N.m.r. Solvent Shifts and the Conformations of αβ-Unsaturated Ketones

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ALTHOUGH attention has been drawn to the use of solvent shifts in the interpretation of n.m.r. spectra only a few isolated measurements have been reported for αβ-unsaturated ketones.[1]

αβ-Unsaturated ketones in general may exist in the two possible approximately coplanar forms together with other less planar forms when there is overcrowding on account of steric interference by bulky substituents.[2] The superscripts, α and β on the substituents indicate the position of the substituents and the superscripts *cis* and *trans* indicate the stereochemistry of the β-substituents, with respect to the CO·R group.

Benzene has previously been shown to act selectively in producing solvent shifts relative to carbon tetrachloride for several αβ-unsaturated carbonyl compounds.[1,3,4] For the present measurements the solvent shift, Δ is defined as:—

$$\Delta \text{ (p.p.m.)} = \tau \text{ in } C_6H_6 - \tau \text{ in } CCl_4$$

all τ-values being measured with respect to tetramethylsilane as internal standard. No attempt was made to keep the concentrations constant, but they were in the range 10 to 20% vol./vol. Separate measurements for mesityl oxide indicated that the τ-values decreased by an average of 0·05 and not more than 0·13 p.p.m. as the concentrations varied from 1—25%. Some typical solvent shifts are shown in the Table. In the Table the solvent shifts are grouped according to the position of the substituent and independently of the nature of the substituent because it was found that variations from H to CH_2 or Me had little effect on the solvent shifts within the range of ketones studied. The labile ketones exist predominantly in the conformations stated, as proved by earlier physical measurements.[2,5,6]

The largest difference in solvent shifts between the *s-cis-* and *s-trans*-series is shown by the $R^{\beta cis}$ substituents. For the *s-cis*-conformations Δ is quite small being usually either slightly positive or slightly negative, whilst for the *s-trans* Δ is much larger and positive. The R and $R^{\beta trans}$ substituents in both the *s-cis-* and *s-trans*-series usually show relatively large and positive Δ-values. The R^{α} substituents show more variable values.

These results can best be explained by recourse to the model recently proposed by Connolly and McCrindle for saturated cyclic ketones in which reference planes were drawn through the carbon atom of the carbonyl group at right angles to the bonds,[7] (see diagram). Benzene complexes with the ketones preferentially behind the reference

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[1] For a review see N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, 1965, p. 159.

[2] *Inter alia*, C. J. Timmons, B. P. Straughan, W. F. Forbes, and R. Shilton, in "Advances in Molecular Spectroscopy," ed. A. Mangini, Pergamon Press, Oxford, 1962, Vol. 2, p. 933.

[3] J. V. Hatton and R. E. Richards, *Mol. Phys.*, 1962, **5**, 153.

[4] J. A. Pople and T. Schaefer, *Mol. Phys.*, 1960, **3**, 547.

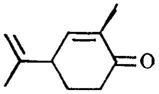
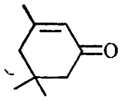
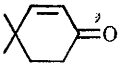
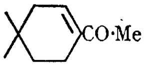
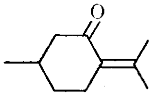
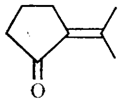
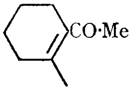
[5] J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 1949, 2957.

[6] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 1960, 3425; K. Noack and R. N. Jones, *Canad. J. Chem.*, 1961, **39**, 2201; M. E. Kronenberg and E. Havinga, *Rec. Trav. chim.*, 1965, **84**, 17.

[7] J. D. Connolly and R. McCrindle, *Chem. and Ind.*, 1965, 379.

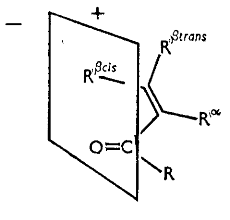
TABLE

Solvent shifts (Δ p.p.m.) for some αβ-unsaturated ketones*

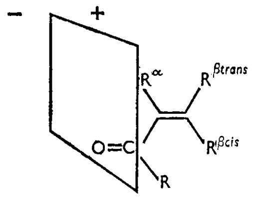
Conformation	Compound	R	Rα	R$^{\beta trans}$	R$^{\beta cis}$
Fixed *s-trans*			−0·07	0·47	
,,		0·03	−0·10	0·32	0·39
,,		0·10	−0·11	0·40	
,,	Cholest-4-en-3-one		−0·19		
Labile *s-trans*	MeCH=CH·CO·Me	0·19	0·07	0·38	0·27
,,	CH$_2$=CMe·CO·Me	0·25	0·04	0·19	0·32
,,	MeCH=CMe·CO·Me	0·19	0·00	0·35	0·38
,,	PhCH=CH·CO·Me	0·22	0·00		0·03
,,		0·21	*ca.* −0·1	*ca.* 0·26	0·34
Fixed *s-cis*				0·26	−0·11
,,				0·32	−0·01
Labile *s-cis*	Me$_2$C=CH·CO·Me	0·17	0·19	0·31	0·03
,,	Me$_2$C=CMe·CO·Me	0·04	0·16	0·21	−0·08
,,	PhCH=CH·CO·CMe$_3$		−0·02		−0·29
,,	PhCH=CH·CO·CH·Me$_2$	0·25	0·06		−0·11
,,		0·17			−0·03

* When the use of benzene as solvent would have obscured part of the spectrum, hexadeuterobenzene was used instead.

plane because the negative oxygen end of the carbonyl group inhibits complex formation with an electron donor. On account of the shielding effect of the benzene, substituents near to the benzene show upfield shifts with respect to tetramethylsilane which similarly to the substituents near to the oxygen does not complex with the benzene. From the diagrams it can be seen that only the R$^{\beta cis}$ substituent in the *s-cis*-conformation is definitely in the vicinity of the oxygen atom



s–cis



s–trans

and does not therefore become shielded. As drawn the R^{α} substituent in the *s-trans*-conformation is close to the reference plane and because its exact position will vary slightly from molecule to molecule it can be understood why it shows a variable solvent shift.

The example of mesityl oxide requires special comment. Its *s-cis*-conformation was first demonstrated by dipole-moment measurements[5] and subsequently confirmed.[2,6] However, several authors have drawn it in the *s-trans*-conformation and this has confused the discussion of its n.m.r. spectrum.[1,3,8] Very recently Baldwin has reinterpreted the n.m.r. spectrum on the basis of the established *s-cis*-conformation.[9]

The present work both illustrates the use of solvent effects in n.m.r. spectra in distinguishing the conformations of labile $\alpha\beta$-unsaturated ketones and emphasises the importance of measuring Δ- as well as τ- and J-values when studying molecules containing polar groups.

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[8] J. C. D. Brand and G. Eglinton, "Applications of Spectroscopy to Organic Chemistry," Oldbourne Press, London, 1965, p. 73.

[9] E. Baldwin, *J. Org. Chem.*, 1965, **30**, 2423.