

renes are not practically obtainable from *trans*- β -bromostyrene at the elevated temperature, when tetrahydrofuran is used as solvent.) However the *cis/trans* ratios of β - d_1 -styrene mixtures remain almost unchanged.

Details will be reported in a later paper.

BASIC RESEARCH LABORATORIES
TOYO RAYON COMPANY
KAMAKURA, KANAGAWA, JAPAN

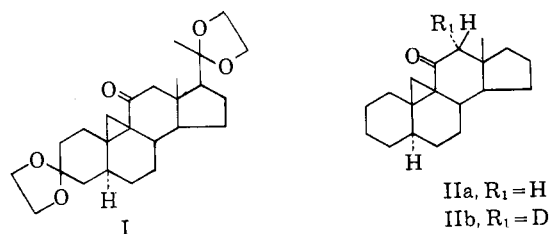
TSUNEO YOSHINO
YASUO MANABE

RECEIVED MAY 25, 1963

Spin-Spin Coupling between Hydrogen and Steroid Angular Methyl Protons

Sir:

Recently¹ it has been demonstrated that in certain fluorosteroids, spin-spin coupling between fluorine and angular methyl protons can occur. To our knowledge, only a single example of a split angular methyl resonance in a steroid nucleus not containing fluorine has been reported; *viz.* the C-18 methyl resonance in the n.m.r. spectrum of the 9,19-cyclo-11-keto steroid I occurred as a three-proton doublet ($J = 0.7$ c.p.s.).² It was tentatively suggested that the splitting may be due to long-range coupling. We have observed a similar



coupling in the closely related ketone IIa and, furthermore, have demonstrated that the methyl protons are coupled to the C-12 axial (12- α) proton. In the 100-Mc. n.m.r. spectrum³ (Fig. 1a) of IIa, the C-18 methyl resonance

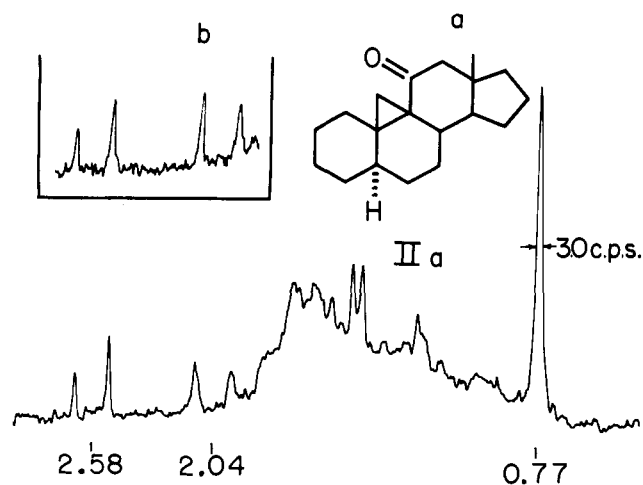


Figure 1.

at $\delta = 0.77$ p.p.m., while not resolvable into a doublet, was broad (half-width = 3.0 c.p.s.). The downfield region of the spectrum showed a pair of doublets at $\delta = 2.58$ and 2.04 p.p.m., due to the C-12 equatorial (12- β) and C-12 axial (12- α) protons, respectively; the coupling constant of the two doublets ($J = 15$ c.p.s.) is consistent with geminal coupling. Limited treat-

(1) A. D. Cross and P. W. Landis, *J. Am. Chem. Soc.*, **84**, 1736 (1962); *ibid.*, **84**, 3784 (1962).

(2) H. Wehrli, M. S. Heller, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **44**, 2162 (1963).

(3) The n.m.r. spectra were obtained on a Varian HR-100 spectrometer. The samples were run as $CDCl_3$ solutions with a trace of tetramethylsilane added to act as internal reference.

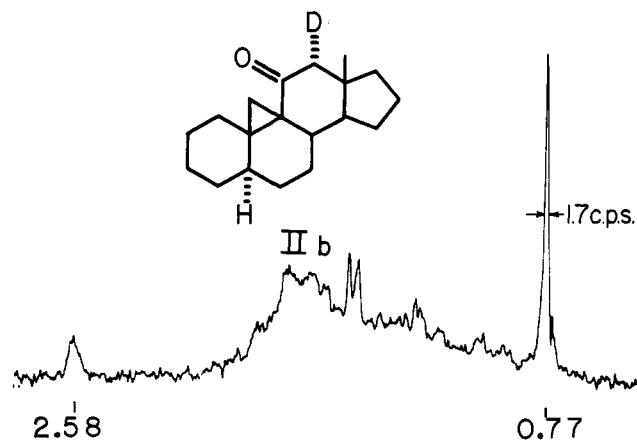


Figure 2.

ment⁴ (0.5-hr. reflux) of IIa with base in deuterium oxide and deuteriomethanol gave the 12 α - d_1 -9,19-cyclo-11-one (IIb) (d_0 , 4%; d_1 , 90%; d_2 , 6% from mass spectral determination), the n.m.r. spectrum of which (Fig. 2) showed, as expected, no signals around $\delta = 2.04$ p.p.m. and only a single resonance at $\delta = 2.58$ p.p.m., broadened due to the small coupling of the C-12 equatorial proton with deuterium. In this spectrum, the half-width of the methyl resonance is now reduced to 1.7 c.p.s.; this is indicative of spin-spin coupling between the angular methyl protons and the C-12 axial hydrogen in IIa. Such a coupling was established conclusively by performing a double resonance experiment⁵ on IIa. On double irradiation at the frequency of the methyl resonance, the doublet at $\delta = 2.04$ p.p.m. was sharpened to give a symmetrical AB system (Fig. 1b), thus clearly demonstrating that the broadening of the C-12 axial proton resonance in the spectrum of IIa (Fig. 1a) is due to coupling with the methyl protons. Alternatively, double irradiation at the frequency of the C-12 axial proton again caused reduction in the half-width of the C-18 methyl resonance, as in the spectrum of the 12 α - d_1 -ketone IIb (Fig. 2).

These results, and those described by us earlier,⁶ along with the reported examples of allylic⁷ and homo-allylic⁸ coupling, again emphasize the caution which must be exercised in the interpretation of n.m.r. spectra.

Acknowledgment.—The work at Stanford University was supported by Grant No. CRTY-5061 from the National Institutes of Health of the U. S. Public Health Service.

(4) D. H. Williams, J. M. Wilson, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 2091 (1963).

(5) N. S. Bhacca, M. E. Wolf, and R. Kwok, *ibid.*, **84**, 4976 (1962), and references cited therein.

(6) D. H. Williams, N. S. Bhacca, and C. Djerassi, *ibid.*, **85**, 2810 (1963).

(7) D. J. Collins and J. J. Hobbs, *Tetrahedron Letters*, **4**, 197 (1963), and references cited therein; T. A. Wittstruck, S. K. Malhotra, and H. J. Ringold, *J. Am. Chem. Soc.*, **85**, 1699 (1963).

(8) J. T. Pinhey, *Tetrahedron Letters*, **4**, 275 (1963).

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA

DUDLEY H. WILLIAMS

VARIAN ASSOCIATES,
PALO ALTO, CALIFORNIA

NORMAN S. BHACCA

RECEIVED JULY 22, 1963

Complexes of Organolithium Compounds with Vacant Orbital Acceptors

Sir:

Organo alkali metal compounds form donor-acceptor complexes with Lewis acids, such as diethylzinc, triethylaluminum, etc. We wish to report that properties, *e.g.*, bond energy, stoichiometry, and association