Characterization of Primary, Secondary, and Tertiary Alcohols Using Proton Magnetic Resonance Techniques

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A NUMBER OF INVESTIGATIONS (*1–3*) have been recently described utilizing NMR techniques for the characterization of alcohols. These methods are based on the reaction of alcohols with various derivatizing groups with subsequent observation of either the characteristic resonance due to the attached group or the alpha resonance of the alcohols which is usually shifted downfield upon derivatization. We describe a proton NMR technique for the characterization of alcohols where both of the previously mentioned effects are operative. This may be accomplished by the preparation of dichloroacetate esters of various alcohols followed by the observation of the characteristic dichloroacetyl proton resonance.

EXPERIMENTAL

The proton magnetic resonance spectra were recorded using a Varian A-60 NMR spectrometer. Resonance positions are given in parts per million relative to tetramethylsilane as an internal standard. The dichloroacetate esters were prepared by either the direct addition of dichloroacetic anhydride (50–100% excess) to the appropriate alcohol followed by extraction with dilute aqueous sodium bicarbonate and drying with anhydrous sodium sulfate, or by the Fisher esterification method. Primary and secondary alcohols reacted completely with dichloroacetic anhydride in several minutes. Tertiary and polyhydroxy alcohols required longer reaction times, but one treatment of alcohol with dichloroacetic anhydride was sufficient to obtain the desired product. All other materials were commercially available reagent grade compounds and used without further purification.

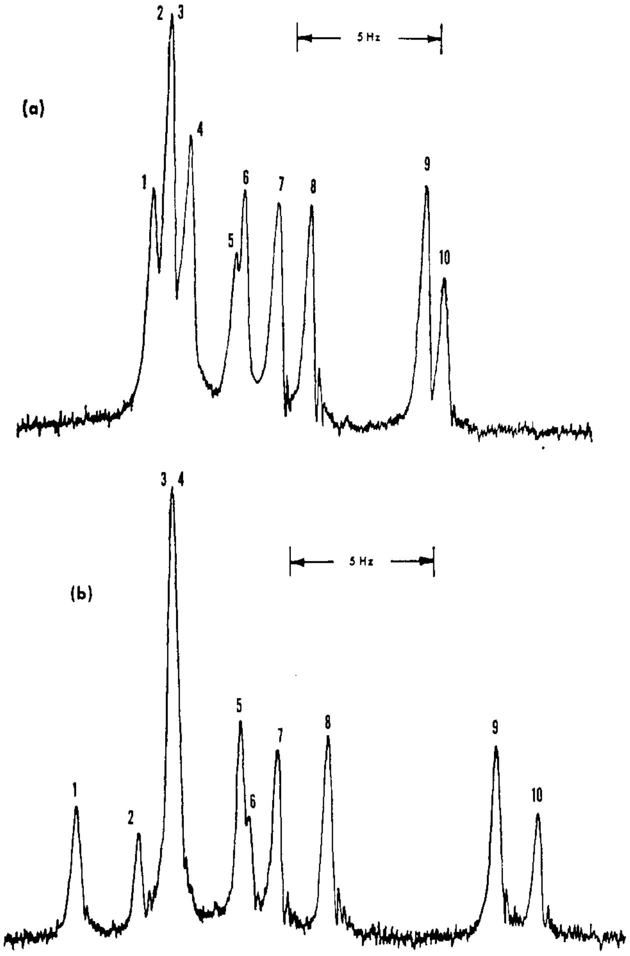

Figure 1. ^{1}H NMR spectra of the dichloroacetyl resonance of some hydroxyl compounds; chemical shifts given in parentheses from TMS. Increasing field to right

(*a*) Mixture in $CDCl_3$; *1*, $C_6H_5CH_2OH$ (6.032); *2* and *3*, $HOCH_2$-CH_2CH_2OH and $CH_3CHOHCH_2$*OH* (6.026); *4*, CH_3OH (6.011); *5*, $HOCH_2CH$*OH*CH_3 (5.988); *6*, CH_3CH_2OH (5.981); *7*, CH_3-$CHOHCH_2CH_3$ (5.961); *8*, $CH_3CHOHCH_3$ (5.941); *9*, $(CH_3)_2$-$(CH_3CH_2)COH$ (5.875); *10*, $(CH_3)_3COH$ (5.860).

(*b*) Mixture in DMSO-d_6; *1*, $C_6H_5CH_2OH$ (6.878); *2*, CH_3-$CHOHCH_2$*OH* (6.841); *3* and *4*, $HOCH_2CH_2CH_2OH$ and CH_3OH (6.818); *5*, CH_3CH_2OH (6.784); *6*, CH_3CH*OH*CH_2OH (6.777); *7*, $CH_3CHOHCH_2CH_3$ (6.761); *8*, $CH_3CHOHCH_3$ (6.730); *9*, $(CH_3)_2(CH_3CH_2)COH$ (6.633); *10*, $(CH_3)_3COH$ (6.608).

RESULTS AND DISCUSSION

The proton resonance of the dichloroacetyl group is removed from most alkyl and aryl resonances and has the additional advantage of giving an extremely sharp resonance line. The latter fact is extremely advantageous when mixtures of dichloroacetate esters are studied. As noted in Figure 1, *a* and *b*, there is a distinct separation between tertiary and the primary and secondary dichloroacetyl resonances. This separation can be enhanced by suitable choice of solvent. Generally, the dichloroacetyl signals follow the order of shielding which is tertiary > secondary > primary resulting in the tertiary resonances falling to higher field and the primary resonances to lowest field. However, there is not the clear separation of primary and secondary resonances as in the case of tertiary and secondary resonances. In deuterochloroform ($CDCl_3$), the dichloroacetyl resonance of ethyl dichloroacetate falls to higher field than the secondary dichloroacetyl resonance of the di-dichloroacetate of 1,2-propanediol. However, when dimethyl sulfoxide-d_6 (DMSO-d_6) is used as a solvent, this anomaly is obviated and the order of shielding, tertiary > secondary > primary, is preserved. The

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use of DMSO as a solvent also enhances the chemical shift separation of the individual dichloroacetyl resonances as well as the tertiary, secondary, and primary group separations. A change in solvent does cause a significant change in chemical shift of the dichloroacetyl resonances,—e.g., shifts in DMSO-d_6 are approximately 0.8 ppm to lower field than those in $CDCl_3$. Concentration variations affect the resonance positions only slightly.

Other dichloroacetates derived from primary alcohols have been studied which are not included in Figure 1, *a* and *b*. The dichloroacetyl resonances of these esters, without exception and independent of degree of branching, fall to lower field than the dichloroacetyl resonance of ethyl dichloroacetate. The advantage of this method lies in the fact that with a single scan of the proton spectrum of a dichloroacetylated alcohol not only may the primary, secondary, and tertiary dichloroacetyl resonances be observed, but also alpha proton paramagnetic shifts may be noted as additional diagnostic features. An additional advantage of the dichloroacetylation-^{1}H method over the ^{19}F method (*1*) is that it can be performed using the more accessible proton spectrometer systems. The trifluoroacetylation-^{19}F method (*1*) for alcohol characterization provides larger chemical shift differences between primary, secondary, and tertiary resonances but approximately the same separations within each group. The same chemical shift tendencies within groups have been noted when compared with the ^{19}F results. The dichloroacetylation-^{1}H method has been applied with success to polymer systems containing hydroxyl groups, specifically polyethers derived from various initiators. In addition to obtaining the types of hydroxyl groups present in these polyethers, one can obtain the amount of hydroxyl with respect to initiator and monomer.

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Rapid Precision Determination of Composition of Continuous Solid Solutions by X-Ray Techniques

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SOLID SOLUTIONS have found considerable application commercially as phosphors, photoconductors, etc. By varying the composition of such solutions, it is possible to adjust their properties—for example, to control the band gap. Thus, it has become increasingly more important to be able to determine precisely and promptly the composition of solid solutions.

A continuous series of solid solutions can form whenever the atoms or ions involved are similar in size and have similar electronic structure. Because this generally means similar chemical properties, problems frequently arise when chemical techniques are used for composition determination. In general, physical methods can be both more rapid and precise. In addition, they frequently require less material than chemical methods.

The techniques we have used are based on X-ray diffraction and fluorescence spectrometry. Basically, the net intensity of X-ray emission by the constituent atoms of the solid solution is calibrated against emission from physical mixtures. These solid solutions are then used as secondary standards for Debye-Scherrer photographs, which can be measured rapidly and require less than 0.1 mg of sample.

The X-ray fluorescence spectrometry method utilizes a ratio technique—i.e., a ratio of the net emission intensities of the constituents *a* and *b* (a binary system is assumed here). It can be shown (*1*) that

$$\ln \frac{I_a}{I_b} \cong \ln K + n \ln \frac{C_a}{C_b} \tag{1}$$

where n and K are constants. If the materials being analyzed can be put into solution, then the matrix effect is considerably reduced and the relationship between the ratio of emitted intensities and the ratio of concentrations is virtually linear. It is also possible to prepare solid pellets with a nonabsorbing dilutant (*2*).

Although X-ray emission spectrometry frequently yields precise results, greater relative precision can be achieved through the use of X-ray diffraction in a rapid technique which we call the "inner ring" method. "Inner rings" refer to Debye-Scherrer diffraction rings having high 2θ values, which are highly sensitive to changes in lattice spacings, and, therefore, in most solid solutions, are highly sensitive to changes in composition. This technique is most useful when the solid solution gives reasonably sharp diffraction lines in the back-reflection region and when the constituents of the solid solution have appreciably different lattice parameters.

If the diameter of an inner ring is defined in terms of S, the line separation, where S is measured in the same units as the camera radius, and d is the lattice spacing, then

$$\cos \frac{S^\circ}{4} = \frac{\lambda}{2d} \tag{2}$$

For a continuous series of solid solutions crystallizing in the cubic phase and obeying Vegard's law—i.e., having lattice constant proportional to the mole per cent of the constituents, a plot of $(\cos S/4)^{-1}$ *vs.* X_i, the mole fraction of the ith component, is linear. The same is true of hexagonal and tetragonal systems when the c/a ratio is independent of the composition. As the latter is generally a good approximation in most systems, the plot of $(\cos S/4)^{-1}$ *vs.* X_i is a very useful one. Greater precision can be achieved if care is taken to eliminate errors due to film shrinkage, absorption, etc. (see Appendix).

To utilize the inner ring method, a set of standard solid solutions is necessary. Their compositions can be determined

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