

dark red needles, m.p. 222–223° dec. (*Anal.* Found: N, 11.19). Similarly monodehydro[14]annulene (II or III) with 1,3,5-trinitrobenzene gave a 1:1 adduct as long red needles, m.p. 182–183° dec. (*Anal.* Found: C, 61.66; H, 3.80; N, 11.20). No comparable complex could be obtained from [14]annulene (IV).

The reaction of the 14-membered ring conjugated compounds with maleic anhydride also appears to be related to their aromatic nature. Thus, 1,8-bisdehydro[14]annulene on treatment with an excess of the anhydride in boiling benzene for 1 hr. was completely unchanged, monodehydro[14]annulene under these conditions was recovered to the extent of 85%, while less than 10% of the nonaromatic [14]annulene was unaffected.

Acknowledgment.—We are indebted to Dr. A. Melera, Varian A. G., Zürich, Switzerland, for determining the 100 Mc./sec. n.m.r. spectra.

DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

YEHIEL GAONI
FRANZ SONDEHEIMER

RECEIVED OCTOBER 28, 1963

The Hyperfine Coupling Constants and Rates of Exchange for $C^{13}N^-$ with the Axial and Equatorial Positions in $Cr(CN)_5NO^{-3}$

Sir:

It has been recently reported^{1,2} that the magnetic hyperfine interaction of C^{13} was observable in the paramagnetic resonance spectrum of aqueous solutions of $Cr(CN)_5NO^{-3}$. It seemed probable that this interaction was only due to the equatorial CN^- , but the possible axial coupling remained unknown. In a preliminary report³ of the exchange with $C^{13}N^-$ we were also unable to differentiate between the axial and equatorial positions. We have now been able to prepare the complex by exchange with C^{13} substituted primarily in the axial position and by synthesis with every cyanide substituted by $C^{13}N^-$. Both the hyperfine interaction and the rates of exchange of the axial and equatorial positions have now been clearly resolved:

Samples of $K_3Cr(CN)_5NO$ were synthesized⁴ utilizing NaCN enriched to 55% in C^{13} isotope. The largest hyperfine splitting in the p.m.r. spectrum of $Cr(CN)_5NO^{-3}$ should arise from the species containing⁵ Cr^{53} , N^{14} , and five C^{13} . In the X-band spectrum of the enriched sample, clearly resolved lines occur 62.4 gauss above and below the center of the spectrum. Since these lines must be due to a combination of axial and equatorial C^{13} hyperfine interaction, this splitting can be combined with the previously assigned^{1,2} Cr^{53} , N^{14} , and C^{13} equatorial splittings to yield a value of 8.55 ± 0.4 gauss for the axial C^{13} coupling constant.

A prominent hyperfine line can also be observed between the C^{12} and the expected equatorial C^{13} lines when the complex is exchanged in solutions containing nearly equal amounts of C^{13} enriched CN^- and HCN. Direct measurement of this line gives 8.93 ± 0.2 gauss for the axial C^{13} coupling constant. Our values can be compared to the 8.43 ± 0.2 gauss reported by Kuska and Rogers⁶ from a resolution of the complex pattern observed for both axial and equatorial C^{13}

TABLE I
HYPERFINE COUPLING CONSTANTS

	A, gauss
Cr^{53}	18.39 ± 0.05
N^{14}	5.27 ± 0.05
C_e^{13}	12.64 ± 0.2
C_a^{13}	8.80 ± 0.3

substitution. A summary of our coupling constants is given in Table I.

In the temperature range 60–100°, the exchange with $C^{13}N^-$ can be observed without decomposition of the complex. We have followed the decrease in the signal due to unsubstituted complex and the increase in the signal resulting from equatorial C^{13} substitution while the samples were held at constant temperature in the microwave cavity of a p.m.r. spectrometer. In solutions ranging from 0.015 to 0.035 *F* in complex and 0.1–0.2 *F* in NaCN (55% in C^{13} isotope), we followed the adjacent lines for unsubstituted and C^{13} equatorial-substituted complex for the Cr^{53} species until approximately 50% of the complex was substituted with one $C^{13}N^-$. These experiments were conducted in the nearly complete darkness of the cavity. In separate experiments no pronounced light catalysis, as reported for other cyanide complexes,⁷ was observed.

These exchange data were fit by rate laws assuming first order in unsubstituted complex and zero order in total CN^- concentration. An integrated rate law was used which took into account the possible substitution of the axial and one of the four possible equatorial CN^- . The total rate constant $k_a + 4k_e$ can be directly obtained from the decrease in the unsubstituted complex and the equatorial rate constant k_e can be evaluated by successive approximation from the growth of the equatorial C^{13} signal. At 75° we obtain $k_a = 1 \times 10^{-4}$ sec.⁻¹ and $k_e = 7 \times 10^{-6}$ sec.⁻¹. Over the range of temperatures we get $\Delta H_a^* = 33.5 \pm 4$ kcal./mole, $\Delta S_a^* = 18 \pm 8$ e.u., $\Delta H_e^* = 30.5 \pm 4$ kcal./mole, and $\Delta S_e^* = 5 \pm 8$ e.u. In the solutions prepared by adding NaCN to neutral solutions of the complex, the ratio $k_a/4k_e = 4 \pm 2$ over the full range of temperature.

The apparent large positive value for ΔS_a^* indicates⁸ that the activated complex for axial exchange is a protonated species. The formation of $HCr(CN)_5NO^{-2}$ by the removal of the proton from HCN could contribute about 40 e.u. to the apparent entropy of activation. When exchange experiments are conducted in acidified solutions so that both CN^- and HCN have nearly equal concentrations, the axial rate is accelerated. In this case, as previously mentioned, a line due to axial substitution becomes prominent before the equatorial line is clearly observable. It seems probable that the formal charge of +1 on the NO group makes the axial CN^- more likely for protonation than the more adjacent equatorial CN^- . It is possible from our data, however, that the equatorial exchange is also partly acid-catalyzed.

The similar values for the N^{14} and both C^{13} coupling constants do not give any clear contradiction or support to the bonding scheme proposed⁹ for these complexes. The axial CN^- is more labile to exchange in aqueous solution primarily because of greater protonation at this position, and the enthalpies of activation are equally large for both positions. The theory for the isotropic hyperfine interaction in these compounds is necessarily complex, and both the signs of the coupling constants

(7) A. G. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.*, **76**, 4222 (1954).

(8) We wish to thank Professor R. E. Connick for suggesting this possibility to us.

(9) H. B. Gray, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3404 (1962).

(1) R. G. Hayes, *J. Chem. Phys.*, **38**, 2580 (1963).

(2) I. Bernal and S. E. Harrison, *ibid.*, **38**, 2581 (1963).

(3) J. B. Spencer and R. J. Myers, presented before the Inorganic Division of the American Chemical Society, 144th National Meeting, Los Angeles, Calif., April, 1963.

(4) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 872 (1959).

(5) There is no observable hyperfine interaction from the N^{14} in the CN^- ; Cr^{53} is 9.5% abundant.

(6) H. A. Kuska and M. T. Rogers; we wish to thank Professor Rogers for sending us a pre-publication copy of their work.

and the anisotropic terms should be determined before a serious effort is made to explain the axial and equatorial coupling constants in terms of bonding.

Acknowledgment.—This work was supported by a grant from the United States Atomic Energy Commission to the Inorganic Materials Research Division of the Lawrence Radiation Laboratory.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA

J. BROCK SPENCER
ROLLIE J. MYERS

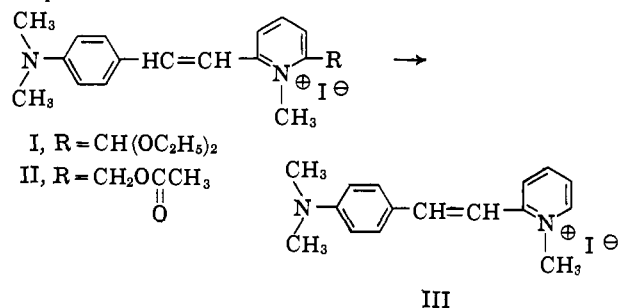
RECEIVED DECEMBER 9, 1963

An Unexpected Cleavage in the Pyridine Series

Sir:

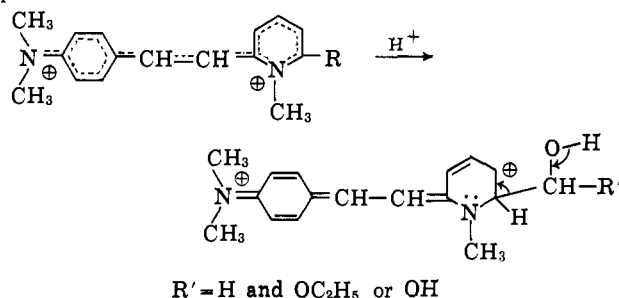
We have observed that an acetoxymethyl group and an aldehyde group, as the acetal, are cleaved from the pyridine nucleus under mild conditions.

The methiodide prepared from the diethyl acetal of 2-methyl-6-pyridinecarboxaldehyde reacted normally with *p*-dimethylaminobenzaldehyde to yield the expected stilbazole I. *Anal.* Calcd. for $C_{21}H_{29}O_2NI$: C, 53.82; H, 6.16; N, 5.85. Found: C, 53.85; H, 6.26; N, 6.07. However, attempts to hydrolyze the acetal linkage in dilute acid resulted in the loss of the group R to yield the known stilbazole III¹ with m.p. 269–270° alone or when mixed with an authentic sample; the infrared and ultraviolet spectra of the two samples were also identical.



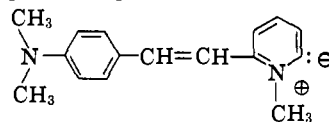
2-Acetoxymethyl-6-methylpyridine methiodide was treated with dimethylaminobenzaldehyde in ethanol and again a cleavage occurred, this time with loss of the acetoxymethyl group. Although stilbazole II was not isolated, it seems reasonable to believe that it was formed and subsequently cleaved in the reaction mixture as for compound I.

Previous work^{2,3} has not suggested that 2-acetoxymethylpyridines or the acetals (or hemiacetals) of 2-pyridine aldehydes are unstable. Therefore, it seems likely that the *p*-dimethylaminophenyl group must in some way facilitate the cleavage reaction. A tentative mechanism for this reaction uses the electron pair of the dimethylamino group to increase the electron density of the pyridine ring so that protonation can take place.



- (1) A. P. Phillips, *J. Org. Chem.*, **12**, 333 (1947).
(2) V. Boekelheide and W. J. Linn, *J. Am. Chem. Soc.*, **76**, 1286 (1954).
(3) W. Mathes and W. Sauermilch, *Chem. Ztg.*, **80**, 475 (1956).

In order for this mechanism to explain the second cleavage it is necessary that the acetic acid resulting from the alcoholysis of the acetoxymethyl group be able to serve as a proton donor. A variation of this mechanism would allow the cleavage to occur before protonation, generating ion IV as an intermediate.



IV

However, the dimethylaminophenyl group plays no part in this mechanism.

Further experiments to determine the scope of the reaction and to illuminate its mechanism further are in progress.

Acknowledgment.—This work was performed as a part of a program supported by Contract DA CML 18 108 G 42 with the U. S. Army Chemical Center.

SCHOOL OF CHEMISTRY
RUTGERS THE STATE UNIVERSITY
NEW BRUNSWICK, NEW JERSEY

RODERICK A. BARNES
ADORJAN ASZALOS

RECEIVED DECEMBER 5, 1963

Cyclization to a Five-Membered Ring in the Free-Radical Reaction of Iodoperfluoroalkanes with 1,6-Heptadiene

Sir:

Cyclic polymerization of 1,6-heptadiene to saturated polymeric chains containing six-membered ring units has been reported.^{1–3} Free-radical chain reaction of 1,6-heptadiene with 1-iodoperfluoropropane (R_FI), initiated by 2 mole % of azobisisobutyronitrile, gave an olefinic monoadduct (1), a bisadduct (2), and two isomeric methylcyclopentane derivatives (4a,b) in the ratio of 84:16. Surprisingly, cyclization gave a five-membered ring rather than the anticipated cyclohexane derivatives. Gas chromatography (g.l.c.) showed no other products were formed. Analogous reaction of R_FI with either 1,5-hexadiene or 1,7-octadiene, however, gave only the olefinic and saturated noncyclic adducts resulting from addition of one or two R_FI molecules, respectively.

Cyclization of the perfluoroalkylheptenyl radical 1a exclusively to a methylcyclopentane structure indicates an unusual degree of kinetic control of products. Secondary radicals such as 1a or the cyclohexyl radical 5a are generally thought to be more stable than primary radicals such as 3a,b. Cyclohexane is known to be more stable than methylcyclopentane.⁴ It seems possible that approach of the large and strongly electronegative R_FI to within bonding distance of the radical site on 1a may be hindered by the R_F group already present on the adjacent carbon. For radicals 3a,b this approach is to the fourth carbon removed; for 5a it is also to the fourth carbon, but steric and conformational effects in the cyclohexane system may serve to raise the energy and entropy of the transition state intermediate leading to 6a (or isomer) having bulky R_FCH₂ and iodine groups.⁵ Studies now under-

- (1) For reviews up to 1960, see (a) C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y. (1963), p. 446; (b) G. B. Butler, *J. Polymer Sci.*, **48**, 279 (1960); (c) C. S. Marvel, *ibid.*, **48**, 101 (1960).
(2) (a) C. S. Marvel and E. J. Gall, *J. Org. Chem.*, **25**, 1784 (1960); (b) N. D. Field, *ibid.*, **25**, 1006 (1960).
(3) S. G. Matsoyan, G. M. Pogoyan, R. K. Skripnikova, and A. V. Mush-egyan, *Vysokomolekul. Soedin.*, **5**, 183 (1963).
(4) R. C. Lamb, D. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).
(5) (a) N. O. Brace, *J. Org. Chem.*, **28**, 3093 (1963); (b) *J. Am. Chem. Soc.*, **84**, 3020 (1962); (c) *ibid.*, in press.