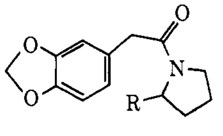
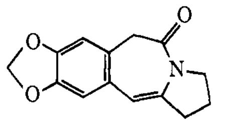
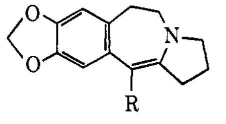


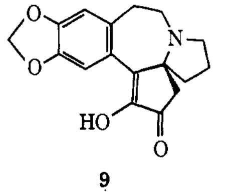
2, R = CH_2OH
3, R = CHO



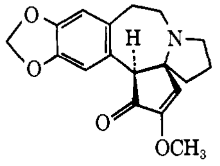
4



5, R = H
6, R = $COCH(OAc)CH_3$
7, R = $COCHOHCH_3$
8, R = $COCOCH_3$



9



10

suspended sodium bicarbonate gave the crystalline vinylogous amide **6**, mp 132–133° (75%) [nmr peaks ($CDCl_3$) at δ 1.12 (3 H, d, J = 7 Hz), 2.09 (3 H, s), 5.60 (1 H, q, J = 7 Hz); ir max ($CHCl_3$) 1740 and 1650 cm^{-1}]. Hydrolysis of **6** with potassium carbonate in aqueous methanol afforded alcohol **7**, mp 139–141°, in 95% yield [nmr peaks ($CDCl_3$) at δ 0.85 (3 H, d, J = 7 Hz), 4.75 (1 H, q, J = 7 Hz); ir max ($CHCl_3$) 3300 cm^{-1}]. Alcohol **7** was converted to the oily yellow α-dicarbonyl compound **8** (80%) upon brief refluxing with lead dioxide in toluene [nmr peak ($CDCl_3$) at δ 2.22 (3 H, s)].[9,9a]

Without purification **8** was treated with magnesium methoxide in methanol[10] resulting in formation of crystalline pentacyclic desmethylcephalotaxinone (**9**),[11,12] mp 104–107°, upon recrystallization from methanol (52%) [found for **9**: nmr ($CDCl_3$) δ 1.8 (4 H, m), 2.60 (2 H, s), 2.9–3.6 (6 H, m), 5.10 (1 H, br s, OH), 6.00 (2 H, s), 6.75 (1 H, s), 7.00 (1 H, s); uv max (C_2H_5OH-HCl) 324 nm (ϵ 8700), 262 (8500), 232 (7800); uv max (C_2H_5OH-KOH) 341 nm (ϵ 13,100); ir max ($CHCl_3$) 3475, 3300, 1700, and 1645 cm^{-1}; m/e 299.1158].

Desmethylcephalotaxinone (**9**), upon refluxing in methanol–dioxane solution with excess 2,2-dimethoxypropane in the presence of 3 equiv of p-toluenesulfonic acid, was converted to naturally occurring cephalotaxinone (**10**) (40%), mp 180–183°.[4b,13,14] Reduction of **10** with sodium borohydride in methanol at room temperature was stereospecific and gave racemic cephalotaxine (**1**) (80%).[13]

Acknowledgment. This investigation was supported by the Research Corporation and the National Cancer Institute, National Institutes of Health (Grant No. CA12568).

---

(9) H. H. Inhoffen, K. Radscheit, U. Stache, and V. Koppe, *Justus Liebigs Ann. Chem.*, **684**, 24 (1965).

(9a) NOTE ADDED IN PROOF. Enamine **5** can be converted to α-dicarbonyl compound **8** in a single step in 80% yield by treatment with the mixed anhydride prepared from pyruvic acid and ethyl chloroformate using a modification of the procedure of R. A. Raphael, *et al. J. Chem. Soc., Perkin Trans. 1*, 860 (972). We are grateful to Professor Raphael for bringing this procedure to our attention and to Mr. R. Cvetovich for carrying out this experiment.

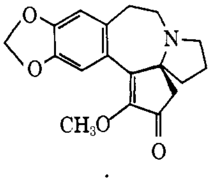
(10) H. Muxfeldt, M. Weigele, and V. Van Rheenen, *J. Org. Chem.*, **30**, 3573 (1965).

(11) Mr. R. G. Powell and Mr. K. L. Mikolajczak, USDA, Peoria, Ill., have informed us that they recently isolated desmethylcephalotaxinone (**9**) from *Cephalotaxus harringtonia*. Comparison of our synthetic material with their natural material indicated that the two are identical. As part of their structure proof, these workers have converted desmethylcephalotaxinone to cephalotaxine. Their borohydride reduction of the intermediate cephalotaxinone was stereospecific. We are indebted to Mr. Powell and Mr. Mikolajczak for their cooperation and for making information available to us in advance of publication.

(12) By this sequence of reactions it is possible to prepare gram quantities of **9**.

(13) This compound was identical in ir, nmr, mass spectrum, and tlc with authentic material of natural origin kindly supplied by Mr. R. G. Powell.

(14) This step also produced some other, as yet unidentified, products but surprisingly did not give any of the isomeric vinyl ether i. Des-



i

methylcephalotaxinone (**9**), upon treatment with diazomethane, forms i in high yield.

(15) Postdoctoral Research Associate, 1971–present.

Joseph Auerbach,[15] Steven M. Weinreb*
Department of Chemistry, Fordham University
Bronx, New York 10458

Received June 7, 1972

Coordinated Nitrene Formation by the Photolysis of Azido Pentaammine Complexes of Rhodium(III) and Iridium(III)

Sir:

Investigations of the photolysis of several different azido–metal complexes suggest the formation of azido radical which then reacts with itself to generate nitrogen.[1] However, this is not the photochemical behavior of the azido group for hydrozoic acid and for organic azides. The photolysis of hydrozoic acid yields the active intermediate nitrene (NH),[2] and organic azides react photochemically to produce substituted nitrenes (NR).[3] We wish to report that the photochemical reactions of $[M(NH_3)_5N_3]^{2+}$, where M = Ir(III) and Rh(III), result in the decomposition of the azido group *via* a coordinated nitrene (M–NH) intermediate.

Photolysis experiments with aqueous solutions of $[Ir(NH_3)_5N_3](ClO_4)_2$ were performed using a Hanovia 8A36 medium-pressure mercury arc lamp and a 270-nm cutoff filter solution (5% benzene in methanol solution). $[Ir(NH_3)_5N_3](ClO_4)_2$ (1 g) was dissolved in 250 ml of 0.1 M HCl, and the solution was irradiated. Irradiation was stopped when the uv spectrum of the solution showed that the absorption band at 258 nm

---

(1) (a) S. A. Penkett and A. S. Adamson, *J. Amer. Chem. Soc.*, **87**, 2514 (1965); (b) J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, **74**, 1021 (1970); (c) C. Bartocci and F. Scandola, *Chem. Commun.*, 531 (1970); (d) W. Beck and K. Scharpp, *Angew. Chem., Int. Ed. Engl.*, **9**, 735 (1970); (e) A. Vogler, *J. Amer. Chem. Soc.*, **93**, 5912 (1971); (f) R. F. Ziolo, J. A. Thich, and Z. Dori, *Inorg. Chem.*, **11**, 626 (1972).

(2) K. H. Welge, *J. Chem. Phys.*, **45**, 4373 (1966); I. Burak and A. Tremin, *J. Amer. Chem. Soc.*, **87**, 4031 (1965).

(3) E. Wasserman, G. Smolinsky, and W. A. Yager, *ibid.*, **86**, 3166 (1964); E. Koch, *Tetrahedron*, **23**, 1747 (1967).

(characteristic of the $[Ir(NH_3)_5NH_2Cl]^{3+}$ ion[4]) reached a maximum optical density corresponding to an 80% yield of the chloramine complex and the band at 279 nm (characteristic of the starting material, $[Ir(NH_3)_5N_3]^{2+}$) disappeared. At this point, the solution was passed through a cation-exchange column (AG50W-X2) which was eluted with about 40 ml of 4 *M* HCl. The eluent was concentrated to dryness by vacuum. The solid residue was then dissolved in a minimum amount of water and concentrated $HClO_4$ was added to precipitate $[Ir(NH_3)_5NH_2Cl](ClO)_3$ in 45% yield. *Anal.* Calcd for $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$: N, 13.40; H, 2.73; NH_2Cl, 8.21; ClO_4^-, 47.57. Found: N, 12.93; H, 2.56; NH_2Cl, 7.75; ClO_4^-, 47.48. The percentage of NH_2Cl was determined by the reaction of the complex with I^- and a determination of the I_2 produced.[4]

The amount of gas liberated by the photochemical reaction was determined using a solution containing 20 mg of $[Ir(NH_3)_5N_3](ClO_4)_2$ dissolved in 2 ml of 0.1 *M* HCl. The solution was degassed by several freeze–thaw cycles, and after irradiation the noncondensable (at liquid nitrogen temperature) gas was collected making use of a Toepler pump. The gas was N_2 with trace amounts of H_2 and O_2, as shown by mass spectrometry. Three experiments gave values of 1.12, 1.15, and 1.10 mol of gas per mole of $[Ir(NH_3)_5N_3](ClO_4)_2$. The 10% excess of gas may result from the photochemical reaction of the product $[Ir(NH_3)_5NH_2Cl]^{3+}$, because under identical conditions irradiation of a solution of $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ yielded 0.14 mol of gas per mole of compound. Again the gas was N_2 with traces of H_2 and O_2.

The photolysis of $[Ir(NH_3)_5N_3](ClO_4)_2$ was also repeated in the presence of added iodide ion (2.9×10^{-3} *M* starting material and 1.7×10^{-3} *M* NaI) and of 1 *M* acrylamide. This was done because it had been reported that the presence of iodide ion[1a–c] or acrylamide[1c] quenched the formation of nitrogen for the photochemical reactions of azido metal complexes which proceed through an azide radical. However, the photochemical reaction of $[Ir(NH_3)_5N_3]^{2+}$ liberates exactly 1 mol of N_2 per mole of complex, even in the presence of added iodide ion or acrylamide. In the presence of iodide ion, $[Ir(NH_3)_6]^{3+}$ and I_2 are formed.

The results observed for the photolysis of $[Ir(NH_3)_5N_3]^{2+}$ are consistent with the reaction scheme

$$\begin{tikzcd}
{[(NH_3)_5IrN_3]^{2+}} \arrow[r, "h\nu", "-N_2"'] & {[(NH_3)_5Ir\text{–}\ddot{N}:]^{2+}} \arrow[d, "H^+"] & \\
 & {[(NH_3)_5Ir\text{–}\ddot{N}H]^{3+}} \arrow[r, "HCl"] & {[(NH_3)_5IrNH_2Cl]^{3+}}
\end{tikzcd}$$

Evidence for the same coordinated nitrene, Ir–NH, intermediate and its reaction with HCl to yield the chloramine product was reported[4] for the thermal reaction of this complex with acid at high concentrations of hydrochloric acid. Clearly, the photochemical decomposition of the azido group in this complex cannot involve the formation of azide radical because the presence of iodide ion or acrylamide does not quench the evolution of nitrogen.

The reaction of $[Rh(NH_3)_5N_3]^{2+}$ with acid does not generate nitrogen,[5] but its photochemical reaction (irradiation at 2537 Å) does evolve nitrogen and also produces the chloramine product $[Rh(NH_3)_5NH_2Cl]^{3+}$. Furthermore, the evolution of nitrogen is not quenched by the addition of iodide ion. These observations suggest that the decomposition of the azide group occurs in the same manner as that outlined above for the corresponding iridium(II) complex.

Irradiated solutions of $[Rh(NH_3)_5N_3]^{2+}$ were monitored at various times for decomposition of the azido complex and formation of $[Rh(NH_3)_5NH_2Cl]^{3+}$. This was done both by measuring the spectra of the resulting solutions and by adding an excess of iodide ion to the solutions and determining the amount of iodine liberated. The results show that the primary photochemical decomposition of the azido complex generates the chloramine in 86% yield; *e.g.*, $\Phi_{NH_2Cl}/\Phi_{dec} = 0.86 \pm 0.02$. However, the rhodium product obtained from the cation-exchange column, as described above for iridium, is a mixture of about 60% $[Rh(NH_3)_5NH_2Cl](ClO_4)_3$ and 40% $[Rh(NH_3)_6]/(ClO_4)_3$. The source of the hexaamminerhodium(III) complex is not known, and it may arise from thermal reactions on the column. The nitrogen content of the isolated material is always high, indicating that photoaquation[6] was not extensive.

Acknowledgment. We thank Dr. Bruce Lane and Mr. Richard Terrell for having done some of the initial experiments on these systems. The research is supported by a grant from the National Science Foundation. The rhodium and iridium were loaned to us by the Matthey Bishop Co.

---

(4) B. C. Lane, J. W. McDonald, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **94**, 3786 (1972).

(5) C. S. Davis and G. C. Lalor, *J. Chem. Soc. A*, 445 (1970).

(6) T. L. Kelly and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 1797 (1972).

James L. Reed, Francis Wang, Fred Basolo*
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received May 11, 1972

Carbene Radical Anions. A New Species of Reactive Intermediate

Sir:

Our interest in the mechanism of reaction of sodium naphthalene with alkyl,[1] vinyl,[2] and aryl[3] halides inevitably led to a consideration of the possible consequences of reaction of this radical anion with polyhaloorganic substrates.[4] Sodium naphthalene (**1**) reacts with alkyl halides *via* dissociative electron transfer to generate an alkyl free radical.[1,5] The free radicals thus produced undergo facile reduction to alkyl anions (or sodium alkyls).[5] One can thus envision two possible mechanistic pathways for the reaction of sodium naphthalene with alkyl geminal dihalides. Initial electron transfer would be expected to generate an α-haloalkyl free radical which could suffer further reduc-

---

(1) G. D. Sargent and G. A. Lux, *J. Amer. Chem. Soc.*, **90**, 7160 (1968); G. D. Sargent, J. N. Cron, and S. Bank, *ibid.*, **88**, 5363 (1966).

(2) G. D. Sargent and M. W. Browne, *ibid.*, **89**, 2788 (1967).

(3) G. D. Sargent, *Tetrahedron Lett.*, 3279 (1971).

(4) For a preliminary report of a reaction which follows a different course from those described here, see G. D. Sargent, *J. Amer. Chem. Soc.*, **93**, 5268 (1971).

(5) A review: J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971); see also J. F. Garst and F. E. Barton II, *Tetrahedron Lett.*, 587 (1969); J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, **88**, 4260 (1966).