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THE HYDROXYMETHYLENE KETONE - ALDO ENOL EQUILIBRIUM

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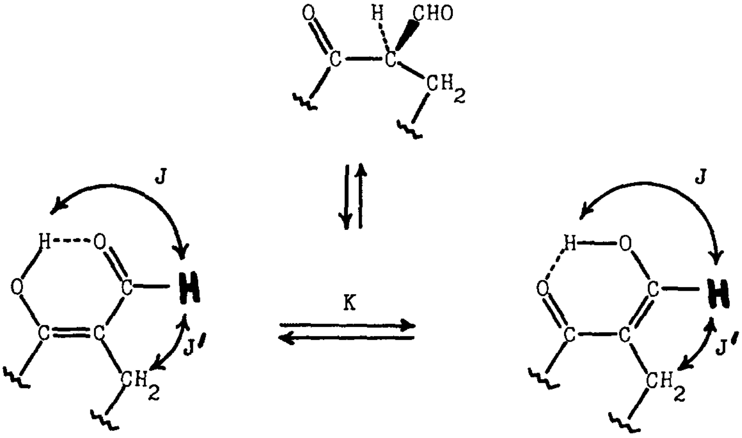
We would like to comment on the recent note[2] by Deutsch and Deutsch in which they interpret data[3] germane to the direction of enolization of α-formyl ketones. Their arguments appear to be erroneous due to an unrecognition of the fundamental difference between the nuclear magnetic resonance consequences of intramolecular and intermolecular proton exchange.



I

II

The direction of enolization (K) of α-formyl ketones may be estimated by NMR spectroscopy through the use of equation (1) where P^o is the observed

$$K = (P^o - P_I)/(P_{II} - P^o) \tag{1}$$

parameter and P_I and P_{II} are those parameters determined from model systems of I and II, respectively. There may be as many as three independent sets of parameters, P, that lead to as many independent solutions to the problem.

These are:

(a) $P = J$

(b) $P = \delta \mathbf{H}$

(c) $P = J'$

Excellent agreement between results using parameters (a) and (b) already have been demonstrated.[3] Forsén has implied[4] the applicability of parameters (c) to equation (1). We have found[5] that results derived therefrom are in reasonable agreement with those deriving from the use of parameters (a) and (b).

The frequency of exchange between I and II must be greater than the frequency difference ΔP (i.e., $|P_I - P_{II}|$) in order to validate the use of equation (1). There is ample reason to expect, a priori, that this condition applies[3] and our reported results[3] seem to demonstrate a realization of this expectation. However, Deutsch and Deutsch reason[2] erroneously, by use of analogy to intermolecular proton exchange phenomena, that under this condition of rapid exchange between I and II, J^o should vanish. As the spin state of a rapidly exchanging proton is preserved during the intramolecular exchange, such a process between I and II does not lead to a decoupling of J^o.[3b] The proton spin coupling, J^o, does not vanish in practice[3] and Deutsch and Deutsch force themselves to conclude erroneously that only II must exist ($J_I \approx 0$ and $J_{II} = 12.6$ Hz).

We have found J^o to vary between 1 and 12 Hz depending upon the system[3,5] and to be linearly correlated with the value of N_{II} (mole fraction of II) determined by use of parameters (b). This, of course, is required if equation (1) applies to both sets of parameters (a) and (b). To account for this linear relationship using the supposition that only II exists, Deutsch and Deutsch reason with no apparent justification that J^o increases as a result of a decrease in the intramolecular hydrogen bond strength and that somehow $\delta \mathbf{H}$ responds linearly in an inverse relationship. This reasoning, although it has no substance because of anteceding misconceptions, leads us to substantiate further the idea[3] that J^o is not dependent significantly upon the strength of the hydrogen bond, within the limits encountered. As a measure of the strength of the intramolecular hydrogen bond we use τ_{OH}. The τ-values for hydrogen bonded protons are known to vary inversely with the strength of these bonds.[6] The figure shows the relationship between J^o and τ_{OH} and demonstrates a marked insensitivity of τ_{OH} to J^o except for No. 1 where an exceptionally weak hydrogen bond is encountered.

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REFERENCES

1) A. P. Sloan Foundation Research Fellow

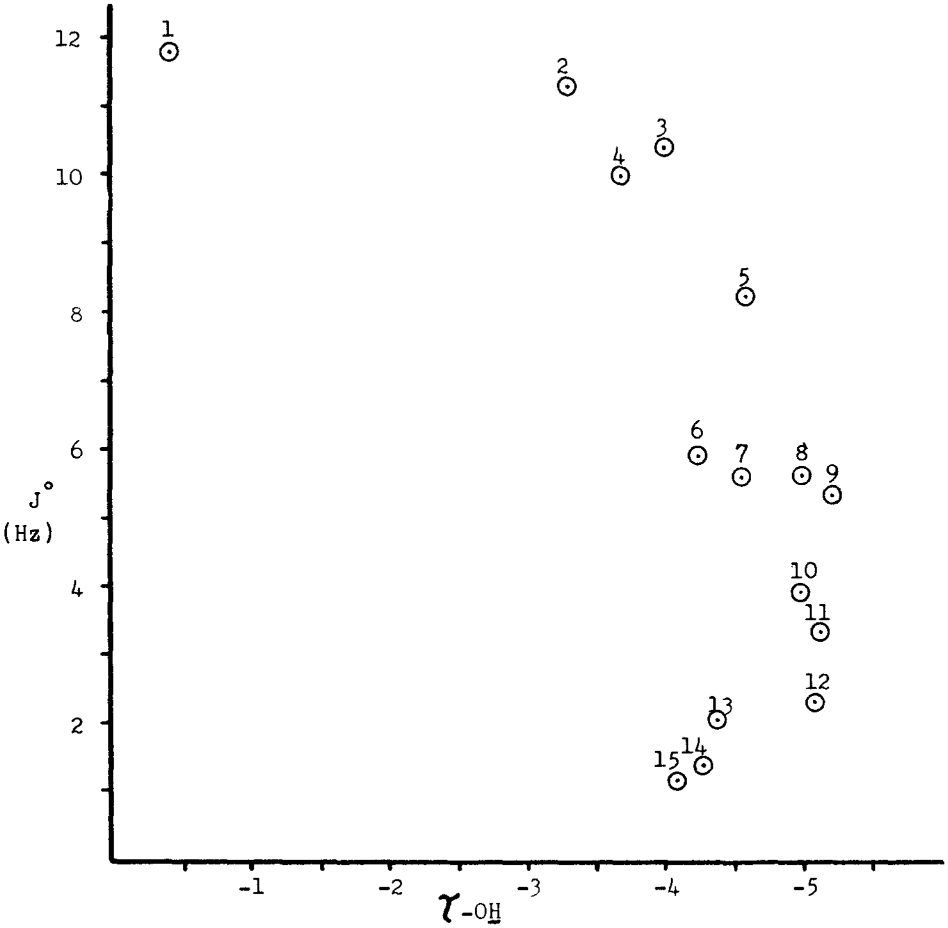
2) I. Deutsch and K. Deutsch, Tetrahedron Letters, 1849 (1966).

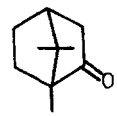
3) (a) Edgar W. Garbisch, Jr., J. Am. Chem. Soc., **85**, 1696 (1963).
(b) ibid., reference 9. See also ibid., **87**, 505 (1965) for further considerations of the hydroxymethylene ketone - also enol equilibrium.

4) S. Forsén, Acta Chem. Scand., **18**, 1208 (1964).

5) Unpublished results of J. G. Russell.

6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., New York, N. Y., 1959, p. 407ff; and A. L. Porte, H. S. Gutowsky, and I. M. Hunsberger, J. Am. Chem. Soc., **82**, 5057 (1960).





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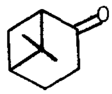

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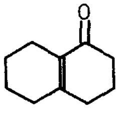

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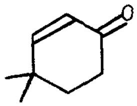

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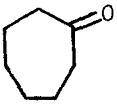

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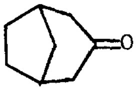

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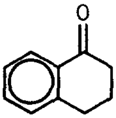

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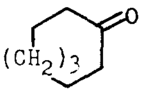

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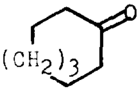

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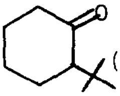

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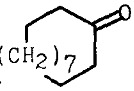

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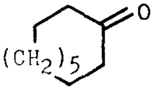

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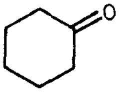

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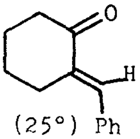

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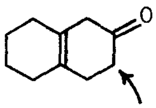

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