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DIFFERENTIATION OF *cis* AND *trans* ISOMERS OF THIONOCARBAMATE ESTERS BY USE OF TRIS(DIPIVALOMETHANATO)EUROPIUM(III)

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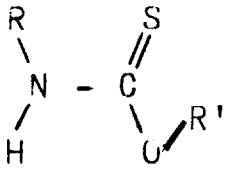
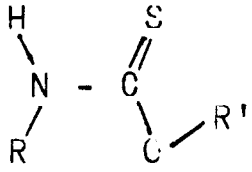
Several reports[1] have appeared on the usefulness of tris(dipivalomethanato)europium(III) [$Eu(DPM)_3$] for simplifying the nmr spectra of alcohols by causing paramagnetic shifts, the magnitude of which depends on the distance of the protons through bonds or space from the europium atom complexed to the oxygen atom. In this paper is presented a new use for this reagent as a sensitive probe for conformation in certain sulfur compounds.

The ability of $Eu(DPM)_3$ to complex with sulfur compounds is not as great as for the oxygen analogs; e.g., we found that O-ethyl thioacetate in CCl_4 solution showed no shifts when treated with the reagent, whereas all the protons of ethyl acetate were affected. This may be due to insufficient electron density at the sulfur atom, because when this is increased by resonance effects as in thionocarbamate esters, complexation can occur if the stereochemistry is favorable.

It has been shown[2] that thionocarbamate esters exist in solution as unequal mixtures of *cis* and *trans* isomers that can be differentiated by nmr spectroscopy.



cis



trans

When such an ester (data for the O-methyl[2] and O-isobutyl[2] esters of methylthiocarbamic acid are given in the Table) was treated in CCl_4 solution with increasing increments of $Eu(DPM)_3$, signals for each of the proton types of the minor isomer underwent large downfield shifts, whereas signals for the major isomer changed by only a small amount. In the isomer ratio itself there was no change, as shown by integration before and after complexation. Even when enough $Eu(DPM)_3$ was used to complex on a 1:1 basis with both isomers of O-isobutyl methylthiocarbamate, the signals for the major isomer, while severely broadened, could still be seen only a few Hz from the original positions; also there were large peaks in the 0-1 and 3.5-4δ regions which are those of uncomplexed $Eu(DPM)_3$ reagent.

The isomer found to complex most strongly witn $Eu(DPM)_3$ was previously[2] assigned the trans conformation by comparison with thioamides and by aromatic solvent-induced shifts. The behavior with $Eu(DPM)_3$ can then be rationalized by assuming a weak attraction between the reagent and thiocarbonyl sulfur which is effectively circumvented by the presence of an alkyl substituent in proximity to the sulfur.

Substantiation of this was obtained by examining O-methyl dimethylthiocarbamate[3], in which the steric situation is equally unfavorable for both the rotational isomers. Here neither of the separate N-methyl signals nor the O-methyl signal shifted in the presence of $Eu(DPM)_3$, although the former broadened considerably. In O-methyl dimethylcarbamate[4] the unfavorable geometry does not prevent complexation with carbonyl oxygen, and both N-methyl and O-methyl signals were shifted, again with broadening of the former.

TABLE OF CHEMICAL SHIFTS*

Compound						Concn.	$Eu(DPM)_3$ Concn.
CH_3	NH	C(S)O	CH_3			.2M	
183.0, 172.0	380, 455		235.5, 241.0				0
183.5, 178.5	388, 505		238.5, 263.5				.02M
186.5, 186.5	395, 560		245 , 309				.04
CH_3	NH	C(S)O	CH_2	CH	$(CH_3)_2$	.28M	
182.5, 172.5	380, 454		248.0, 251.5		56.5, 59.5		0
183.5, 174.5	380, 480		250.0, 267.5		57.5, 64.5		.026M
185.5, 190	385, 610		252.0, 337.5		58.5, 87.5		.038
186 , 224	390, 900		257 , 495		60 , 138		.082
$(CH_3)_3C$	NH	C(S)O	CH_3			.2M	
88, 81.5	368, 427		228, 240				0
88, 81.5	375, 450		230, 250				.02M
88, 80	380, 477		236, 266				.04
88, 79	388, 500		240, 280				.06

*Reported in Hz downfield from internal TMS at 60 MHz, the shift for the cis isomer being given first. The spectra were run in CCl_4 solution at the normal probe temperature in a Jeolco Minimar 60 spectrometer.

One further example is O-methyl tert-butylthiocarbamate which was found in the earlier work[2] to be abnormal in that the trans isomer appeared to predominate. With $Eu(DPM)_3$ it was this major isomer which underwent downfield shifts of its protons, thus supporting the previous assignment.

The difficulties in assignment of conformation to amide and thionamide isomers have been reviewed recently[6], and some errors caused by reliance on the known methods of assignment have been noted[7]. It is suggested that the $Eu(DPM)_3$ reagent may be a sensitive probe to establish the stereochemistry of such systems.

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2. R. A. Bauman, J. Org. Chem., 32, 4129 (1967).
3. Prepared from $(CH_3)_2NCSCl$ and $NaOCH_3$, this compound had an nmr spectrum agreeing with that reported previously[5].
4. Prepared from $(CH_3)_2NCOCl$ and $NaOCH_3$, this compound had an nmr spectrum agreeing with that reported previously[5].
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