side of the C_5H_6 ring nearer to the metal atom. By analogy, it is suggested that the X-protons lie closer to Pd than the M-protons in I as illustrated perspectively above. The bond between the allyl group and Pd is delocalized, somewhat analogously to the π-cyclopentadiene–metal bond in metallocenes. However, in contrast to the metallocenes, the allyl carbons do not have the same unpaired spin densities. The unpaired spin density in an allyl radical is $+ {}^2/_3$ at each of the two terminal carbon atoms and is $- {}^1/_3$ at the middle carbon atom.[5] Consequently, it is reasonable to visualize that the Pd in I is situated off center and is closer to the terminal carbon atoms as shown in the perspective figure above.

The non-classical structure of II eliminates the possibility of geometrical isomerism. Spin-lattice relaxation time measurements[6] indicate that the cyclopendiene groups in ferrocene are freely rotating. We have looked carefully for geometric isomers of II and found none. The crude product obtained as a tan, methylene chloride-soluble solid in 96.5% yield, was chromatographed analytically on alumina. Elution with methylene chloride–acetonitrile (65 fractions) gave an 88.6% yield of II. The n.m.r. spectra of the first and last fractions were identical.

The non-classical structures proposed for the organometal part in I and II are further supported by infrared spectra.[7] The C–H stretching region in the spectrum of I has only three strong bands at 3012, 3053 and 3081 cm.$^{-1}$ with relative absorbance of 0.1, 0.22 and 0.27, respectively. These bands may be assigned to the C–H$_{\rm A}$, C–H$_{\rm M}$ and C-H$_{\rm X}$ stretching modes. These three bands are present also in the spectrum of II together with the bands due to the methyl group. In II, the relative absorbance of the 3081–cm.$^{-1}$ peak decreased in magnitude and became comparable to the 3012–cm.$^{-1}$ peak.

It is realized that the structures proposed are tentative and that further evidence from X-ray study on single crystals is necessary.

Even though a hyperfine splitting of 0.2 c.p.s. can be detected easily, there is no measurable coupling between the M- and the X-protons. Karplus and Anderson[8] showed that it is the non-perfect-pairing valence-bond structures which contribute most to the contact coupling constants. The absence of coupling between the M- and the X-protons suggests that interference by the Pd d-orbitals may have reduced the contribution of the non-perfect-pairing structures to the ground state wave functions. Another possible explanation is that the HCH dihedral angle is 125°, in which case[9] the value of $J^{\rm HH}_{\rm gcm}$ is zero. It is possible that both mechanisms contribute to the observed zero $J_{\rm MX}$ value.

The 60-mc. spectrum of allylcobalt tricarbonyl[10] is similar to that of I in all respects which suggests strongly the symmetrical non-classical structure for the allylcobalt portion of the molecule.

---

[5] H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **27**, 984 (1957); H. M. McConnell, *ibid.*, **28**, 1188 (1958).

[6] C. H. Holm and J. A. Ibers, *ibid.*, **30**, 885 (1959).

[7] We are indebted to Mr. J. A. Gailey for the infrared determinations and interpretations; $CDCl_3$, $CHCl_3$ and CCl_4 were used as solvents.

[8] M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **30**, 6 (1959); M. Karplus, *ibid.*, **30**, 11 (1959).

[9] H. S. Gutowsky, M. Karplus and D. M. Grant, *ibid.*, **31**, 1278 (1959).

[10] R. F. Heck and D. S. Breslow, THIS JOURNAL, **82**, 750 (1960).

RESEARCH CENTER HENRY C. DEHM
HERCULES POWDER COMPANY JAMES C. W. CHIEN
WILMINGTON, DELAWARE

RECEIVED MAY 9, 1960

FACILE BROMINATION OF PYRIDINE-TYPE HETEROCYCLES AT THE β-POSITION[1]

Sir:

The extremely vigorous conditions required to effect (presumably electrophilic) substitution into the pyridine ring are well-known,[2] and substitution into a pyridine derivative already containing an electron-withdrawing group is virtually impossible, except in special cases. However, we have found that refluxing a solution of bromine (1.5 moles) and nicotinyl chloride hydrochloride (I)[3] (1 mole) in excess thionyl chloride (II) for 13–19 hr. produced, after hydrolysis, 70–75% yields of 5-bromonicotinic acid (III)[4] (purified m.p. 189–190°; lit. m.p.'s 183°[4] and 182–183°[5]), identified by conversion *via* the acid chloride (ammonia in chloroform) to 5-bromonicotinamide[6] [80% yield, m.p. 219–219.5° (from aqueous ethanol) calcd. for $C_6H_5N_2OBr$: C, 35.85; H, 2.51; N, 13.95. Found:[7] C, 36.15; H, 2.65; N, 13.66] and thence by a Hofmann reaction (sodium hypobromite) to the known 3-amino-5-bromopyridine (65–67% yield, m.p. 69–69.5°; lit. m.p.'s, 65°[8] and 66–67°[9]), whose diazonium salt was reduced[10] to the known 5-bromo-3-pyridylhydrazine, m.p. 111–115°, lit. m.p. 109–110°.[10]

Dropwise addition (cooling) of 50 ml. of II to 40 ml. of pyridine (IV) and then 65 ml. of bromine (during 2 hr. at 90°) and heating the resulting solution at 88–91° for 5 hr. afforded, after removal of excess bromine and II, steam distillation of the basified residue, and vacuum sublimation, 20–28% of almost analytically pure 3,5-dibromopyridine (V), m.p. 111–112° (lit. m.p.'s 110–111°[11] and 110°[12]), identical (mixed m.p. and infrared spectrum) with

---

[1] (a) Taken, in part, from the doctoral dissertation of C. V. Greco. (b) Supported, in part, by a research grant (CY-2962) from the National Cancer Institute of the Public Health Service and by the U.S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 18-(603)-127. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] For a recent review, see K. Thomas and D. Jerchel, *Angew. Chem.*, **70**, 719 (1958).

[3] A. L. Mndzhoyan, *J. Gen. Chem.* (*U.S.S.R.*), **16**, 1029 (1946); *C.A.* **41**, 2737 (1947).

[4] G. B. Bachman and D. D. Micucci [THIS JOURNAL, **70**, 2381 (1948)] prepared III in 87% yield by heating I with bromine for 10 hr. at 150–170° and then hydrolyzing.

[5] H. Gilman and S. M. Spatz, *J. Org. Chem.*, **16**, 1485 (1951).

[6] Also prepared in 50–65% yield (based on nicotinic acid) by direct reaction of the bromination product from I with ammonia in chloroform.

[7] Combustion analyses by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

[8] H. J. den Hertog and J. P. Wibaut, *Rec. trav. chim.*, **55**, 122 (1936).

[9] R. Graf, E. Lederer-Ponzer, M. Kopetz, R. Pukrert and P. Laszlo, *J. prakt. Chem.*, **138**, 244 (1933); *C.A.*, **28**, 769 (1934).

[10] C. Zwart and J. P. Wibaut, *ibid.*, **74**, 1062 (1955).

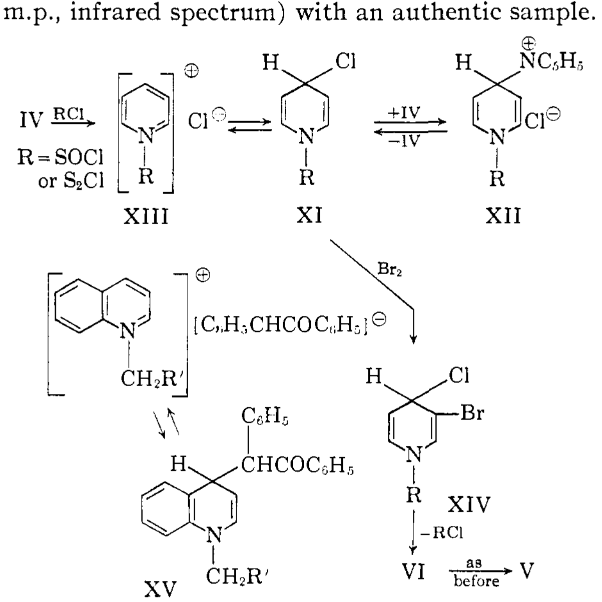
[11] S. M. E. Englert and S. M. McElvain, THIS JOURNAL, **51**, 863 (1929).

[12] H. Maier-Bode, *Ber.*, **69**, 1534 (1936).

an authentic sample. From the steam distillate a small amount of 3-bromopyridine (VI) and about 25% of unchanged IV were isolated. Replacement of II by sulfur monochloride (VII) permitted a higher reaction temperature (125–130°), an easier work-up, and increased the yield of V to 33–40%. VI in II and in VII afforded V in 15[13] and 50% yields, respectively.

Quinoline (VIII) is much more reactive than IV toward bromination in a solution of VII. Best results were obtained by use of equimolar amounts VIII, VII and IV with a slight excess of bromine, the reagents being added (cooling) to VIII in the order named. On heating the solution in a bath at about 95° for about 1 hr. a solid formed. The filtered solid was treated with aqueous alkali, sulfur removed by filtration, the filtrate extracted with ether, and the extract distilled to yield 65% of almost analytically pure 3-bromoquinoline (IX),[14] b.p. 115–120° at 1 mm., $n^{25}\text{D}$ 1.6613, whose infrared spectrum was identical with that of an authentic sample[15] kindly supplied by Dr. J. Eisch.

Bromination of isoquinoline in VII has not yet been studied thoroughly, but we have obtained 4-bromoisoquinoline, m.p. 34–37°, identical (mixed m.p., infrared spectrum) with an authentic sample.



R' = 2,6-dichlorophenyl

Characteristic of these reactions is the entry of the bromine at the beta-position to the ring nitrogen, regardless of the nature of the substituent (—H, —Br, or —COCl) already present. The mild conditions used, even with I, militate against a straightforward electrophilic substitution. Much more likely is the view that the species being brominated is a 1,2- or 1,4-dihydropyridine derivative (XI) or its reaction product (XII) with IV, all of which probably exist in equilibrium with the pyridinium salt formed by addition of either VII or II to IV. Electrophilic bromination of XI or XII (each has a vinylamine structure) would certainly proceed readily to yield (from XI) XIV, which could lose RCl to form the observed products. It is noteworthy that XII has been suggested as an intermediate in the reaction of IV with either II or VII to form the 4-pyridyl-pyridium chloride hydrochloride.[16,17] The mechanism is strikingly similar to those independently suggested to explain the bromination of compounds like XV[18] and the nitration (with benzoyl or acetyl nitrate) of quinoline 1-oxide,[19] both of which occur at the 3-position under very mild conditions.

It seems likely that the above ideas can be extended to other pyridine-type heterocycles and to other substitution reactions. Furthermore, II and VII probably can be replaced by a variety of similar reagents. Work along some of these lines is in process in this Laboratory. We believe that reactions like those described open important new perspectives in the chemistry of pyridine-type heterocycles.

---

(13) No attempt was made to achieve maximum yield.

(14) A. Edinger [*Ber.*, **29**, 2456 (1896)] reported a low yield of IX from the exothermic reaction of VIII with sulfur monobromide (X), free bromine being produced by decomposition of X.

(15) J. Eisch, *Chemistry and Industry*, 1449 (1959).

(16) E. Koenigs and H. Greiner, *Ber.*, **64**, 1049 (1931).

(17) E. Koenigs and H. Greiner, German Patents 536, 891 (1931), and 566,693 (1932), as cited by H. Maier-Bode and J. Altpeter in "Das Pyridin und seine Derivate," Verlag von Wilhelm Knapp, Halle (Saale), 1934, Photo-Lithoprint Reproduction by Edwards Brothers, Inc., Ann Arbor, Mich., 1943, pp. 99, 289, and 292.

(18) F. Kröhnke and I. Vogt, *Chem. Ber.*, **90**, 2227 (1957).

(19) E. Ochiai and C. Kaneko, *Pharm. Bull.* (*Tokyo*), **5**, 56 (1957); *Chem. Pharm. Bull.* (*Tokyo*), **7**, 267 (1959).

(20) To whom all inquiries should be sent at Department of Chemistry, University of Massachusetts, Amherst, Massachusetts.

DEPARTMENT OF CHEMISTRY EDWARD E. GARCIA
FORDHAM UNIVERSITY CLAUDE V. GRECO
NEW YORK 58, NEW YORK I. MOYER HUNSBERGER[20]

RECEIVED JULY 20, 1960

THEORY OF PROTON COUPLING CONSTANTS IN UNSATURATED MOLECULES

Sir:

A number of recent papers[1-5] concerned with the n.m.r. spectra of unsaturated molecules have reported the magnitudes of 1.5 to 7 c.p.s. for the coupling constants between protons separated by three or four carbon atoms. Since theoretical calculations[6] and experimental measurements[7] have shown that the sigma-electron contribution to such coupling constants is less than 0.5 c.p.s., the large size of the observed values has aroused some interest. We wish to point out in this communication that the inclusion of pi-electron terms in the coupling interaction provides a quantitative explanation of the experimental results.

A second-order perturbation formalism has been developed for the calculation of the pi-electron contribution to the proton coupling constants for unsaturated systems in which the formal separation into sigma and pi electrons is possible. The

---

(1) S. Alexander, *J. Chem. Phys.*, **28**, 355 (1958); J. Waugh, *ibid.*, **30**, 944 (1956); C. N. Banwell, A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Chem. Soc.*, 266 (1955).

(2) E. B. Whipple, J. H. Goldstein, L. Mandell, G. S. Reddy and G. R. McClure, THIS JOURNAL, **81**, 1321 (1959); P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, to be published.

(3) E. B. Whipple, J. H. Goldstein and L. Mandell, *ibid.*, **30**, 1109 (1959); E. B. Whipple, J. H. Goldstein and W. E. Stewart, THIS JOURNAL, **81**, 4761 (1959).

(4) R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960).

(5) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).

(6) M. Karplus, unpublished calculations.

(7) P. T. Narasimhan, private communication; Shimizu, Matsuoka, Hafferi and Seudo, *J. Phys. Soc.* (*Japan*), **14**, 683 (1959).