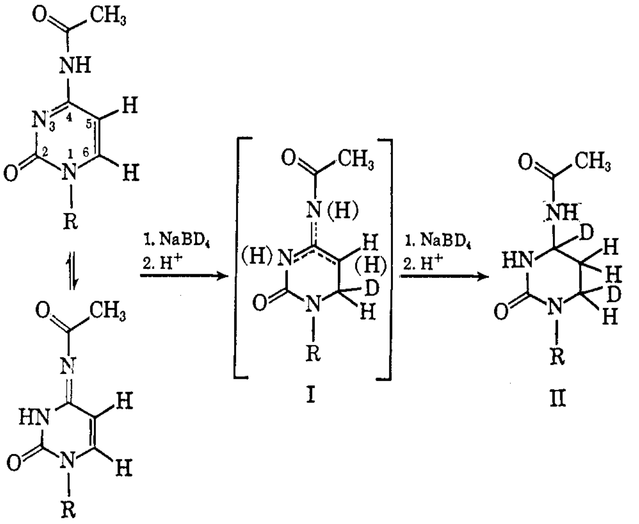
44% cytidine was formed. If the reaction was carried out under ultraviolet irradiation (2537 A) the yield for the reduction product was 76% and for cytidine 21% (14 *M* excess of $NaBH_4$).[10]

The two components of the reduction mixture, cytidine and N^4-acetyl-3,4,5,6-tetrahydrocytidine, were separated by column chromatography on Dowex 50W-X8 (H^+). The structure of the reduction product was derived from the nmr spectrum (in D_2O). A triplet at 5.30 ppm ($J = 4.5$ cps, 1 H) was attributed to the proton at C_4 and a multiplet centered at 3.39 ppm (2 H) to the methylene protons at C_6. A multiplet at higher field was superimposed by a singlet originating from the methyl group of the acetyl substituent (singlet at 1.99 ppm) and was attributed to the methylene protons at C_5. The signal at 5.30 ppm disappeared and the multiplet at 3.39 ppm was simplified and lowered in intensity if the reduction was carried out with sodium borodeuteride. The product of the reduction with sodium borodeuteride is therefore N^4-acetyl-3,4,5,6-tetrahydrocytidine-d_4,d_6 (II). The isotope distribution in II suggests the following reaction steps: (1) 1,4 addition of a hydride (deuteride) ion (at C_6) and a proton (at N^3 or N^4) to an α,β-unsaturated imine, and (2) further reduction of the intermediate N^4-acetyldihydrocytidine (I) by the attack of a second hydride (deuteride) ion at C_4.



R=β-D-ribofuranose

This novel reaction was used for the synthesis of copolymers of cytidylic acid and N^4-acetyl-3,4,5,6-tetrahydrocytidylic acid by the reduction of copolymers of cytidylic acid and N^4-acetylcytidylic acid.[11] The polymers were exposed to a large excess of sodium borohydride in 0.05 *M* sodium carbonate buffer at pH 9.8 for 40 min at room temperature. The polymers were purified by repeated precipitation with cold ethanol and by passage through Sephadex G-25. The composition of the polymers was determined spectrophotometrically and with the orcinol assay after total digestion with pancreatic ribonuclease. In contrast to the behavior of the monomer no significant deacetylation was observed. Polymers containing 8, 16, and 29% N^4-acetyl-3,4,5,6-tetrahydrocytidylic acid were prepared by this method, and their physical properties are now being investigated. The characterization of the polymers is given in Table I. The presence of N^4-acetyl-3,4,5,6-tetrahydrocytidine in the reduced polymer was demonstrated in experiments using sodium borotritiide as a reducing agent. The components of the ribonuclease digest were separated on Dowex 50W-X4 (H^+). The fractions containing radioactive material were treated with alkaline phosphomonoesterase and their content was compared to authentic N^4-acetyl-3,4,5,6-tetrahydrocytidine by thin layer chromatography (silica gel G, 85% 2-propanol). Identical R_f values were found for the radioactive compound derived from the polymer and for N^4-acetyl-3,4,5,6-tetrahydrocytidine obtained from the reduction of the monomer. No radioactivity was found in the eluates containing cytidylic acid.

Table I. Characterization of the Polymers

Compn before reduction, %		Compn after reduction, %	
Cytidine 3′-phosphate[a]	N^4-Acetylcytidine 3′-phosphate[a]	Cytidine 3′-phosphate[b]	N^4-Acetyl-3,4,5,6-tetrahydrocytidine 3′-phosphate[b]
68	26	73	29
81	18	84	16
90	7	90	8

[a] The amounts of cytidine 3′-phosphate and N^4-acetylcytidine 3′-phosphate were calculated from the absorbance of the nucleotide mixture obtained from the digestion of the polymers with pancreatic ribonuclease in 0.05 *M* NH_4HCO_3, pH 7.5, at 270 and 294 mμ (ϵ_{270} cytidine 3′-phosphate 9×10^3; ϵ_{294} cytidine 3′-phosphate 10^3; ϵ_{270} N^4-acetylcytidine 3′-phosphate 4.4×10^3; ϵ_{294} N^4-acetylcytidine 3′-phosphate 8.6×10^3). To accomplish complete deacetylation the samples were then kept for 6 hr at 65–70° and the cytidine 3′-phosphate content was determined from the absorbance at 280 mμ (ϵ 1.3×10^4, pH 1). This value was taken as 100% for the calculation of the base composition of the polymers. [b] The amount of cytidine 3′-phosphate was determined from the absorbance of the nucleotide mixture obtained from the digestion of the reduced polymers with pancreatic ribonuclease at 280 mμ (ϵ 1.3×10^4, pH 1). The content of N^4-acetyl-3,4,5,6-tetrahydrocytidine 3′-phosphate was measured with the orcinol assay. Total polymer phosphate was determined according to B. N. Ames and D. T. Dubin, *J. Biol. Chem.*, **235**, 769 (1960), and taken as the basis for the calculation of the base composition of the polymers.

Attempts are now being made to synthesize copolymers of cytidylic acid and 3,4,5,6-tetrahydrocytidylic acid by the reduction of N^4-formylated and N^4-trifluoroacetylated polycytidylic acid followed by deacylation.

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Rate Constants and the Mechanism for the Transfer of Triplet Excitation Energy

Sir:

The intramolecular transfer of triplet excitation from one chromophore to another has been measured for

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(10) No spectral changes were detected if N^4-acetylcytidine was irradiated under the analogous conditions for 70 min in the absence of $NaBH_4$.

(11) A. M. Michelson and M. Grunberg-Manago, *Biochim. Biophys. Acta*, 91, 92 (1964).

molecules I and II shown in Figure 1. The triplet donor in I is the ester of benzophenone-4-carboxylic acid, and the triplet donor in II is the carbazole chromophore. The triplet acceptor in both cases is the naphthalene chromophore. The absorption spectrum of each molecule is the sum of the absorption spectra of their composite chromophores. The lowest singlet state of both triplet donors is lower in energy than the lowest singlet state of naphthalene. This makes it possible to excite these donors with long wavelength radiation which is not absorbed by the naphthalene chromophore. All emission measurements were made at 77°K in a rigid glass matrix.[1]

The phosphorescence spectrum of a very dilute solution (3×10^{-5} *M*) of II shows emission from both the carbazole chromophore ($\sim$63%) and the naphthalene chromophore ($\sim$37%). The intensity of phosphorescence from II is about 67% as strong as the intensity of phosphorescence of an equimolar mixture of naphthalene and III at the same concentration. The lifetime of the carbazole emission from II is 5.7 sec,[2] while the lifetime of the carbazole emission from III is 7.2 sec. The difference of the first-order rate constants (reciprocal lifetimes) indicates that 21% of the triplet excitation energy is transferred and that the rate constant for the transfer process is about 0.04 sec^{-1}. The agreement between these three completely different types of measurements for the amount transferred is very good. The first method is the least accurate because it involves a knowledge of the phosphorescence quantum yields for the two chromophores, and it involves intensity measurements at different wavelengths.[3] No corrections were made for the change in sensitivity of the apparatus as a function of wavelength.

The phosphorescence spectrum of a very dilute solution (1×10^{-4} *M*) of I shows emission from both the naphthalene and the benzophenone chromophore. The lifetime of the phosphorescence from the benzophenone chromophore is almost 1000 times shorter than the phosphorescent lifetime of the naphthalene chromophore. A measurement of the ratio of the intensities of the fast and slow components of I indicated that about 39%[4] of the triplet excitation energy was transferred to the naphthalene chromophore. The phosphorescence from I is about 65% as intense as the phosphorescence from an equimolar mixture of IV and naphthalene. This indicates that about 35% of the triplet excitation energy is transferred. The lifetime of the benzophenone emission from I is 4.9×10^{-3} sec and from IV is 5.6×10^{-3} sec. The difference of the first-order rate constants indicates that 12% of the energy is transferred and that the rate constant for the transfer process is 25 sec^{-1}. The agreement between the three sets of measurements is not quite as good for

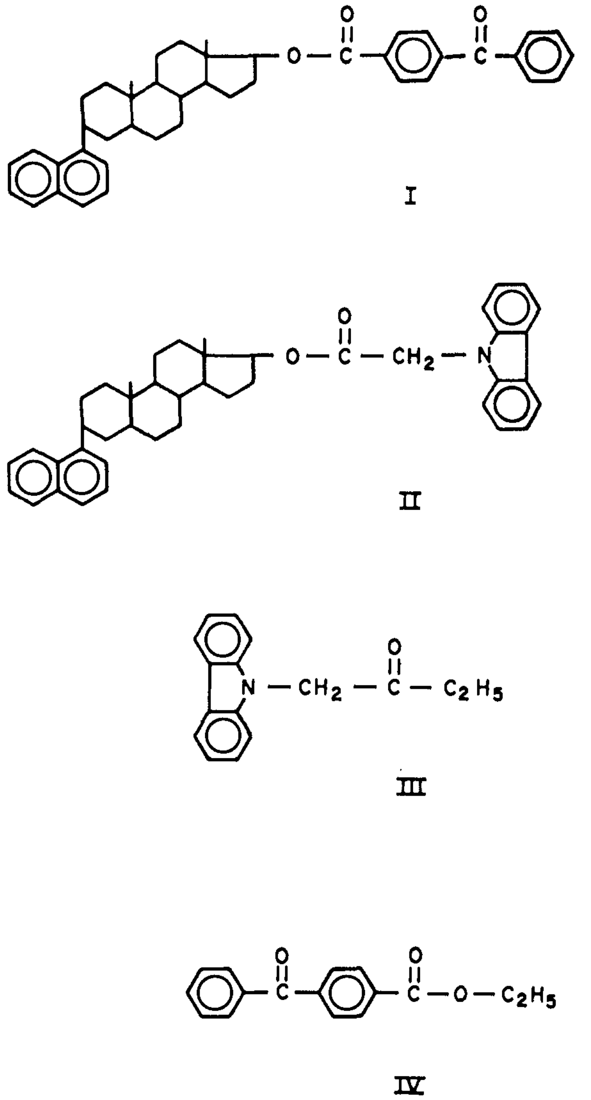

Figure 1. Molecules studied: (I) 3-(α-naphthyl)-5α-androstan-17β-ol 17-*p*-benzoylbenzoate, (II) 3-(α-naphthyl)-5α-androstan-17β-ol 17-(9-carbazole)acetate, (III) ethyl (9-carbazole)acetate, (IV) ethyl *p*-benzoylbenzoate.

I as it is for II, but all measurements agree within a factor of 3. The lifetime measurement is probably the most accurate because it does not involve a comparison of two intensities or an assumption of quantum yields.

The transfer of singlet excitation energy from the naphthalene chromophore to the two donor chromophores was measured by comparing the intensity of the naphthalene emission from an equimolar mixture of naphthalene and either III or IV to the intensity of the naphthalene emission from I or II; 2985-A radiation was used for excitation. These measurements indicated that in I, 70% of the singlet excitation energy is transferred and in II, 95% of the singlet excitation energy is transferred. A dipole–dipole coupling mechanism was assumed to be responsible for the transfer of singlet excitation energy and Förster's equation[5] was used to calculate the distance between the chromophores. The distances were found to be 14 A for I and 15 A for II. These numbers agree very well with

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(1) 30% butyl alcohol and 70% isopentane.

(2) The decay was very slightly nonexponential at very short times. This may be due to a distribution in the distances between the chromophores. The lifetime quoted was from the exponential part of the curve.

(3) The quantum yields of naphthalene and carbazole were assumed to be the same for this calculation. The intersystem quantum yields for both of these compounds were found to be the same by A. A. Lamola and G. S. Hammond, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p 209.

(4) No corrections were made for the sensitivity of the apparatus as a function of wavelength. The phosphorescent quantum yield of the benzophenone chromophore was assumed to be ten times the phosphorescence quantum yield of the naphthalene chromophore.

(5) Th. Förster, *Discussions Faraday Soc.*, **27**, 7 (1959). The exponent on π should be 5 instead of 6; see S. A. Latt, H. T. Cheung, and and E. R. Blout, *J. Am. Chem. Soc.*, **87**, 995 (1965).

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.

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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.

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(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.

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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]

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(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