was obtained after three recrystallizations from acetone–ligroin, mp 194–196°, $\nu_{C=O}$ 1775 cm^{-1}.

Treatment of the ketone with 2,4-dinitrophenylhydrazine dissolved in a mixture of phosphoric acid and ethanol afforded the corresponding hydrazone derivative, mp 262–263° dec, $\nu_{C=O}$ 1775 cm^{-1}. *Anal.* Calcd for $C_{14}H_{12}N_4O_6$: C, 50.60; H, 3.64; N, 16.86. Found: C, 50.37; H, 3.61; N, 16.81.

A thioketal derivative was prepared by the method of Fieser,[26] mp 134°. *Anal.* Calcd for $C_{10}H_{12}O_2S_2$: C, 52.60; H, 5.30. Found: C, 52.46; H, 5.18.

4-*exo*-Tosyloxy-6-oxatricyclo[3.2.1.1^{3,8}]nonane (7). 4-*exo*-Hydroxy-6-oxatricyclo[3.2.1.1^{3,8}]nonane,[22] 4.5 g, and *p*-toluenesulfonyl chloride, 9.0 g, were dissolved in 12 ml of dry pyridine. The reaction mixture was allowed to stand at room temperature overnight. At the end of this time, ice was added, and the precipitate which deposited was collected and washed thoroughly with water. After drying at room temperature, the crude crystalline product was recrystallized from ether–pentane, 7.6 g (76%), mp 86–87°. *Anal.* Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16. Found: C, 61.50; H, 6.27.

Acknowledgment. Discussions of the spectra of the compounds reported in this paper with Dr. B. Franzus of Esso Co., Linden, N. J., and with D. Dreyer of the U. S. Department of Agriculture, Pasadena, Calif., are gratefully acknowledged. P. von R. Schleyer, Princeton University, also contributed critical discussion of much value.

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New Heteroaromatic Compounds. XXV.[1] Studies of Salt Formation in Boron Oxyacids by ^{11}B Nuclear Magnetic Resonance

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Abstract: The ^{11}B nmr spectra of several compounds containing the group BOH have been measured in neutral and alkaline solution. Salt formation shifts the ^{11}B resonance far upfield (>13 ppm) in the case of boric acid and simple arylboronic acids, the line width remaining unchanged or becoming narrower; this indicates that such compounds behave as Lewis acids toward base. The B–OH derivatives of several borazaro[3] compounds are quite different in this respect, salt formation leading to small downfield shifts (3–7 ppm) in the ^{11}B resonance, and also to extreme broadening of the lines. Here salt formation must involve proton transfer, in agreement with earlier conclusions[3] and implying that compounds of this type are indeed aromatic.

Trivalent boron compounds are well known to behave as Lewis acids, combining with base to form coordination compounds (*e.g.*, $H_3N \rightarrow BF_3$); an ambiguity therefore exists in the case of compounds which contain the grouping BOH and so could act either as protic acids, or as Lewis acids, toward base. Thus hydroxide ion could either deprotonate such a compound to give a planar ion, R_2BO^- (eq 1), or it could add to boron to form an ion in which boron is now quadricovalent and tetrahedral (eq 2).

$$R_2BOH + OH^- \longrightarrow R_2BO^- + H_2O \qquad (1)$$

$$R_2BOH + OH^- \longrightarrow R_2B^-(OH)_2 \qquad (2)$$

The Raman spectrum of boric acid in alkali indicates that it behaves as a Lewis acid,[4] forming the ion $B(OH)_4^-$, and the available evidence, while scanty, seems to suggest[5] that arylboronic acids act likewise. On the other hand, B–OH derivatives of borazaro compounds[3] seem to behave as protic acids, judging by comparisons of their ultraviolet spectra in neutral and alkaline solution; this difference has been attributed to the aromaticity of the boron-containing rings in compounds of this kind, the boron being consequently reluctant to adopt a tetrahedral geometry.

It seemed to us that ^{11}B nmr spectroscopy could provide a definite distinction between the two possible modes of salt formation. Conversion of trivalent planar boron to quadrivalent tetrahedral boron would be expected[6] to produce a large upfield shift in the ^{11}B resonance, due to the greater shielding of boron in compounds where four pairs of valence electrons surround the boron atom; the available evidence supports this conclusion. Thus the ^{11}B chemical shifts (relative to trimethyl borate) of quadrivalent boron compounds almost all lie above 7 ppm, while compounds with lower chemical shifts contain planar trivalent boron.[7] Salt formation according to eq 2 should therefore lead to a large upfield shift of the ^{11}B resonance, while salt formation according to eq 1 should produce a much smaller change.

Conversion of boric acid to borate ion is indeed accompanied[7] by a large upfield shift (17.5 ppm) in the ^{11}B resonance, as would be expected if the ion has the tetra-

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[1] Part XXIV: M. J. S. Dewar and J. L. Von Rosenberg, Jr., *J. Am. Chem. Soc.*, **88**, 358 (1966).

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