The Concentration Effect of the Long-range Proton Spin-spin Coupling Constant in Ketones

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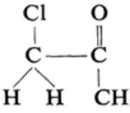
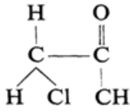
A previous communication[1] has reported that the multiplet structures have been observed in the spectra of the methyl group adjacent to the carbonyl group in ethyl methyl ketone and in isopropyl methyl ketone. Such a coupling has also been investigated in some substituted acetones, CH_3COCH_2X or CH_3COCHX_2 ($X=Cl$ and Br), and it has been pointed out: (1) the more electronegative X is, the less the coupling constant becomes, and (2) this coupling will be dependent upon the dihedral angle between the C–H bond and the π-orbital of the carbon atom in the carbonyl group.[2] Therefore, it is plausible to consider that the coupling will be dependent upon the population of the rotational isomers in each ketone. The four compounds have been examined briefly in the pure liquid and in a 5 mol. % solution in carbon tetrachloride, at 60 Mc. and 22.8±0.5°C. The experimental results are shown in Table I. Although the differences are very small, the variation of the coupling constants is clearly real. This result is acceptable on the basis of the following consideration about the rotational isomers. In chloroacetone, Mizushima[3] and Bellamy[4] suggested two rotational isomers, I and II, on the basis of the infrared and dipole moment studies. The carbonyl-stretching frequencies of this compound were observed at 1752 and 1726 cm^{-1} in a carbon tetrachloride solution,[4] corresponding to the two rotational isomers, the cis-form (I) and the trans-form (II) with respect to the Cl atom and the CO group, respectively. The former is more polar than the latter, so that a very marked change in the relative intensities of these bands was observed when the compound passed from the pure liquid to the solution in carbon tetrachloride. The contribution of each hydrogen in I and II, depending upon the dihedral angle (ψ), to the long-range coupling in chloroacetone is supposed to be:

TABLE I. THE LONG-RANGE PROTON-PROTON COUPLING CONSTANTS IN KETONES (IN C. P. S.)

Compound	Pure	in CCl_4
$CH_3COCH(CH_3)_2$	0.45±0.05[1]	0.44±0.03
CH_3COCH_2Br	0.40±0.01	0.37±0.01[2]
CH_3COCH_2Cl	0.33±0.03	0.22±0.03[2]
$CH_3COCHCl_2$	0.24±0.03	0.30±0.01[2]


I


II

$$a \sim P_{\mathrm{I}}[a(30^\circ)+a(30^\circ)]+P_{\mathrm{II}}[a(30^\circ)+a(90^\circ)]$$

$$a(\psi)\propto\cos^2\psi$$

where a corresponds to the hyperfine constant as defined by Karplus[5] and where P_i is the population of the i isomer. Therefore, the contribution of II is half that of I. The decrease in the coupling constant in a carbon tetrachloride solution may be caused by the increase in the population of II as compared with that of I. This kind of variation in the long-range coupling constants has not yet been reported in the literature. Detailed results will be published later in this Bulletin.

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