had become constant (−0.905°) and did not change thereafter during the succeeding 19 hr. The first-order rate constant, calculated from the observed data, was ln 8.8 × 10^{-2} min.$^{-1}$. At the completion of the reaction the solution was washed with aqueous sodium bicarbonate, and dried over sodium sulfate. A sample of the solution was applied directly to a column (0.25 in. × 6 ft.) of 1% SE 30 on Gaschrom P (Silanized)[13] at 250° (flame-ionization detector). The two anomeric methyl 2,3,5-tri-*O*-benzyl-D-arabinofuranosides were well resolved and, from the area under the peaks, the mixture was estimated to consist of 92% of the β-anomer and 8% of the α-anomer.

Methanolysis of 2,3-Di-O-benzyl-5-O-p-nitrobenzoyl-α-D-arabinofuranosyl Chloride (VII). The halide VII (62.2 mg., 0.125 mmole) was dissolved in dichloromethane to a volume of 5.0 ml. and the solution was then diluted with methanol (0.50 ml.). The progress of the resulting solvolysis was followed polarimetrically at 20°. The first-order rate constant, calculated from the observed data, was ln 11 × 10^{-3} min.$^{-1}$. When mutarotation had ceased, 1 ml. of 1 *N* sodium methoxide was added and the solution left for 6 days. The solution was then filtered and concentrated to a sirup which was dissolved in 80% aqueous methanol (v./v.) and deionized with Amberlite MB-1. Filtration and concentration yielded a product contaminated with methyl *p*-nitrobenzoate. In order to remove this, the mixture was dissolved in dioxane and the resulting solution, diluted with 2 ml. of 1 *N* sodium hydroxide, heated on a steam bath for 2 hr. After concentration and evaporation, the mixture was dissolved in 80% aqueous methanol and the solution deionized with Amberlite MB-1. Filtration and concentration then gave a mixture of the anomeric methyl 2,3-di-*O*-benzyl-D-arabinofuranosides. The benzyl groups were removed by hydrogenolysis over freshly prepared and well-washed palladium black suspended in methanol. After filtration and concentration the sirupy mixture was dried *in vacuo* for 2 days. Conversion to the trimethylsilyl derivatives was carried out as described by Sweeley, *et al.*,[14] and vapor phase chromatography was performed on a column (0.25 in × 5 ft.) of 3% SE 52 on Gaschrom A.[13] The mixture was found to consist of 10% of the α-anomer and 90% of the β-anomer. Both authentic methyl α- and β-arabinopyranoside separate completely from authentic methyl β-D-arabinofuranoside when run as their tri-*O*-trimethylsilyl derivatives under these conditions.

Methanolysis of 2-O-Benzyl-3,5-di-O-p-nitrobenzoyl-α-D-arabinofuranosyl Chloride (XIV). 2-*O*-Benzyl-3,5-di-*O*-*p*-nitrobenzoyl-α-D-arabinofuranosyl chloride (70.8 mg., 0.127 mmole) was methanolyzed as described for VII above, the rotation becoming constant at a value of −2.365° after 99 hr., k = ln 8.3 × 10^{-4} min.$^{-1}$. Sodium methoxide in methanol (1 *N*, 2 ml.) was added to the solution and, after 24 hr., the solution was concentrated. Water was added, the methyl *p*-nitrobenzoate was removed by filtration, and the filtrate was deionized with Amberlite MB-1. Concentration of the solution gave a crystalline residue which was dried *in vacuo* and converted to its trimethylsilyl ether. Vapor phase chromatography, using a column (0.25 in. × 6 ft.) of 3% SE 52 on Gaschrom A[13] and programming the temperature from 50 to 230°, revealed two peaks which were identified through the use of authentic samples of the bis-*O*-trimethylsilyl ethers of the two anomeric methyl 2-*O*-benzyl-D-arabinofuranosides. The peak areas of the signals indicated that the mixture contained 2% of the α-anomer and 98% of the β-anomer.

Acknowledgment. We are indebted to Dr. J. D. Stevens for his interpretation of the n.m.r. spectrum of IXb and to the Section on Analytical Services and Instrumentation for spectra and elemental analyses.

(13) Applied Science Laboratories, Inc., State College, Pa.

(14) C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Am. Chem. Soc.*, **85**, 2497 (1963).

Communications to the Editor

A Paramagnetic Octahedral Rhodium(III) Complex

Sir:

Although paramagnetic octahedral complexes of rhodium(III) have been neither known nor anticipated,[1] we wish to report the synthesis and certain properties of a complex that apparently involves retention of the 3+ oxidation state and (distorted) octahedral symmetry.

During study of the deprotonation of diamagnetic tris(ethylenediamine)rhodium(III) iodide[2] by reaction with potassium amide in liquid ammonia at −33.5° by methods described earlier,[3] stepwise deprotonation of $[Rh(en)_3]I_3$ led to the isolation and characterization of *diamagnetic* $[Rh(en\text{-}H)(en)_2]I_2$, $[Rh(en\text{-}H)_2(en)]I$, and $[Rh(en\text{-}H)_3]$, where (en-H) denotes an ethylenediamine (en) ligand from which one proton has been removed. Efforts to effect further deprotonation at −33.5° resulted in incomplete reaction; however, completion of the next deprotonation step was achieved by the use of excess potassium amide at 25°, as follows.

A solution and suspension of 1.0489 g. of $[Rh(en)_3]I_3$

(1) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p. 840.

(2) G. W. Watt and J. K. Crum, forthcoming publication.

(3) G. W. Watt, L. E. Sharif, and E. P. Helvenston, *Inorg. Chem.*, **1**, 6 (1962).

in 20 ml. of liquid ammonia was treated in a Faraday tube with 20 ml. of potassium amide solution [formed from 0.3414 g. (*ca.* 5 molar equiv.) of potassium] at 25° for 8 days with frequent agitation.

In some experiments, conversion of potassium to potassium amide was catalyzed by iron wire. In order to minimize or eliminate the possibility of contamination of the product with ferromagnetic or paramagnetic impurities, other experiments employed bright platinum foil catalysts.

The initially yellow solid product changed progressively to very dark green crystals. These were washed up to six times with 30-ml. portions of liquid ammonia, dried under reduced pressure, and thereafter maintained in a dry helium atmosphere. (This salt is hygroscopic but appears to be stable indefinitely in dry helium or dry air.) The μ_{eff} value at 25° is 1.5 ± 0.1 B.M. (cor.).

Anal. Calcd. for $K[Rh(en\text{-}2H)(en\text{-}H)_2]$: Rh, 32.3; C, 22.6; H, 6.3. Found: Rh, 31.7; C, 22.8; H, 6.0.

Using Cu Kα radiation, exposure times up to 24 hr. were required to obtain X-ray powder diffraction patterns in which the lines were rather broad and diffuse. The *d*-spacings (Å.) and relative intensities (in parentheses) were as follows: 4.01 (0.1), 3.70 (0.1), 3.13 (0.2), 2.92 (0.4), 2.68 (1.0), 2.44 (0.1), 2.29 (0.2), 1.98 (0.6), 1.83 (0.1), and 1.63 (0.1).

The infrared spectrum (Nujol mulls) showed bands at 885, 1057, 1088, 1575, 1600, 1660, 3120, 3230, and 3510 cm.$^{-1}$; this spectrum was not different in any major respects from those of the parent complex and the three deprotonated precursor complexes. Thus the over-all close similarity of the spectra of these five species is indicative of retention of essentially octahedral symmetry; the significance of the small differences that are observed in relation to the deprotonation process will be discussed elsewhere.[2]

Treatment of $K[Rh(en\text{-}2H)(en\text{-}H)_2]$ in water with aqueous HI resulted in quantitative reconversion to $[Rh(en)_3]I_3$ which was identified by its X-ray diffraction pattern.[2]

As an oxidation state determination, 118.3 mg. of $K[Rh(en\text{-}2H)(en\text{-}H)_2]$ in 40 ml. of liquid ammonia at −33.5° was treated with 69.5 mg. of K in 15 ml. of ammonia. During the course of the reaction, a black solid was formed and 8.3 cc. of hydrogen (at STP) was collected. After correction for potassium consumed in (catalyzed) amide formation, the ratio K/K-$[Rh(en\text{-}2H)(en\text{-}H)_2]$ = 2.8, thus indicating Rh^{3+} in the complex. This conclusion is supported by the regeneration of $[Rh(en)_3]I_3$ under nonoxidizing conditions as described above.

The paramagnetic susceptibility value reported above is the average of eight measurements made by three different operators using samples of different size taken from six independently prepared products. After one measurement on a relatively large sample, it was washed exhaustively with liquid ammonia at −33.5°; the measurement was then repeated using a smaller sample without change in the value found. The Curie–Cheneveau torsion balance employed was calibrated between measurements against $HgCo(SCN)_4$.

The origin of the paramagnetism remains obscure. We believe that we have virtually eliminated the possibility of contamination by ferromagnetic or other impurities. In view of the environments to which the compound in question has been subjected, oxidation to Rh^{4+} (d^5) is untenable and the data given herein appear to preclude the possibility of reduction to Rh^{2+} (d^7). The infrared spectrum provides no evidence for the presence of Rh–H bonds.

Acknowledgment. This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

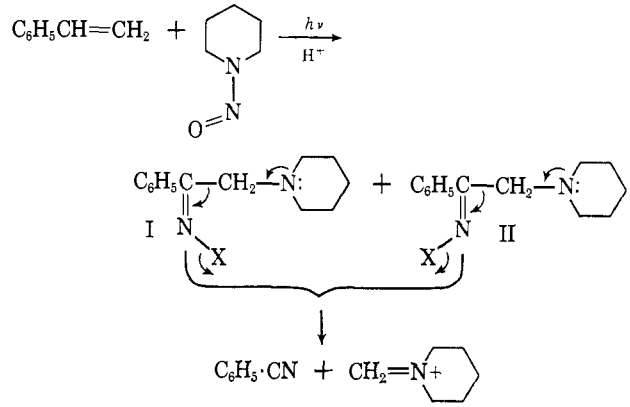
George W. Watt, John K. Crum, James T. Summers
Department of Chemistry, The University of Texas
Austin, Texas 78712
Received July 2, 1965

Carbon–Carbon Double Bond Cleavage by Photoaddition of N-Nitrosodialkylamine to Olefins

Sir:

We have reported[1] recently a photoaddition of N-nitrosodialkylamines to cyclohexene to give, *via* intermediaries of the nitroso derivatives,[2] 2-dialkylaminocyclohexanone oxime. Application of this interesting reaction to various unsymmetrically substituted olefins reveals that the dialkylamino group goes to the less-substituted carbon atom. Thus the addition of N-nitrosopiperidine to styrene[3] gave a quantitative yield of a mixture of two geometrical isomers Ia (m.p. 117–117.5°, lit.[4] m.p. 117–118°) and IIa (m.p. 136–138°, lit.[4] m.p. 136–138°). Tosylation of the mixture in triethylamine cleanly cleaved the compounds to benzonitrile (91%), following the well-established mechanism reported by Grob and co-workers.[5] The similar cleavage of 2-dimethylaminocyclohexanone oxime has been described.[5]

The combination of the photoaddition and the electromerically assisted Beckmann reaction[6] provides a new



Ia, IIa; X = OH; Ib, IIb; X = OTs

pathway for cleavage of mono- and symmetrically disubstituted olefins.

(1) Y. L. Chow, *Can. J. Chem.*, in press.
(2) The dimer of 1-piperidino-2-nitrosopentane can be isolated in a pure state from photoaddition of N-nitrosopiperidine to 1-pentene.
(3) The experimental condition follows the same as described in ref. 1 unless stated otherwise.
(4) H. P. Fischer and C. A. Grob, *Helv. Chim. Acta*, **45**, 2528 (1962).
(5) H. P. Fischer, C. A. Grob, and E. Renk, *Helv. Chim. Acta*, **45**, 2539 (1962); H. P. Fischer and C. A. Grob, *ibid.*, **46**, 936 (1963); C. A. Grob, H. P. Fischer, H. Link, and E. Renk, *ibid.*, **46**, 1190 (1963).
(6) Other types of electromerically assisted Beckmann reactions are reviewed in ref. 5 and also described in a recent communication [R. L. Autrey and P. W. Scullard, *J. Am. Chem. Soc.*, **87**, 3284 (1965)].