Long-range Proton Spin-Spin Interactions in Ketones[*]

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Long-range spin-spin interactions between protons, separated more than three bonds in unsaturated and in aromatic compounds, recently have been reported by many. In the present communication, we should like to present two examples of such a coupling in ketones. We have selected simple systems such as CH_3-X-C_2H_5 and CH_3-X-$CH(CH_3)_2$

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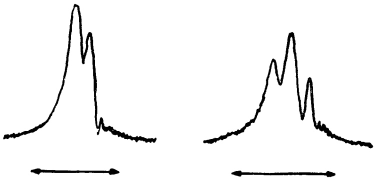
where X=S, O and C=O. The four compounds have been examined; ethyl methyl sulfide, ethyl methyl ketone, methyl isopropyl ether and methyl isopropyl ketone. All spectra were taken in pure liquid state for the samples in sealed glass tubes (5 mm. outside diameter, 3 mm. inside diameter), at 40 Mc and 22°C, the usual spinning technique was employed. The spacing of the multiplet structure was calibrated by running acetaldehyde with its known splitting of 2.85 c. p. s.

In methyl isopropyl ketone, the spectrum of the methyl group attached to carbonyl group is a doublet with a spacing of 0.45±0.05 c. p. s. This shows the coupling between the methine proton and the methyl protons four formal single bonds apart, through carbonyl group. The coupling of similar magnitude was also observed in the spectrum of ethyl methyl ketone in which the methyl proton spectrum in question has a triplet structure with a spacing of 0.48±0.05 c. p. s., shown in Fig. 1.



(a) (b)

Fig. 1. The proton magnetic resonance spectra of the methyl group attached to carbonyl group; (a) methyl isopropyl ketones, (b) ethyl methyl ketone. Applied magnetic field increases from right to left.

In order to observe these small couplings, the degassed procedure for the samples is much effective. In non-degassed ethyl methyl ketone, the methyl proton spectrum in question shows only a broad peak. The samples must be carefully degassed before sealing. The proton spin-spin coupling between two methyl groups in acetone, arising from the natural abundant $^{12}CH_3CO^{13}CH_3$, was also observed recently by Holmes and Kivelson, it to be 0.54±0.05 c. p. s.(1). This value is consistent with our present result.

However, in the NMR spectra of ethyl methyl sulfide and methyl isopropyl ether, where no resolved multiplet structures were observed in the methyl proton spectra attached to oxygen or sulfur. We estimate the values of the proton spin-spin coupling constants between the methine proton and the methyl protons or between the methylene protons and the methyl protons in these compounds, not greater than 0.4 c. p. s., based on the observed line widths.

It can be assumed, as pointed out also by Holmes and Kivelson(1), that the observed long-range proton spin-spin coupling in ketone may be due to the pi-electronic framework in the vicinity of C=O group. Another example is *N, N*-dimethylformamide, where the C=O group can be also considered to play an important role to the long-range proton spin-spin coupling. In *N, N*-dimethylformamide, the spectra of two methyl groups shows the doublet structures with the spacing of 0.7 and 0.5 c. p. s., respectively(2). Similar observations were reported also in *N*-methylformamide(3), *N, N*-dimethylformamide(3-5), *N*-methylacetamide(6) and *N, N*-dimethylacetamide(3). Further investigations along this line are now in progress for the systems containing other functional groups, X.

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