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THE NMR SPECTRA AND CONFORMATIONS OF CYCLIC COMPOUNDS—V:

PROTON COUPLINGS AND CHEMICAL SHIFTS IN BRIDGED CYCLOBUTANES

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Abstract—The PMR spectra of twelve pinene derivatives are reported, analysed and assigned.

The proton couplings in the bridged cyclobutane group are compared with those of other strained cyclobutanes, and the relationship between $^2J_{HH}$ and the C.CH$_2$.C angle is shown to be anomalous in these systems, suggesting unusually small H.C.H. angles in cyclobutanes.

The very large values of $^4J_{HH}$(eq-eq) in buckled cyclobutanes are interpreted in terms of current M.O. theory and also given a simple geometric rationalisation based on the direct mechanism.

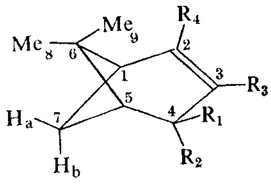
The various couplings in the pinene skeleton are discussed in terms of present theories and minor conformational effects in these molecules. Substituent chemical shift (SCS) values for Me and OH groups around the pinene skeleton are obtained, and shown not to agree with calculations based on present theories of chemical shifts.

PMR SPECTROSCOPY has been relatively little used, other than as a finger-print in the study of pinene derivatives,[1,2,3] even though it can provide configurational and conformational data needed for the rationalisation of pinene rearrangements.[4]

The difficulties in the interpretation of the PMR spectra in these systems are mainly due to the small spread of the proton chemical shifts and extensive long range coupling, which give broad unresolved spectra. Nevertheless by modern techniques (e.g. high fields, shift reagents) much useful data can be obtained and we report complete assignments for twelve pinene derivatives (**1** to **12**, Scheme 1).

Trivial rather than systematic names are still in predominant use in pinene chemistry[4] and are employed here (*cf.* Table 1). It should also be noted that the nomenclature of Scheme 1 will be used throughout even though this contradicts at times the systematic numbering and name, e.g. **6** and **7**.

The pinene skeleton is essentially a Y shape[5] (Scheme 1) with $C_1C_2C_3C_4C_5$ planar



	R$_1$		R$_2$	R$_3$	R$_4$
(1)		C=O		H	Me
(2)	OH		H	H	Me
(3)	H		OH	H	Me
(4)	H		H	H	Me
(5)	H		H	H	H
(6)	Me		OH	H	H
(7)	OH		Me	H	H
(8)		C=O		H	H
(9)	H		OH	H	H
(10)	OH		H	H	H
(11)	H		H	Me	H
(12)	Me		H	H	H

SCHEME 1

or nearly so. The dihedral angle of the cyclobutane part has been found to be *ca.* 150° in α-pinene[5] and *ca.* 137° in the analogous, saturated bicyclo[3,1,1]hexane.[6]

Spectral analysis and results

Some typical spectra are given in the spectral supplement (Spec. Nos. 0494 to 0496 in Supplement).

The spectra of verbenone (**1**) and the *cis*- and *trans*-verbenols (**2**) and (**3**) have been given previously.[1]

α-pinene (**4**). A full computer analysis of the 100 MHz spectrum has been given previously,[2] though the claimed accuracy of the parameters is doubtful.[2,7]

In the present work 100 MHz, 220 MHz and 300 MHz spectra of **4** have been obtained. The 300 MHz spectrum (Spec. No. 0494 in Supplement) resolves the **4a** and **4b** proton resonances with $J_{4a4b} \approx 18$ Hz. The rest of the analysis is analogous to that of the verbenols (**2**) and (**3**).

*Cis- and trans-pin-*3*-en-*2*-ol, apopinenone* (**6**), (**7**) *and* (**8**). In **6** the olefinic protons gave first order patterns at 100 MHz, with splittings *ca.* 0·9, 6·0 and 8·7 Hz in the low field region and 0·9, 2·0 and 8·7 Hz in the high field region. The common splitting is assigned as J_{23} and the splitting of 6 Hz as J_{12}. Decoupling the olefinic protons in turn showed that the upfield cyclobutane proton is coupled to H_3 only, and is therefore H_5, whereas the central region is coupled to both H_2 and H_3, and is therefore H_1. The low field region is accordingly H_{7a}, which exhibits a long range coupling to H_2. Compounds **7** and **8** are analogous (*cf.* Tables 1 and 2).

Cis- and trans-apopinenol (**9**) *and* (**10**). In the *cis*-isomer (**10**) the analysis is straightforward, especially at 220 MHz. The narrower range of chemical shifts in the *trans*-isomer means that even at 220 MHz the shifts of H_1, H_5 and H_{7a} cannot be accurately obtained. Addition of Eu $(DPM)_3$[8] produced the expected dramatic changes in chemical shifts and enabled the analysis to be confirmed.

Cis-δ-pinene (**12**). This spectrum bears a similarity to that of **6** and may be partially analysed by comparison. The only new couplings in **12**, which are not found in **6**, are J_{24}, J_{34} and J_{45}. The latter has not been picked out, as H_4 and H_5 are both ill-resolved multiplets, but J_{34} can be discerned as ~3 Hz from H_3 and J_{24} as ~2 Hz from H_2.

Apopinene (**5**). Again the analysis is similar to that of **6** and **7**, but H_1 and H_5 overlap as do H_{4a} and H_{4b}, such that couplings to these protons cannot be rigorously obtained. From H_3, J_{34} can be obtained as *ca.* 3 Hz.

3*-methyl apopinene* (**11**). This is similar to **5**. It is of interest that the 3-CH_3 group is a 1:2:2:2:1 quintet with J_2—CH_3 1·8 Hz and J_4—CH_3 1·0 Hz.

The NMR data ($CDCl_3$ solution) for **1** to **12** are given in Tables 1 and 2. With the exception of **5**, **11** and **12**, the parameters quoted have been refined by use of LAOCN 3.[9] Because each observed 'line' consists of several unresolved transitions as calculated by LAOCN 3, the refinement process does not give highly accurate data, and so the chemical shifts are in general only considered accurate to *ca.* ±0·01 ppm and the coupling constants to *ca.* ±0·3 Hz.

DISCUSSION

Coupling constants

Before discussing the individual coupling constants, we need to consider possible conformational differences in **1** to **12**. Examination of molecular models suggests

TABLE 1. CHEMICAL SHIFTS OF PINENE DERIVATIVES δ_{ppm} ($CDCl_3$)

		Proton									
	Compound	1	2	3	4	5	7_a	7_b	8	9	Other protons
Verbenone	**(1)**	2·42	—	5·72	—	2·64	2·80	2·07	1·50	1·01	$R_4 = CH_3$:2·01
cis-verbenol	**(2)**	1·96	—	5·35	4·45	2·28	2·44	1·29	1·35	1·07	$R_4 = CH_3$:1·73
trans-verbenol	**(3)**	2·02	—	5·34	4·25	2·16	2·24	1·35	1·34	0·87	$R_4 = CH_3$:1·71
α-pinene	**(4)**	1·92	—	5·17	{2·15 2·23	2·06	2·33	1·17	1·27	0·83	$R_4 = CH_3$:1·66
Apopinene	**(5)**	2·1	6·14	5·51	2·3	2·1	2·37	1·21	1·26	0·90	
cis-pin-3-en-2-ol	**(6)**	2·20	6·26	5·52	—	2·05	2·40	1·49	1·37	0·94	$R_1 = CH_3$:1·32
trans-pin-3-en-2-ol	**(7)**	2·17	6·21	5·54	—	2·17	2·50	1·42	1·36	1·14	$R_2 = CH_3$:1·28
Apopinenone	**(8)**	2·61	7·53	5·94	—	2·56	2·86	2·13	1·52	1·04	
trans-apopinenol	**(9)**	2·18	6·31	5·64	4·30	2·18	2·25	1·40	1·32	0·89	
cis-apopinenol	**(10)**	2·15	6·31	5·68	4·51	2·30	2·49	1·37	1·34	1·10	
3-methyl apopinene	**(11)**	2·05	5·78	—	2·17	2·05	2·34	1·17	1·26	0·82	$R_3 = CH_3$:1·65
cis-δ-pinene	**(12)**	2·1	6·05	5·55	2·65	2·05	2·45	1·25	1·25	1·0	$R_1 = CH_3$:1·05

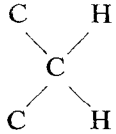
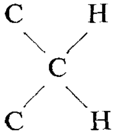
TABLE 2. COUPLING CONSTANTS IN THE PINENES (Hz)

Molecule	J_{12}	J_{13}	J_{15}	J_{17a}	J_{23}	J_{24}	J_{34}	J_{35}	J_{45}	J_{57a}	$J_{7a,7b}$	Other couplings
(1)	—	1·5	6·3	5·5	—	—	—	1·6	—	5·4	8·9	$J(\text{Me} - 3) = 1{\cdot}6$;
(2)	—	1·5	5·7	5·1	—	—	3·0	1·5	3·0	5·9	8·7	$J(\text{Me} - 3) = 1{\cdot}5$; $J(\text{Me} - 4) = 1{\cdot}5$
(3)	—	1·5	5·5	5·3	—	—	3·0	1·5	3·0	5·7	8·7	$J(\text{Me} - 3) = 1{\cdot}5$; $J(\text{Me} - 4) = 1{\cdot}5$
(4)	—	1·5	5·4	5·2	—	—	3·2	1·5	2·8	5·7	8·5	$J(\text{Me} - 3) = 1{\cdot}6$; $J(\text{Me} - 4) = 2{\cdot}0$; $J_{4a,4b} = 18$
(5)	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	$J_{34} = 3$; $J_{27a} = 0{\cdot}8$; $J_{23} = 8{\cdot}5$
(6)	6·0	0·8	5·3	5·4	8·8	—	—	2·1	—	5·5	9·0	$J_{27a} = 1{\cdot}0$
(7)	6·3	0·7	5·8	5·2	8·7	—	—	2·2	—	5·8	8·9	$J_{27a} = 0{\cdot}8$
(8)	6·1	1·0	6·2	5·0	8·8	—	—	1·7	—	5·9	8·8	$J_{27a} = 1{\cdot}0$
(9)	6·4	[a]	5·8	5·8	9·1	[a]	[a]	[a]	[a]	5·8	9·2	
(10)	6·2	1·0	6·0	5·7	9·0	1·1	2·9	1·9	2·9	5·7	8·9	$J_{27a} = 1{\cdot}1$
(11)	[a]	—	[a]	[a]	—	[a]	—	—	[a]	[a]	[a]	$J(\text{Me} - 2) = 1{\cdot}8$; $J(\text{Me} - 4) = 1{\cdot}0$
(12)	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	$J_{34} = 3$; $J_{24} = 2$

[a] These couplings ill defined from spectrum.

that steric repulsions are only important for the interaction of the 9-Me group with a *cis*-4-Me group (R_1 = Me) as in **6** and **12**. In these circumstances the closest approach of two H atoms in the opposed methyl groups is *ca.* 0·6 Å, as compared to the sum of the Van der Waal's radii, 2·0 Å. In these circumstances, it is likely that there will be small conformational distortions to relieve steric compression, even in a system as seemingly rigid as the pinene skeleton. Similar distortions have recently been demonstrated[10] in the norbornane skeleton, which was previously thought to be rigid. In the remaining molecules there is no *a priori* reason to expect that conformational differences exist (*vide infra*).

The $^2J_{HH}$, $^3J_{HH}$ and $^4J_{HH}$ coupling constants in the cyclobutane moiety of pinenes are compared with other bridged ring compounds in Tables 3, 4 and 5.

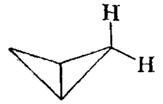
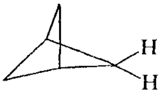
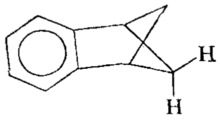
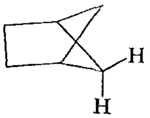
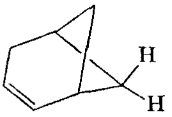
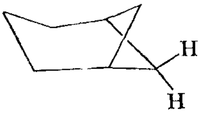
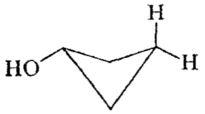
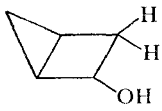
$^2J_{HH}$. The values of $^2J_{HH}$ in bridged cyclobutanes become more negative as the dihedral angle of the cyclobutane ring increases.[2] This correlation presumably reflects bond angle changes in the  fragment which are concomitant with the buckling of the cyclobutane ring and suggests[2] that the HCH bond angle increases with the dihedral angle. Such data on HCH bond angles as are available (Table 3, column 2) do not lend support to this suggestion, however, although the accuracy of some of the data is poor. There is, however, a rather better correlation between $^2J_{HH}$ and the CCC angle of the  fragment (Fig. 1). Previous workers[11] have noted this correlation in other systems where substituent electronegativity effects are similarly unimportant and have remarked that cyclobutane itself did not fit in with the trend for other hydrocarbons. In Fig. 1 we have distinguished between cyclobutanes (shown □) and other hydrocarbons (○). It is clear that cyclobutane derivatives exhibit a correlation rather different to that of other rings.

This anomalous behaviour has important practical consequences. Thus in Ref. 2, a value for the $C_5C_7C_1$ bond angle in pinenes of *ca.* 97° was deduced from the value of $J_{7a,7b} \approx -9$ Hz, using the correlation shown as (○) in Fig. 1. This is obviously an unjustified interpolation and it can be seen that a value for $C_5C_7C_1$ of *ca.* 87° is in much better accord with $J_{7a,7b}$ when the correct (□) correlation is used, as well as being in agreement with the value for $C_5C_7C_1$ (87·1°) determined by election diffraction[6] for the analogous saturated bicyclo[3,1,1]hexane.

The reason for the anomalous behaviour of cyclobutanes is still not clear. It has been tentatively suggested that this arises because the HCH angles in cyclobutane are smaller than would be deduced from the CCC angles.[11] More data are necessary to test this proposal, but certainly the values of the HCH angles in bicyclo[1,1,1]-pentane[12] (103·8 ± 5°) and bicyclo[2,1,1]hexane[13] (98·8 ± 6°) are much smaller than tetrahedral.

$^3J_{HH}$. Examination of molecular models suggests that the dihedral angles made by the C—H_{7b} and C—H_1 bonds, and also by the C—H_{7b} and C—H_5 bonds are close to 85° in the pinenes. Thus the lack of observable couplings $J_{1,7b}$ and $J_{5,7b}$ may be

TABLE 3.[a] GEMINAL COUPLINGS IN BRIDGED CYCLOBUTANES

System	$^{2}J_{HH}$[b] (Hz)	HCH angle[b] (degrees)	CCC angle[b] (degrees)	Dihedral Angle of cyclobutane (degrees)
	(−1·7)[c] 0·5[e]	115·6[d]	59·95[d]	122·7[d]
	−3·0[f]	103·8 ± 5[g]	73·3[g]	120[g]
	−4·9[h]			
	(−5·4)[i] −6·5 to 7·5[k]	98·8 ± 6[j]	85·4[j]	129·5[j]
	−8·8[l]			(150)[n]
	−8·5 to 9·5[k]	113·1[m]	87·1[m]	137[m]
	−10·95[p]	112[q]	~88[q]	145 to 150[q]
	−11·54[p]	108 ± 4[r]	86·5[r]	180[r]

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[a] Literature references for Tables 3, 4 and 5 are combined after Table 5; parameters in parenthesis are regarded as doubtful in view of later work.

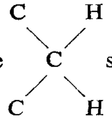
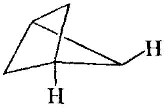
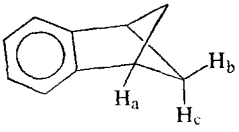
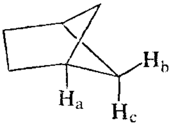
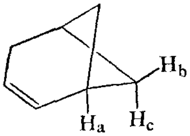
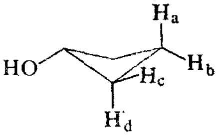
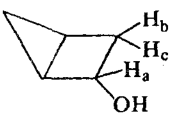
[b] Parameters refer to the  $\begin{array}{ccc} C & & H \\ & C & \\ C & & H \end{array}$ system whose protons are shown.

TABLE 4.[a] VICINAL COUPLINGS IN BRIDGED CYCLOBUTANES

System	$^3J_{HH}$ (Hz)	Dihedral Angle of HCCH system[b] (degrees)	Cyclobutane dihedral angle (degrees)
	0[g]	~65	120[g]
	J_{ab} 2·4[h] J_{ac} 0[h]		
	J_{ab} 2 to 3[i] J_{ac} 0[i]	~40 ~80	129·5[j j]
	J_{ab} 5·1 to 5·9[l] J_{ac} 0[l]	~40 ~85	
	J_{ac} 7·9 to 9·7[p] J_{ad} 10·4[p] J_{bc} 2·3[p]	~25 ~160 ~105	145 to 150[q]
	J_{ab} 9[p] J_{ac} 3·5[p]	0 ~125	180[r]

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[a] Literature references for Table 3, 4 and 5 are combined after Table 5.

[b] These angles have been measured on molecular models and are therefore likely to be accurate to no better than ±5°.

rationalised in terms of the Karplus cos^2 ϕ relationship.[14] For J_{17a} and J_{57a}, for which the dihedral angles in each case are *ca.* 40°, the couplings of *ca.* 5·5 Hz are also reasonable. Not all the changes in $^3J_{HH}$ with increasing cyclobutane dihedral angle can be ascribed to dihedral angle changes in the HCCH fragment, however. $^3J_{HH}$ is also very sensitive to changes in HCC bond angles[15,16] and these are also likely to increase as the cyclobutane ring becomes more buckled. This would serve to reduce $^3J_{HH}$ values in the buckled rings, independently of dihedral angle considerations.

TABLE 5. LONG RANGE COUPLINGS ($^4J_{HH}$) IN CYCLOBUTANES AND RELATED MOLECULES

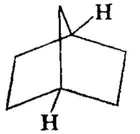
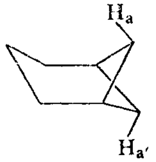
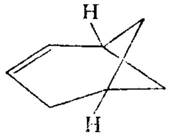
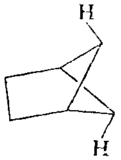
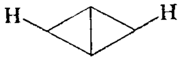
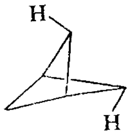
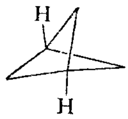
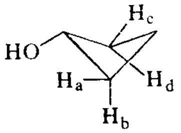
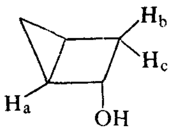
System	$^4J_{HH}$ (Hz)
	1·5[t] ~3·0[u]
	5·5 to 6[j]
	5·4 to 6·3[l]
	7 to 8[k]
	(10)[c] 5[e]
	10[f]
	18[f]
	J_{ac} 5·16[p] J_{bd} 0[p] J_{ad} −1[p]

TABLE 5. (*continued*)

System	$^4J_{HH}$(Hz)
	J_{ab} ±1[p] J_{ac} ~0[p]

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[c] S. Masamune, *Tetrahedron Letters* 945 (1965).
[d] K. W. Cox, M. D. Harmony, G. Nelson and K. S. Wiberg, *J. Chem. Phys.* **50**, 1976 (1969).
[e] K. Wüthrech, S. Meiboom and L. C. Snyder, *J. Chem. Phys.* **52**, 230 (1970).
[f] A. Padwa, E. Shefter and E. Alexander, *J. Am. Chem. Soc.* **90**, 3717 (1968).
[g] Ref. 12.
[h] M. Pomerantz, *J. Am. Chem. Soc.* **88**, 5349 (1966).
[i] Ref. 24.
[j] Ref. 13.
[k] K. B. Wiberg, B. R. Lowry and B. J. Nist, *J. Am. Chem. Soc.* **84**, 1594 (1962).
[l] Present work.
[m] Ref. 6.
[n] Ref. 5.
[p] K. B. Wiberg and D. E. Barth, *J. Am. Chem. Soc.* **91**, 5124 (1969).
[q] Values for cyclobutyl fluoride and chloride; *cf.* Ref. 12.
[r] Value for bicyclo[2.1.0]pentane, R. K. Bohn and Y.-H. Tai, *J. Am. Chem. Soc.* **92**, 6447 (1970).
[s] Ref. 25.
[t] K. C. Ramey, D. C. Lini, R. M. Moriarty, K. Gopal and H. G. Welsh, *J. Am. Chem. Soc.* **89**, 2401 (1967).
[u] Value for norbornene: Ref. 28.

As we have discussed above, the accuracy of coupling constant data in the present work is unikely to be better than *ca.* ±0·3 Hz. With this condition, however, Table 2 shows that in general $J_{57a} \geqslant J_{17a}$. Earlier workers[2] have deduced from the same observation in a single case that the relevant dihedral angles were not equal and inferred that this arose from a lack of coplanarity in the $C_1C_2C_3C_4C_5$ fragment. We cannot agree that this inference has to be drawn. Regardless of the coplanarity of $C_1C_2C_3C_4C_5$, the lack of molecular symmetry about a plane through $H_aC_7H_b$ necessarily means that the $C_2C_1H_1$ and $C_4C_5H_5$ bond angles will not be identical, and so neither will the dihedral angles of the C_1—H_1 and C_5—H_5 bonds with C_7—H_a be identical. Furthermore, in all cases, C_1 is attached to an sp^2 hybridised C atom, C_2, whereas in the majority of cases (except **1** and **8**) C_5 is attached to an sp^3 C atom. Since an sp^2 C atom is effectively more electronegative than an sp^3 C atom (2·74 *versus* 2·50 on the Pauling scale[17]), it would be expected[18] that this would cause J_{57a} to be larger than J_{17a}—as observed.

$^4J_{HH}$. The coupling J_{15} found in the pinenes has been shown to be of positive sign.[3] Inspection of Table 2 suggests that introduction of a keto group at C_4 increases the coupling from *ca.* 5·5 to *ca.* 6·2 Hz. This may reflect some slight change in molecular dimensions, or else may be occasioned by the presence of an additional coupling pathway via the $\alpha\beta$ unsaturated keto system.

Table 5 shows that in bridged cyclobutanes $^4J_{HH}$ between pairs of pseudo equatorial protons increases rapidly as the cyclobutane ring buckles. It is perhaps worth

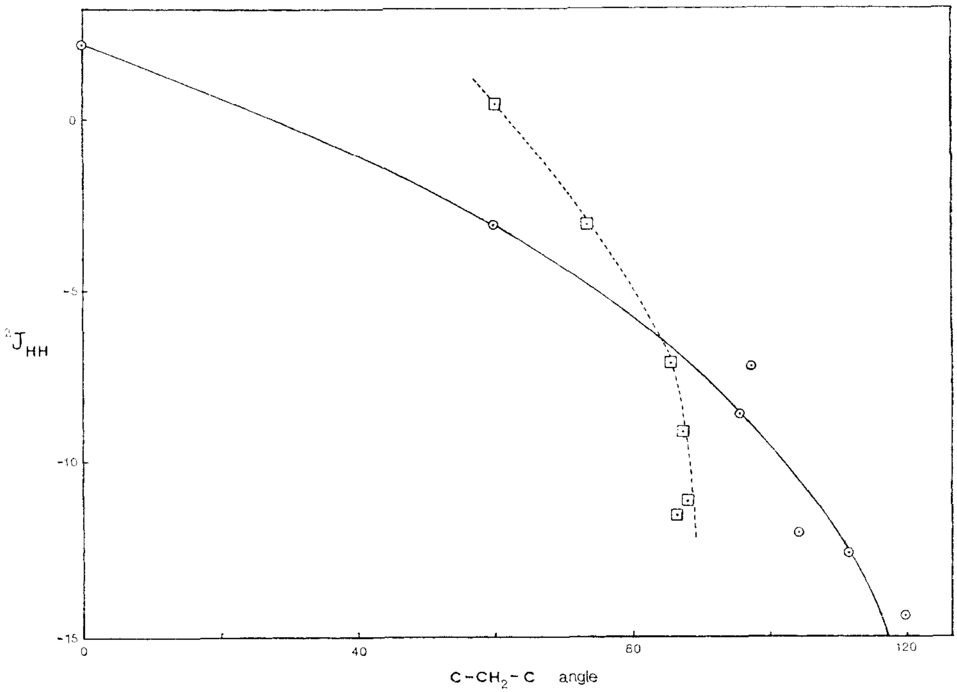
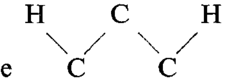


FIG. 1. The correlation between $^2J_{HH}$ and CCC angles in the C—CH$_2$—C system. Points marked □ are from Table 3, while points marked ○ are from Ref. 11.

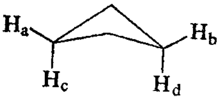
Key to points marked ○, in order of increasing C—CH$_2$—C angle, are:- ethylene; cyclopropane; *exo* 1,2 diphenyl bicyclo[2,2,1]heptene (7 CH$_2$); benzobicyclo[2,2,1]-heptene (7 CH$_2$); 2-methylbicyclo[2,2,1]heptane-2-*exo* carboxylic acid (3 CH$_2$); cyclohexane d_8; *cis*-2,6-dibromo-3,3,5,5-tetramethylcyclohexanone.

stressing that in the majority of examples shown, the large magnitude of $^4J_{HH}$ is not associated with a fully coplanar 'W' configuration.[19] Thus in bicyclo[2,1,1]hexane,[13] the two C—H bonds of the  $\overset{\text{H}}{\text{C}}\;\overset{\text{C}}{}\;\overset{\text{H}}{\text{C}}$ coupling system make dihedral angles of *ca.* 60° with each of the CCC planes and are not coplanar with the latter, as has been implied in one review.[20]

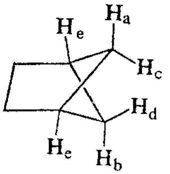
Recent calculations of $^4J_{HH}$ in propanic fragments[21] have shown using the INDO method[22] that the coupling in a planar 'W' system decreases rapidly as the CCC angle is increased, whereas in non coplanar systems a change in the CCC angle has almost no effect on this coupling. This was interpreted as implying the importance of a 'direct' mechanism between the C—H bonds in the coplanar 'W' fragment and the much lesser significance of such a "direct" mechanism when coplanarity is lost.

Encouraged by the above results, we have attempted in two ways to gain further insight into the mechanisms responsible for large values of $^4J_{HH}$ in certain buckled cyclobutanes. First, we have calculated INDO proton-proton bond orders $(\pi_{HH})^{22}$ for a range of proton orientations in some buckled cyclobutanes. The results are given in Table 6 and Fig. 2. To a crude, but intuitively useful approximation,[23] coupling constants are proportional to the square of the bond order, such that trends in couplings in a series of similar molecules may be investigated by reference to the bond

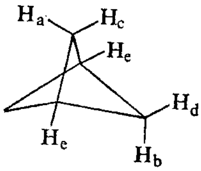
TABLE 6. SCF BOND ORDERS (INDO) FOR $^4J_{HH}$ IN CYCLOBUTANES



(I)[a]



(II)[b]



(III)[c]

	System	Bond order (×10²)			
		H_a H_b	H_a H_d	H_c H_d	H_e H_e
(I)	$\theta = 0°$	−3·34	−1·24	−3·34	—
(I)	$\theta = 15°$	−4·70	−1·20	−2·94	—
(I)	$\theta = 35°$	−6·74	+0·43	−1·42	—
(I)	$\theta = 45°$	−7·80	+1·53	−1·31	—
(II)		−7·82[d]	−0·44	−0·08	−6·99
(III)		−7·53[d]	1·47	2·29	−11·78

[a] θ = angle of buckle of cyclobutane ring.

[b] Using geometry found in Ref. 13.

[c] Using geometry found in Ref. 12.

[d] Because the experimental geometries are used for II and III, as opposed to rather idealised geometries for I, the HCH angles in II and II are much smaller than in I (see Discussion). This will possibly explain the lack of smooth trends in certain couplings, e.g. J_{ab} of this Table.

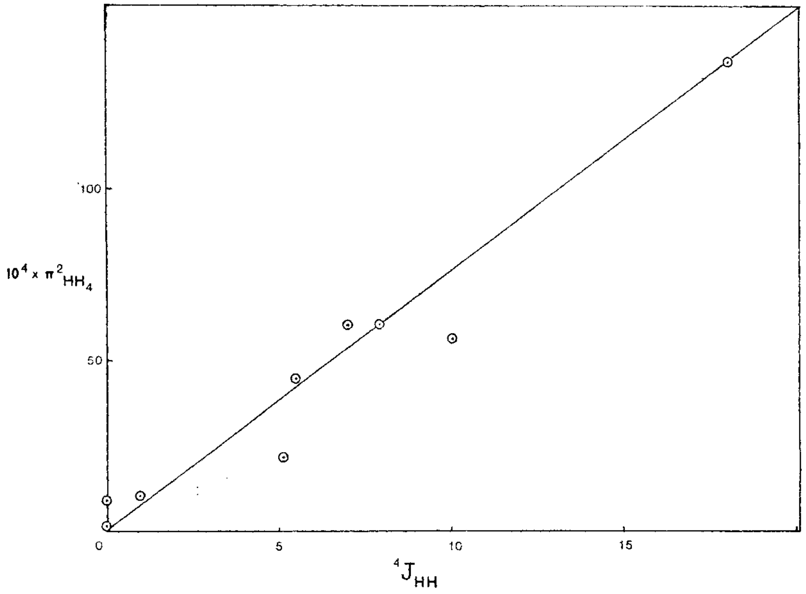


FIG. 2. The correlation between the square of the INDO/2 bond order (π^2_{HH}) and $^4J_{HH}$ in cyclobutane derivatives. For convenience the full range of π^2_{HH} *vs.* $^4J_{HH}$ is not shown where $^4J_{HH}$ is too small to be observed and π^2_{HH} is less than 10 × 10⁻⁴.

orders. Figure 2 shows that the correlation between $^4J_{HH}$ and the square of the bond order in buckled cyclobutanes is very reasonable. As the ring is buckled, π^2_{HH} increases very rapidly for protons A and B, but the change is much less marked for other orientations of the protons. π^2_{HH} for protons 'e' in III (Table 6) is the largest of all, in agreement with experiment. At this level of approximation therefore, molecular orbital theory seems to account well for the large values of $^4J_{HH}$.

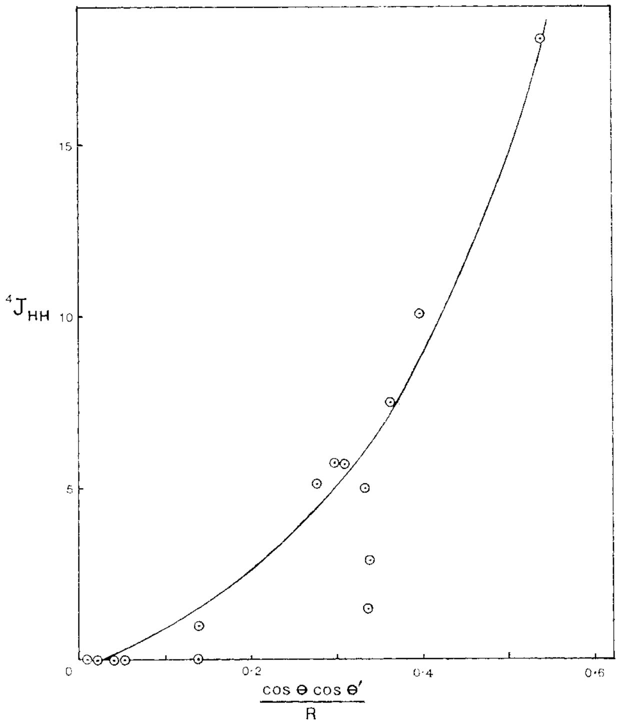
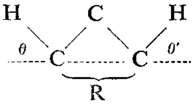


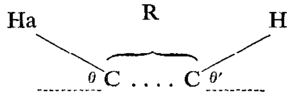
FIG. 3. The correlation between $^4J_{HH}$ and cos θ cos θ'/R in the system



.

Data from Table 5.

Second, we have attempted to assess the importance of a 'direct' interaction mechanism between the C—H bonds by an empirical method. If in the system



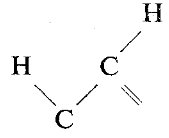
the four atoms are coplanar, then we should expect that any electron overlap, which may be equated with the coupling J_{ab}, at least on an intuitive basis,[24] would be proportional[25] to cos θ cos θ'/R. This prediction is tested in Fig. 3. The correlation is reasonable: since mechanisms other than the 'direct' one can contribute ~1 to 2 Hz to $^4J_{\mathrm{HH}}$, no significance need be attached to deviations of this order from the correlation. The only points remaining with deviations larger than this are the two disagreeing values of $^4J_{\mathrm{HH}}$ across the bridge in norbornane. Here the coupling is in a buckled cyclopentane ring, and not, as in the rest of the examples, in a buckled cyclobutane. This suggests that the correlation must not be taken too far. Nevertheless, the data seem to suggest a significant direct mechanism and the simple treatments presented here may serve to stimulate more extensive theoretical work.

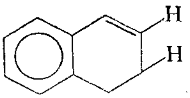
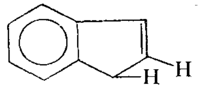
$C_1C_2C_3C_4C_5$ fragment

$^2J_{\mathrm{HH}}$. In **4**, $J_{4a,4b}$ is found to be $\sim|18|$ Hz–presumably negative. Undoubtedly there is a large negative contribution to this coupling from hyperconjugation with the p orbital on C_3.[7,11,26] This confirms that the $C_1C_2C_3C_4C_5$ fragment is essentially planar.

$^3J_{\mathrm{HH}}$. The values of J_{23} in **6** to **10** are found to be $\sim$8·8 to 9·0 Hz. This value lies between the magnitude of the *cis*-olefinic couplings in cyclopentene (5·57 Hz) and cyclohexene (10·11 Hz), and fits in well with the trends observed in other bridged cyclohexenes.[16]

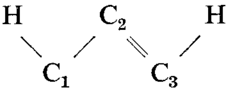
The correlation between H—C═C—H bond angles and $^3J_{\mathrm{HH}}$ couplings in cycloalkenes has recently been extensively discussed.[16]

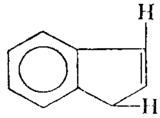
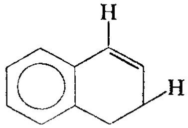
The coupling J_{12} is found as *ca.* 6·0 to 6·4 Hz in **6** to **10**. There do not seem to be in the literature a wide range of values for eclipsed couplings in  fragments. The analogous coupling in bicyclo[2,2,2]octene[27] is *ca.* 6·4 Hz, which is very similar to that in the present work. In the much more strained bicyclo[2,2,1]-heptene,[28] the analogous coupling is greatly reduced (2·89 Hz), although since this system is not eclipsed, but has a dihedral angle of *ca.* 20°, the coupling would have to be increased by *ca.* 0·4 Hz (to $\sim$3·3 Hz) to allow for this dihedral dependence before comparison would be valid. As with J_{23}, J_{12} seems sensitive to slight changes in molecular geometry, but there are insufficient data for quantitative discussion.

J_{34} is found as *ca.* 3·0 Hz in **2** to **4** and **10**. This value is intermediate between the values[29,30] of 4·4 Hz in  and 2·02 Hz in . This seems reasonable for a bridged cyclohexene system. The coupling J_{34} is apparently little affected by substitution of H by OH at C_4. By analogy with substituted ethanes[18] substitution of OH for H at C_4 in the *gauche* orientation of C_3—H and C_4—H would be expected to increase J_{34}. Possibly this increase in the pinene system is too small to be observed. There is also the possibility that the electronegativity effect of the OH is offset by a slight change in molecular geometry which alters the dihedral angle between the C_3—H and C_4—H bonds.

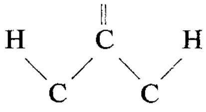
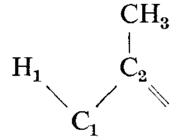
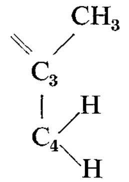
J_{45} is also *ca.* 3·0 Hz in **2** to **4** and **10**, and as in the case of J_{34}, does not seem greatly influenced by OH substitution at C_4.

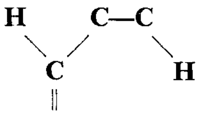
$^4J_{HH}$ allylic couplings

J_{13} is found to be *ca.* 0·8 to 1·0 Hz in the planar  system, but is rather larger, *ca.* 1·5 Hz, when C_2 is methyl substituted. In the case of **1**, the coupling has been shown to be positive.[3] This is in line with theory;[31] the C_1—H_1 bond lies in the node of the p orbital on C_2, so that π-electron contributions to the coupling are expected to be negative, while the σ-electron contribution is calculated as *ca.* +1·3 Hz. More sophisticated calculations[21,31] further suggest that introduction of a methyl at C_2 would cause the σ-contribution to increase-as observed here. More detailed experimental evidence of substitution effects of planar allylic systems has been given.[32]

J_{24} occurs only in **10** and **12**, where the values are |1·1| and ~|2| Hz, respectively. The values of analogous couplings in  and  are −1·98 and −1·86 respectively, which are similar to the value in **12**. Calculations[21,31] have suggested that substitution of OH for H on C_4 should make the coupling more positive, as found in the present work.

Isopropylidenic couplings.

These are defined as $^4J_{HH}$ couplings in the system . Their behaviour differs[31] somewhat from the analogous fully saturated system, on which the coupling is calculated as most positive for a 'W' orientation of bonds and falls off rapidly as coplanarity is lost. In the isopropylidenic system, $^4J_{HH}$ has a large π-electron contribution when the three central C atoms are in one plane and the two C—H bonds are perpendicular to this. In the pinenes, isopropylidenic couplings are of two types, namely , which in all cases is too small to be observed experimentally (⩽0·3 Hz) and the solitary example of  in **11**, which is *ca.* |1·0| Hz. Using dihedral angles found in models, calculations[31] of the σ-contribution in the two cases give +0·8 and +0·1 Hz, respectively, while the π-contributions are ~0 and ~ −1·8 Hz. Thus we calculate values of *ca.* +0·8 and −1·7 Hz in the two cases. Current theory therefore suggests that the coupling in **11** is likely to be more easily observed, as found, but the quantitative agreement is poor.



couplings

This coupling has not received separate theoretical treatment[31] but is regarded as analogous to the all-sp^3 carbon case.

In the pinenes, examples of this coupling are found as J_{27a} in **6** to **8** and **10** where the value is |0·8| to |1·1| Hz. The other example is J_{35} in **1** to **4**, |1·5| Hz; **6** and **7**, |2·1| Hz; **8**, |1·7| Hz and **10**, |1·9| Hz.

J_{35}. Here the coupling nuclei form a planar, or nearly so, 'W' system so that the coupling is presumably positive.[31] The coupling is apparently little affected by the hybridisation of the central C_4 atom, which is commonly sp^3, but sp^2 in **1** and **8**. Although the data are limited, the coupling is apparently increased by substitution of either CH_3 or OH for H at C_4. This is in line with theory.[21,31]

J_{27a}. Examination of molecular models gives the dihedral angles made by the C_2—H and C_{7a}—H bonds with the $C_2C_1C_7$ plane as *ca.* 80° and *ca.* 30°. These orientations correspond to only a small coupling constant in terms of a σ-contribution,[21,31] although a value of *ca.* |1| Hz is obtained experimentally. In contrast, for the coupling $J_{4a,7a}$, which in practice is too small to be observed ($\leqslant 0{\cdot}3$ Hz) the dihedral angles are both *ca.* 25°, which in terms of current theory would correspond to a larger coupling constant for $J_{4a,7a}$ than for $J_{2a,7a}$. Presumably, therefore, the p orbital on C_2 plays a significant effect in transmission of J_{27a}. Further theoretical work seems required.

$^5J_{HH}$—Homoallylic couplings

J(2Me-4) is found to be *ca.* |1·5| Hz in **2** and **3**, and *ca.* |2·0| Hz in α-pinene (**4**). Assuming an HC_4H angle of *ca.* 112°, the calculated value[21] is *ca.* $+1{\cdot}7$ Hz in good agreement with experiment. It is not known if the apparent substituent effect of $^5J_{HH}$ being reduced by OH substitution at C_4 is significant or not and no theoretical work on this is available.

Chemical shifts

In the series **1** to **12**, CH_3 and OH substituents have been introduced into the basic apopinene skeleton. The chemical shift data should therefore be of use for investigating current theories of the effect of the substituents on chemical shifts.

We began by noting that for the compounds **1** to **12**, equivalent changes in substitution pattern would be expected to give rise to equal changes in chemical shifts, provided that molecular geometry is not distorted by the substitution. The substituent induced chemical shifts are compared in Table 7 A to D.

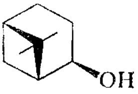
The chemical shifts produced by introducing a methyl group in place of hydrogen at R_4 are generally consistent. The only notable exceptions are for H_3 and H_5 in **8** → **1**, when the shifts of the protons are both $\sim$0·12 ppm smaller than in the other three examples. In both **8** and **1**, however, H_3 and H_5 are flanking a conjugated carbonyl group. It is possible that the anomaly arises because methyl substitution affects the anistropy of the conjugated carbonyl groups, or because methyl substitution causes a redistribution of electron density in the vicinity of H_3 and H_5 via the conjugated π-electron system of C_2, C_3 and C_4. Such an electron redistribution effect would be expected to be much less when C_4 is sp^3 hybridised.

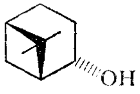
TABLE 7. EFFECTS OF EQUIVALENT SUBSTITUTIONS ON CHEMICAL SHIFTS IN PINENES

Example	H_1	H_3	H_{4a}	H_{4b}	H_5	H_{7a}	H_{7b}	CH_3-8	CH_3-9
A—Replacement of H *by* CH_3 *at* R_4: Upfield shifts (ppm) are positive									
(5) → **(4)**	0·18	0·34	—	—	0·04	0·04	0·04	−0·01	0·07
(8) → **(1)**	0·19	0·22	—	—	−0·08	0·06	0·06	0·02	0·03
(10) → **(2)**	0·19	0·33	—	0·06	0·02	0·05	0·08	−0·01	0·03
(9) → **(3)**	0·16	0·30	0·05	—	0·02	0·01	0·05	−0·02	0·02
B—Replacement of H *by* CH_3 *at* R_1									
(9) → **(6)**	−0·02	0·12	—	—	0·13	−0·15	−0·09	−0·05	−0·05
(5) → **(12)**	0·00	−0·04	—	—	0·05	−0·08	0·04	−0·04	0·10
C—Replacement of H *by* OH *at* R_2									
(4) → **(3)**	−0·10	−0·17	—	—	−0·10	0·09	−0·18	−0·07	−0·04
(12) → **(6)**	−0·10	0·03	—	—	0·00	0·05	−0·24	−0·12	0·06
(5) → **(9)**	−0·08	−0·13			−0·08	0·12	−0·19	−0·06	0·01
D—Replacement of H *by* OH *at* R_1									
(4) → **(2)**	−0·04	−0·18	—	—	−0·22	−0·11	−0·12	−0·08	−0·24
(5) → **(10)**	−0·05	−0·17	—	—	−0·20	−0·12	−0·16	−0·08	−0·20

The shifts produced by introduction of a methyl group at R_1 are much less consistent (Table 7B). The introduction of an OH group at R_2 (Table 7C) and at R_1 (Table 7D) give more consistent shifts, apart from H_3 and H_5 **12** → **6** (Table 7C). The greatest discrepancies are for the positions closest to the substitution, i.e. H_3 and H_5, and the spatially close positions 9-CH_3 and H_{7b}. As noted earlier, molecular models indicate that there is appreciable steric interaction only between the 9-methyl group and a methyl at R_1. Thus when a methyl group is introduced at R_1, it is likely that there is some change in molecular geometry at C_9 (or C_8) and C_4. The latter will probably lead to slight changes in the positions of both R_1 and R_2. The effect of this distortion upon chemical shifts is likely to be most pronounced when R_2 is an OH group, since these shifts are very sensitive to the orientation of this electronegative group. Substitution shifts for H_3, H_5 and 9-CH_3 are consistent between the cases **4** → **3** and **5** → **9**, (Table 7C), where there is no methyl group at R_1, but not with **12** → **6**, where there is a methyl at R_1 which agrees with the above reasoning. Similarly, in the introduction of a methyl group at R_1 (Table 7B) the subsequent distortion has little effect on the chemical shifts for **5** → **12**, but in **9** → **6** the resultant slight change in position of the OH on R_2 provides an important mechanism for changes in chemical shift. Thus the chemical shifts in **6** and **12** may have to be viewed with reserve for comparative purposes.

For the *cis/trans* isomer pairs (**2** and **3**, **6** and **7** and **9** and **10**), the 8-methyl is in all cases at $\delta = 1{\cdot}35$ ($\pm 0{\cdot}03$) ppm. The 9-methyl is at $\delta = 1{\cdot}10$ ($\pm 0{\cdot}04$) ppm for **2**, **7** and **10**, however, but at $\delta = 0{\cdot}90$ ($\pm 0{\cdot}04$) ppm for **3**, **6** and **9**. The 9-methyl resonance would be expected to be more susceptible to OH substitution at C_4 than would the 8-methyl, and hence the NMR evidence confirms the *cis/trans* assignments for OH substitution.[1] Similar behaviour of the **8** and **9** methyl resonances has recently been noted in the pinane series.[33] In the α- and β-nopinols,



and


and related molecules,

whose configurations and conformations are established independently by synthesis and coupling constant data, it is found that the 8-Me proton remains relatively constant at $\delta = 1{\cdot}20 \pm 0{\cdot}04$ ppm, while the 9-methyl is at $\delta = 0{\cdot}80 \pm 0{\cdot}04$ for a *trans*-hydroxyl and $\delta = 1{\cdot}00 \pm 0{\cdot}08$ ppm for a *cis*-hydroxyl. This pattern of chemical shifts parallels the situation in the present work, although the absolute values of δ are rather different, presumably because of the influence of the double bond both on chemical shifts and on the conformational flexibility of the pinenes.

In the steroid series, Zürcher[34] has shown how the changes in chemical shift of methyl groups may be calculated when the skeleton is substituted by, among others, —OH and C═O substituents. For the OH substituent his treatment calculates the electric field effect of the C—O dipole along the C—H bond, while for C═O substitution the electric field effect together with the C═O bond anisotropies are regarded as important. Recently Tribble *et al.*[35] have extended this type of treatment to the calculation of absolute chemical shifts in hydrocarbons using bond-anisotropy and Van-der-Waal's mechanisms, and claim reasonable agreement though with some notable exceptions, e.g. adamantane.

Our attempts to reproduce the trends in chemical shift of protons in the pinene skeleton upon OH or C═O substitution, using Zürcher's formalism, gave poor agreement with experiment. We conclude that the success claimed by Zürcher for steroids is not universal. Indeed Zürcher's treatment has been criticised[35] for being oversimplified and particularly for ignoring contribution due to Van-der Waal's forces.

Our attempts to reproduce the effects of methyl substitution using the procedure of Tribble *et al.* also gave results in direct contradiction to experiment. This can be easily visualised as follows. The introduction of a methyl group at R_4 will produce, due to the C—C bond anisotropy, low field shifts of all protons except H_1 and H_3, which are situated at the side of the C—C bond. The Van-der-Waal's term gives low field shifts at all positions. We observed, however, high field shifts for all positions. Thus calculations based on only these mechanisms do not begin to predict proton chemical shifts.

Tribble *et al.*'s treatment can be further criticised in that unlike all previous treatments which calculate differences in chemical shifts on substitution, they calculate absolute δ values. Thus the chemical shift difference between the CH_3 protons in ethane and TMS is explained as due to C—C bond anisotropy plus Van-der-Waal's contributions *without any mention of the effect of the* C—C *versus the* C—Si *bonds.* This we suggest contradicts most chemical thinking and illustrates the dangers of an uncritical approach towards these calculations.

EXPERIMENTAL

The spectra were measured in $CDCl_3$ solution, concentration *ca.* 150 mgs/ml, on a Varian HA-100 spectrometer, and occasionally on Varian 220 MHz and 300 MHz spectrometers.

Preparation of materials

Optical rotations were determined for chloroform solutions in a 1-dm tube. Infrared spectra were determined using a Perkin-Elmer Infracord. Analytical gas-liquid chromatography (GLC) was carried out on a Perkin-Elmer F.11 chromatograph with a 100-ft. capillary column coated with PEG 400 and preparative work on a Wilkins Aerograph A700 with an 18 ft. × $\frac{3}{8}$ in. copper column packed with 12% Carbowax 20 M on 60 to 80 mesh Celite.

Myrtenal. Redistilled α-pinene (272 g), α_{22}^{D} − 36·9° (neat, 1 dm) was oxidised[36] with selenium dioxide (234 g) in dry ethanol, to give myrtenal (150 g, 50%) b.p. 57 to 59°/1 mm. Analytical GLC showed this to be 91% pure.

Apopinene. Myrtenal was decarbonylated[36] to apopinene b.p. 139·5°/746 mm, α_D^{22} − 15·9° (neat, 1 dm), 98·5% pure by analytical GLC.

trans-Apopinenyl Acetate. (−)-apopinene (13·6 g), α_D^{22} − 15·9° (neat, 1 dm) was oxidised by refluxing with lead tetra-acetate (49 g) and calcium carbonate (20 g) in dry benzene (150 mls) for 6 hrs. Work-up and distillation yielded the product (7·3 g, 36%) b.p. 53 to 55°/1 mm plus a distillation residue (12 g). Analytical GLC indicated a purity of 90%. Preparative GLC at 140° gave a 99% pure sample of *trans*-apopinenyl acetate, $[\alpha]_D^{22}$ + 48·6° (c.10) ν_{max} 1730, 899, 739 and 728 cm^{-1}. (Found: C, 73·6; H, 8·8. $C_{11}H_{16}O_2$ requires C, 73·3; H, 9·0%).

trans-Apopinenol. (+)-*trans*-apopinenol acetate (1·43 g, 90% pure) was reduced with lithium aluminium hydride (0·18 g) in ether to give a product (1·10 g) consisting of 90% *trans*-apopinenol. Preparative GLC at 140° gave a pure sample of *trans*-apopinenol, $[\alpha]_D^{22}$ + 47·8° (c 10) ν_{max} 3420, 1624, 1033, 872 and 725 cm^{-1}. (Found: C, 78·0; H, 10·2. $C_9H_{14}O$ requires C, 78·2; H, 10·2%), *p*-nitrobenzoate, m.p. 74·5 to 75·5°.

Apopinenone. (+)-*trans*-apopinenol (3·0 g, 90% pure) was oxidised with manganese dioxide in pentane[37] for 24 hrs to give a pale yellow product (2·9 g). Preparative GLC at 140° gave a pure sample of apopinenone, m.p. 25 to 27°, $[\alpha]_D^{22}$ + 85·5° (c.9·8). ν_{max} 1685 cm^{-1}.

Hydrogenation of apopinenone gave nopinone $[\alpha]_D^{19}$ + 11·1° (c 10) compared with the values of $[\alpha]_D^{22}$ + 33 (c 10) of material from β-pinene which had $[\alpha]_D^{22}$ − 18·4 (neat, 1 dm). Clearly, the lead tetraacetate oxidation involves loss of approximately two thirds of the optical activity of the starting material.

cis-Apopinenol. (+)-apopinenone (0·50 g) was reduced at 0°C with lithium aluminium hydride (0·10 g) in ether to give a white crystalline solid (0·51 g) m.p. 48 to 70°. Analytical GLC showed a mixture of *cis*- and *trans*-alcohols in the ratio 30:1. Preparative GLC at 140° gave a pure sample of *cis*-apopinenol m.p. 77·5 to 78·5°. (Found: 78·2%; H, 10·3%. C_9H_4O requires C, 78·2%; H, 10·2%).

trans-Pin-3-ene-2-ol. To a solution of apopinenone (0·50 g, 95% pure) in ether (15 mls) at −70° was added 5·0 mls of 0·92 M methyl lithium in ether over 10 mins. Decomposition of the complexes with water followed by extraction gave a pale yellow liquid (0·51 g). Analytical GLC indicated *ca.* 1% *cis*-pin-3-ene-2-ol and 95% of the *trans*-isomer. Preparative GLC at 130° gave a pure sample of *trans*-pin-3-ene-2-ol, m.p. 44 to 46°, (Lit.[9] m.p. 44°), ν_{max} 3320, 1668, 1620, 929, 919 and 741^{-1}.

cis-Pin-3-ene-2-ol. Prepared by the method of Whitham.[38]

cis-δ-Pinene. This was prepared by the general method of Shapiro and Heath.[39]

3-*Methyl-apopinene.* The authors are grateful to Dr E. Klein of Dragoco, Holzminden, for a generous gift of a sample of this compound.[40]

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