

## $n-\pi$ Interaction between an Oxygen Lone Pair and $\pi$ -Electrons in Cyclic Allylic Alcohols and Ethers; Carbon-13 Nuclear Magnetic Resonance Spectra, Catalytic Hydrogenation, and CNDO/2 Calculations

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In order to elucidate the  $n-\pi$  interaction between an oxygen lone pair and  $\pi$ -electrons,  $^{13}\text{C}$  n.m.r. spectra have been obtained for several cyclic allylic alcohols and ethers. The chemical shifts for  $sp^2$ -carbons of these compounds are compared with those of the corresponding hydrocarbons. The chemical shift differences ( $\Delta\delta$ ) between compounds in which the oxygen atoms are placed at an anticlinal position with respect to the double bond and the corresponding hydrocarbons are different from those of a set of compounds, the oxygens of which are synperiplanar. We have also studied catalytic hydrogenation of and CNDO/2 calculations for these cyclic allylic compounds. These results are discussed in terms of homoconjugation.

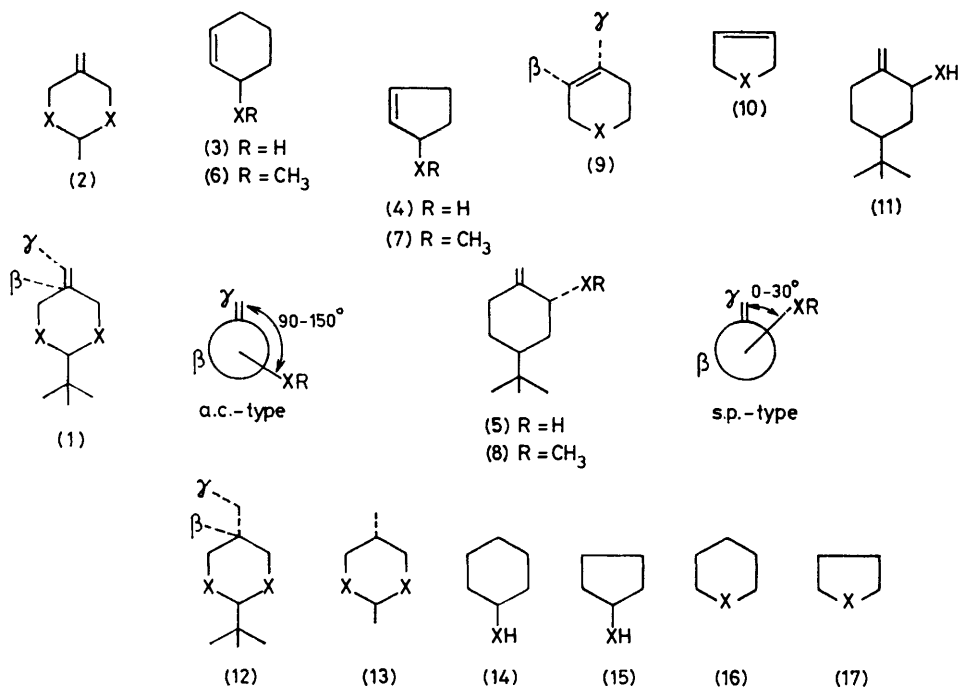
RECENTLY photoelectron (p.e.) spectroscopy has proved to be extremely useful in evaluating the interactions of non-adjacent groups in the ground state, assuming the validity of Koopmans' theorem.<sup>1</sup> Heilbronner *et al.*<sup>2</sup> have described interactions between  $\pi$ -electrons ( $\pi-\pi$  interactions) in conjugated or non-conjugated systems. Interactions between lone pair and  $\pi$ -electrons ( $n-\pi$  interactions),<sup>3</sup> and between lone pair electrons ( $n-n$  interactions)<sup>4</sup> have been also investigated for various cases.

On the other hand, much effort has been spent in elucidating the  $\pi$ -charge density dependence of carbon-13 chemical shifts in unsaturated compounds.<sup>5-7</sup> The results support the original finding that shielding is connected with high charge density and indicates a simple

linear relation of the type<sup>5</sup>  $\Delta\sigma = K\Delta Q$  where  $\Delta\sigma$  is the difference in shielding,  $\Delta Q$  is the charge density difference, and  $K$  is a proportionality constant.

As the intramolecular orbital interactions which have been examined thoroughly by p.e. spectroscopy contain intraorbital charge transfer interactions,  $^{13}\text{C}$  n.m.r. chemical shifts which sharply reflect molecular electronic structures serve as a useful tool for evaluating the properties of such interactions.

Morishima *et al.* have reported structural effects on homoconjugative<sup>8</sup> and bishomoconjugative<sup>9</sup> interactions between a nitrogen lone pair and  $\pi$ -electrons with the aid of  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. measurements. However, studies on the non-bonded interaction between an oxygen lone pair and non-adjacent  $\pi$ -electrons are few.



(1a) - (17a) X = O

(1b) - (5b), (9b) - (17b) X = CH<sub>2</sub>

We have attempted to examine the  $n_{\text{O}}-\pi_{\text{CC}}$  interaction of several cyclic allylic alcohols and ethers by  $^{13}\text{C}$  n.m.r. spectroscopy, since p.e. spectra of some allylic ethers indicate that the double bond is undoubtedly influenced by the presence of oxygens.<sup>10</sup> Two types of substrates were selected; one is a series of compounds in which the oxygen is anticlinal (a.c.) and the other in which it is synperiplanar (s.p.) with respect to the double bond. In the series of compounds, 5-methylene-1,3-dioxans are particularly interesting because the two oxygens are in a symmetrical position at the  $\sigma$  face containing the  $\pi$ -orbital, and catalytic hydrogenation indicates exclusively high stereoselectivity compared with that of the corresponding methylenecyclohexanes.<sup>11</sup> A  $^{13}\text{C}$  n.m.r. study, particularly of the chemical shifts of the  $sp^2$ -carbons of allylic compounds and corresponding unsaturated hydrocarbons, together with a set of saturated compounds, was carried out.

The stereochemistry of the catalytic hydrogenation of 2-alkyl-5-methylene-1,3-dioxans (1a) and (2a), and the corresponding methylenecyclohexanes (1b) and (2b), is discussed in relation to non-adjacent  $n-\pi$  interactions. Moreover, CNDO/2 calculations of 5-methylene-1,3-dioxan (18a), methylenecyclohexane (18b), 1-hydroxy-2-methylenecyclohexane (19a), and 1-methyl-2-methylenecyclohexane (19b) were carried out in order to evaluate the electron density of the  $sp^2$ -carbons.

## RESULTS

(1) *Carbon-13 N.m.r. study.*—The chemical shift differences ( $\Delta\delta$ ) between resonances for  $sp^2$ -carbons of cyclic allylic ethers and alcohols (1a)—(8a) in which the oxygen atoms are placed in an a.c. position with respect to the double bond, and those of the corresponding unsaturated hydrocarbons (1b)—(5b), were obtained. The  $\Delta\delta$  values thus obtained are compared with those of a set of saturated compounds (12)—(17). These values are tabulated in Table 1.

TABLE 1

Chemical shift differences ( $\Delta\delta$ ) of  $\beta$ - and  $\gamma$ -carbons in a.c.-type unsaturated compounds and corresponding saturated compounds

Unsaturated compounds	$\Delta\delta$	
	$\beta$	$\gamma$
(1a) — (1b)	-10.0	+3.5
(2a) — (2b)	-10.2	+3.2
(3a) — (3b)	-3.6	+3.3
(4a) — (4b)	-2.9	+4.2
(5a) — (5b)	-3.0	+3.1
(6a) — (3b)	-2.3	+2.1
(7a) — (4b)	-1.9	+1.4
(8a) — (5b)	-6.1	+4.8
Saturated compounds	$\Delta\delta$	
	$\beta$	$\gamma$
(12a) — (12b)	-2.9	-10.3
(13a) — (13b)	-1.9	-11.2
(14a) — (14b)	-0.6	-2.1
(15a) — (15b)	+0.2	-2.0

The  $\Delta\delta$  values for  $\beta$ - and  $\gamma$ -carbons of *trans*-5-methyl-2-*t*-butyl-1,3-dioxan (12a), *trans*-2,5-dimethyl-1,3-dioxan (13a), and the corresponding cyclohexanes (12b) and (13b), whose alkyl substituents take an exclusively equatorial orientation,

are -2.9 to -1.9 and -11.2 to -10.3 p.p.m., respectively. On the other hand, those of 5-methylene-1,3-dioxans (1a) and (2a) and the corresponding methylenecyclohexanes (1b) and (2b) are -10.2 to -10.0 and +3.2 to +3.5 p.p.m., respectively. The upfield shifts of  $\beta$ -carbon resonances of 5-methylene-1,3-dioxans compared with the resonances of the corresponding hydrocarbons are larger than those of the saturated compounds. The  $\gamma$ -carbon resonances of 5-methylene-1,3-dioxans are moved downfield compared with those of the corresponding hydrocarbons. This situation is the reverse of that in saturated compounds.

Similar trends were observed for the  $\Delta\delta$  values of (3a)—(8a) and (3b)—(5b) in which X is anticlinal. The upfield  $\beta$ - and downfield  $\gamma$ -shifts for the methoxy-substituted compounds (6a) and (7a) are smaller than those of the hydroxy-substituted compounds (3a) and (4a). However, the upfield  $\beta$ - and downfield  $\gamma$ -shifts of (8a) are larger than those of (5a) in spite of the methoxy-substituted compound.

This trend was barely evident for the carbon chemical shift differences between the cyclic allylic ethers and alcohol (9a)—(11a) and the corresponding unsaturated hydrocarbons (9b)—(11b) in which X is placed at an s.p. position with respect to the double bond (Table 2).

TABLE 2

Chemical shift differences ( $\Delta\delta$ ) of  $\beta$ - and  $\gamma$ -carbons in s.p.-type unsaturated compounds and corresponding saturated compounds.

Unsaturated compounds	$\Delta\delta$	
	$\beta$	$\gamma$
(9a) — (9b)	-2.7	-0.2
(10a) — (10b)	-4.2	
(11a) — (11b)	-1.7	-0.5
Saturated compounds	$\Delta\delta$	
	$\beta$	$\gamma$
(16a) — (16b)	-0.5	-3.6
(17a) — (17b)	-0.4	

(2) *Catalytic Hydrogenation.*—The catalytic hydrogenation of (1a), (1b), (2a), and (2b) was examined over a variety of the Group VIII transition metals in ethanol. Table 3 shows the equatorial selectivities for hydrogen addi-

TABLE 3

Stereochemistry in hydrogenation of 2-alkyl-5-methylene-1,3-dioxans (1a) and (2a), and corresponding hydrocarbons (1b) and (2b)

Catalyst	<i>cis</i> (%)			
	(1a)	(1b)	(2a)	(2b)
Raney Fe	95	56	88	53
Raney Co	80	35	73	37
Raney Ni	89	43	89	45
Ru-carbon	87	84	88	77
Rh-carbon	92	69	87	61
Pd-carbon	97	24	90	26
Os-carbon	90	84	88	62
Ir-carbon	82	70	76	66
Pt-carbon	88	54	84	64
PtO <sub>2</sub>	98	71	98	64
Pt black	98	69	95	62

tion. The products from 2-alkyl-5-methylene-1,3-dioxans (1a) and (2a) were principally (73—99%) the thermodynamically less stable *cis*-isomers, independent of the catalyst metal. The stereoselectivity over palladium catalyst (*cis* 90—97%) is particularly surprising in view of the fact that

hydrogenation over this catalyst generally proceeds to give the more stable of two possible products.<sup>12</sup>

The results for the hydrogenation of the corresponding methylenecyclohexanes (1b) and (2b) show that the proportion of *cis*-product is 24–84%. A preponderance of *cis*-addition to give the more stable *trans*-isomer is observed with Raney Co, Raney Ni, and Pd–C catalysts.

(3) *CNDO/2 MO Calculations*.—In order to estimate the intramolecular orbital interactions, semi-empirical calculations were carried out on (18a) and (19a) [only the axial hydroxy conformation is investigated for (19a)] in which the oxygen atom was placed at an a.c. position with respect

TABLE 4

Total and  $\pi$ -electron densities ( $D_T, D_\pi$ ) of  $\beta$ - and  $\gamma$ - $sp^2$  carbons in 5-methylene-1,3-dioxan (18a), 1-hydroxy-2-methylenecyclohexane (19a)<sup>a</sup> and corresponding hydrocarbons (18b) and (19b) by CNDO/2 calculation

		$\beta$	$\gamma$
	$D_T$	3.9940	4.0566
	$D_\pi$	1.0054	0.9979
	$D_T$	3.9541	4.0869
	$D_\pi$	0.9465	1.0911
(18a) - (18b)	$\delta D_T$	+0.0399	-0.0303
	$\delta D_\pi$	+0.0589	-0.0932
	$D_T$	3.9803	4.0741
	$D_\pi$	0.9575	1.0710
	$D_T$	3.9820	4.0721
	$D_\pi$	0.9598	1.0686
	$D_T$	3.9801	4.0707
	$D_\pi$	0.9610	1.0674
	$D_T$	3.9531	4.0938
	$D_\pi$	0.9401	1.1028
	$D_T$	3.9538	4.0933
	$D_\pi$	0.9404	1.1023
	$D_T$	3.9547	4.0923
	$D_\pi$	0.9419	1.1004
	$D_T$	3.9540	4.0927
	$D_\pi$	0.9416	1.1008
(19a) - (19b) <sup>b</sup>	$\delta D_T$	+0.0254	-0.0182
	$\delta D_\pi$	+0.0156	-0.0294

<sup>a</sup> Only axial hydroxy conformation is employed for (19a).

<sup>b</sup> The  $\delta D$  values for  $\beta$ -carbon were calculated by the difference between the smallest value of (19a) and the largest one of (19b), and those for  $\gamma$ -carbon were calculated by the reverse method.

to the double bond, and the corresponding unsaturated hydrocarbons (18b) and (19b) by the CNDO/2 method<sup>13</sup> which was successful in predicting the electron density of the double bond. Total and  $\pi$ -electron densities of the double bond for various conformations of the hydroxy- or the methyl-group are shown in Table 4, from which the dif-

ference in electron densities can be calculated between compounds containing oxygen and the corresponding hydrocarbons. The  $\delta D_T$  values for  $\beta$ - and  $\gamma$ -carbons for (18a and b) are +0.0399 and -0.0303, and the  $\delta D_\pi$  values are +0.0589 and -0.0932, respectively. The electron density of the  $\beta$ -carbon for (18a) is larger than that for (18b), but the electron density of the  $\gamma$ -carbon is smaller.

This trend also occurs for (19a and b), which bear an axial substituent at the 2-position. The  $\delta D_T$  values for the  $\beta$ - and  $\gamma$ -carbons of (19a and b) are +0.0254 and -0.0182, and the  $\delta D_\pi$  values are +0.0156 and -0.0294, respectively. Though the  $\delta D_T$  and  $\delta D_\pi$  values indicate a similar trend for  $\beta$ - and  $\gamma$ -carbons, the difference in  $\delta D_\pi$  is notably greater than that in  $\delta D_T$  for (18a and b). In the case of (19a and b), the  $\delta D$  values for the  $\beta$ -carbon were calculated by the difference between the smallest value for (19a) and the largest one for (19b), and those for the  $\gamma$ -carbon were calculated by the difference between the largest value of (19a) and the smallest one of (19b).

## DISCUSSION

Eliel and his co-workers<sup>14</sup> found that the upfield shifts of the *anti*-carbon  $\gamma$  to the oxygen atom in a saturated ring system are larger than those of the *gauche*  $\gamma$ -carbon. They suggested that this may be due to a hyperconjugative-type (through-bond) interaction of the free electron pairs centred on the oxygen atom with the  $C_\alpha$ - $C_\beta$  bond, accompanied by subsequent alternation of the electron density at the  $\gamma$ -antiperiplanar carbon (Figure 1). The

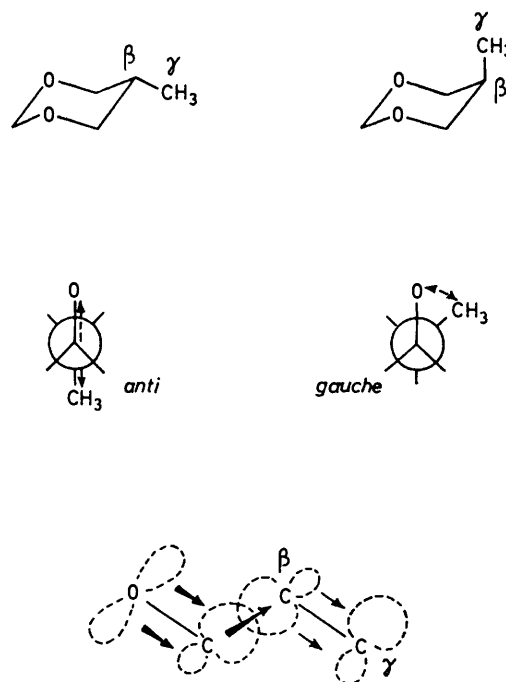


FIGURE 1 Hyperconjugative charge transfer from free-electron pairs on the X atom to the *anti*- $\gamma$ -carbon<sup>14</sup>

appreciable upfield  $\beta$ - and downfield  $\gamma$ -shifts which occur when the oxygen atoms are located at the homoallylic position (*cf.* Table 1), however, cannot be explained only by the hyperconjugative-type interaction in the saturated system. Although it is assumed that the

appreciable upfield  $\beta$ - and downfield  $\gamma$ -shifts caused by the delocalisation of  $\pi$ -electrons depend on the electronegativity of the oxygen atom, it is difficult to insist that such homoconjugation takes place only when the oxygen is placed at an a.c. position with respect to the double bond (Figure 2).

Hoffmann *et al.*<sup>15</sup> reported that, if X is more electronegative than H in Figure 3, then the anion will prefer con-

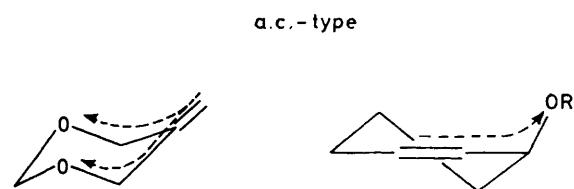


FIGURE 2 Homoconjugation in cyclic allylic alcohols and ethers

formation A as a result of a polar C-X, while the cation favours B. They further reported that the 1,3 through-space interaction D, significant in that it may lead to bridging as a consequence, appears to be important only in the unstable A conformations of  $\text{FCH}_2\text{-CH}_2^+$  and  $\text{BH}_2\text{CH}_2\text{-CH}_2^-$ . Their conclusions on  $\sigma$ - $\pi$  conjugation have a bearing on our  $^{13}\text{C}$  n.m.r. results.

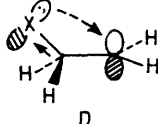
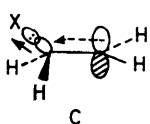
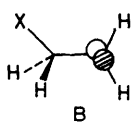
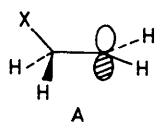
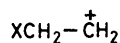
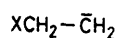


FIGURE 3 Conformations (A,B) of anion  $\text{XCH}_2\text{-CH}_2^-$  or cation  $\text{XCH}_2\text{-CH}_2^+$  and orbital interactions (C,D)<sup>15</sup>

When the oxygen atoms are fixed at an a.c. position with respect to the double bond, the through-space interaction between the  $\pi$ -type  $n$ -orbital of the oxygen atom and the vacant  $p$ - $\pi^*$ -orbital results in a decrease of the electron density at the oxygen atoms. The enhanced effective electronegativity of these oxygen atoms, therefore, induces a homoconjugative through-bond interaction between the C-O  $\sigma$ -orbital and the  $p$ - $\pi$ -orbital (Figure 4). We envisage that electron delocalisation of the  $\pi$ -orbital by such through-space and through-bond interactions results in an upfield shift of the  $\beta$ -carbon resonances and a downfield shift of the  $\gamma$ -carbon resonances.



FIGURE 4 Through-space and through-bond interactions in a.c.-type compounds

This trend was hardly found for the carbon chemical shifts of (9a)—(11a) in which the oxygen atom is fixed at a synperiplanar position with respect to the double bond (*cf.* Table 2). This may be due to the following two reasons. First, the through-space interaction of the  $\pi$ -type  $n$ -orbital with the  $p$ - $\pi^*$ -orbital is inhibited by the antisymmetric  $p$ - $\pi^*$ -orbital of another  $sp^2$ -carbon. Secondly, there is little homoconjugative interaction of the  $p$ - $\pi$ -orbital and the C-O  $\sigma$ -orbital because these two orbitals are placed almost perpendicular to each other (Figure 5).



FIGURE 5 Through-space and through-bond interactions in s.p.-type compounds

The chemical shift differences of the  $sp^2$ -carbons on the methoxy-substituted compounds (6a) and (8a) have a similar trend to the hydroxy-substituted compounds (3a) and (5a), and those of (8a) are larger than (6a) (*cf.* Table 1). These may be caused by a change in the steric environment. When the through-space interaction operates between the  $\pi$ -type  $n$ -orbital of the oxygen atom and the vacant  $p$ - $\pi^*$ -orbital in (6a), the methyl substituent of the methoxy-group is repulsed sterically by the axial hydrogen on C-5; this interaction does not exist in (8a) (Figure 6). As a result, chemical shift differences of (8a) become larger than those of (6a).

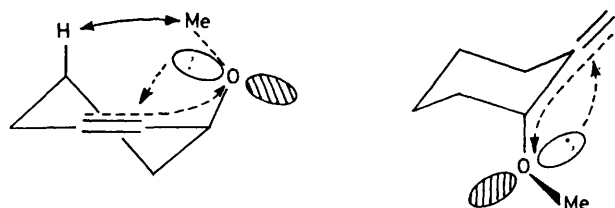


FIGURE 6 Variance of steric environment in the methoxy-substituted compounds (6a) and (8a)

The large chemical shift differences in  $^{13}\text{C}$  n.m.r. spectra revealed a through-bond and through-space interaction between the  $\pi$ -type  $n$ -orbital of the two oxygen atoms and the  $\pi$ -orbital of the exocyclic double bond of (1a) and (2a). Consequently, the electron densities of the axial and equatorial sides of the double bond are unequal. This should become manifest in the relative rates of electrophilic attack on each face of the double bond. Klein has reached similar conclusions for

the orbital interaction between the  $\beta_{C-O}$  single bond and the exocyclic double bond in (1b) and (2b).<sup>16</sup> We studied the axial : equatorial ratios of the hydrogenation products of (1a) and (2a), and corresponding unsaturated hydrocarbons (1b) and (2b), over a variety of the Group VIII transition metals. The results show (*cf.* Table 3) that the axial/equatorial selectivities for hydrogen addition to (1a) and (2a) are significant compared with those for (1b) and (2b). These high stereoselectivities for (1a) and (2a) may be the consequence of homoconjugation between an oxygen lone pair and  $\pi$ -electrons by through-space and through-bond interactions (Figure 7) which result in the

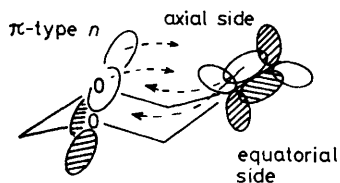


FIGURE 7 Orbital interactions at the axial side in 5-methylene-1,3-dioxan

upfield shift of  $\beta$ -carbon resonances and the downfield shift of  $\gamma$ -carbon resonances. The adsorption of the substrate onto the surface of the metals and/or the attack of hydrogens on the double bond from the axial side greatly perturbs the through-space interaction at the transition state of the hydrogenation. On the other hand, the adsorption and/or attack of the hydrogens from the equatorial side does not perturb such orbital interactions at the transition state.

In order to estimate the intramolecular orbital interactions, the electron density of the double bond was calculated using the CNDO/2 method<sup>13</sup> (*cf.* Table 4). A good correlation was found between the  $\delta D$  values of the electron density and  $\Delta\delta$  values of the <sup>13</sup>C n.m.r. chemical shifts. The  $\beta$ -carbon resonances moved to higher field with an increase in the electron density, while those of the  $\gamma$ -carbon moved to lower field with a decrease in the electron density. Anteunis *et al.*<sup>17</sup> reported that the vicinity around the double bond of 5-methylene-1,3-dioxans shows a flattened conformation by comparison with the corresponding methylenecyclohexanes. This result also suggests that repulsion between the two oxygen atoms is attenuated by a decrease in the electron density of the oxygen atoms which is caused by through-space interaction with the vacant  $p-\pi^*$ -orbital.

**Conclusions.**—The results of the <sup>13</sup>C n.m.r. experiments and CNDO/2 MO calculations on allylic ethers and alcohols in which the oxygen atom is placed at an anticlinal position with respect to the double bond are attributed to the electron delocalisation of the  $\pi$ -orbital by homoconjugation between the oxygen atom and the double bond owing to orbital interactions. Such orbital interactions increase the *cis*-stereoselectivity of the hydrogenation of 2-alkyl-5-methylene-1,3-dioxans over Group VIII transition metals. The study of reactions of a variety of electrophiles with these compounds is under investigation.

## EXPERIMENTAL

**N.m.r. Spectra.**—Carbon-13 Fourier transform n.m.r. spectra were obtained at 25.15 MHz with a JEOL JNM-MH-100 instrument equipped with a JNM-MFT-100 Fourier transform accessory; the instrument was controlled with a JEC-6 computer. Samples were dissolved into CDCl<sub>3</sub>, the deuterium signal of which provided a field frequency lock; concentrations were 15–20% (w/v). Measurement conditions were as follows; pulse width 27.5  $\mu$ s (*ca.* 45°); repetition time 4 s; spectral width 6.25 kHz; data points 8 192. Noise-modulated proton decoupling was carried out at a nominal power of 20 W. Chemical shifts ( $\delta$ ) are expressed in p.p.m. downfield from internal Me<sub>4</sub>Si. Each observed chemical shift is estimated to be accurate to within  $\pm 0.1$  p.p.m.

**Materials.**—Compounds (1a),<sup>18</sup> (2a),<sup>18</sup> (3a),<sup>19</sup> (4a),<sup>20</sup> (5a),<sup>21</sup> (8a),<sup>22</sup> (9a),<sup>23</sup> (11a),<sup>22</sup> (12a),<sup>14</sup> (13a),<sup>14</sup> (1b),<sup>24</sup> (2b),<sup>24</sup> (5b),<sup>11b</sup> (11b),<sup>11b</sup> (12b),<sup>14</sup> and (13b)<sup>14</sup> have been previously reported. Compounds (6a) and (7a) were prepared from (2a) and (3a) according to the method of Heathcock and Kelly.<sup>22</sup> Compounds (10a), (14a), (15a), (16a), (17a), (3b), (4b), (9b), (10b), (14b), (15b), (16b), and (17b) were commercially available. The structure of each compound was confirmed by <sup>1</sup>H n.m.r. and analytical g.l.c.

**Catalytic Hydrogenation.**—The following general procedure was used. A known amount of substrate and catalyst in the solvent was stirred with H<sub>2</sub> at ambient temperature. After reaction the catalyst was removed and the mixture was analysed by g.l.c.

**G.l.c. Analysis.**—Hitachi F-6 and K-53 gas chromatographs equipped with flame ionization detectors were used with an Infotronics digital integrator. The products were analysed on a 45 m  $\times$  0.25 mm Goley column of PEG 400 at 70 °C.

**CNDO/2 Calculations.**—For CNDO/2 calculations the following geometrical parameters were used for each compound. 5-Methylene-1,3-dioxan: angles 126 [C-4-C-5(*sp*<sup>2</sup>)-C-7(*sp*<sup>2</sup>)], 111 (C-2-O-C-4) and (C-2-O-C-6), 109.5 (for any other carbon set), 120 [C-5(*sp*<sup>2</sup>)-C-7(*sp*<sup>2</sup>)-H], 109.5°  $\dagger$  [H-C(*sp*<sup>3</sup>)-H]; distances 1.37 (C=C), 1.41 (C-2-O), 1.435 (C-4-O and C-6-O), 1.50 [C-4-C-5(*sp*<sup>2</sup>) and C-6-C-5(*sp*<sup>2</sup>)], 1.09 Å  $\dagger$  (C-H). Methylenecyclohexane: angles 117 [C-2-C-1(*sp*<sup>2</sup>)-C-6], 121.5 [C-2-C-1(*sp*<sup>2</sup>)-C-7(*sp*<sup>2</sup>) and C-6-C-1(*sp*<sup>2</sup>)-C-7(*sp*<sup>2</sup>)], 109.5 (for any other carbon set), 120 [C-1(*sp*<sup>2</sup>)-C-7(*sp*<sup>2</sup>)-H], 109.5° [H-C(*sp*<sup>3</sup>)-H]; distances 1.37 (C=C), 1.54 (C-C), 1.09 Å (C-H).

$\dagger 1^\circ = (\pi/180)$  rad; 1 Å = 10<sup>-8</sup> m.

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