Detection of Organic Dianions by Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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Summary Dianions of organic substrates can be generated in dimethyl sulphoxide by using the dimsyl anion, and their structures can be proved unambiguously by the splitting patterns and chemical shifts of their ^{13}C n.m.r. spectra.

Although organic dianions formed by removal of at least one proton from carbon are important in syntheses,[1] their spectroscopic properties have not been studied systematically. There was originally controversy over whether the intermediates in question were truly dianions, and although their dianionic nature is almost completely accepted now, many of the synthetic results could be explained in terms of sequential production of various monoanions. We have sought definitive evidence for organic dianions *via* carbon-13 n.m.r. spectroscopy. Previous use of this technique has been restricted to monoanions[2] or aromatic dianions, *e.g.*, the cyclo-octatetraene dianion. Dimethyl sulphoxide (DMSO) was used as solvent and the dimsyl anion ($MeSOCH_2^-$) as the agent for proton removal, since extensive acidity data are available for DMSO.[3] The pK_a of DMSO is *ca.* 35.1[4] so that substrates with second pK_a's close to this value will not give dianions. At present, there is no direct information on the second pK_a values.

Anionic species were produced by treatment of 0·3—0·4 M solutions of the substrate with 0·8 M solutions of $MeSOCH_2^-$ Na^+. All manipulations, including transfer to the 8 mm n.m.r. tubes used, were carried out under nitrogen. Both coupled and ^{1}H-decoupled ^{13}C n.m.r. spectra were recorded, with the DMSO peak as reference. These chemical shifts were converted to the Me_4Si scale by adding 40·5 p.p.m. Depending on the second pK_a of the substrate, this procedure produced dianions, monoanions, or mixtures. Dianions were obtained from Ph_2CHCO_2H, $PhSCH_2CO_2H$, $Ph(SO_2)CH_2CO_2H$, $EtO_2CCH_2C(:O)CH_2CO_2Et$, and indan-2-one, monoanions from $MeC(:O)CH_2C(:O)Me$ and $MeC(:O)CH_2CO_2Et$, and mixtures from $PhCH_2CO_2H$, p-$MeC_6H_4CH_2CO_2H$, and p-$FC_6H_4CH_2CO_2H$. All these substrates could be recovered quantitatively from the n.m.r. samples by treatment with water under acidic conditions.

Of the 8 substrates that gave a dianion either wholly or in part, 6 are monocarboxylic acids. Dianion formation in these cases was indicated by the change in the α methylene carbon resonance in the ^1H-undecoupled spectrum from a triplet in the starting material or the monoanion to a doublet in the dianion (or from a doublet to a singlet for the methinyl carbon in the single case of Ph_2CHCO_2H). In the 2 remaining cases, indan-2-one and $EtO_2CCH_2C(:O)CH_2CO_2Et$, both methylene resonances became doublets on treatment with dimsyl anion. Monoanions were clearly indicated for $MeC(:O)CH_2C(:O)Me$ and $MeC(:O)CH_2CO_2Et$ by a doublet resonance for the carbon between the carbonyl groups and a quartet structure for the terminal methyl groups. All these signals became clean singlets on proton irradiation.

Dianion formation was normally accompanied by a downfield shift of the resonance for the carbon atom from which the proton had been removed. The large downfield shift caused by change of the hybridization of carbon from sp^3 to sp^2 is partially offset by an upfield shift from the fractional negative charge present on that carbon. The dianion carbon atoms resonate in the range 64—85 p.p.m. (except for a value of 36 p.p.m. for $PhSCH_2CO_2H$), compared to the normal alkene range of 105—145 p.p.m. and the range for the same carbon atoms in the neutral starting materials of 35—64 p.p.m. The one-bond coupling constants $^1J(^{13}C–^1H)$ give further evidence for sp^2 hybridization in the dianion, as their values are in the range 140—168 Hz, typical for trigonal carbons bearing negative charge.

At the level of basicity in these solutions, a methyl hydrogen α to a carbonyl group is insufficiently acidic in the presence of the first negative charge to be removed, as in $MeC(:O)CH_2C(:O)Me$ and $MeC(:O)CH_2CO_2Et$. Removal is complete if the second proton is on a carbon atom that is either between two carbonyl groups or between one carbonyl group and a carbon atom bearing two phenyl groups, a sulphide bond, or a sulphone bond. These second pK_a values must be well below 35. If the proton is on a carbon atom between one carbonyl group and a carbon atom bearing one phenyl group, as in the phenylacetic acids, removal is only partial. These second pK_a values must approach that of DMSO. Orbital overlap is more favorable in indan-2-one, so that the dianion is fully formed. Negative charge delocalization is manifested in the indan-2-one dianion by upfield shifts of the aromatic carbon resonances. In the carboxylic acids, the second negative charge is concentrated as far away as possible from the carboxylate group. Thus the largest shifts for the phenylacetic acid dianions (from the neutral species) are observed for the *para* carbon atoms. Valence bond resonance effects are small in the sulphide and sulphone, so that the second negative charge in these substrates should reside primarily on the carbon atom next to the carbonyl group. The strong inductive effect of the sulphone provides some downfield shift, but the observed value of 64·1 p.p.m. is still at higher field than that of all other dianions, save the sulphide. For the sulphide, the lack of either resonance or inductive effect causes a concentration of charge and a resonance at rather high field (36·4 p.p.m.). $^1J(^{13}C–^1H)$ values are 163 and 168 Hz, respectively, in the sulphide and the sulphone, so the carbon atoms are clearly sp^2 hybridized.

In summary, ^{13}C n.m.r. spectroscopy provides an unambiguous method to recognize dianion formation. The ^{13}C chemical shifts are useful for mapping charge delocalization, and the one bond $^{13}C–^1H$ coupling constants are useful in determining hybridization changes.

We thank the National Science Foundation and NATO for support, and Dr. Giorgio A. Pagani, University of Milan, for the procedure to obtain anionic solutions suitable for examination by n.m.r. spectroscopy.

(*Received, 28th October* 1977; *Com.* 1127.)

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