Pyrazoline Stereochemistry: Use of Nuclear Magnetic Resonance Shift Reagents with Azo-compounds

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Summary $Eu(fod)_3$ shifts the n.m.r. spectra of *cis*-azo-compounds, whereas *trans*-azo-compounds remain almost unaffected; shifts obtained from pyrazolines have been related to their stereochemistry.

We report the results of a study on the effect of the shift reagent $Eu(fod)_3$ on azo-compounds. Although the use of such n.m.r. shift reagents is commonplace, only passing reference has been made to their use with pyrazolines[1] and several reports have appeared claiming azo-compounds do not complex.[2,3] In the course of a synthesis of the sesquiterpene marasmic acid,[4] we determined the stereochemistry of pyrazoline intermediates. In order to determine the effect of $Eu(fod)_3$ on azo-compounds, a study of *trans*-azobenzene (**1**), *cis*-azobenzene (**2**), azo-2-methylpropane (**3**), and 1,4-dimethyl-2,3-diazabicyclo[2,2,2]oct-2-ene (**4**) was undertaken. We found that the *cis*-azo-compounds (**2**) and (**4**) complex strongly with the reagent, whereas the *trans*-azo-compounds (**1**) and (**3**) remain virtually unaffected. The n.m.r. spectrum of the *cis*-azobenzene (**2**), for example, shows the *ortho*-protons shifting to a multiplet at δ 13·2 with one equivalent of $Eu(fod)_3$. When three pyrazoline intermediates were studied, the lines for the shifts of the methylene AB quartet adjacent to the azo-linkage possess identical slopes and the greatest shifts. Equivalent environments of the azo-linkage in the three compounds can be inferred by the similarly identical slopes of other corresponding protons. The *cis*-azo-linkage complexes less strongly than OH but more strongly than CO or CO_2Me.

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[1] R. G. Bergman and R. A. Keppel, *J. Amer. Chem. Soc.*, 1972, **94**, 1350.

[2] C. Beate, Z. W. Wolkowski, and N. Thoai, *Chem. Comm.*, 1971, 700.

[3] R. E. Rondeau, M. A. Berwick, R. N. Steppel, and M. P. Serve, *J. Amer. Chem. Soc.*, 1972, **94**, 1096, footnote 16.

[4] S. R. Wilson and R. B. Turner, *J. Org. Chem.*, in the press.