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THE SYNTHESIS, CIRCULAR DICHROISM AND ABSOLUTE CONFIGURATION OF (1S) 4,4-DIDEUTERIOADAMANTAN-2-THIONE (II)

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The contribution of deuterium to the sign and magnitude of rotation of chiral cyclic ketones has been of continuing interest[1,2,3] since early studies by Djerassi and coworkers indicated an anti octant behavior for the isotope. The availability in our laboratory[3,4] of optically active 4,4-dideuterio adamantan-2-one (I) of known enantiomeric and isotopic purity and absolute configuration naturally led to the idea that the transformation of the carbonyl group would allow entry into a series of novel chiral deuterated compounds.

We report herewith the synthesis of optically active (1S) 4,4-dideuterio adamantan-2-thione (II). Following the procedure reported by Greijdanus for the preparation of adamantane-2-thione,[5] 100 mg of I,[3,4] $|\alpha|^{21}_{578}$ = -3.4 (c=0.53, isooctane, optical purity 84 ± 3%) was converted to II using P_4S_{10} in pyridine. The crude thione was carefully sublimed to remove traces of adamantanone and polymeric material and was pure by GLC.

The following spectroscopic data were obtained: I.R. (nujol): C=S, 1160 cm^{-1}, C-D 2100, 2200 cm^{-1}; U.V.: λ_{max} 507 nm, ε=11.1 (c=0.07 mole $liter^{-1}$, isooctane); specific rotation $|\alpha|^{21}_{578}$ = -14.5, (c=1,1 isooctane); C.D, λ_{max} 507 nm, $\Delta\varepsilon$=-0.38.

The optical purity of II is expected to be the same as I (34 ± 3%), assuming the enantiomeric ratio did not change during the reaction, and isolation of the product.

The few chiral thiones which have been studied[1a,7,8] exhibited normal octant rule[9] behavior for the Cotton effect of the n-π^* transition. In fig (1) the circular dichroism spectrum of II is shown. Naturally II must have the same absolute configuration (1S) as the starting material

I.[2,4] Once again[1,2,4] we would predict a positive Cotton effect if deuterium showed normal octant rule[9] behavior and once again unmistakingly anti octant rule behavior is exhibited by the strongly negative Cotton effect of the 507 nm n-π^* transition. The rotation $|\alpha|^{21}_{578}$ - 14.5, unusually high for a compound whose chirality is due to deuterium substitution only is understandable since the measurement is carried out close to the λ_{max} of the n-π^* transition (507 nm).

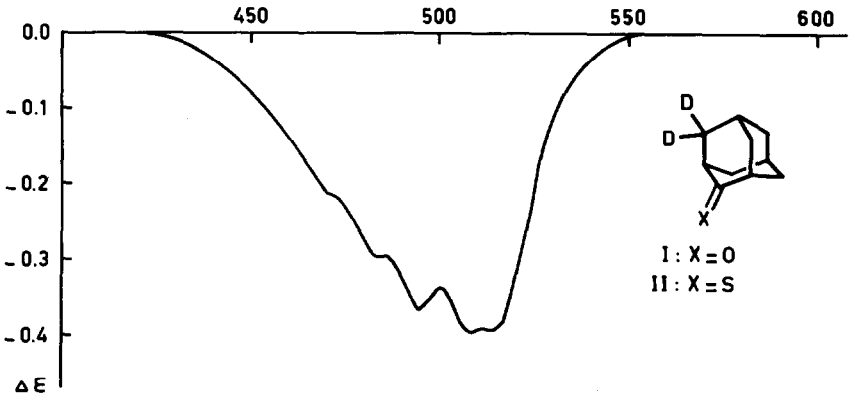

fig. (1): C.D.-curve of II, in isooctane ($c = 0.07$ mole.liter^{-1})

References

1a. C. Djerassi and D. Herbst, J. Org. Chem., 26, 4675 (1961).
b. C. Djerassi and B. Tyrsch, J. Am. Chem. Soc., 86, 4609 (1961); See P. Sundaraman and
c. C. Djerassi, Tetrahedron Lett. 2457 (1978) for the latest publications from this group and references cited therein.
2. D.A. Lightner, T.C. Chang and J. Horwitz, Tetrahedron Lett. 3019 (1977).
3. H. Numan, C.B. Troostwijk, J.H. Wieringa and H. Wynberg, Tetrahedron Lett. 1761 (1977).
4. H. Numan and H. Wynberg, J. Org. Chem., 43, 2232 (1978).
5. J.W. Greijdanus, Can. J. Chem., 48, 3530 (1970).
6. J.P. Engelbrecht, G.D. Anderson, R.E. Linden, C. Barth, E. Bunnenberg and C. Djerassi, Spectr. Acta Part A, 31A, 507 (1975).
7. R.E. Ballard and S.F. Mason, J. Chem. Soc., 1624 (1963).
8. C.A. Emeis, diss. Leiden 1968.
9. W. Moffitt, R.B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, J. Am. Chem. Soc., 83, 4013 (1961).
10. C. Djerassi, C.L. van Antwerp and P. Sundaraman, Tetrahedron Lett. 535 (1978).
11. Stereochemistry, Ed. H.B. Kagan, Thieme Publ. Stuttgart, Vol. 2 (1977).

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