measurements of the distances made on molecular models.

In summary, the rate constant for triplet excitation transfer in I (25 sec^{-1}) is about 1000 times greater than in II (0.040 sec^{-1}). The transfer distance is about the same in both cases. The mechanism suggested by these results involves spin-orbital coupling to the singlet system in the donor chromophore combined with dipole-dipole coupling between the singlet systems of the two chromophores and spin-orbital coupling back to the triplet system in the acceptor chromophore. The difference of 1000 in the rate constant for transfer is the result of the large difference in spin-orbital coupling between III and IV which is exemplified by the large difference (again a factor of 1000) in their phosphorescent lifetimes. A mechanism involving exchange integrals would not be expected to lead to such a large difference in the transfer properties of the two compounds. Also, it is unlikely that an exchange integral mechanism could be operative at such large distances.

A more complete description of these measurements is currently in preparation.

Richard A. Keller
National Bureau of Standards
Washington, D. C. 20234
Lloyd J. Dolby[6]
Department of Chemistry, University of Oregon
Eugene, Oregon 97403

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[6] Alfred P. Sloan Research Fellow. L. J. D. gratefully acknowledges financial support from the Public Health Service Carrier Program Award 1-K3-NB-28, 105 from the National Institute of Neurological Diseases and Blindness.

Preparation and Properties of Monocesium Chloroxenate ($CsClXeO_3$)[1]

Sir:

We wish to report preparation of a stable, crystalline cesium xenon(VI) compound containing chloride similar to the cesium fluoroxenate ($CsFXeO_3$) reported by Selig[2] and Spittler, *et al.*[3] The crystalline cesium chloroxenate can be prepared either from aqueous solutions at pH 8 to 9 or from acetonitrile. A crystalline precipitate is obtained by mixing ice-cold solutions of approximately 2.0 ml of 1.5 *M* cesium chloride with 0.4 ml of 1.5 *M* xenon trioxide or by adding xenon trioxide to cesium chloride dropwise until permanent turbidity appears. Then the solution is left in the icebox for approximately 3 hr. The supernatant solution is sucked off, and the crystals first are washed with several portions of ice-cold water and finally with acetonitrile. The contents are dried in a vacuum desiccator. Preparation of cesium chloroxenate must be carried out in slightly alkaline medium otherwise chloride is oxidized to chlorine oxides and forms highly explosive solutions. Crystalline cesium chloroxenate also can be prepared by mixing approximately equal volumes of 0.1 *M* cesium chloride and 0.1 *M* xenon trioxide dissolved in moist acetonitrile. The precipitation in acetonitrile is less dependent on pH, but is more subject to coprecipitation of the reagent which is present in excess. The resulting precipitate compares well to the aqueous preparations: infrared spectra and analyses are almost identical.

The chloride in the cesium chloroxenate is determined by Fajans method after the decomposition of xenate with dilute hydrogen peroxide. Cesium is determined either as cesium perchlorate or indirectly as cesium chloride titrimetrically, and the oxidation equivalent is determined iodometrically by "hi-lo" titration. The analyses of chloride, cesium, and oxidation equivalent yield the empirical formula weight 347, 348, and 344, respectively, as compared to the calculated formula weight 346.5 for $CsClXeO_3$.

Cesium chloroxenate is considerably more stable than xenon trioxide. It loses some xenon and oxygen at approximately 150° and on further heating evolution of xenon and oxygen diminishes. At temperatures higher than 190°, xenon and oxygen are evolved rather rapidly and the sample explodes at approximately 205° *in vacuo*, leaving cesium chloride residue. Cesium chloroxenate is shock sensitive and should be handled with care. Cesium chloroxenate, upon addition to concentrated sulfuric acid, yields chlorine, chlorine oxides, oxygen, and xenon.

Crystalline cesium chloroxenate shows a number of infrared bands at 818 (s), 793 (s), 766 (m), 749 (m), 663 (w), and 400 (m) cm^{-1}. The strong bands at 818 and 749 cm^{-1} are similar to cesium fluoroxenate at 807 and 757 cm^{-1} as reported by Selig.[2] The X-ray powder diffraction pattern is different from cesium chloride and xenon trioxide calculated *d* values.[4] However, the general pattern of lines resembles that of $CsFXeO_3$ as prepared in our laboratory.[3] The *d* spacings for the $CsClXeO_3$ are: 4.03 (w), 3.82 (m), 3.34 (m), 3.20 (w), 2.68 (m), 2.34 (m), 2.00 (s), and 1.74 (w) A. (Some of these weak lines may be due to the decomposition of crystals in the X-ray beam as has been observed in the study of various xenon(VI) compounds.)

We are continuing our investigations on the nature of the halide interactions with xenon trioxide.

[1] This work is supported by the grant from the National Science Foundation (GP-5045).

[2] H. Selig, *Inorg. Chem.*, **5**, 183 (1966).

[3] T. M. Spittler, B. Jaselskis, and J. L. Huston, presented at the 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967.

[4] D. H. Templeton, A. Zalkin, J. D. Forrester, and S. M. Williamson, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago, Chicago, Ill, 1963, p 229.

Bruno Jaselskis, T. M. Spittler, J. L. Huston
Department of Chemistry, Loyola University
Chicago, Illinois 60626

Received February 1, 1967

Dibenzoequinene. A Novel Heptacyclic Hydrocarbon from the Photolysis of [2.2]Paracyclonaphthane

Sir:

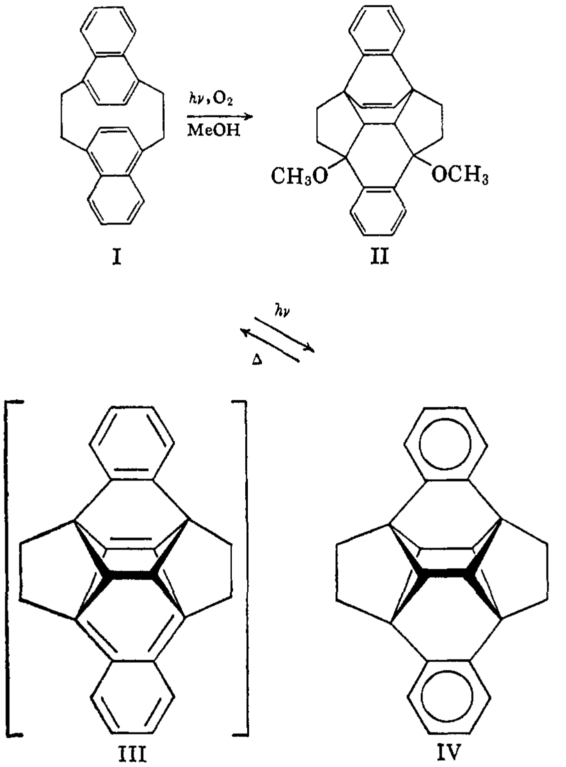
In a recent communication[1] we reported that [2.2]paracyclonaphthane (I)[2] undergoes photosensitized autoxidation to form the dibenzo dimethoxy polycyclic system II. We have now found that, in the presence of ultraviolet light,[3] I is converted to the novel hydrocarbon IV, "dibenzoequinene."[4]

[1] H. H. Wasserman and P. M. Keehn, *J. Am. Chem. Soc.*, **88**, 4522 (1966).

[2] D. J. Cram, C. K. Dalton, and G. R. Knox, *ibid.*, **85**, 1088 (1963).

[3] In our initial dye-photosensitized autoxidation studies we used a 150-w floodlamp as light source. This was replaced by a sunlamp in order to decrease reaction time and improve yields. Compound IV was observed as a minor product in the photosensitized autoxidations

Ultraviolet irradiation[6] of [2.2]paracyclonaphthane (I) in degassed benzene-methanol (1:1) for 10 days yielded IV (50%), after chromatography on silica gel and recrystallization from hexane. *Anal.*[7] Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54; mol wt, 308. Found: C, 93.53; H, 6.20; mol wt (mass spectroscopy), 308.



The photolysis product did not exhibit a sharp melting point. At about 190–200° a change in the crystalline structure was observed, and melting finally took place at 294–298° dec. (The reported melting point of I is 299–301°.) Examination of the ultraviolet spectrum of material which had been heated to 200° clearly showed that a thermal reversal of IV to I had taken place.

Further spectroscopic examination of product IV revealed the following. (i) The infrared spectrum ($CHCl_3$) contains broad (CH) absorption in the 2800–3100-cm^{-1} range with no bands in the regions associated with alcohol or ether groups. (ii) The mass spectrum (like the spectrum of I) shows only a base peak at *m/e* 154 and a molecular ion peak at *m/e* 308, suggesting a hydrocarbon of molecular formula $C_{24}H_{20}$ which has a high degree of symmetry. (iii) The ultraviolet spectrum of the hydrocarbon (Figure 1) bears a very close resemblance to the spectrum of II, and also to that of *o*-xylene. (iv) The nmr spectrum is remarkaly uncomplicated, showing three sharp singlets, in the ratio 2:2:1, at τ 2.65 (8 aromatic H), 7.60 (8 H at positions a), 8.36 (4 H at positions b). The upfield shift of the four protons at b is in accord with previous observations on the chemical shifts of equatorial hydrogens on the four-membered rings of bicyclo[2.1.1] systems.[8]

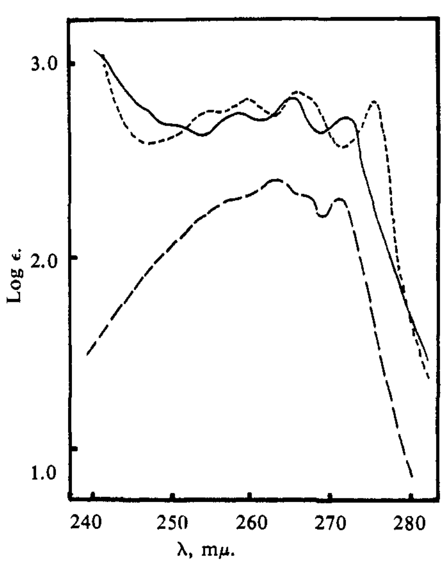
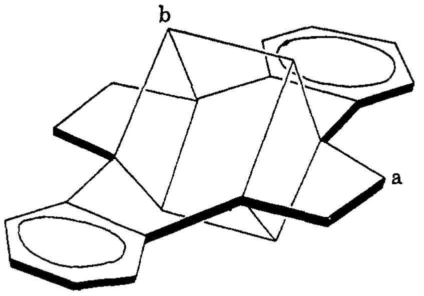


Figure 1. Ultraviolet spectrum of dibenzoequinene (IV) in hexane (- - - - -); the dimethoxy polycyclic system (II) in ethanol (——); and *o*-xylene in hexane (– – –).



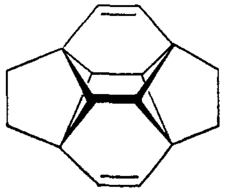
IV

The structural representation for the $C_{24}H_{20}$ hydrocarbon which is clearly in accord with all of the above information is the hydrocarbon IV. This product appears to form by a light-induced intramolecular cyclization[9] possibly through the intermediate III. Other products formed in this photochemical reaction are under investigation.

An independent X-ray structure determination on dibenzoequinene is in progress by Dr. Albert Fratini of the U. S. Naval Research Laboratories, Washington, D. C.[9a]

carried out in the presence of ultraviolet light, but it was the main product in the purely photochemical reaction in the absence of oxygen.

(4) We suggest the trivial name "equinene" for the parent $C_{16}H_{16}$ heptacyclic diene (i) which has not yet been prepared. As has been pointed out earlier,[5] this hydrocarbon would be formed if [2.2]-paracyclophane were to undergo a twofold intramolecular Diels–Alder reaction.



i

(5) R. C. Helgeson and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 509 (1966).

(6) An air-cooled Rayonet Photochemical Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) and a Pyrex reaction vessel were used. The light source consisted of 16 lamps at 3500 A.

(7) We thank Dr. Robert Rittner of the Olin Mathieson Chemical Corp. for assistance in obtaining the microanalytical data.

(8) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962).

(9) Recent studies on [2.2]paracyclophane[5] have shown that, on irradiation with ultraviolet light, this system undergoes ring opening without formation of i.

(9a) NOTE ADDED IN PROOF. Dr. Fratini has recently informed us that he has confirmed structure IV by X-ray analysis.

Acknowledgments. This work was supported by Grant GM 13854 from the National Institutes of Health. We wish to thank Drs. S. Lipsky and W. McMurray for help in determining the mass spectra of products formed in this and related work. We also thank B. von Klock for technical assistance.

(10) National Institutes of Health Predoctoral Fellow, 1966–1967.

Harry H. Wasserman, Philip M. Keehn[10]
Department of Chemistry, Yale University
New Haven, Connecticut 06520
Received January 21, 1967

Peptide Bond Formation and Subsequent Hydrolysis at a Cobalt(III) Center

Sir:

We wish to report the rapid formation of a peptide bond in nonaqueous solutions at room temperature using the Co(trien)$^{3+}$ (trien = triethylenetetramine) moiety as a N-terminal protecting group and as an activating center. This discovery was made during a preparative study of cobalt(III) complexes containing monodentate amino acid amides and esters.

Treatment of α- or β-[Co(trien)(TBP)$_2$]$^{3+}$ [1] or β_2-[Co(trien)Cl(glyOEt)](ClO$_4$)$_2$[2] with glycine ethyl ester in dry TBP, and sulfolane or dimethylformamide solutions, respectively, results in the rapid condensation of two glycine ester residues and the formation of the β_2-[Co(trien)glyglyOEt]$^{3+}$ ion. The reactions (eq 1–3) are complete within 2 min at 25°.

$$\alpha\text{-[Co(trien)(TBP)}_2]^{3+} + 2\text{glyOEt} \xrightarrow{\text{TBP}} \beta_2\text{-[Co(trien)glyglyOEt]}^{3+} + \text{HOEt} + 2\text{TBP} \quad (1)$$

$$\beta_2\text{-[Co(trien)ClglyOEt](ClO}_4)_2 + \text{glyOEt} \xrightarrow[\text{(DMF)}]{\text{sulfolane}} \beta_2\text{-[Co(trien)glyglyOEt]}^{3+} + \text{HOEt} + 2\text{ClO}_4^- + \text{Cl}^- \quad (2)$$

$$\beta\text{-[Co(trien)(TBP)}_2]^{3+} + 2\text{glyOEt} \xrightarrow{\text{TBP}} \beta_2\text{-[Co(trien)glyglyOEt]}^{3+} + \text{HOEt} + 2\text{TBP} \quad (3)$$

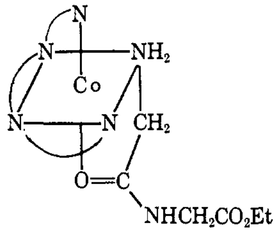
Chromatography on cation ion-exchange paper (Whatman cellulose phosphate P81) showed almost quantitative formation of the dipeptide ester complex, and analytically pure β_2-[Co(trien)glyglyOEt](ClO$_4$)$_3\cdot$H$_2$O was isolated in high yield ($\backsim$80%) from each of the reactions. (*Anal.* Calcd: C, 21.17; H, 4.74; N, 12.35. Found: C, 20.86; H, 4.82; N, 12.16). An identical product was isolated following treatment of β-[Co(trien)(H$_2$O)$_2$]$^{3+}$ with glycylglycine ethyl ester in aqueous solution at pH 7.5–8.0 for 1 hr at 25° and addition of NaClO$_4$ (reaction 4).

$$\beta\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} + \text{glyglyOEt}\cdot\text{HCl} \longrightarrow \beta_2\text{-[Co(trien)glyglyOEt]}^{3+} + 2\text{H}_2\text{O} + \text{H}^+ + \text{Cl}^- \quad (4)$$

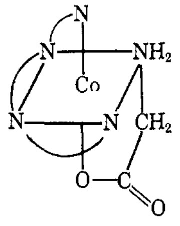
The equivalence of the products isolated from reactions 1–4 was established by comparisons of pmr (δ 1.3 (triplet), 4.36, 4.27, and 4.25 ppm (masked quartet); intensity ratio 3:2:2:2), infrared (1735 cm^{-1} ester carbonyl, 1630 cm^{-1} coordinated amide carbonyl), and visible (ϵ_{346} 153; ϵ_{478} 141) spectra, as well as by their chromatographic behavior and analytical data. The compound β_2-[Co(trien)glyglyOEt](ClO$_4$)$_3\cdot$H$_2$O is easily recrystallized without change from neutral or acidic solutions, but undergoes hydrolysis in basic solutions (pH $\geq$8) liberating 1 equiv of glycine ethyl ester (reaction 5). The resulting glycine chelate β_2-[Co(trien)gly]$^{2+}$ ion was isolated as its I$^-$ and ClO$_4^-$ salts (*Anal.* Calcd for $[\mathrm{CoC_8H_{22}O_2N_5}](\mathrm{ClO_4})_2\cdot 0.5\mathrm{H_2O}$: C, 19.72; H, 4.75; N, 14.38. Found: C, 19.82; H, 4.53; N, 14.33) and is identical with that obtained in the reaction of β-[Co(trien)(H$_2$O)$_2$]$^{3+}$ with glycine (ϵ_{346} 145 ϵ_{478} 134).[3] In view of reactions 4 and 5 and structure I below, it is now proposed that the β_2-[Co(trien)glyglyOEt]$^{3+}$ ion is the intermediate in the hydrolysis of peptide esters and amides catalyzed by the β-[Co(trien)OH(H$_2$O)]$^{2+}$ ion.[4]

$$\beta_2\text{-[Co(trien)glyglyOEt](ClO}_4)_3 + \text{OH}^- \longrightarrow \beta_2\text{-[Co(trien)gly]}^{2+} + \text{glyOEt} + 3\text{ClO}_4^- \quad (5)$$

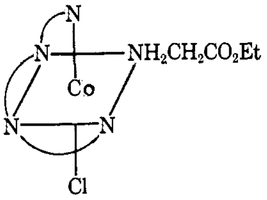
An X-ray structural study of β_2-[Co(trien)glyglyOEt](ClO$_4$)$_3\cdot$H$_2$O establishes its geometrical configuration as I[5] in which glycylglycine ethyl ester functions as a bidentate ligand by attachment to cobalt through the terminal amino nitrogen and peptide carbonyl oxygen atoms. This, together with the experiments below, establishes the geometrical structure of the hydrolyzed product, β_2-[Co(trien)gly]$^{2+}$, and reactant, β_2-[Co(trien)Cl(glyOEt)]$^{2+}$, as II and III, respectively, in agreement with previous assignments.[3]



I



II



III

To establish that formation of the peptide bond does occur at the cobalt(III) center, β_2-[Co(trien)Cl(glyOEt)](ClO$_4$)$_2$ (1 g) (*Anal.* Calcd: C, 22.13; H, 5.02; N, 12.91. Found: C, 21.98; H, 5.12; N, 12.99) containing C^{14}-labeled glycine ethyl ester (4850 ± 17 cpm/mg of complex) was treated with 2 equiv of freshly prepared inactive glycine ethyl ester (0.4 g) in sulfolane (10 ml) and the reaction quenched after 2 min by addition of ethanol and ether. The β_2-[Co(trien)glyglyOEt](ClO$_4$)$_3\cdot$H$_2$O obtained after two recrystallizations from hot water (*Anal.* Calcd: C, 21.17; H, 4.74; N, 12.35. Found: C, 21.25; H, 4.42; N, 12.40) and unreacted glycine ethyl ester recovered by chromatography were analyzed for their C^{14} content, and

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(1) α and β refer to the geometrical arrangement of triethylenetetramine about the metal atom: G. H. Searle and A. M. Sargeson, *Inorg. Chem.*, **4**, 45 (1965). TBP = tri(*n*-butyl) phosphate.

(2) Subscripts β_1 and β_2 are used to distinguish between the two nonequivalent positions in the β structure; see II and III below.

(3) L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, **6**, 1042 (1967).

(4) D. A. Buckingham, J. P. Collman, D. A. R. Happer, and L. G. Marzilli, *J. Am. Chem. Soc.*, **89**, 1082 (1967).

(5) M. Fehlmann, H. Freeman, D. A. Buckingham, and A. M. Sargeson, to be published.