

The conversion to 3-cyclopropyl-2-propanones appears to be a general reaction of  $\alpha,\beta$ -unsaturated ketones containing a quaternary carbon at the  $\gamma$ -position. Under similar conditions, 4,5,5-trimethyl-3-hexen-2-one (Ib) (1.1 g. in 400 ml. of ether, irradiation for 31 hr.) is converted to the isomeric ketone IIb in 55% yield (based on reacted starting material; approximately 10% starting ketone recovered), isolated by vapor phase chromatography (found: C, 76.96; H, 11.30),  $\gamma_{\text{max}}^{\text{CCl}_4}$  3055, 1724 and 1712 (shoulder)  $\text{cm}^{-1}$ , semicarbazone, m.p. 143–144° (found: C, 60.99; H, 9.90; N, 21.00). The n.m.r. spectrum revealed an unsymmetrical two-proton doublet at 7.65  $\tau$  ( $J_{AB} = 3$  c.p.s.), three-proton singlets at 7.98, 8.90, 8.96 and 9.00  $\tau$  and a characteristic high field cyclopropane methylene singlet at 9.83  $\tau$ , corroborating the structural assignment as 3-(1,2,2-trimethylcyclopropyl)-2-propanone (IIb). The mechanism and scope of this reaction are being investigated.

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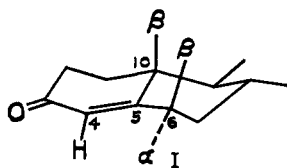
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#### CONCERNING THE STERIC REQUIREMENTS FOR THE ALLYLIC 1,3-SPIN-SPIN COUPLING OF PROTONS<sup>1</sup>

Sir:

Although the long range 1,3-spin-spin coupling of a vinylic proton with an allylic proton is a well recognized<sup>2–5</sup> phenomenon, there is a paucity of information concerning the steric requirements for such interaction. The only definitive studies that we are aware of involve acyclic  $\Delta^1$ -olefins with preferred conformations about the C<sub>2</sub>-C<sub>3</sub> bond due to dipole repulsions<sup>4</sup> or to steric hindrance<sup>5</sup> and indicate strongly that coupling is minimal when the C-1 methylene group and allylic proton are eclipsed,<sup>4,5</sup> while there appears to be no simple relationship of coupling constants to *cis-trans* geometrical configuration.<sup>3,6</sup> We wish to present evidence that in a



number of  $\Delta^4$ -3-keto steroids (structure I) the vinylic C-4 proton is strongly 1,3-coupled ( $J = 1.5$ – $2.0$  c.p.s.) to the axial  $6\beta$ -proton and, in 19-nor steroids, to the axial  $10\beta$ -proton as well, while coupling with the equatorial  $6\alpha$ -proton is negligible. This defines in a rigid system the conditions for minimal and for significant (probably maximal) 1,3-coupling.

The C-4 vinyl proton of a number of representative  $\Delta^4$ -3-keto steroids (e.g., testosterone) appears in the n.m.r. spectrum as a single peak at about 344 c.p.s.<sup>7</sup>

(1) Supported in part by Grants A-4044 and CY-4550, U. S. Public Health Service, and T-185, American Cancer Society.

(2) S. Alexander, *J. Chem. Phys.*, **28**, 355 (1958); **32**, 1700 (1960).

(3) R. R. Fraser and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961), and references therein.

(4) E. B. Whipple, J. H. Goldstein and G. R. McClure, *J. Am. Chem. Soc.*, **82**, 3811 (1960); E. B. Whipple, *J. Chem. Phys.*, **35**, 1039 (1961).

(5) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); A. A. Bothner-By, C. Naar-Colin and H. Gunther, *ibid.*, **84**, 2748 (1962).

(6) Cf. D. R. Davis and J. D. Roberts, *ibid.*, **84**, 2252 (1962).

(7) All spectra were obtained using a Varian 4300 n.m.r. spectrometer, with field homogeneity control unit, at a frequency of 60 Mc.p.s. The

with an average line width<sup>8</sup> of 3.4 c.p.s. Examination of the C-4 proton peak of the  $6\beta$ -deuterio derivatives of androst-4-ene-3,17-dione, testosterone and cholest-4-en-3-one revealed a marked sharpening of the peak with a line width of 2.3 c.p.s. in each case which suggested that despite the absence of a split C-4 proton peak there is a 1,3-coupling between the C-4 and C-6 $\beta$  protons in the undeuterated steroid. Three  $6\beta$ -methyl- $\Delta^4$ -3-ketones similarly exhibited sharpened C-4 proton peaks with an average line width of 2.3 c.p.s. (2.1, 2.4 and 2.5 c.p.s.), further indication of C-4,  $6\beta$  proton-proton coupling in the unsubstituted cases.

In contrast, the examination of four  $6\alpha$ -methyl- $\Delta^4$ -3-ketones demonstrated in each case a doublet for the C-4 proton with  $J = 1.5$ – $2.0$  c.p.s.,<sup>9</sup> while the  $6\alpha$ -methyl group itself exhibited the normal doublet splitting pattern of a methyl group on a carbon atom bearing a single proton. These results can be interpreted only as C-4,  $6\beta$  proton-proton coupling.

A similar pattern was found in the isomeric 6-bromoandrost-4-ene-3,17-diones. The  $6\beta$ -bromo isomer exhibited a sharpened C-4 proton peak of width 2.4 c.p.s. at 355 c.p.s. (average frequency) while the  $6\alpha$ -proton, due to coupling with the C-7 protons, appeared as a typical ABX quartet centered at 296 c.p.s. The  $6\alpha$ -bromo isomer, however, showed a doublet for the C-4 proton centered at 391 c.p.s.,  $J = 2.0$  c.p.s., and an octet for the  $6\beta$ -proton (center 304 c.p.s.) due to coupling with the two C-7 protons and the C-4 proton.

It is apparent that 1,3-coupling is significant only in the case of the axial  $6\beta$ -proton while the effect of the  $6\alpha$ -equatorial proton appears to be negligible. Sterically, the  $6\beta$ -axial C-H bond but not the  $6\alpha$ -equatorial bond is positioned for efficient overlap with the  $\pi$  orbitals of the double bond and the transmission of spin information may be pictured as proceeding *via* the electrons associated with the C-6 proton directly to the  $\pi$ -electrons.<sup>10</sup> These findings appear to confirm the prediction of Karplus<sup>10</sup> that the position of the allylic proton with respect to the  $\pi$ -orbitals of the double bond will be the predominant factor in determining the magnitude of 1,3-coupling. It may be noted that although the  $6\alpha$ -proton in  $\Delta^4$ -3-keto steroids geometrically approximates the eclipsed conformation of the olefins in ref. 4 and 5, and confirms that coupling is minimal in this position, 1,3-coupling should also be minimal when the two protons are *trans* if the two C-H bonds are in the same plane.

It was predictable that 19-nor- $\Delta^4$ -3-keto steroids should exhibit evidence of  $10\beta$ -hydrogen as well as  $6\beta$ -hydrogen coupling with the C-4 proton since the C-H bond in both cases is approximately perpendicular to the plane passing through the C-4, 5 and 6 carbon atoms and hence in an optimal position for  $\sigma$ - $\pi$  overlap. A number of 19-nor- $\Delta^4$ -3-ketones, unsubstituted at C-6, were investigated and all exhibited marked broadening of the C-4 proton peak (av. line width 4.3 c.p.s.) indicative of additional coupling with the  $10\beta$ -proton but no definite splitting was observed. However, the C-4 proton of  $6\beta$ -methyl-19-norandrost-4-ene-3,17-dione appeared as a sharp doublet at 353.5 c.p.s.,  $J = 2.0$  c.p.s.,

samples were dissolved in deuteriochloroform and the spectra were calibrated using the side-band technique. Peak positions are reported in c.p.s. downfield from tetramethylsilane (internal reference).

(8) The full line widths were measured in each case at half-height. The homogeneity of the magnetic field was such that the average line width of the tetramethylsilane reference peak was 1.2 c.p.s. The uncertainty in measurement is estimated to be  $\pm 0.2$  c.p.s.

(9)  $6\alpha$ -Methyltestosterone, 2.0 c.p.s.;  $6\alpha$ -methylprogesterone, 2.0 c.p.s.;  $6\alpha$ -methyl-17 $\alpha$ ,21-dihydroxypregn-4-ene-3,20-dione, 1.5 c.p.s.;  $6\alpha$ -methyl-17 $\alpha$ -hydroxypregn-4-ene-3,20-dione, 1.5 c.p.s.  $J$ -values are estimated to be accurate to  $\pm 0.2$  c.p.s.

(10) M. Karplus, *J. Am. Chem. Soc.*, **82**, 4431 (1960); *J. Chem. Phys.*, **33**, 1842 (1960).

TABLE I  
N.M.R. SPECTRUM OF C-4 PROTON OF  $\Delta^4$ -3-KETOSTEROIDS

Substituent at C-6	Average $\delta$ (c.p.s.) <sup>7</sup>	Average line width (c.p.s.) <sup>8</sup>	No. of compounds	
None	344.2	3.4	6	
6 $\beta$ -D	343.5	2.3	3	
10-Methyl	6 $\beta$ -CH <sub>3</sub>	344.3	2.3	3
	6 $\beta$ -Br	355.0	2.4	1
	6 $\alpha$ -Br	390.6	$J = 2.0$	1
	6 $\alpha$ -CH <sub>3</sub>	347.4	$J = 1.7$	4
10-H	None	350.0	4.3	4
(19-Nor)	6 $\beta$ -CH <sub>3</sub>	353.5	$J = 2.0$	1

which almost certainly is due to C-4, 10 $\beta$  proton-proton coupling.

The appearance of the C-4 proton as a broadened peak when two protons are present at C-6 but as a sharp doublet in the presence of a 6 $\alpha$ -substituent may be rationalized by a first-order treatment<sup>11</sup> of the C-4 and two C-6 protons as an ABX system which indicates that two of the possible six lines are of near zero intensity while the remaining four are so closely spaced as to be unresolved by the present instrument and appear as a broadened signal. When the 6 $\alpha$ -proton is replaced by halogen or methyl the system under consideration reduces to the AX type in which the X portion consists of only two lines.

(11) Cf. J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961, p. 71.

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#### LINKAGE ISOMERISM: SYNTHESIS OF THIOCYANATO AND ISOTHIOCYANATO ISOMERS OF SOME PALLADIUM(II) COMPLEXES

Sir:

The first example of linkage isomerism for metal complexes was reported in 1893 by Jørgensen<sup>1</sup> for nitro (Co-NO<sub>2</sub>) and nitrito (Co-ONO) ammines of cobalt(III). Recently, it was possible to extend this type of isomerism to include complexes of rhodium(III), iridium(III) and platinum(IV).<sup>2</sup> These have been the only examples of linkage isomers in metal complexes.

The thiocyanate ion is often suggested as an example of another ligand that might possibly be used to produce linkage isomers. Typical of textbook statements is the following: "the thiocyanate ion coordinates through sulfur in some complexes and through nitrogen in others but no isomeric pair has as yet been found".<sup>3</sup>

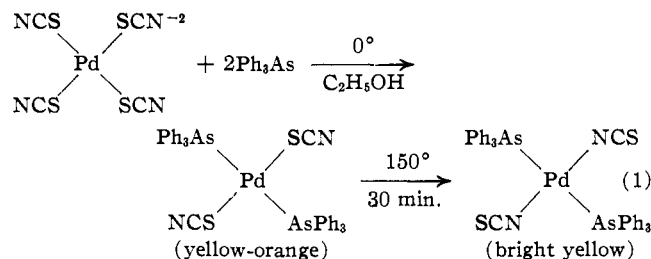
We wish to report the synthesis of thiocyanato (Pd-SCN) and isothiocyanato (Pd-NCS) isomers of some palladium(II) complexes. The method used is based on the interesting and significant observation made by Turco and Pecile.<sup>4</sup> They found that, for Pd(II) and Pt(II) complexes, coordinated thiocyanate ion is either S- or N-bonded, depending on the nature of the other ligands present. Thus, the systems [M(SCN)<sub>4</sub>]<sup>-2-</sup> and [M(NH<sub>3</sub>)<sub>2</sub>(SCN)<sub>2</sub>] are S-bonded, whereas [M(PR<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub>] is N-bonded. It follows that in these systems there should be some borderline ligands for which the energy difference between the M-SCN and M-NCS isomers is small. Triphenylarsine, Ph<sub>3</sub>As, was found to be such a ligand. Using this ligand it is possible to obtain the unstable kinetic product before it rearranges to the stable isomer (1).

(1) S. M. Jørgensen, *Z. anorg. allgem. Chem.*, **5**, 169 (1893).

(2) F. Basolo and G. S. Hamaker, *J. Am. Chem. Soc.*, **82**, 1001 (1960); *Inorg. Chem.*, **1**, 1 (1962).

(3) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 538.

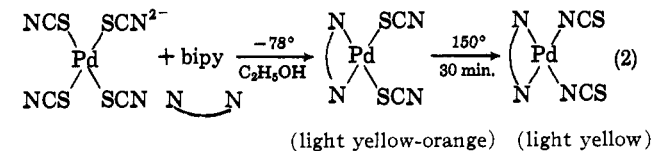
(4) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).



In a typical preparation, 1.03 g. (2.47 mmoles) of K<sub>2</sub>Pd(SCN)<sub>4</sub>, dissolved in 25 cc. of absolute ethanol and 5 drops of water, and 1.52 g. (4.95 mmoles) of triphenylarsine, dissolved in 25 cc. of absolute ethanol and 5 drops of ethyl ether, were cooled to 0°, then mixed in a vessel surrounded by an ice bath. After stirring for 1 min., the yellow-orange S-bonded product was precipitated by the addition of 50 cc. of ice water, isolated, washed with ice-cold ethanol and ethyl ether and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub> (yield, 1.87 g. or 91%).

Anal. Calcd. for [Pd(AsPh<sub>3</sub>)<sub>2</sub>(SCN)<sub>2</sub>]: C, 54.7; H, 3.6; N, 3.4. Found, before heating: C, 54.5; H, 3.8; N, 3.3; after heating: C, 55.0; H, 3.8; N, 3.6.

The S-bonded isomer is stable at room temperature in the solid state for weeks but rearranges readily at elevated temperatures and in solution it immediately gives the N-bonded form. Because of the possible complication due to the chance of concurrent geometric isomerism, it was necessary to prepare a system containing a bidentate ligand. This was accomplished using 2,2'-bipyridine, bipy, at the temperature of a Dry Ice-acetone mixture (2).



When alcoholic solutions of equimolar quantities of K<sub>2</sub>Pd(SCN)<sub>4</sub> and 2,2'-bipyridine, pre-cooled to -78°, were mixed in a reaction vessel surrounded by a Dry Ice-acetone bath, no formation of solid took place. The solution was removed from the bath and, after about 10 min., had become opaque. An unidentified orange solid was removed by filtration and the desired S-bonded isomer immediately separated in the filtrate. This was isolated, washed with -78° ethanol and ethyl ether and dried in a vacuum desiccator over Mg(ClO<sub>4</sub>)<sub>2</sub>.

Anal. Calcd. for [Pd(bipy)(SCN)<sub>2</sub>]: C, 38.0; H, 2.1; N, 14.8. Found, before heating: C, 38.2; H, 2.5; N, 15.0; after heating: C, 38.5; H, 2.4; N, 14.8.

The nature of the thiocyanate bonding in these two sets of isomers was determined by examining the infrared spectra of Nujol mulls of the solid compounds. It has been shown<sup>4,5</sup> that the C-S stretching vibrations of coordinated thiocyanates fall into two ranges: M-SCN, 690-720 cm.<sup>-1</sup>; M-NCS, 780-860 cm.<sup>-1</sup>. The C-S stretching frequencies found were [Pd(AsPh<sub>3</sub>)<sub>2</sub>(SCN)<sub>2</sub>], blank in M-NCS range, obscured by phenyl absorption in M-SCN range; [Pd(AsPh<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub>], 854 cm.<sup>-1</sup>; [Pd(bipy)(SCN)<sub>2</sub>], 700 cm.<sup>-1</sup>; [Pd(bipy)(NCS)<sub>2</sub>], 842 cm.<sup>-1</sup>.

Under high resolution, the frequencies of the C-N stretching vibrations were also observed to vary, in accordance with the order predicted by Mitchell and Wil-

(5) M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959); J. Lewis, R. S. Nyholm and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).