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Carbon-13 NMR and IR Spectroscopic Studies on Some 7-Oxabicyclo[2.2.1]heptanes and -heptenes. n-π Interaction and Hydrogen Bonding

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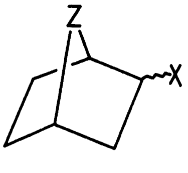
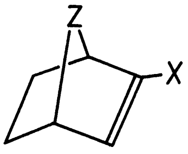
The ^{13}C NMR spectra of diastereomeric pairs of the title compounds together with some tetrahydrofurans were examined and the chemical shifts were compared with those for the corresponding bicyclo[2.2.1]heptanes and -heptenes. The intramolecular interaction between the n-orbital of an oxygen atom and the π-orbital of an olefinic bond was found in 2-methylene-7-oxabicyclo[2.2.1]heptane. Intramolecular hydrogen bonding between the 7-oxygen and the hydroxyl group occurs in *exo*-7-oxabicyclo[2.2.1]heptane-2-methanol.

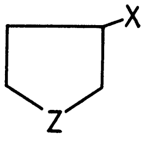
The ^{13}C NMR spectra of substituted 7-oxabicyclo[2.2.1]heptanes (**1**—**6**) and -heptenes (**7** and **8**) and some tetrahydrofurans (**9** and **10**) were examined. The chemical shifts were compared with those for analogous carbocyclic compounds. Some intramolecular interactions were expected between the oxygen atom introduced at the 7-position of a bicyclo[2.2.1]heptane skeleton and the functional group in the molecule. The hydrogen bonding in 7-oxabicyclo[2.2.1]heptane-2-methanol (**4**) and the n-π interaction in 2-methylene-7-oxabicyclo[2.2.1]heptane (**6**) were also studied.



	X	Z
1:	H	O
2:	CH_3	O
3:	$COOCH_3$	O
4:	CH_2OH	O
5:	CH_2OCOCH_3	O
6:	$=CH_2$	O
11:	$=CH_2$	CH_2
13:	CH_3	CH_2



7:	H	O
8:	CH_3	O



9:	$=CH_2$	O
10:	CH_2OH	O
12:	$=CH_2$	CH_2
14:	CH_3	O
15:	CH_3	CH_2

Results and Discussion

The new compounds employed in this study were **6** and 2-methyl-7-oxabicyclo[2.2.1]hept-2-ene (**8**). The former was prepared by the thermal decomposition of 7-oxabicyclo[2.2.1]heptane-2-methanol acetate (**5**) over Pyrex chips at 450 °C and the latter was obtained by a Diels-Alder reaction of 3-methylfuran with ethylene.

Table 1 summarized the ^{13}C chemical shifts of **1**—**10**. The introduction of an oxygen atom to the 7-position of a bicyclo[2.2.1]heptane skeleton caused a downfield shift of 38 ppm for the carbon α to the oxygen atom,[1)] but no appreciable shift was observed on the carbon β to the oxygen atom. The γ carbons, which are the carbons of the substituents attached to the 7-oxabicyclo[2.2.1]heptane skeleton, showed small upfield shifts compared to those for the corresponding bicyclo[2.2.1]heptanes.[1)] Considerable shielding differences were observed in two diastereomeric 7-oxabicyclo[2.2.1]heptane derivatives. The signals for C2, C6, and the carbon of the substituent attached to the ring skeleton of endo-isomers always appeared at higher fields than those for exo-isomers. The resonances for C2, C6, and the methyl group of *endo*-2-methyl-7-oxabicyclo[2.2.1]heptane (*endo*-**2**) were shielded by 4.0, 6.1 and 5.3 ppm, respectively, compared to those for *exo*-**2**. The signals for other ring carbons of endo-isomers did not always appear at higher fields than those for exo-isomers. No significant shielding difference between the two diastereoisomers was found for carbons which were not directly bonded to the bicyclic skeleton. The shielding difference of the methyls between stereoisomeric methoxycarbonyl groups was 0.2 ppm and that for the acetoxyl groups was only 0.1 ppm. The resonances for the methyl carbons of diastereomers **2** appeared at δ 21.3 (exo) and 16.0 (endo). These values are comparable with those of the equatorial and axial methyls on a cyclohexane ring in a chair conformation.[2)]

In the 7-oxabicyclo[2.2.1]hept-2-ene series (**7** and **8**), the introduction of a methyl group into an sp^2 carbon causes an upfield shift of the other sp^2 carbon compared to the parent compound. The methyl carbon signal for the sp^2 carbon also appeared at a higher field than that for the sp^3 carbon of compound **2**, as experienced on bicyclo[2.2.1]hept-2-enes.[1)]

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Table 1. ^{13}C Chemical Shifts of 7-Oxabicyclo[2.2.1]heptanes, -heptenes and Related Compounds[a)]

Compound		Chemical shift (δ) Ring C1	C2	C3	C4	C5	C6	Substituent C8	C9	C10
7-oxabicyclo[2.2.1]heptane										
Parent (**1**)		76.1	30.3	30.3	76.1	30.3	30.3			
2-Methyl- (**2**)	exo	81.9	40.0	37.8	76.6	29.7	29.7	21.3		
	endo	80.2	36.0	39.1	77.5	31.1	23.6	16.0		
-2-carboxylic acid methyl ester (**3**)	exo	78.8	51.8	48.0	76.3	34.5	29.5	173.8	29.7	
	endo	77.7	51.7	47.9	77.5	33.3	26.4	172.8	29.9	
-2-methanol (**4**)	exo	77.9	45.8	34.0	76.3	30.0	29.5	65.0		
	endo	78.3	44.2	34.3	77.0	30.6	24.2	63.6		
-2-methanol acetate (**5**)	exo	75.5	42.5	34.1	76.0	29.9	29.3	66.5	170.7	20.9
	endo	77.9	40.6	34.4	76.8	30.5	24.3	65.4	170.5	20.8
2-Methylene- (**6**)		80.6	150.9	39.1	77.2	29.5	30.6	102.5		
7-Oxabicyclo[2.2.1]hept-2-ene										
Parent (**7**)		77.7	134.6	134.6	77.7	23.4	23.4			
2-Methyl- (**8**)		82.1	142.6	128.2	78.8	26.0	23.3	12.3		
3-Methylenetetrahydrofuran (**9**)			71.0	148.1	32.9	68.6		105.5		
Tetrahydrofuran-3-methanol (**10**)			70.6	41.5	28.7	67.8		64.0		

a) The carbon numbering is as follows:

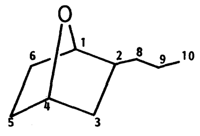
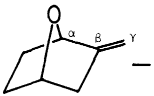
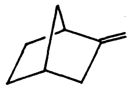
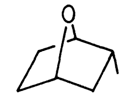
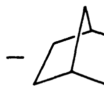
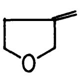
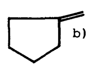
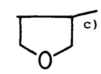
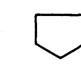


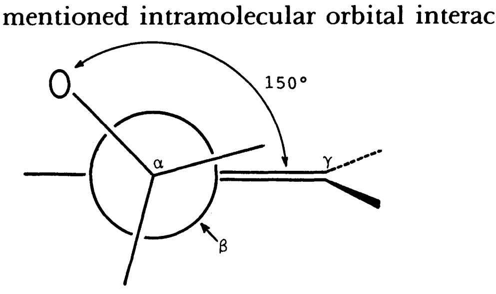
Table 2. Differences in β- and γ-Carbon Resonances between Unsaturated Compounds and between the Corresponding Saturated Ones (ppm)

Unsaturated compound	β	γ	Saturated compound	β	γ
 **6** –  **11**	−4.7	+0.7	 endo-**2** –  endo-**13**	+1.5	−1.5
 **9** –  **12**	−0.5	+0.6	 **14** –  **15**	−1.5	−3.0

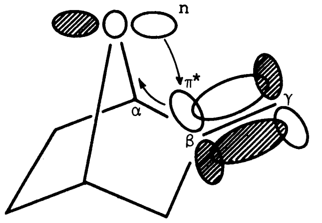
The chemical shifts were taken from[a)] Ref. 1. b) S. H. Grover and J. B. Stothers, *Can. J. Chem.*, **53**, 589 (1975). c) E. L. Eliel, V. S. Rao and K. M. Pietrusiewicz, *Org. Magn. Reson.*, **12**, 461 (1979). d) M. Christl, H. J. Reich and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 3463 (1971).

The ^{13}C chemical shifts for sp^2 carbons of **6** and 3-methylenetetrahydrofuran (**9**) were compared with those for the corresponding hydrocarbons (Table 2). The shielding differences, thus obtained, were compared with those for saturated compounds. The Δδ value for the carbon β to the oxygen atom between *endo*-**2** or 3-methyltetrahydrofuran (**14**) and the corresponding hydrocarbons (**13** or **15**) are +1.5 or −1.5, respectively, and that for the carbon γ to the oxygen atom being −1.5 or −3.0 ppm, respectively. On the other hand, the Δδ value between **6** or **9** and the corresponding hydrocarbon (**11** or **12**) are −4.7 and −0.5 for the β-carbon, and +0.7 and 0.6 ppm for the γ-carbon, respectively. The β carbon resonances for the unsaturated system which contains an oxygen atom were located at a higher field than those for the corresponding hydrocarbons. The γ carbon resonances, on the contrary, moved downfield compared to those for the corresponding hydrocarbons.

Molecular orbital interactions have been found between a nonbonding orbital of an oxygen and the π-orbital of the olefinic bond in a series of cyclic allylic ethers and alcohols in which the oxygen is placed at the anticlinal position with respect to the double bond.[3)] The Newman projection formula, viewed from C1 along the C1-C2 bond of **6** indicates that the dihedral angle between the O7-C1 bond and the C2-C8 (*exo*-methylene carbon) double bond is approximately 150°. This suggests the presence of the previously mentioned intramolecular orbital interac-



tion in this compound. The through-space interaction between the π-type n-orbital in the oxygen atom and the vacant p-π^*-orbital results in a decrease in the electron density at the oxygen atom. The enhanced effective electronegativity of the oxygen atom, therefore, induces a homoconjugative through-bond interaction between the C-O σ-orbital and the p-π-orbital.



The electron delocalization of the π-orbital by such through-space and through-bond interaction results in an upfield shift of the β carbon resonances and a downfield shift of γ carbon resonances. The shielding differences observed in a series of **9** infer the presence of an analogous orbital interaction.

The stereochemistry of the hydrogenation of 2-substituted 5-methylene-1,3-dioxanes over Group-VIII transition metals made a sharp contrast with that of 4-substituted 1-methylenecyclohexanes.[3b] A high cis selectivity was observed with the former, while the latter exhibited a wide variety of diastereomeric product distributions. The stereochemistry of the reaction was interpreted in terms of the n-π orbital interaction. The hydrogenation of **6** and 2-methylenebicyclo[2.2.1]heptane (**11**) was performed over Group-VIII noblemetal catalysts in order to examine the stereochemistry of the reaction. In this case, the steric factor was always predominant, giving more than 58% endo-isomer (Table 3). The introduction of an oxygen atom into the 7-position of the bicyclo[2.2.1]heptane skeleton resulted in an increase in the attack of the hydrogen from the endo side, which is the opposite side of the oxygen atom. This also supports the presence of the n-π orbital interaction in **6**.[3b]

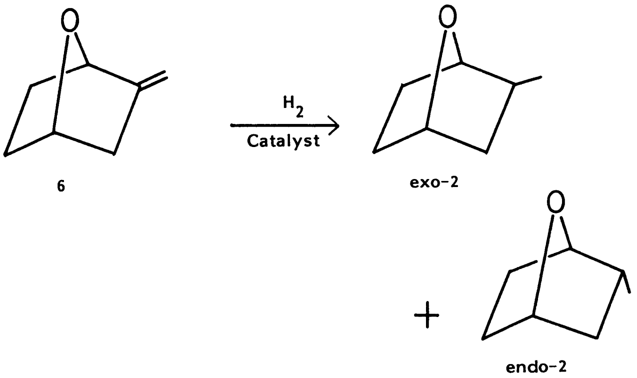


Table 3. Stereochemistry on the Hydrogenation of **6** and **11**

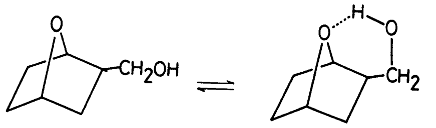
Catalyst	Starting olefin	
	6	**11**
	Product (*endo*/%)	
Ru-black	71	74
Rh-black	69	73
Pd-black	82	90
Os-black	70	79
Ir-black	62	77
Pt-black	58	84

Table 4. The OH Stretching Absorption of Some Hydroxylic Compounds (cm^{-1})

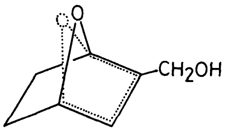
Compound	ν_{OH}	ε	$\Delta\nu_{1/2}$ [a)]	$\Delta\nu$ [b)]
10	3639	86	22	
	3610	sh [c)]	—	29
exo-**4**	3654	55	24	
	3533	17	84	121
endo-**4**	3653	91	22	

a) Half-band width. b) Separation of free and bonded hydroxyl bands. c) Shoulder.

No evidence of intramolecular hydrogen bonding has been found in either *endo*- or *exo*-**4** by proton NMR spectroscopy.[4] In this work, the ν_{OH} vibration was carefully examined in these two diastereomers together with tetrahydrofuran-2-methanol (**10**) which corresponds to the partial structure of **4**. The spectra were obtained under such conditions as suppress intermolecular hydrogen bonding (in carbon tetrachloride at 4×10^{-3} M). Table 4 shows the infrared absorption frequencies in a hydroxyl stretching region. Alcohol **10** showed absorption for a free hydroxyl group at 3639 cm^{-1} and a bonded hydroxyl group at 3610 cm^{-1} as a shoulder of the main absorption. The absorption of *endo*-**4** at 3653 cm^{-1} could be associated with a free hydroxyl group, while the absorptions of *exo*-**4** appeared at 3654 and 3533 cm^{-1} corresponded to a free and a bonded hydroxyl group, respectively. Since the apparent areas of the absorption of both bonded and free hydroxyl bands of *exo*-**4** are roughly equal, the hydrogen bonded conformers and the alternative seem to be of equal population. Such an equilibrium between the bonded and free hydroxyl species in the system may make it difficult to determine the hydrogen bonding in an NMR time scale. Essentially, free pseudo-rotation occurs between the half-chair (C_2) and the envelope (C_s) conformation of the tetrahydrofuran skeleton of **10**, with the former form slightly preferred.[5] In some conformations intramolecular hydrogen-bond formation is possible, but the bonded conformation is insufficiently stabilized by the formation of the hydrogen bond. Consequently, only a very weak absorption of a bonded hydroxyl appears. As expected, no hydrogen bond is formed in *endo*-**4** in which the C1-O7 and C2-CH_2OH bonds are in opposite direction. The tetrahydrofuran ring in **4** has a fixed C_s form with the oxygen atom out of the five-membered ring plane.[5] The structural



analysis of tetrahydrofuran and 7-oxabicyclo[2.2.1]heptane homologs by X-ray diffraction,[6] electron diffraction[7] and microwave analysis[8] suggests that the degree of puckering of the tetrahydrofuran moiety of 7-oxabicyclo[2.2.1]heptane skeleton is a little greater than that of tetrahydrofuran itself. Consequently, the distance between O7 and the hydroxyl oxygen becomes smaller than that for **10**. This also supports the formation of stronger hydrogen bonding in the bicyclic system. Using either the equation derived by Kuhn[9] or the modified equation by Brutcher and Bauer[10] relating the $\Delta\nu$ to the hydrogen bonded distance, the distance between O7 and hydroxyl hydrogen in *exo*-**4** was estimated to be 1.28 or 1.74 Å, respectively. Since Ouellette et al. reported that the minimum O7-hydroxyl oxygen distance is 2.6 Å from the examination of the model,[4] the distance between the hydroxyl hydrogen and O7 was estimated to be 1.64 Å by assuming that the distance between the hydrogen and the oxygen of a hydroxyl group is 0.96 Å. This is in fair agreement with the results obtained in the present work. If it is possible to apply the enthalpy vs. shift difference of the ν_{OH} band relationship ($-\Delta H$ (kcal mol^{-1})$=0.016\ \Delta\nu_{OH}+0.63$)[11] to this system, $-\Delta H$ between the free and bonded species is then 10.7 kJ mol^{-1}. In this connection, $-\Delta H$ of the hydrogen bonding between benzyl alcohol and dioxane is 8.8 kJ mol^{-1}.[12]



Experimental

Materials. Diels-Alder reaction of furan and methyl acrylate by refluxing for 5 weeks followed by hydrogenation over Pd-C gave 7-oxabicyclo[2.2.1]heptane-2-carboxylic acid methyl ester (**3**) in a yield of 19%.[13] The two diastereomers of **3** were separated by fractional distillation. Ester **3** was reduced with LAH in ether to give **4**, (72%)[13] which was treated with acetic anhydride in pyridine to give **5** (70%).[13] The tosylate of **4** was reduced with LAH to give **2** (60%).[13] 1,4-Cyclohexanediol was heated over Al_2O_3 to give 7-oxabicyclo[2.2.1]heptane (**1**) (45%).[14] Diels-Alder reaction of furan with ethylene at 155 °C for 6 h gave 7-oxabicyclo[2.2.1]hept-2-ene (**7**) (5%).[15] A Wittig reaction of tetrahydrofuran-3-one and of bicyclo[2.2.1]heptan-2-one with methyltriphenylphosphonium bromide gave **9** (65%)[16] and **11** (65%),[17] respectively. Tetrahydrofuran-3-carboxylate was reduced with LAH to give **10** (65%).[18]

2-Methylene-7-oxabicyclo[2.2.1]heptane (6). The acetate (18 g, 0.106 mol) was passed through a heated (440—450 °C) Pyrex tube (50 cm×10 mm) packed with Pyrex chips. The crude mixture was digested with pentane which was washed with a saturated $NaHCO_3$ solution and a saturated NaCl solution and then dried over $CaCl_2$. Distillation yielded **6** (3.2 g, 0.029 mol, 27%), bp 37 °C/40 mmHg. Found: C, 76.56; H, 9.58%. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15%. ^1H NMR (100 MHz, $CDCl_3$) δ=1.49—2.16 (6H), 4.73 (3H, m), 4.89 (1H, brs).

2-Methyl-7-oxabicyclo[2.2.1]hept-2-ene (8). After the mixture of 3-methylfuran (20 g, 0.244 mol) and ethylene (40 kg cm^{-2}) was stirred in a 200-ml autoclave at 150 °C for 24 h, the crude product was extracted with pentane. Distillation gave **8** (2 g, 0.018 mol, 7%), bp 115—120 °C. Found: C, 76.53; H, 9.53%. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15%. ^1H NMR (100 MHz, $CDCl_3$) δ=1.17 (2H, m), 1.27 (2H, m), 1.80 (3H, d, J=1.4 Hz), 4.69 (1H, brd, J=3.7 Hz), 4.87 (1H, brs), and 5.75 (1H, brs).

Catalytic Hydrogenation. The substrate (0.5 mmol) and the catalyst (5 mg) in ethanol (3 ml) were stirred with hydrogen at atmospheric pressure and room temperature. After the reaction was completed the catalyst was removed by the centrifugal method and the mixture was analyzed by GLC.

Spectra. ^1H NMR spectra were obtained with a Jeol FX-100 spectrometer and ^{13}C NMR spectra were obtained with a Jeol MH-100 and FX-100 spectrometers in an FT-mode using TMS as an internal standard. $CDCl_3$ was used as a solvent. IR spectra were measured with a Hitachi model 260-10 spectrometer using a 30-mm optical-length quartz cell. CCl_4 was used as a solvent.

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