Spectroscopic Studies. Part III.[1] Proton Magnetic Resonance Spectra and Solvent Shifts of Some αβ-Unsaturated Ketones

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The ^{1}H n.m.r. spectra of several αβ-unsaturated ketones of fixed and labile conformations have been determined in benzene and carbon tetrachloride solutions and their solvent shifts recorded. Although the solvent shift data are consistent with the known conformations of these ketones, only an approximate relationship between solvent shift and degree of coplanarity could be found.

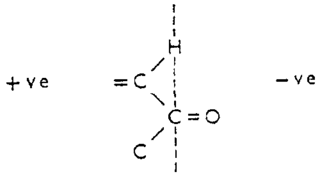
The approximate conformation of αβ-unsaturated ketones may also be determined using solvent shift data in solvents other than aromatic complexing solvents.

RECENTLY, several authors have demonstrated the use of ^{1}H n.m.r. solvent shift data in determining the conformations of ketones.[2-8] In the case where carbon tetrachloride is used as the reference solvent and benzene as the complexing solvent, the solvent shift, Δ, for a given proton is defined by

$$\Delta_{C_6H_6-CCl_4} = \delta_{C_6H_6} - \delta_{CCl_4}$$

where the chemical shifts are in τ units. Thus a positive chemical shift corresponds to a shielding of the proton by the benzene ring current.

It has been shown that for αβ-unsaturated ketones all protons lying behind a plane drawn through the carbonyl carbon atom, perpendicular to the double bond, experience a shielding which increases with distance from the plane, and conversely protons on the oxygen side of the plane are deshielded relative to their chemical shift in carbon tetrachloride solution.[2-4] Protons in or near the plane generally experience either a very small positive shift or none at all.



The aim of this present investigation is to test the validity of conformational deductions from solvent shift data for a number of αβ-unsaturated ketones, the conformations of most of which have been determined by other means.

The following compounds were investigated, and their ^{1}H n.m.r. solvent shifts are listed in Table 1: $\mathrm{CH_2{=}CH{\cdot}COMe}$ (I), $\mathrm{MeCH{=}CH{\cdot}COMe}$ (II), $\mathrm{Me_2C{=}CH{\cdot}COMe}$ (III), $\mathrm{Me_2C{=}CMe{\cdot}COMe}$ (IV), $\mathrm{Me_2C{=}CMe{\cdot}COEt}$ (V), $\mathrm{Me_2C{=}CMe{\cdot}COPr^i}$ (VI), $\mathrm{Me_2C{=}CMe{\cdot}COBu^t}$ (VII), *cis*-$\mathrm{Et(Me)C{=}CH{\cdot}COPr^i}$ (VIIIa), *trans*-$\mathrm{Et(Me)C{=}CH{\cdot}COPr^i}$ (VIIIb), *cis*-$\mathrm{Et(Me)C{=}CH{\cdot}COBu^t}$ (IXa), *trans*-$\mathrm{Et(Me)C{=}CH{\cdot}COBu^t}$ (IXb), 3-Methylcyclopent-2-enone (X), 10-Methyl-$\Delta^{1(9)}$ octalin-2-one (XI), 4,4-Dimethylcyclohex-2-enone (XII), Pulegone (XIII), *trans*-2-Ethylidenecyclohexanone (XIV), and 1-Acetyl-2-methylcyclohexene (XV).

EXPERIMENTAL

Materials.—The preparation and purification of the above compounds, with the exception of (I), (II), (VIII), (IX), (XII), and (XIV), have been described.[1] All the products were finally purified by g.l.c. on a Wilkens Autoprep A700 with a 20 ft. × ⅜ in. silicone oil column or 25 ft. × ⅜ in. Carbowax 20M column, or on a Varian Aerograph 712 with a 50 ft. × ⅜ in. Carbowax 20M column.

Methyl Vinyl Ketone (I).—A commercial sample purified by fractional distillation and g.l.c. on a 50 ft. Carbowax 20M column had n_D^{25} 1·4089. The ketone was used as soon as possible after purification as it polymerised rapidly.

Ethylideneacetone (II).—A commerical sample was purified by fractional distillation under reduced pressure, b. p. 30°/13 mm. Final purification was carried out by g.l.c. on a 50 ft. Carbowax 20M column. The pure liquid had n_D^{26} 1·4341.

2,5-*Dimethylhept*-4-*en*-3-*one* (VIII).—This was prepared by the method of Colonge and Mostafavi from isobutyryl chloride and 2-methylbutene in the presence of stannic chloride.[9] The olefin was prepared by the Wittig olefin synthesis from methylenetriphenylphosphorane and ethyl methyl ketone.[10] As the olefin had a very low boiling point (31°) and tended to form an azeotrope with ether, the final reaction of the ylid with ethyl methyl ketone was carried out in benzene, and the olefin then distilled off and reacted with the acid chloride. The final yields were very low. Although all impurities were removed by distillation and g.l.c., it was found to be impossible to separate the *cis*- and *trans*-isomers, even on the 50 ft. g.l.c. column. The mixture of conformers was colourless and had a distinctive odour, very different to that of the isomeric ketone (VI).

The ^{1}H n.m.r. spectra of the mixture were determined, and the assignment of peaks was made by assuming that the *trans*-form was more abundant than the *cis*, as there is less steric hindrance in the former. From the ratio of peak

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[1] Part II, F. H. Cottee, B. P. Straughan, C. J. Timmons, W. F. Forbes, and R. Shilton, *J. Chem. Soc.* (*B*), 1967, 1146.

[2] (*a*) N. S. Bhacca and D. H. Williams, *Tetrahedron Letters*, 1964, 3127; (*b*) N. S. Bhacca and D. H. Williams, *Tetrahedron*, 1965, **21**, 2021.

[3] C. J. Timmons, *Chem. Comm.*, 1965, 576.

[4] D. H. Williams, *Tetrahedron Letters*, 1965, 2305.

[5] J. D. Connolly and R. McCrindle, *J. Chem. Soc.* (*C*), 1966, 1613.

[6] D. H. Williams and D. A. Wilson, *J. Chem. Soc.* (*B*), 1966, 144.

[7] P. C. Cherry, W. R. T. Cottrell, G. D. Meakins, and (Mrs.) E. E. Richards, *J. Chem. Soc.* (*C*), 1967, 181.

[8] I. Ronayne and D. H. Williams, *J. Chem. Soc.* (*B*), 1967, 540.

[9] J. Colonge and K. Mostafavi, *Bull. Soc. chim. France*, 1939, **6**, 335.

[10] M. F. Ansell and D. A. Thomas, *J. Chem. Soc.*, 1961, 539.

intensities the relative abundance of the *trans*-form was estimated to be about 70%

2,2,5-*Trimethylhept*-4-*en*-3-*one* (IX).—This was prepared by the method of Colonge and Mostafavi from pivaloyl chloride and 2-methylbutene in the presence of stannic chloride.[9] The olefin was prepared by dehydration of t-pentyl alcohol with syrupy phosphoric acid and careful separation of the isomers on a spinning-band column. Although yields of the olefin were higher using this method, it was found to be impossible to obtain the required isomer in greater than 60% purity as it formed an azeotrope with the higher boiling isomer (b. p. 38°).

The ketone was again purified by fractional distillation and g.l.c., but, as for compound (VIII), the *cis*- and *trans*-isomers could not be separated. The ^{1}H n.m.r. spectra of the mixture were determined and the ratio of *trans* : *cis* found to be 7 : 3.

4,4-*Dimethylcyclohex*-2-*enone* (XII).—This was prepared by the method of Bordwell and Wellman from isobutyraldehyde and methyl vinyl ketone.[11] The product was purified by fractional distillation under reduced pressure, the fraction, b. p. 53—56°/4 mm., being further purified by g.l.c. on a 25 ft. Carbowax column. The pure liquid was colourless and had n_D^{22} 1·4737 (lit.,[11] n_D^{25} 1·4696).

trans-2-*Ethylidenecyclohexanone* (XIV).—This was prepared by the method of Dubois and Dubois from acetaldehyde and cyclohexanone in base followed by dehydration in acid.[12] The product was purified by fractional distillation under reduced pressure, the fraction, b. p. 88—95°/8 mm. being further purified by g.l.c. on a 25 ft. Carbowax column. The *cis*- and *trans*-isomers were shown to be in the ratio of about 1 : 20 but there was insufficient of the *cis*-isomer present to condense in the collecter bottles. The *trans*-isomer was colourless and had n_D^{25} 1·4892.

^{1}H n.m.r. spectra were determined using 0·5M-solutions at 33·5° on a Perkin-Elmer R10 spectrometer (60 Mc./sec.) with 1% TMS as internal reference. All solvents were spectroscopic grade, and were dried over 5 Å molecular sieve before use. Double resonance experiments were performed with a Perkin-Elmer spin-decoupling accessory using the frequency scan mode.

The spectra of (II) and (IX) were determined in the concentration range 0·05—2·0M in carbon tetrachloride and benzene solutions in order to calculate the proton chemical shifts at infinite dilution. In all cases the difference between the chemical shift at 0·5M and that at infinite dilution was found to be less than 0·01 p.p.m. and as solvent shift differences of this order are not really significant, particularly as smaller values of solvent shift have an error considerably less than this maximum limit, it was considered sufficiently accurate to determine the remaining spectra at a concentration of 0·5M.

As the methyl peaks for ketones (V)—(VII) were extremely close together in carbon tetrachloride solution it was difficult to assign them correctly. This problem was overcome by determining spectra in a series of mixtures of carbon tetrachloride and benzene of varying composition. By plotting the position of each resonance relative to TMS as a function of benzene concentration it was relatively easy to find the appropriate resonance position in carbon tetrachloride solution by extrapolation.

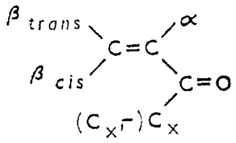
The analysis of the spectra of compounds (XI), (XIII), and (XV) was facilitated by determining the spectra of the deuteriated ketones. Deuteriation of all positions α to the carbonyl group and the carbon–carbon double bond was accomplished by refluxing the ketones for 30 min. in a 3 : 1 mixture of deuteriomethanol and 15% sodium deuteroxide in deuterium oxide.[13] The resulting cooled mixture was then shaken with equal parts of ether and water, and the ethereal extract was washed with water and dried. After removal of ether the ^{1}H n.m.r. spectra showed at least 90% deuteriation in all cases.

The spectra of methyl vinyl ketone (an ABC system) were analysed by trial and error fitting of calculated spectra using a KDF9 Algol programme adapted from a Fortran programme written by Wiberg.[14] Initial parameters were obtained from the spectrum of (I) in benzene, which approximates to an ABM type system.

RESULTS AND DISCUSSION

The ^{1}H n.m.r. benzene solvent shift data of some αβ-unsaturated ketones are listed in Table 1. The solvent shifts of ketones (II)—(IV) in a series of solvents of increasing dielectric constant, excluding benzene, are shown in Table 2.

The protons in an αβ-unsaturated ketone are most conveniently labelled by the use of the letters α, β, or X to define their position relative to the carbonyl group, and the subscripts *cis* or *trans* to distinguish between the two possible β-positions.[3]



Of the labile ketones included in this study, it is known from u.v. spectroscopy and other physical methods that (I) and (II) exist in the *s*-*trans*-conformation, although i.r. spectral data also suggest the presence of small concentrations of *s*-*cis*-conformers.[15,16] The remaining labile ketones are all predominantly *s*-*cis*, although the series (IV)—(VII) exhibits a rapid departure from coplanarity due to steric hindrance caused by the increasing bulk of the X-substituent.[1]

Using the compounds of fixed conformation as models it can be seen that the solvent shifts are approximately consistent with the picture of a reference plane through the carbonyl carbon atom, although in the case of the labile ketones particularly it should be emphasised that there are several anomalies which cannot be explained on this basis.

From the results obtained it is unnecessary to know the stereochemistry of the solvent–solute complex in order to assign an approximate conformation to a given ketone

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[11] F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, 1963, **28**, 1347.

[12] J. E. Dubois and M. Dubois, *Compt. rend.*, 1963, **256**, 715.

[13] D. H. Williams, J. M. Wilson, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 2091.

[14] K. B. Wiberg, 'Physical Methods in Organic Chemistry,' Wiley, New York, 1964, p. 549.

[15] J. Kossanyi, *Bull. Soc. chim. France*, 1965, 704.

[16] K. Noack and R. N. Jones, *Canad. J. Chem.*, 1961, **39**, 2225.

as, particularly for nearly planar conformers, the difference in solvent shift between protons at corresponding sites in *s-cis*- and *s-trans*-conformers is sufficiently large to make an unambiguous assignment possible.

For the ketones studied here the most significant indication of conformation is given by the β_{trans}-solvent shifts. For the fixed *s-trans*-ketones the β_{trans}-solvent shifts are in the range +0·45 to +0·57 p.p.m. and this compares well with the values of +0·58 and +0·54 p.p.m. for (I) and (II). For the fixed *s-cis*-ketones (XIII)—(XV) $\Delta_{\beta_{trans}}$ lies in the range +0·27 to +0·36 p.p.m. However, it is known from molecular polarisability data that pulegone is non-planar [17] and therefore the higher values for $\Delta_{\beta_{trans}}$ are probably more representative of a nearly planar *s-cis*-conformer.

The labile *s-cis*-ketones exhibit β_{trans}-solvent shifts in the range +0·39 to +0·06 p.p.m. The largest $\Delta_{\beta_{trans}}$-value is for mesityl oxide which is known from molecular polarisability data to adopt an *s-cis*-conformation with an inter-planar angle of 38°.[17] Compounds (VIII) and (IX) would be expected to be somewhat less planar due to the presence of the bulky terminal alkyl substituents, and accordingly the β_{trans}-solvent shift drops to about 0·29 p.p.m. The remaining *s-cis*-ketones (IV)—(VII) become less planar with increasing size of the terminal substituent and the solvent shift correspondingly shows a drop from +0·24 to +0·06 p.p.m.

It can thus be concluded that the β_{trans}-solvent shift for αβ-unsaturated ketones is substantially larger for the planar *s-trans*-conformation (approximately 0·5 to 0·6 p.p.m.) than for the planar *s-cis*-conformation (0·3 to 0·4 p.p.m.). In both cases, however, steric hindrance to coplanarity results in a reduction of these values, so that care would be required for example in attempting to apply only these criteria to a compound which may have a non-planar *s-trans*-conformation.

TABLE 1

Benzene solvent shift data for some αβ-unsaturated ketones

	Chemical shift in CCl_4				Chemical shift in benzene				Solvent shift			
Compound	δ_{α}	$\delta_{\beta_{cis}}$	$\delta_{\beta_{trans}}$	δ_{X}	δ_{α}	$\delta_{\beta_{cis}}$	$\delta_{\beta_{trans}}$	δ_{X}	Δ_{α}	$\Delta_{\beta_{cis}}$	$\Delta_{\beta_{trans}}$	Δ_{X}
(I)	3·82	3·85	4·20	7·80	4·00	4·35	4·78	8·21	+0·18	+0·50	+0·58	+0·41
(II)	3·98	3·28	8·09	7·87	4·10	3·69	8·63	8·15	0·12	0·41	0·54	0·28
(III)	3·93	7·90	8·12	7·92	4·19	7·91	8·51	8·13	0·26	0·01	0·39	0·21
(IV)	8·24	8·19	8·19	7·89	8·59	8·21	8·43	8·10	0·35	0·02	0·24	0·21
(V)	8·21	8·21	8·23	CH_2 7·55 Me 8·94	8·53	8·22	8·40	CH_2 7·78 Me 8·98	0·32	0·01	0·17	CH_2 0·23 Me 0·04
(VI)	8·25	8·20	8·26	CH 7·18 Me 8·97	8·57	8·32	8·40	CH 7·35 Me 9·04	0·32	0·12	0·14	CH 0·17 Me 0·07
(VII)	8·30	8·25	8·43	8·86	8·58	8·40	8·49	8·88	0·28	0·15	0·06	0·02
(VIIIa)	4·02	CH_2 7·46 Me 8·97	8·14	CH 7·40 Me 8·96	4·16	CH_2 7·38 Me 8·99	8·43	CH 7·74 Me 9·08	0·14	CH_2 −0·08 Me +0·02	0·29	CH 0·34 Me 0·12
(VIIIb)	3·98	7·91	CH_2 7·87 Me 8·92	CH 7·40 Me 8·96	4·07	7·87	CH_2 8·17 Me 9·18	CH 7·62 Me 8·98	0·09	−0·04	CH_2 0·30 Me 0·26	CH 0·22 Me 0·02
(IXa)	3·83	CH_2 7·50 Me 8·95	8·12	8·90	4·16	CH_2 7·39 Me 9·02	8·41	8·93	0·33	CH_2 −0·11 Me 0·07	0·29	0·03
(IXb)	3·77	7·95	CH_2 7·83 Me 8·91	8·90	3·75	7·86	CH_2 8·12 Me 9·16	8·90	−0·02	−0·09	CH_2 0·29 Me 0·25	0·00
(X)	4·15	7·44	7·85	7·69	4·21	8·10	8·42	7·93	0·06	0·66	0·57	0·24
(XI)	4·42	Me 8·78	~7·73	7·73 X′ 8·21	4·24	Me 9·22	8·18	7·78 X′ 8·63	−0·18	Me 0·44	0·45	0·05 X′ 0·42
(XII)	4·29	Me 8·83	3·50	7·66 X′ 8·17	4·22	Me 9·27	3·96	7·80 X′ 8·63	−0·07	Me 0·44	0·46	0·14 X′ 0·46
(XIII)	7·91	8·04	8·21	7·53 Me 8·98	8·20	7·92	8·48	7·51 Me 9·23	0·29	−0·12	0·27	−0·02 Me 0·25
(XIV)	7·57	3·41	8·29	7·69	8·01	3·16	8·65	7·80	0·44	−0·25	0·36	0·11
(XV)	7·76	8·18	7·90	7·89	~8·0	8·16	~8·19	8·08	0·24	−0·02	0·29	0·19

TABLE 2

Solvent shift data for some labile ketones

	(II)				(III)				(IV)			
Solvent	Δ_{α}	$\Delta_{\beta_{cis}}$	$\Delta_{\beta_{trans}}$	Δ_{X}	Δ_{α}	$\Delta_{\beta_{cis}}$	$\Delta_{\beta_{trans}}$	Δ_{X}	Δ_{α}	$\Delta_{\beta_{cis}}$	$\Delta_{\beta_{trans}}$	Δ_{X}
n-Hexane	+0·01	+0·04	+0·09	+0·08	+0·02	0·00	+0·05	+0·07	+0·06	+0·01	+0·01	+0·04
$CDCl_3$	−0·09	−0·12	−0·01	−0·09	−0·10	−0·06	−0·03	−0·09	−0·01	−0·05	−0·05	−0·11
$C_2H_4Cl_2$	−0·03	−0·10	+0·03	−0·04	−0·08	−0·01	0·00	−0·03	+0·03	+0·01	+0·01	−0·04
EtOH	−0·07	−0·22	−0·01	−0·08	−0·17	−0·02	−0·04	−0·07	−0·02	−0·03	−0·03	−0·09
MeOH	−0·09	−0·28	−0·01	−0·09	−0·20	−0·02	−0·05	−0·08	−0·03	−0·02	−0·02	−0·10
D_2O	−0·12	−0·40	−0·03	−0·11	−0·25	+0·01	−0·07	−0·15	−0·02	0·00	0·00	−0·18

A large value for the β_{cis}-solvent shift is a reliable indication of an *s-trans*-conformation, the values found in this study being +0·66 p.p.m. for the fixed *s-trans*-ketone (X) and +0·50 and +0·41 p.p.m., respectively, for (I) and (II) which are known to contain an increasing percentage of *s-cis*-conformer. Even when there is no β_{cis}-proton or methylene group, methylene or methyl groups attached to the β_{cis}-carbon atom still exhibit a solvent shift in the range +0·44 to +0·48 p.p.m. It should be noted that the bond angles in (X) will be different from those in the remaining *s-trans*-ketones owing to the strain encountered in a five-membered ring. For ketones with an *s-cis*-conformation the β_{cis}-solvent shift is very small or negative. For the fixed *s-cis*-ketones (XIII)—(XV) the range is −0·25 to −0·02

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[17] D. Izsàk and R. J. W. LeFèvre, *J. Chem. Soc.* (*B*), 1966, 251.

p.p.m. Ketones (VIII), (IX), and (III) which show only moderate deviation from coplanarity also exhibit solvent shifts in this range, but the much larger interplanar angles for (VI) and (VII) result in the solvent shift increasing rapidly to +0·15 p.p.m. for (VII). The β_{cis}-solvent shift will not differentiate between non-planar and nearly planar *s-cis*-conformers unless the molecule deviates greatly from coplanarity, as can be seen from the Δ values for (IV) and (V), which, although less planar than mesityl oxide, nevertheless have very similar $\Delta_{\beta_{cis}}$-values.

The solvent shift values for α groups lie over an extremely wide range and although it is possible to distinguish between *s-cis*- and *s-trans*-conformers with their aid, it is difficult to differentiate between nearly planar and substantially non-planar forms. For *s-trans*-ketones the Δ values are either negative or slightly positive, the values becoming more negative with increasing substitution on the β-carbon. Thus the values range from +0·18 p.p.m. for (I) (no β-substituents) to −0·18 p.p.m. for (XI) where the β-carbon is part of a cyclohexane ring. The Δ values for the *s-cis*-ketones are generally higher, lying in the range +0·44 p.p.m. for the fixed *s-cis*-ketone (XIV) to +0·26 p.p.m. for mesityl oxide. However, the results are widely scattered, although there does appear to be a decrease in Δ with decreasing coplanarity in the series (IV)—(VII).

The Δ_X-values appear to be of no diagnostic value for the fixed ketones. For the labile ketones the values are higher for *s-trans*-conformers (+0·28 to 0·41 p.p.m.) than for *s-cis* (+0·17 to +0·23 p.p.m.).

Many attempts have been made to correlate results of this type with models of donor–acceptor complexes between the benzene molecule and the positive end of the carbonyl group involving varying degrees of stereospecificity. Several authors have pointed out that the solvent shifts of axial and equatorial methyl groups α to a carbonyl group can be rationalised in terms of the 'reference plane' mentioned in the introduction.[2a,4,6,7] However, a cursory glance at the α-solvent shifts for such compounds as (X), (XI), and (XII), where the distances of the vinyl proton and the α-methylene group from the 'reference plane' are in fact very similar, shows that this is an over simplification. For the labile ketones this picture is even less satisfactory as can be seen for example in ketone (III). Molecular models show that the β_{cis}-methyl group would be well in front of the 'reference plane' and yet the solvent shift of nearly zero is indicative of a position actually in the plane of zero shielding. Thus although the 'reference plane' picture enables one to differentiate between axial and equatorial α-methyl groups in ring compounds, and between predominantly *s-cis*- and *s-trans*-conformations for $\alpha\beta$-unsaturated compounds, it does not allow an estimation of the degree of deviation from coplanarity which may exist for a given compound.

Williams has postulated a 1 : 1 stereospecific complex between the benzene solvent molecule and the positive end of the carbonyl dipole in order to explain the solvent shifts in a large number of ketones.[6,8] However, as other authors have pointed out,[18] it is unlikely that such a specific complex would be formed at room temperature in view of the high thermal energy of the solvent molecules and the relatively long period of an n.m.r. measurement. It is therefore much more realistic to talk in terms of a solvation shell around the carbonyl group. The distance of closest approach will be smallest above and below the plane of the molecule and the benzene molecules will tend to approach so that their π-electron clouds are as far as possible from the oxygen end of the carbonyl group. Consequently there will be a region of deshielding in front of the carbonyl group and a much larger shielding region behind it, the shielding values increasing with distance from the carbonyl group up to a distance of something over the radius of a benzene ring, and then falling off again. Also for a given distance from the carbonyl group, protons in or near the plane of the solute molecule will tend to be shielded less than those which project above or below the plane.

Obviously the degree of complex formation will be very much dependent on steric hindrance, and bulky groups behind the carbonyl group will prevent the benzene molecules from approaching as close to the carbonyl group as they would in an unsubstituted molecule. Also, in order for the benzene molecule to be able to interact with the positive end of the carbonyl group it will be necessary for it to approach at a steeper angle to the plane of the solute molecule, thus increasing the extent of the deshielding region in front of the carbonyl group, and bringing protons behind the carbonyl group nearer to the shielding node calculated by Johnson and Bovey.[19] This is one of the reasons for the decreasing value of Δ_α with increasing substitution of the β-carbon atoms. Non-planarity of the $\alpha\beta$-unsaturated chromophore will have the same effect, as this too tends to make the carbonyl carbon atom less accessible. This steric effect is illustrated by the fact that the sum of the solvent shifts for the compounds (IV)—(VII) decreases with decreasing coplanarity of the system. It is also noteworthy that there appears to be a correlation between $\Delta_{\beta_{trans}}$ and the interplanar angle calculated from u.v. ε values. Figure 1 shows plots of $\Delta_{\beta_{trans}}$ against interplanar angles calculated from u.v. spectra in hexane and ethanol solutions, assuming a value of 38° for mesityl oxide.

It is also possible to distinguish between *s-cis*- and *s-trans*-conformations using solvents other than benzene by determining the solvent shifts in a series of solvents of increasing polarity. Results are given in Table 2 for compounds (II)—(IV) as solutions in n-hexane, deuteriochloroform, carbon tetrachloride, 1,2-dichloroethane, ethanol, methanol, and water. Figure 2 is a representative plot of these solvent shifts (relative to

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[18] R. Grigg, J. A. Knight, and P. Roffey, *Tetrahedron*, 1966, **22**, 3301.

[19] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

the chemical shift in carbon tetrachloride) against the square root of the solvent dielectric constant, ε.[20] It is worth commenting that the shift values in deuteriochloroform solution lie well off the curves joining the other values, and this anomalous shift is one very good reason for not using this solvent as the reference solvent when determining benzene solvent shifts.

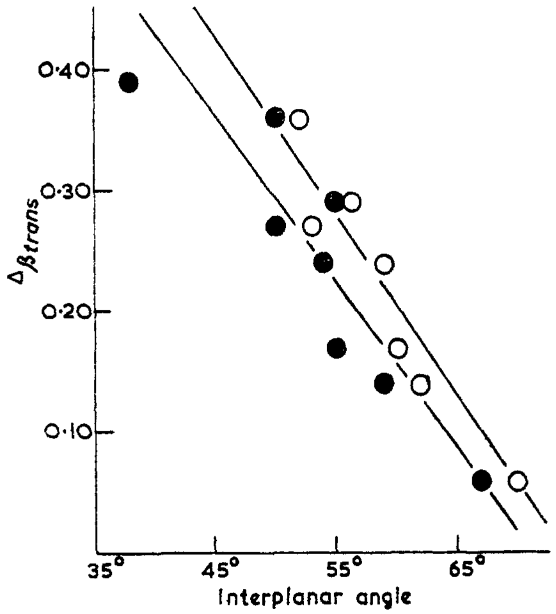

FIGURE 1 Plot of $\Delta\beta_{trans}$ against interplanar angle for the *s-cis*-$\alpha\beta$-unsaturated ketones (III)—(VII) and (XIII)—(XV); angle calculated from hexane solution spectra ●; angle calculated from ethanol solution spectra ○

If one pictures a solvation shell about the solute molecule with an induced dipole opposing the carbonyl dipole then protons in the line of the induced dipole will be increasingly shielded with increasing solvent polarity owing to perturbation of the electronic configuration of the carbon–hydrogen bond.[21] Protons nearer the edge of the solvation shell do not show such a strong deshielding effect, and hence a plot of solvent shift against some function of solvent polarity will readily show whether the α- or β_{cis}-proton is more strongly deshielded; in other words whether the molecule is *s-cis* or *s-trans*.

In conclusion, it has been shown that *s-cis*- and *s-trans*-conformations of $\alpha\beta$-unsaturated ketones can be readily differentiated by means of ^{1}H n.m.r. solvent shift data. In the case of solvent shifts using non-aromatic solvents the two conformers can be distinguished by the fact that for a plot of solvent shift against $\varepsilon^{\frac{1}{2}}$ of solvent the α-proton solvent shifts have a greater slope than those for the β_{cis}-proton in the case of an *s-cis*-compound. The reverse is true for *s-trans*-ketones.

In the case of benzene solvent shifts the 'shielding plane' model allows one to distinguish between the two conformations, but is incapable of explaining all the solvent shifts. In particular it is not easy to recognise non-planar forms. However, using model compounds it has been shown that, particularly for labile *s-cis*-ketones, certain trends are recognisable in the solvent shift data for $\alpha\beta$-unsaturated ketones with decreasing planarity. Probably the most useful of these is the decrease in the β_{trans}-solvent shift, which shows an approximately linear relationship with the interplanar angle.

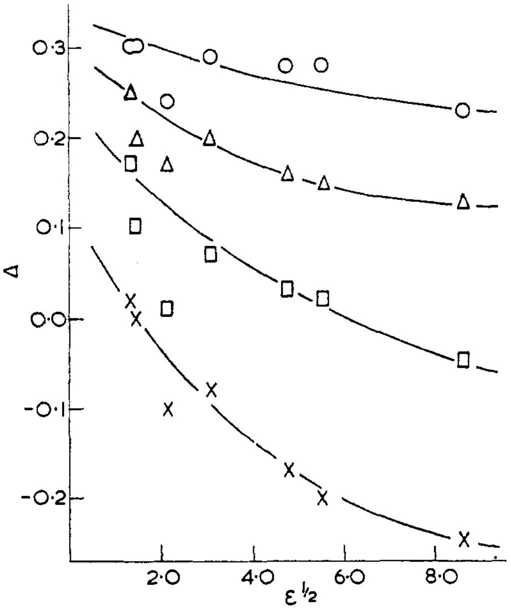

FIGURE 2 Plot of solvent shift against root of solvent dielectric constant for compound (III); Δ_{α}, ×; Δ_{x}, □ (displaced by +0·1 p.p.m.); $\Delta\beta_{trans}$, △ (displaced by +0·2 p.p.m.); $\Delta\beta_{cis}$, ○ (displaced by +0·3 p.p.m.)

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