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Ruthenium Nitrosyl Complexes from Solutions of Ruthenium(III) Ammines in Dilute Perchloric Acid

Sir:

Unknown brown-black solutions have been reported when dilute perchloric acid reacts with the chloropentaammineruthenium(III) cation.[1] We now find that nitrosyl complexes of ruthenium may be isolated from such solutions, the NO group being readily identified by its characteristic infrared absorption spectrum.

At steam-bath temperatures, reaction between the metal complex (concentration $\sim 10^{-3}$ *M*) and 0.1 *M* perchloric acid is evident by the marked color development after approximately 10 min. After a further 2 hr deep purple solutions are obtained, and by slow (48 hr) fractional crystallization on the steam bath both purple-black and yellow solids may be isolated. The infrared spectrum of the yellow product in potassium bromide has the following bands (cm^{-1}) for which assignments are given in parentheses: 3500 br s (H_2O), 3220 s, 3120 s (N–H), 1850 s (N–O), 1620 br w (N–H, H_2O), 1300 m (N–H), 1140 s, 1120 s, 1080 s, 940 w (ClO_4^-), 840 br m (N–H) (br = broad; s = strong; m = medium; w = weak). This spectrum agrees with that reported for the $[RuOH(NH_3)_4NO]^{2+}$ cation with the inclusion of the ClO_4^- modes.[2,3] The less-soluble purple-black fractions showed a strong absorption at 1925 cm^{-1} in addition to the above list. This is attributed to the presence of some $[RuH_2O(NH_3)_4NO](ClO_4)_3$ for which frequencies are expected in the 1910–1920-cm^{-1} region, the exact location depending upon the counterion.[4] The intense dark colors of the solutions and certain of the solids isolated are no doubt due to chloronitrosyl complexes. Thus, from the more soluble fractions, solids having strong additional absorption at 1880 cm^{-1} are obtained. Also, decomposition of the purple solids with sodium hydroxide followed by acidification and treatment with silver nitrate shows the presence of chloride ion.

When a chloride-free preparation of $[RuH_2O(NH_3)_5](ClO_4)_3$ is used in these experiments, chloride ion may be detected among the reaction products. Hexaammineruthenium(III) chloride also reacts with 0.1 *M* perchloric acid when heated in solution on the steam bath to yield nitrosyl complexes. For similar concentrations of reagents, the reaction is distinctly slower than for the pentaammine complexes, suggesting that coordination of ClO_4^- may be the initial step in this unusual reaction.

Acknowledgment. Financial support for this research by Hercules, Inc., is gratefully acknowledged.

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(1) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).

(2) E. E. Mercer, W. A. McAllister, and J. R. Durig, *ibid.*, **5**, 1884 (1966).

(3) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

(4) M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, **22**, 359 (1966).

(5) On sabbatical leave from the Australian National University, Canberra, Australia.

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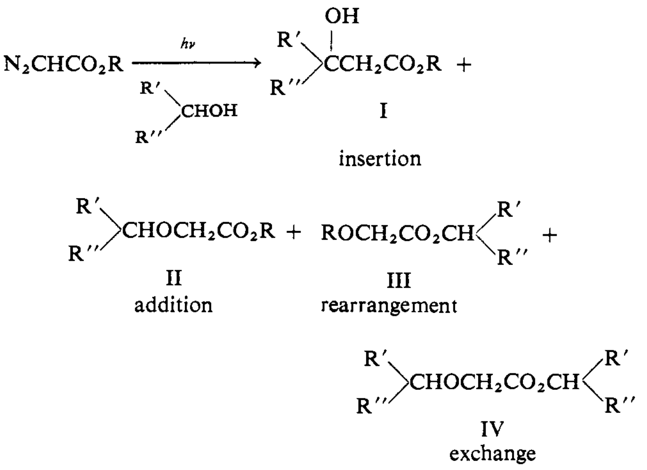
Photochemistry of Diazo Esters. II. A Novel Reaction Path

Sir:

Photolysis of diazo compounds is generally assumed to proceed by a carbene mechanism.[1-3] Our current study on a series of diazoacetates in alcohols, however, indicates a novel reaction path not involving carbene intermediates.



Products I, II, and III have been rationalized in terms of carbalkoxymethylene reactions.[2-4] The formation of IV, with a net exchange of the alcohol moiety, is the main concern of the present communication. The reaction is quite general since exchange products were found in each system studied (Table I), and the exchanged alcohol could also be detected. The efficiency of exchange varies with respect to substituents in the order PhO $\simeq$ MeO > EtO > *i*-PrO $\simeq$ AllylO $\simeq$ *t*-BuO, and with respect to the solvent, Me < Et < *i*-Pr < *t*-Bu alcohol. Evidently steric effects are not important, and all esters exchange freely in *t*-butyl alcohol; moreover, the *t*-butyl ester solvolyzes as readily as its isopropyl and allyl analogs.

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(1) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964.

(2) O. P. Strausz, T. DoMinh, and H. E. Gunning, *J. Am. Chem. Soc.*, **90**, 1660 (1968).

(3) F. Weygand, W. Schwenke, and H. J. Bestmann, *Angew. Chem.*, **73**, 409 (1961).

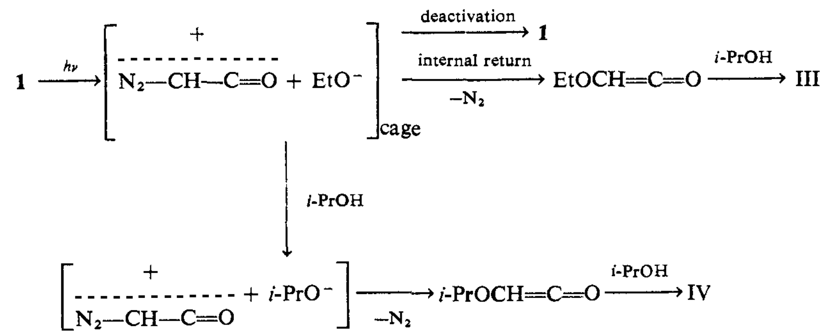
(4) (a) J. Shafer, P. Baranowsky, R. Laursen, F. Finn, and F. H. Westheimer, *J. Biol. Chem.*, **241**, 421 (1966); (b) F. H. Westheimer, private communication.

Table I. Photolysis[a] and Thermolysis[b] of Diazo Esters in Alcohols

	Relative product yields,[c] %															
	Insertion, I				Addition, II				Rearrangement, III				Exchange, IV			
Ester	MeOH	EtOH	*i*-PrOH	*t*-BuOH	MeOH	EtOH	*i*-PrOH	*t*-BuOH	MeOH	EtOH	*i*-PrOH	*t*-BuOH	MeOH	EtOH	*i*-PrOH	*t*-BuOH
Methyl	10	34	8	35		25	37	28		23	35	15	(90)[d]	18	20	22
Ethyl	9	15[e]	12	17	54	40[e]	33	33	32	32[e]	39	29	5	13[e]	16	21
Ethyl[b]			4				75				2				19	
i-Isopropyl	7	15	12	7	55	41		37	36	37		40	2	7	(88)[d]	16
Allyl	2	9	10		57	45	38		38	39	39		3	7	13	
t-Butyl	7	26	17	5	58	25	24		33	43	46		2	6	13	(95)[d]
Phenyl	6	6	5	3	44	36	35	32	34	40	40	42	16	18	20	23

[a] Alcohol solution (5%) in Pyrex vessel irradiated for 1 hr with a Hanovia 450-W medium-pressure mercury lamp. [b] Heated at 180° for 6–10 hr in sealed glass tubes. [c] Total product yields are ~65–80%. [d] Products due to exchange, addition, and rearrangement are indistinguishable. [e] Photolysis in both EtOH and EtOH-d_2. All products, with the exception of the phenyl and *t*-butyl esters and the phenoxyacetates, are stable. Phenyl esters undergo the photo-Fries reaction (J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963); R. A. Finnegan and J. J. Mattice, *Tetrahedron*, **21**, 1015 (1965)), phenoxyacetates undergo an analogous rearrangement (F. H. Westheimer, private communication), and the *t*-butyl esters undergo a photodecomposition which has not been fully characterized.

Scheme I



In the elucidation of the mechanism the following additional considerations have to be taken into account. (a) The exchange step is a photoinduced process; control experiments under comparable conditions, but without irradiation, did not afford more than mere traces of products. (b) The exchange does not involve carbenes; neither does it occur in the starting materials. Both possibilities should lead to the appearance of the exchanged insertion products, which in spite of careful search could not be detected. Furthermore, detailed exposure time studies indicated that the appearance of the exchange products did not exhibit an induction period. (c) Gas-phase photolysis of ethyl diazoacetate (**1**) (5 Torr) in the presence of isopropyl alcohol (50 Torr) yielded only III and products derived from ethoxyketene.[2] (d) The quantum yield of disappearance of **1** in ethanol is wavelength dependent and has been reported to have values[5] of 1.1 at 2804 Å, 0.34 at 3130 Å, and 0.15 at 3650 Å. The effect is less pronounced in heptane with values of 1.0, 0.54, and 0.31, respectively.[5] We have also noticed a slight wavelength dependence for the exchange reactions, the yields being somewhat higher at longer wavelengths. (e) Thermolysis of **1** gave II and IV, with I and III strongly suppressed.

On these grounds we consider it unlikely that either carbenes or solvolyzed parent compounds[6] would be implicated in the exchange mechanism. Instead we suggest Scheme I in which ion pairs are produced by a light-induced heterolysis.

Cage recombination of the geminate ions may be partly responsible for the lower than unit efficiency of decomposition, while "internal returns" on C_2 with loss of nitrogen may contribute to the formation of III. The resonance-stabilized ketenediazonium ions may live long enough to allow the fraction of the ethoxide ions which escape the solvent cage to undergo anion exchange and eventually form IV. Stable aliphatic diazonium ions of similar structures[7] have been synthesized, and analogous ion pairs[8] have been considered in the decomposition of diazoalkenyl esters of the type $>C{=}CHCN_2C(OAc)<$ derived from the photolysis of pyrazolenines. There is in fact a close similarity between the two systems, and our results are fully consistent with Day and Whiting's view[8] that diazo compounds with a leaving group may be expected to undergo heterolysis. Our results also indicate that the rearrangement may involve carbalkoxymethylenes at least in the gas phase,[2] while in solution it may be attributed to both carbenes and ion pairs. The intervention of a presumably unstable, isomeric diazo ether[9] as an ion precursor, although a distinct possibility, cannot yet be ascertained.

Finally, with an appropriate choice of solvent the

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(5) E. Wolf, *Z. Physik. Chem.*, **B17**, 46 (1932).

(6) In this connection, a phototransesterification of phenyl *p*-nitrobenzoate has recently been reported: R. A. Finnegan and D. Knutson, *J. Am. Chem. Soc.*, **90**, 1670 (1968). By contrast the reaction is remarkably sensitive to steric effects.

(7) K. Bott, *Angew. Chem. Intern. Ed. Engl.*, **3**, 804 (1964).

(8) A. C. Day and M. C. Whiting, *J. Chem. Soc.*, *B*, 991 (1967), and references cited therein.

(9) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y., 1961, pp 149–150, 224.

reaction may be utilized in introducing an ether functionality under mild and neutral conditions. As an example, the simple esters (Me, Et, *i*-Pr, and *t*-Bu) were photolyzed in the corresponding alcohols to give ether esters of general structure $ROCH_2CO_2R$ in 65–80% yields. Further studies are in progress.

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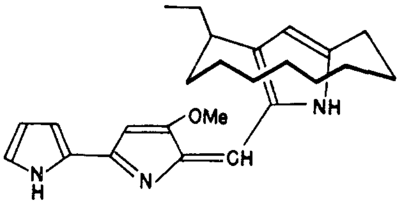
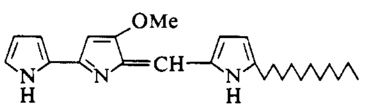
Metacycloprodigiosin, a Tripyrrole Pigment from *Streptomyces longisporus ruber*

Sir:

We have recently reported the structure and synthesis of undecylprodigiosin (II), a C-25 prodigiosin analog isolated from a strain of *Streptomyces*.[1] At that time it was noted that another more complex C-25 prodigiosin-like pigment was formed concurrently with II. In this communication we describe the isolation and structure determination of this product. Formulated as I,[2] this new tripyrrole pigment incorporates the unusual structural feature of a *meta*-bridged pyrrole, the first such system to be observed in a natural product. We propose the trivial name metacycloprodigiosin for this new pigment (I),[3] the synthesis of which is described in the accompanying report.[4]



I



II

Streptomyces longisporus ruber, strain M-3,[5] was grown on a soymeal–mannitol medium in shake culture for 1–3 weeks. Methylene chloride extraction of the lyophilized cells followed by acid and base washing and removal of the solvent *in vacuo* yielded a dark amorphous solid. Chromatography of the solid on basic alumina yielded two fractions, the first containing the new C-25 base (I), and the second containing a mixture of I and undecylprodigiosin (II). The new pigment was obtained as orange-brown crystals from petroleum ether, mp 208–209°, $[\alpha]^{20}{}_D$ −2370°; hydrochloride, mp 214–216°. *Anal.* Calcd for $C_{25}H_{33}N_3O \cdot HCl$: C, 70.12; H, 8.02; N, 9.81; Cl, 8.28. Found: C, 69.89; H, 8.10; N, 9.53; Cl, 8.08. The high-resolution mass spectrum of the hydrochloride has a molecular ion peak at *m/e* 391.2625 corresponding to the free base, $C_{25}H_{33}N_3O$ (*m/e* 391.2610).

The spectroscopic properties of the pigment and its hydrochloride clearly show it to be a member of the prodigiosin series.[6,7] In particular, the absorption spectrum of the free base exhibits a peak at $\lambda_{max}^{MeOH\ (0.5\%\ KOH)}$ 467 mμ (ε 30,600), while the hydrochloride has a peak at λ_{max}^{MeOH} 530 mμ (ε 75,900) as well as a shoulder at 500 mμ (ε 31,500). In the infrared, the free base of the new pigment shows bands at 1620, 1602, 1548, 1063, and 968 cm^{-1}. Likewise, the hydrochloride has characteristic bands at 1629, 1601, 1570, 1542, 1528, and 961 cm^{-1}.

The nmr spectrum of metacycloprodigiosin exhibits peaks due to N–H, and aromatic and methoxyl protons nearly identical with the corresponding absorptions shown by other prodigiosins,[6,7] and, in addition, the free base has a broad multiplet at τ 7.13–8.06 (3 H) and a multiplet at τ 8.13–9.42 (19 H). More specifically, the peak (1 H) at τ 4.08 is in accord with the presence of a β proton in the dialkylpyrrole residue.[6,7]

Pyrolysis of the pigment over soda lime gave a C-15 pyrrole containing four elements of unsaturation. *Anal.* Calcd for $C_{15}H_{25}N$: C, 82.13; H, 11.49; N, 6.38; mol wt, 219.1980. Found: C, 81.82; H, 11.80; N, 6.58; mol wt (high-resolution mass spectrum), 219.1985. The nmr spectrum clearly shows that the pyrrole is disubstituted, with one free α and one free β position: τ 2.69 (1 H), 3.71 (1 H multiplet, α-ring H), 4.18 (1 H multiplet, β-ring H), 7.5 (2 H triplet, $J = 6$ Hz), 7.8 (1 H multiplet), 8.3–9.2 (19 H, unresolved methyl–methylene region). Vapor phase reduction of the pyrrole (platinum-on-glass column)[8] yielded a hydrocarbon, $C_{15}H_{30}$, which was identified by mass spectrometry, nmr, and independent synthesis[9,10] as 1-ethyl-2-methylcyclododecane (III).

Of the $C_{15}H_{25}N$ pyrroles which may lead to III on reduction, only structures IV and V would exhibit nmr spectra consistent with that observed. To distinguish between these possibilities, the 2-formyl derivative was prepared[11] for nmr examination. *Anal.* Calcd for

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(1) H. H. Wasserman, G. C. Rodgers, and D. D. Keith, *Chem. Commun.*, 825 (1966); see also K. Harashima, N. Tsuchida, T. Tanaka, and J. Nagatsu, *Agr. Biol. Chem.*, **31**, 481 (1967); K. Harashima, N. Tsuchida, and J. Nagatsu, *ibid.*, **30**, 309 (1966).

(2) Structure I is not stereochemically definitive, as the absolute configuration of the pigment has not been determined.

(3) There have been numerous reports of C-25 analogs of prodigiosin of undetermined structure; these substances, some of which show considerable antibiotic activity, most probably correspond to I or II, or mixtures of the two pigments. (a) E. Dietzel, *Naturwissenschaften*, **35**, 345 (1948); (b) E. Dietzel, *Z. Physiol. Chem.*, **284**, 262 (1949); (c) F. Arcamone, A. DiMarco, M. Chione, and T. Scotti, *Giorn. Microbiol.*, **4**, 77 (1957); (d) R. A. Nicolaus, R. Nicoletti, and F. Arcamone, *Ric. Sci.*, **28**, 2314 (1958); (e) J. J. Perry, *Nature*, **191**, 77 (1961); (f) Yu. M. Khokhlova, A. V. Puchnina, and O. I. Artamonova, *Biokhimya*, **29**, 841 (1964); (g) Y. Chi-sheng, *Mikrobiologiya*, **31**, 254 (1962); (h) N. A. Krasil'nikov and G. I. El'-Registan, *ibid.*, **35**, 581 (1966); (i) M. N. Bekhtereva, Yu. M. Khokhlova, N. V. Tarasova, V. E. Khizhanovskaya, and G. A. Kasymova, *ibid.*, **35**, 586 (1966); (j) E. P. Feofilova and E. I. Filippovich, *ibid.*, **36**, 396 (1967), and references contained therein; (k) N. F. Kirillova, *ibid.*, **36**, 274 (1967).

(4) H. H. Wasserman, D. D. Keith, and J. Nadelson, *J. Am. Chem. Soc.*, **91**, 1264 (1969).

(5) We thank Dr. K. Haider, Institut fur Biochemie des Bodens, Braunschweig, Germany, for providing us with strains of *Streptomyces longisporus ruber*.

(6) H. H. Wasserman, J. E. McKeon, L. A. Smith, and P. Forgione, *Tetrahedron Suppl.*, **8**, Part II, 647 (1966), and references contained therein.

(7) D. J. Friedland, Ph.D. Thesis, Yale University, 1968.

(8) C. J. Thompson, H. J. Coleman, C. C. Ward, and H. T. Rall, *Anal. Chem.*, **34**, 151 (1962). Reduction of model pyrroles by this method indicated no rearrangement of alkyl substituents.

(9) Synthesized by Dr. Jeffrey Nadelson from 2-methylcyclododecanone.

(10) Satisfactory analytical and spectral data were obtained for all new compounds.

(11) R. M. Silverstein, E. E. Ryskiewicx, C. Willard, and R. C. Koehler, *J. Org. Chem.*, **20**, 668 (1955).