

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  $\mu_{\text{eff}}$  value at 25° is  $1.5 \pm 0.1$  B.M. (cor.).

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

Using Cu  $K\alpha$  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  $\text{cm}^{-1}$ ; 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.<sup>2</sup>

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

As an oxidation state determination, 118.3 mg. of  $\text{K}[\text{Rh}(\text{en-2H})(\text{en-H})_2]$  in 40 ml. of liquid ammonia at  $-33.5^\circ$  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  $\text{K}/\text{K}-[\text{Rh}(\text{en-2H})(\text{en-H})_2] = 2.8$ , thus indicating  $\text{Rh}^{3+}$  in the complex. This conclusion is supported by the regeneration of  $[\text{Rh}(\text{en})_3]\text{I}_3$  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  $-33.5^\circ$ ; 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  $\text{HgCo}(\text{SCN})_4$ .

The origin of the paramagnetism remains obscure. We believe that we have virtually eliminated the possibility of contamination by ferromagnetic or other im-

purities. In view of the environments to which the compound in question has been subjected, oxidation to  $\text{Rh}^{4+}$  ( $d^5$ ) is untenable and the data given herein appear to preclude the possibility of reduction to  $\text{Rh}^{2+}$  ( $d^7$ ). The infrared spectrum provides no evidence for the presence of Rh-H bonds.

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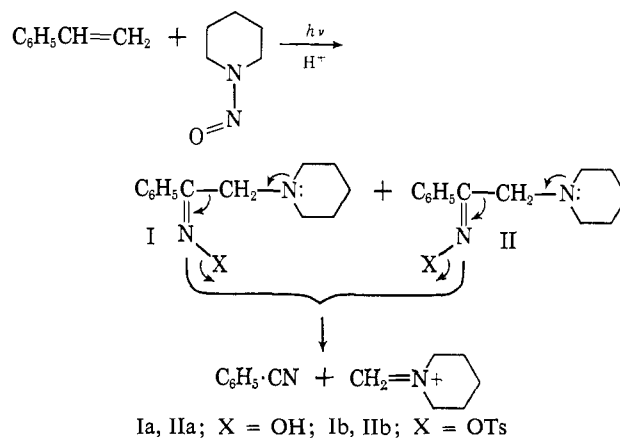
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## Carbon-Carbon Double Bond Cleavage by Photoaddition of N-Nitrosodialkylamine to Olefins

Sir:

We have reported<sup>1</sup> recently a photoaddition of N-nitrosodialkylamines to cyclohexene to give, *via* intermediaries of the nitroso derivatives,<sup>2</sup> 2-dialkylamino-cyclohexanone 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<sup>3</sup> gave a quantitative yield of a mixture of two geometrical isomers Ia (m.p. 117–117.5°, lit.<sup>4</sup> m.p. 117–118°) and IIa (m.p. 136–138°, lit.<sup>4</sup> 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.<sup>5</sup> The similar cleavage of 2-dimethylaminocyclohexanone oxime has been described.<sup>5</sup>

The combination of the photoaddition and the electrochemically assisted Beckmann reaction<sup>6</sup> provides a new



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.

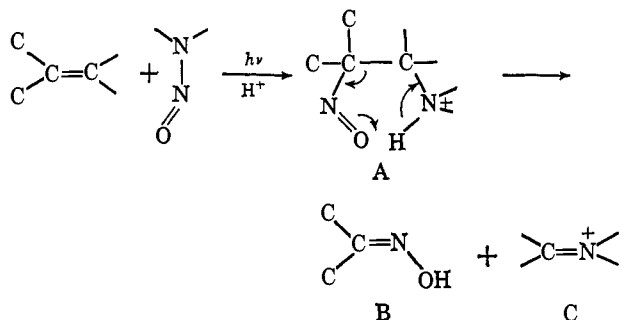
(3) The experimental condition follows the same as described in ref. 1 unless stated otherwise.

(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 electrochemically 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)].

The observed pattern of orientation predicts that the photoaddition of a nitrosamine to an unsymmetrically disubstituted or more complex olefin should give an adduct (A) in which the nitroso group can no longer tautomerize to an oxime. An intramolecular proton transfer followed by redistribution of bonding electrons



(see A) would offer an alternative pathway resulting in cleavage of the original olefin bond to give B and C. Such an expectation has now been unambiguously borne out by our experiments, providing a new, yet remarkably simple, technique of cleaving a carbon-carbon double bond.

Using N-nitrosopiperidine as the reagent,  $\alpha$ -methylstyrene was cleaved to acetophenone oxime (91%) and dipiperidinomethane (82%) while tetramethylethylene gave acetone and its oxime. The latter photolysate was hydrolyzed to acetone and identified as the 2,4-dinitrophenylhydrazone (87%). For 1-methylcyclohexene, where the cleavage product possess both B and C moieties in interacting proximity, N-nitrosodimethylamine in 30% aqueous tetrahydrofuran was found to afford, after a mild hydrolysis, 6-ketoheptanal (59%), b.p. 102–105° (13 mm.); 2,4-DNP m.p. 181–182°. *Anal.* Found: C, 46.95; H, 4.25; N, 22.71.

A mixture of *dl*-camphene (10 g.), N-nitrosopiperidine (5.15 g.), concentrated hydrochloric acid (6 ml.), and methanol (300 ml.) was placed in a water-jacketed Pyrex photocell and cooled externally in an ice bath. While a slow stream of nitrogen was bubbled through, the solution was irradiated with a 250-w. Hanovia mercury lamp until the nitrosamine absorption at 348  $m\mu$  disappeared. Methanol and excess camphene were evaporated under vacuum and the residue was extracted with ether. The usual workup of the ether solution gave a crystalline residue which was recrystallized to give *dl*-camphenilone oxime, m.p. 102–103° (14.6 g.), lit.<sup>7</sup> m.p. 105–107°. The aqueous layer was basified and extracted with ether to give dipiperidinomethane, b.p. 48° (0.2 mm.) (67%), lit.<sup>8</sup> b.p. 115° (15 mm.).

The present cleavage reaction is similar to ozonolysis in the net results except that the two cleavage products derived from an olefin possess different functional groups. An olefin carrying functional groups, particularly those photolabile ones, may conceivably alter the reaction pattern at some stage. The scope and the limitation of this photocleavage reaction will be further investigated. In comparison to the similar photocleavage reported by Büchi and Ayre<sup>9</sup> the present method provides good yields and a simpler reaction.

(7) G. Kommpa, *Ann.*, **366**, 71 (1909).

(8) E. Knoevenagel, *Ber.*, **31**, 2585 (1898).

(9) G. Büchi and D. A. Ayre, *J. Am. Chem. Soc.*, **78**, 690 (1956).

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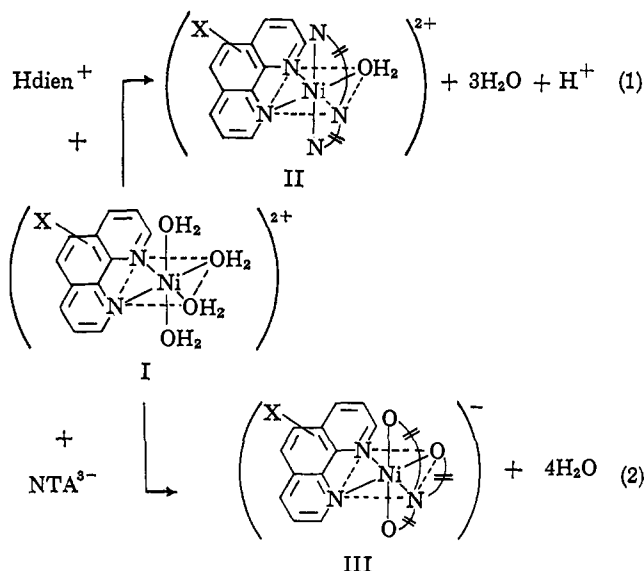
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### Remote Ligand Substituents in Nickel(II) Complexes Affecting the Rate of Loss of Coordinated Water

Sir:

Substituents on position 5 of the ligand in mono(1,10-phenanthroline)nickel(II) complexes influence the rate of replacement of water molecules coordinated to the nickel. Reactions were studied with diethylenetriamine (dien) and with nitrilotriacetate (NTA) leading to the formation of mixed complexes without displacement of the 1,10-phenanthroline or 5-substituted 1,10-phenanthroline (eq. 1 and 2).



Crystalline salts of the phenanthroline complexes were prepared, and in each kinetic experiment fresh solutions of these salts were used to avoid the presence of bis- and tris(1,10-phenanthroline)nickel(II) complexes. The mixed complexes II and III were characterized in solution by spectrophotometric and pH measurements which showed that in the initial reactions the phenanthroline was not displaced from nickel and that dien and NTA were coordinated to nickel. A recording spectrophotometer was used for the reaction in eq. 1 and a stopped-flow apparatus was used for the reaction in eq. 2. The reactions were first order in the  $Ni(phen)^{2+}$  complex and first order in dien and NTA, respectively. The acid dependence of reaction 1 was resolved and showed  $Hdien^+$  to be the primary reactant at pH 6–7.

The substituents are quite remote from the reaction site and their kinetic effect (Table I) cannot be due to steric factors but must be due to changes in metal-ligand electron density. Excellent Hammett free energy relationships were obtained for both reactions (Figure 1). The  $\sigma$  values were calculated from the acid dissociation