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LONG-RANGE COUPLING IN ESTERS.

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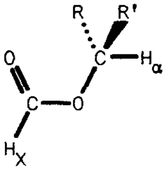
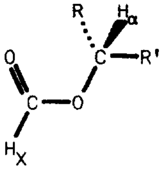
The formyl proton (X) in a number of simple alkyl formates is coupled to the α- and β-protons of the alkyl group, $^4J_{\alpha X}$ being ≈ 0.9 c/s and $^5J_{\beta X}$ being ≈ 0.5 c/s (1). We have confirmed several of the coupling constants previously reported, and add that *tert*-butyl formate shows $^5J_{\beta X}$ ≈ 0.4 c/s. Although it was previously reported (1) not to occur, we have observed resolveable five-bond coupling (confirmed by spin-decoupling) between α and α'-protons of certain non-formate esters *e.g.* the methyl-proton signals of methyl acetate are each quartets, splitting 0.25 c/s.

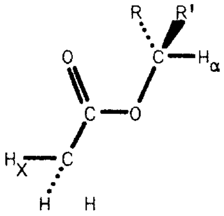
Long-range couplings are usually strongly stereospecific, and may be broadly divided into those primarily communicated through σ-bonds in planar W (^4J) or extended-W (^5J) systems, often saturated, or those primarily communicated through σ-π interactions as in allylic (^4J) or homoallylic (^5J) systems; in the latter cases, maximum coupling occurs for protons making dihedral angles close to 90° with the plane of the unsaturated system (2). The presence of more than one conformation in a variety of esters has been detected by infrared spectroscopy (3) and, as the O-Acyl bond in esters has partial double-bond character, the four-bond couplings in formates and five-bond couplings in acetates might be transmitted primarily by either mechanism as in conformations I*a*, I*b*, II*a*, or II*b*. The microwave spectrum of ethyl formate at -77° shows that, besides the symmetrical conformation I*b* (R=H, R'=CH_3), the *gauche* conformations I*a* (R=H, R'=CH_3; and *vice versa*) are present, the barrier to rotation being ≈ 5 kcal/mole and that for rotation of the methyl group ≈ 2 kcal/mole (4). Such barriers are too small to hinder rotation significantly on the p.m.r. time-scale at room temperature. Couplings where observed are manifested under conditions of sufficiently free rotation about the O-Cα, Cα-Cβ, and carbonyl--methyl C-C bonds as to allow equivalence within each group of protons, as reflected in



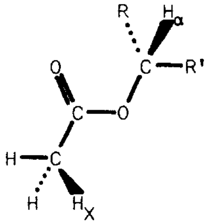
I*a*: planar-W $^4J_{\alpha X}$



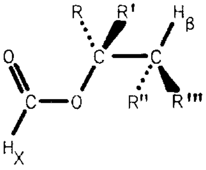
I*b*: allylic $^4J_{\alpha X}$



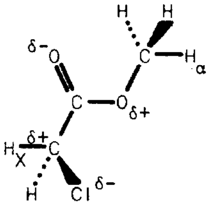
II*a*: extended W $^5J_{\alpha X}$



II*b*: homoallylic $^5J_{\alpha X}$



III: extended W $^5J_{\beta X}$



IV

appropriate symmetry in the multiplet signals of the long-range coupled proton groups, and observed values are time-averages. If then the residence time in a conformation conducive to a particular mechanism becomes very small, coupling due to that mechanism will not be observed. There may be as-yet-undescribed mechanisms, but all long-range couplings here discussed may be ascribed to transmission through planar-W or extended-W σ-bond systems (I*a*, II*a*, or III), the function of the ester group being to maintain the necessary degree of planarity; in any case σ-π interaction (homoallylic) may not be invoked to account for five-bond couplings in formates.

Other effects are doubtless superimposed on the conformational: otherwise one would have expected decreasing values of $^4\underline{J}_{\alpha X}$ in the series, methyl formate (I: R=R'=H) (0.85 c/s), ethyl formate (I: R=H, R'=CH_3) (0.85 c/s), and benzyl formate (I: R=H, R'=Ph) (0.95 c/s), as a result of increasing preference for conformation I*b*. The formyl-proton signal for ethylene diformate is however a sharp singlet, presumably because polar repulsion between the two ester groups essentially fixes the conformation as I*b* (R=H, R'=CH_2OCHO). In the series, methyl acetate (II: R=R'=H) (0.25 c/s), ethyl acetate (II: R=H, R'=CH_3) (0.20 c/s), and benzyl acetate (II: R=H, R'=Ph) (≈ 0.1 c/s, detected by decrease in width at half-height of the acetate-methyl signal upon irradiation of the benzyl-methylene signal) decreasing values of $^5\underline{J}_{\alpha X}$ (in parentheses) do in fact parallel the expected order of increasing preference for conformation II*b*. For isopropyl acetate (II: R=R'=CH_3), $^5\underline{J}_{\alpha X}$ is indetectably small even by irradiation, so the residence time in conformation II*a* is negligible.

Complementary effects are observed upon introducing substituents into the acid residue of methyl esters. Methyl chloroacetate apparently resides in conformation IV sufficiently long to show $^5\underline{J}_{\alpha X}$ ≈ 0.27 c/s, perhaps as a result of dipolar interaction between the chlorine and ethereal oxygen atoms as indicated. Similar interactions would account for the observed $^5\underline{J}_{\alpha X}$ of 0.25 c/s in methyl cyanoacetate, and 0.20 c/s in methyl bromoacetate. In the last case, the dipolar interaction may be somewhat offset by steric repulsion, and the steric effect is dominant in methyl dichloroacetate for which $^5\underline{J}_{\alpha X}$ is indetectably small. We have not examined methyl fluoroacetate because of the extreme toxicity of fluoroacetic acid. Five-bond coupling (≈ 0.15 c/s) may be present in methyl phenylacetate but we have been unable to resolve it and irradiation is impracticable since the methylene and methyl signals are separated by only 2.2 c/s.

This interpretation may be extended to explain our failure to observe five-bond couplings in benzhydryl, cyclohexyl, and βββ-trichloroethyl acetates, ethylene mono- and di-acetates, and in the following methyl esters: acetoacetate, isobutyrate, malonate, lactate, tartrate*, di-*O*-acetyltartrate*, maleate, fumarate*, and cinnamate.*

The conformational conclusions are consistent with those reached on the basis of acylation shifts for primary and secondary alcohols (5), or of coupling constants between carbonyl-^{13}C and alkyl-αH in acetate esters (6).

A sample of pure *tert*-butyl formate was kindly provided by Professor I.A. Lauder. Other samples were commercial or prepared by literature methods. P.m.r. spectra were measured for neat liquids (or deuterochloroform solutions of those marked *) at 30° on a Varian HA-60-IL spectrometer purchased with a grant from the Australian Research Grants Committee.

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