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LONG RANGE COUPLING AND SOLVENT SHIFTS IN THE NMR SPECTRA OF BORNANE DERIVATIVES

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Abstract—Long range coupling between the C_8 and C_9 *geminal* dimethyl groups of bornanes is shown to occur. The use of line widths in assigning the Me groups in the NMR spectra of such compounds is described. Substituent effects on the shifts of bornane Me groups is discussed.

THERE is considerable experimental evidence to show that spin-spin coupling occurs between protons separated by 4σ bonds and is at a maximum when the five atoms involved adopt a "W" configuration.[1,2] In particular, the signals due to a Me group may be broadened or even observably split when one or more hydrogen atoms is suitably located with respect to it.[3–5] Such geometry is found in the *geminal* dimethyl grouping and in cases where the two Me groups are non-equivalent, coupling should be observed. Indeed this has been described in a recent paper,[6] where the Me's concerned are attached to a carbon atom itself attached to an electronegative atom.

We now report long-range coupling between the protons of the C_8 and C_9 Me groups of camphor and its derivatives and the use of spectral line widths, from spectra measured in different solvents, for the correlation of assignments.

The C_{10} Me group of camphor has been identified in the NMR spectrum by the synthesis of 10-d_1-camphor[7] while we have identified the C_9 Me group by synthesis of 9-d_1-camphor (III), 9-d_1-bornane-2,3-dione (IV) (9-d_1-camphorquinone) and the dimers 9,9′-*bi*(bornan-2-one) (V), 9,9′-*bi*(bornane-2,3-dione) (VI) and 9,9′-*bi*(2-ethylenedioxybornane) (XXVIII).[8] Furthermore, comparison of the spectra of camphoric anhydride (XVIII) and apocamphoric anhydride (XIX) allows assignment of the C_{10} Me in this case.

In all the spectra of bornane derivatives measured, two Me resonances were appreciably broader than the third. In each of the cases in which an unequivocal assignment can be made (by deuteration or by formation of a dimer) it is the C_{10} Me group which is the narrowest of the three Me signals in the spectrum while of the other two, the C_8 Me is slightly broader than the C_9 Me. In a comparison of the line widths of camphoric anhydride (XVIII) and apocamphoric anhydride (XIX) it is the narrowest line which is missing from the spectrum of XIX which may therefore be assigned to C_{10}. In camphor, the signals due to the C_8 and C_9 Me protons in $CDCl_3$ had $\Delta W_{\frac{1}{2}}(= W_{\frac{1}{2}} - W_{\frac{1}{2}}\text{TMS})$ of 0·84 and 0·78 c/s respectively, whereas the signal due to the C_{10} Me protons had $\Delta W_{\frac{1}{2}} = 0{\cdot}18$ c/s. Similar results were obtained for a comparison of bornane-2,3-dione (II), 9-d_1-bornane-2,3-dione and its dimer (IV), and also of 2-ethylenedioxybornane (XXII) and its dimer (XXVIII). As a result a new assignment of the Me peaks of bornane-2,3-dione in benzene is given.[cf. 7]

We consider that this broadening of the signals of the *gem* Me groups is due to long-range coupling between them. Coupling through 4σ bonds having a "*W*" configuration is clearly seen in the spectrum of 9-bromobornan-2-one (IX) where the signal due to the C_8 Me group is observed as a doublet ($J = 1{\cdot}0$ c/s) and one of the arms of the AB quartet shown by the CH_2Br grouping is split into a 1:3:3:1 quartet.[9] Similar effects were noted in the spectra of the C_9 sulphonic acid derivatives (XI and XII).

Although coupling constants are not solvent invariant,[10, 11] line widths may be used to correlate assignments made on spectra measured in different solvents. Thus although values of $\Delta W_{\frac{1}{2}}$ were found not to be solvent invariant, all available evidence indicates the relative widths of the 3 peaks were in the same order.

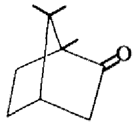
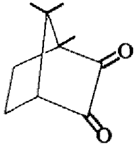
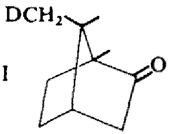
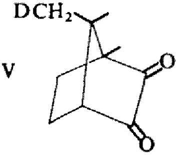
The solvent shifts of a number of bornanones between CCl_4 and benzene have been measured and the results are generally in good agreement with those of Connolly and McCrindle,[7, 12] although substituents within the rest of the molecule also have some effect on the shifts, due in some cases to formation of a collision complex[13] with the substituent. In bornane-2,3-dione (II) and the sulphonic acid derivatives (XI and XII) it is difficult to predict the nature of the complex and its effects, but in general the shifts in these molecules are quite large. In 3-*endo*bromobornan-2-one (VII) and 3-*endo*-9-dibromobornan-2-one (VIII) the shifts of the C_8 Me are very large (0·60 p.p.m.) compared to those in camphor, possibly owing to a different orientation of the benzene in the collision complex caused by the *endo*-bromine. The spectra of a number of bornane derivatives not containing a ketone group were also measured in benzene and shifts of the Me resonances were again noticed although there did not appear to be any correlation of solvent effects with molecular structure.

An investigation was made of the change in resonances of the Me groups when substituents in the basic bornane skeleton were varied. For example it was noted that if a bornan-2-one was converted to its corresponding C_2 ethylenedioxy compound, then there appeared to be a uniform effect through a series of compounds: The C_8 Me became slightly deshielded, while the C_9 and C_{10} Me's were shielded relative to the ketone. However on converting the C_2 carbonyl group to an *exo* hydroxyl group, the effect is far from uniform in a series, even for any one Me group. If a bornan-3-one is converted to an *exo* oxygen function, then the effect seems to be general for C_8 and C_9 (C_8 again deshielded and C_9 shielded), while the effect on C_{10} does not seem to be general. If the C_3 methylene group is replaced by an *exo* oxygen function irrespective of other groups present, then again the general effect is a resultant deshielding of C_8 and shielding of C_9, and a non uniform effect on C_{10}. It appears therefore, that substitution of an *exo* oxygen function at either C_2 or C_3 results in deshielding of C_8 and shielding of C_9, while there is no general effect on C_{10}. It becomes apparent that in work of this type it is inadvizable to make generalizations on the basis of one or two examples.

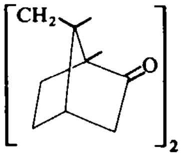
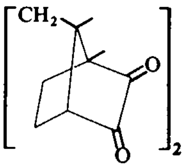
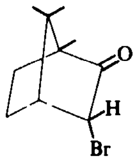
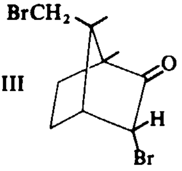
Long-range coupling between the *exo* protons of C_2 and C_6 and of C_3 and C_5 is well known,[1] and during the present work, several more examples were observed. In 3-*endo*bromobornan-2-one (VII), 3-*endo*-9-dibromobornan-2-one (VIII) and 3-*endo*bromobornan-2-one-9-sulphonylchloride (XII) coupling between the *exo* H_3 and H_4 protons in each case is 4·5 c/sec and each arm of the H_3 doublet is further split into a doublet by long-range coupling ($J = 1{\cdot}5$ c/s) with the *exo* H_5 proton.

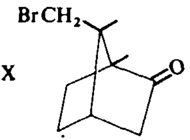
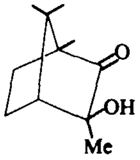
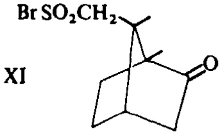
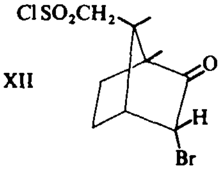
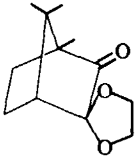
Taken together our results indicate that it is possible to assign the Me peaks of

Line widths and positions in various solvents

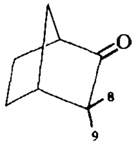
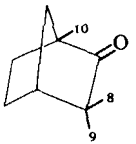
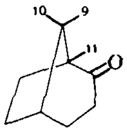
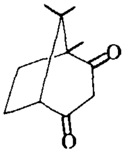
Compound	Me group	CCl_4		Benzene		$CDCl_3$		Pyridine		δCCl_4—δC_6H_6	$\delta CDCl_3$—δC_6H_6	$\delta CDCl_3$—δpy
		$\Delta W_{\frac{1}{2}}$	δ	$\Delta W_{\frac{1}{2}}$	δ	$\Delta W_{\frac{1}{2}}$	δ	$\Delta W_{\frac{1}{2}}$	δ			
I 	8	1·11	0·85	0·78	0·66	0·84	0·83	0·94	0·73	+0·19	+0·17	+0·10
	9	0·86	0·97	0·70	0·75	0·78	0·97	0·82	0·83	+0·22	+0·22	+0·14
	10	0·41	0·87	0·16	0·87	0·18	0·91	0·24	0·89	0·00	+0·04	+0·02
II 	8	0·89	0·92	0·94	0·56	0·76	0·93	1·11	1·01	+0·36	+0·37	−0·08
	9	—	1·05	0·86	0·51	0·60	1·08	1·07	0·78	+0·54	+0·59	+0·30
	10	—	1·05	0·32	0·84	0·42	1·11	0·56	0·86	+0·21	+0·27	+0·25
III 	8	0·84	0·83	—	0·63					+0·20		
	9	t	0·95	t	0·70							
	10	0·45	0·85	—	0·88					−0·03		
IV 	8			—	0·60	—	0·95				+0·35	
	9			t	0·57	t	1·09					
	10			—	0·86	—	1·11				+0·25	

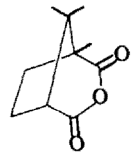
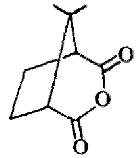
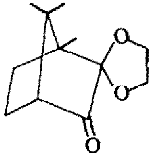
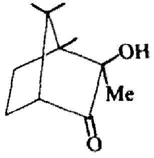
LINE WIDTHS AND POSITIONS IN VARIOUS SOLVENTS

Compound	Me group	CCl_4		Benzene		$CDCl_3$		Pyridine		$\delta CCl_4 - \delta C_6H_6$	$\delta CDCl_3 - \delta C_6H_6$	$\delta CDCl_3 - \delta py$
		$\Delta W_{\frac{1}{2}}$	δ	$\Delta W_{\frac{1}{2}}$	δ	$\Delta W_{\frac{1}{2}}$	δ	$\Delta W_{\frac{1}{2}}$	δ			
V 	8	0·91	0·84	0·81	0·56	—	0·95			+0·28	+0·39	
	10	0·39	0·90	0·55	0·96	—	0·86			−0·06	+0·10	
VI 	8					d $J = 0·9$	0·96					
	10					—	1·12					
VII 	8	1·12	1·09	1·08	0·48					+0·61		
	9	—	0·95	1·00	0·62					+0·33		
	10	—	0·93	0·51	0·79					+0·14		
VIII 	8	d	1·12	d	0·52					+0·60		
	10	0·48	0·99	0·33	0·62					+0·37		

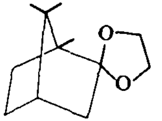
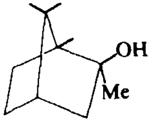
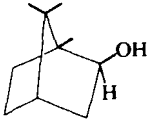
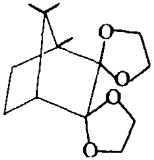
IX		8	d	1·02	d	0·69					+0·33		
		10	0·16	0·93	0·36	0·72					+0·21		
X		8	1·15	0·99	1·52	0·71					+0·28		
		9	1·07	1·05	1·24	1·12					−0·07		
		10	0·31	0·89	0·50	0·89					0·00		
		11	0·37	1·25	0·71	1·08					+0·17		
XI		8	d	1·10	d	0·84	d	1·27			+0·26	+0·43	
		10	—	0·98	0·52	0·53	0·40	0·98			+0·45	+0·45	
XII		8			d	0·76	d	1·30	d	1·47		+0·53	+0·71
		10			0·53	0·54	0·40	1·08	0·67	1·15		+0·54	+0·61
XIII		8	—	0·99	1·04	1·08	1·18	1·04			−0·09	−0·04	
		9	—	0·99	1·02	0·71	1·18	1·07			+0·28	+0·36	
		10	0·36	0·87	0·41	0·87	0·22	0·95			0·00	+0·08	

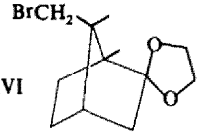
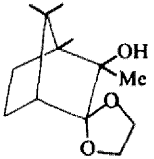
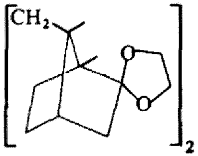
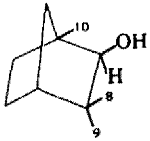
LINE WIDTHS AND POSITIONS IN VARIOUS SOLVENTS

Compound	Me group	CCl_4		Benzene		$CDCl_3$		Pyridine		$\delta CCl_4—\delta C_6H_6$	$\delta CDCl_3—\delta C_6H_6$	$\delta CDCl_3—\delta py$
		$\Delta W_{\frac{1}{2}}$	δ	$\Delta W_{\frac{1}{2}}$	δ	$\Delta W_{\frac{1}{2}}$	δ	$\Delta W_{\frac{1}{2}}$	δ			
XIV 	8	0·83	1·00	—	0·89					+0·11		
	9	0·86	0·99	—	0·89					+0·10		
XV 	8	—	0·99	0·60	0·92					+0·07		
	9	—	0·99	0·98	0·90					+0·09		
	10	0·51	1·09	0·60	1·10					−0·01		
XVI 	9	1·09	0·85	—	0·68					+0·17		
	10	0·94	0·95	—	0·66					+0·29		
	11	0·41	0·92	0·44	1·01					−0·09		
XVII 	9	1·00	0·81	1·21	0·65					+0·16		
	10	0·77	1·03	0·95	0·48					+0·55		
	11	0·45	1·08	0·56	0·93					+0·15		

XVIII		8					0·98	1·12	0·97	0·96		+0·16
		9					0·84	1·04	0·94	0·80		+0·24
		10					0·44	1·30	0·52	1·18		+0·12
XIX		8					0·82	1·24	0·83	1·07		+0·17
		9					0·76	1·08	0·71	0·85		+0·23
XX		8	1·17	1·04	1·12	1·08					−0·04	
		9	1·07	0·96	1·04	0·67					+0·29	
		10	0·39	0·88	0·56	0·89					−0·01	
XXI		8	1·08	0·97	1·13	1·16					−0·19	
		9	0·88	1·09	1·11	0·69					+0·40	
		10	0·42	0·95	1·30	1·05					−0·10	
		11	0·50	1·17	0·39	0·91					+0·26	

LINE WIDTHS AND POSITIONS IN VARIOUS SOLVENTS

Compound		Me group	CCl$_4$	
			$\Delta W_{\frac{1}{2}}$	δ
XXII		8 9 10	1·58 1·27 0·57	1·03 0·86 0·77
XXIII		8 9 10 11	1·56 1·51 0·50 0·74	0·91 1·15 0·87 1·19
XXIV		8 9 10	1·33 1·15 0·78	1·00 0·81 0·87
XXV		8 9 10	1·22 1·08 0·40	1·10 0·84 0·73

XXVI		8	d	1·13
		10	0·40	0·80
XXVII		8	1·53	1·16
		9	1·27	0·86
		10	0·13	1·06
		11	0·41	0·83
XXVIII		8	0·84	0·97
		10	0·54	0·75
XXIX		8	1·13	0·97
		9	1·32	0·84
		10	0·66	1·07

bornane type compounds on the basis of line widths, and more generally, it is possible to correlate Me resonances in different solvents on the basis of their line widths.

EXPERIMENTAL

Line widths for the tertiary Me groups in the NMR spectra of bornane derivatives were measured on a Varian A-60 spectrometer using AR CCl_4, $CDCl_3$, benzene or pyridine as solvents with TMS as internal reference. In all spectra, the line width of TMS was obtained in the range 0·35 to 0·56 c/s and line widths at half-height, expressed as $\Delta W_{\frac{1}{2}} (= W_{\frac{1}{2}} - W_{\frac{1}{2}}\text{TMS})$, were measured at 0·1 c/s/sec sweep time, employing a 50 c/s sweep width. Samples were not degassed.

The preparation of 9-d_1-bornan-2-one (III), 9-d_1-bornane-2,3-dione (IV), 9,9′-*bi*(bornan-2-one) (V), 9,9′-*bi*(bornane-2,3-dione) (VI), 9-bromobornan-2-one (IX), 3-*exo*hydroxy-3-methylbornan-2-one (X), 3-ethylenedioxybornan-2-one (XII), 1,8,8-trimethylbicyclo (3,2,1) octan-2-one (XVI), 2-ethylenedioxybornan-3-one (XX), 2-*exo*hydroxy-2-methylbornan-3-one (XXI), 2-ethylenedioxybornane (XXII), 2,3-*bis*ethylenedioxybornane (XXV), 9-bromo-2-ethylenedioxybornane (XXVI), 3-ethylenedioxy-2-*exo*hydroxy-2-methylbornane (XXVII), and 9,9′-*bi*(2-ethylenedioxybornane) (XXVIII) are described in another paper.[8] Bornane-2,3-dione (II) was prepared according to Evans *et al.*,[14] 3-bromobornan-2-one (VII) according to Kipping and Pope,[15] and 3,9-dibromobornan-2-one (VIII) according to Corey *et al.*[16] Bornan-2-one-9-sulphonylbromide (XI) was prepared according to Kipping and Pope,[17] 3-*endo*bromobornan-2-one-9-sulphonylchloride (XII) according to Delépine *et al.*[18] and 1,8,8-trimethylbicyclo(3,2,1)octane-2,4-dione (XVII) by the method of Eistert *et al.*[19] Apocamphoric anhydride (XIX) was prepared by the method of Marsh and Gardner,[20] 2-*exo*hydroxy-2-methylbornane (XXIII) by the method of Zelinsky[21] and *iso*borneol (XXIV) according to Bunton.[22]

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