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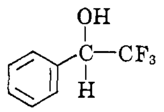
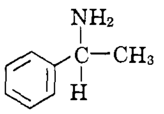
The Nonequivalence of Physical Properties of Enantiomers in Optically Active Solvents. Differences in Proton Magnetic Resonance Spectra. II

Sir:

We have recently reported[1] that the fluorine nmr spectra of the enantiomers of trifluoromethylphenylcarbinol (I) are dissimilar when optically active α-phenethylamine (II) is used as solvent. We now wish to report the first examples of nonequivalence of the proton magnetic resonance spectra of enantiomers in an optically active solvent.


I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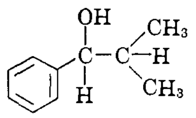
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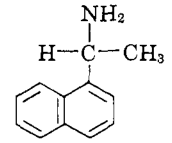
IV

In fluorotrichloromethane, the resonance of the carbinyl proton in racemic phenylisopropylcarbinol (III) appears as a doublet[2] ($|J_{\mathrm{H-H}}|$ = 6.8 cps) at 4.1 ppm from internal tetramethylsilane. When *d*-α-(1-naphthyl)ethylamine (IV) ($[\alpha]^{27}\mathrm{D}$ +75.6° (neat), lit.[3] for the *levo* isomer $[\alpha]^{25}\mathrm{D}$ −80.8° (neat)) is used as the solvent, the carbinyl proton resonances of the enantiomers have different chemical shifts and give rise to two equally intense sets of doublets ($|J_{\mathrm{H-H}}|$ = 6.3 cps).[4] At 60 Mc the sets are separated by 1.6 cps; at 100 Mc the separation is 2.5 cps.[5] The increased separation at the higher frequency rules out the possibility that the increased multiplicity arises from some unusual solvent effect causing long-range coupling which is not observed when fluorotrichloromethane is used as solvent. Further indication that the increased multiplicity has been correctly interpreted arises from the observation that replacement of the optically active amine with racemic amine causes the two sets of doublets to coalesce. This indicates that any given carbinol molecule is solvated by both optical forms of the amine solvent during the time required for nmr measurement. Because of this fast exchange, both carbinol enantiomers are in identical average magnetic environments and no longer have dissimilar spectra. An important consequence of this fast exchange is that *the solvent need not be completely optically pure* in order for one to observe spectral nonequivalence of enantiomeric solutes. The magnitude of the observed nonequivalence will simply be proportional to the optical purity of the solvent in cases where such fast exchange obtains.

The chemical shifts of the enantiomeric carbinyl proton resonances are unequally affected by changes in temperature, ratio of amine to carbinol, and extent of dilution with optically inactive solvents. Hence, the separation between the sets of carbinyl proton resonances is affected by the choice of experimental conditions as well as by the operating frequency of the spectrometer.[6]

Under similar conditions, proton spectral nonequivalence of the enantiomers of trifluoromethylphenylcarbinol, methyl-2-naphthylcarbinol, and methyl-*o*-fluorophenylcarbinol has also been noted. The ability to observe pmr spectral nonequivalence greatly enhances the scope of our previously reported nmr method for optical purity determination.[1] In all cases cited, the extent of nonequivalence is great enough to allow 60-Mc nmr optical purity determinations to be made. The use of higher frequency nmr spectrometers will facilitate these determinations.

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[1] W. H. Pirkle, *J. Am. Chem. Soc.*, **88**, 1837 (1966).

[2] The absence of observable coupling between the carbinyl and hydroxyl protons suggests that the hydroxyl protons are undergoing rapid intermolecular exchange.

[3] E. Samuelsson, *Svensk. Kem. Tidskr.*, **34**, 7 (1922).

[4] It has proven advantageous to use fluorotrichloromethane as a diluent in order to obtain better resolution through diminished viscosity and to shift the carbinyl proton resonances from underneath the methine proton resonance of the solvent amine.

[5] The 100-Mc spectra were obtained by Dr. N. Bhacca of Varian Associates. The 60-Mc spectra were determined by means of a Varian A56/60A spectrometer.

[6] The effect of these parameters upon the extent of enantiomeric spectral nonequivalence is being studied in order to gain a better understanding of the origin of the phenomenon.

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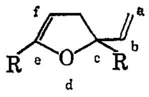
Thermal Rearrangement of 2,5-Dimethyl-2-vinyl-2,3-dihydrofuran to 4-Methyl-4-cycloheptenone

Sir:

Inherent in the simple 2-vinyl-2,3-dihydrofuran structure is the rearrangement-prone bisallylic system of an allyl vinyl ether (I, atoms a–f). Such furan derivatives



I, R = H
II, R = CH_3

have been observed to undergo a variety of rearrangements depending on the conditions imposed and the location and nature of substituents on the basic structure, I; thus, acylcyclopentenes,[1] 1-acyl-2-vinylcyclopropanes,[2] and acyclic dienic carbonyl compounds[3] have been reported as products.

In our continuing interest in Claisen and Cope rearrangements and with a view to exploring the geometric

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[1] J. Wiemann and S. T. Thuan, *Compt. Rend.*, **241**, 503 (1955); *Bull. Soc. Chim. France*, 199 (1958).

[2] J. Wiemann, N. Thoai, and F. Weisbuch, *ibid.*, 2187 (1964).

[3] J. Wiemann, P. Casals, and N. Lefebvre, *ibid.*, 310 (1962); N. Thoai, *ibid.*, 225 (1964).