Because of our interest in antiviral substances, we decided to investigate this reaction in some detail as applied to the pyrimidine antagonist 5-iododeoxyuridine.[12] Dilithium ethyl phosphorothioate[7] (46 mg., 0.3 μmole) was converted to the pyridinium salt by passage over Dowex 50 (pyridinium form) and dried by concentrating its solution in pyridine. The residue was again dissolved in 1 ml. of dry pyridine. 5-Iododeoxyuridine 3'-acetate[13] (II, R' = H, R'' = COCH$_3$), 40 mg. (0.1 mmole), and DCC, 300 mg. (1.5 mmoles), were added and the well-stoppered reaction mixture was shaken in the dark for 48 hr. Water (2 ml.) was added, and the resulting suspension was kept in the refrigerator for 18 hr. The solution was filtered, the precipitate was washed well with water, and the combined filtrate was concentrated to dryness *in vacuo*. The residue was treated for 2 hr. at room temperature with 10 ml. of a 50% aqueous acetone solution containing 85 mg. of iodine and then again concentrated to dryness. Concentrated ammonia, 20 ml., was added; exposure was maintained at room temperature overnight, and the ammonia was removed *in vacuo*. The residue was dissolved in 15 ml. of water, the pH adjusted to 8.5, and the solution charged to a column (1 × 10 cm.) of DEAE–Sephadex A-25 (bicarbonate cycle). A linear gradient consisting of 1 l. of 0.1 M triethylammonium bicarbonate continuously diluting 1 l. of 0.005 M buffer was applied, 15-ml. fractions of eluate being collected. The product, 5-iodo-5'-deoxyuridylic acid[14] (II, R' = PO$_3^{2-}$, R'' = H), emerged as a single peak at 0.06 M buffer, as monitored by ultraviolet absorption. The fractions were combined, concentrated, and lyophilized to give a homogeneous material, 450 optical density units, λ_{pH2}^{max} 286 mμ. (A parallel condensation, using Tener's reagent,[3] gave a 50% yield of the same material.) The material had an organic phosphate content of 0.96 μmole per 5.7 optical density units (theory: 1.0 μmole).

The advantage of the present method was demonstrated by omitting the final hydrolytic step: the corresponding 3'-acetate (II, R' = PO$_3^{2-}$, R'' = COCH$_3$), retaining the base-labile ester group, was isolated in 36% yield. Structure of the latter was proved by dephosphorylation with bacterial alkaline phosphatase[6] to IUdR 3'-acetate (II, R' = H, R'' = COCH$_3$). Finally, by omitting both iodine treatment and alkaline hydrolysis, the intermediate S-alkylphosphorothioate 3'-acetate (II, R' = P-(SC$_2$H$_5$)O$_2^{2-}$, R'' = COCH$_3$) was isolated in 91% yield, its structure following from its diminished electro-

phoretic mobility (7.0 cm.) as compared to the corresponding phosphomonoester and from conversion to the 3'-acetate phosphate (II, R' = PO$_3^{2-}$, R'' = COCH$_3$) by treatment with iodine.

The method is not restricted to the 5-halogenated pyrimidine nucleosides: phosphorylation of thymidine 3'-acetate to 5'-thymidylic acid was carried out in high yield. Its application to the monophosphorylation of other types of molecules is under current study.

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Flash Photolysis of Cobalt(III) Acidopentaammine and of PtBr$_6^{-2}$ and PtI$_6^{-2}$ Complexes

Sir:

We wish to report the results of some current flash photolytic work which serve to distinguish between alternative mechanisms in two cases of interest.

A flash of about 150 joules of 30-μsec. decay time was used to induce about 10% reaction in 10^{-4} M solutions. Intermediates were observed by following their absorption as a function of time after the flash, using a monochromatized scanning light.

The first group of complexes studied consisted of [Co(NH$_3$)$_5$I]Cl$_2$, [Co(NH$_3$)$_5$N$_3$]Cl$_2$, and [Co(NH$_3$)$_5$Br]Br$_2$, prepared by previously described methods.[1,2] Steady light illumination of pH 4–5 aqueous solutions of the above compounds led to photo oxidation–reduction decomposition with conversion of Co(III) to Co(II), and to I$_2$ and N$_2$, but not Br$_2$ production, respectively. It was postulated that the primary chemical act was a homolytic bond fission to produce I, N$_3$, and Br radicals and that the absence of bromine in the last case was due to reaction of Br with the released ammonia. An alternative possibility would be that an ammonia ligand was oxidized directly in the primary step, as appears to be suggested in a study of the pyrolysis of [Co-(NH$_3$)$_5$Br]Cl$_2$.[3]

For aqueous systems we confirm the original mechanism in that aqueous Co(NH$_3$)$_5$Br^{+2} and Co(NH$_3$)$_5$I^{+2} both give strongly the respective halogen atom transients on flashing in either a quartz or a Pyrex cell.[4] Thus the ammonia oxidation in the over-all photolytic reaction of Co(NH$_3$)$_5$Br^{+2} must indeed be due to a secondary reaction of Br atoms produced in the primary step. Interestingly, the decay time of the iodine transient is distinctly less than expected[4]; it may be that the reaction of iodine atoms with unphotolyzed complex is being observed rather than the recombination.[5]

No transient absorption could be located in the case of the Co(NH$_3$)$_5$N$_3^{+2}$ ion, but the presence of azide

tempt to apply this reaction to the phosphorylation of 11-desoxycorticosterone gave yields of at most 0.3% based on steroid. The same principle, the activation of only one of the substituents of phosphorus, underlies the procedure recently published by A. J. Kirby, *Chem. Ind.* (London), 1877 (1963); the latter appears to be subject to the same limitation. Furthermore, the relative inefficiency of the S-alkylthio substituent as an activating group is demonstrated by the absence of disteroid monophosphate in our DCC condensation reactions.

(12) E. S. Perkins, R. M. Wood, M. L. Sears, W. H. Prusoff, and A. D. Welch, *Nature*, 194, 985 (1962).

(13) Prepared from 5-iodouracil 2'-deoxyriboside (II, R' = R'' = H) (W. H. Prusoff, *Biochim. Biophys. Acta*, 32, 299 (1959)) by the standard procedure of 5'-tritylation, acetylation at 3', and subsequent detritylation. All new compounds here described display satisfactory analytical data.

(14) A. Hampton, E. Hampton, and M. L. Eidinoff, *Biochem. Pharmacol.*, 11, 155 (1962).

(1) A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, 80, 3865 (1958).

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(4) T. A. Gover and G. Porter, *Proc. Roy. Soc.* (London), A262, 476 (1961).

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radical is strongly suggested by the observation that in the presence of added iodide ion the iodine atom transient is again observed. No halogen atom transient appears when added bromide ion is present, however; this is consistent with our earlier report that iodide but not bromide inhibited nitrogen gas production in the photolysis of this complex.[2]

Less expected were the results for aqueous $PtBr_6^{-2}$ and PtI_6^{-2}. Again, concentrations of 10^{-4} M were used; all solutions were air saturated unless otherwise noted. Previous work in this laboratory showed that a chain mechanism acted to provide very high quantum yields for the photoexchange of bromide ion with $PtBr_6^{-2}$, and a mechanism was suggested for which the initial step was

$$PtBr_6^{-2} \longrightarrow PtBr_5^{-2} + Br \qquad (1)$$

analogous to the one proposed for the chloride system.[6] The complete mechanism accounted for the small amount of net decomposition observed, the square root dependence of the exchange quantum yield on light intensity, and its dependence on bromide ion concentration.

Our flash photolytic results for $PtBr_6^{-2}$ are as follows: (a) extensive decomposition occurs in either a quartz or a Pyrex cell to give what may be a hydrated form of $PtBr_6^{-2}$ (this is partially repressed by added bromide ion); (b) no indication of any bromine atom transient was present; (c) no free electrons were observed in the degassed system even though we do detect such with dilute ferrocyanide[7]; (d) if 10^{-4} M hydroquinone at pH 5 (itself not affected by flashing) was also present, a new permanent absorption at 244 mμ resulted; however, addition of the hydroquinone immediately after flashing gave no effect; (e) PtI_6^{-2} plus iodide solutions showed a long-lived transient with a half-life of about 0.1 sec. absorbing at 410 mμ.

Observation d indicates that a short-lived oxidizing species is present and therefore that the primary photochemical act is in nature oxidation–reduction. Observation b rules out reaction 1 and c, the possibility of free electron production, so that the primary reaction apparently must be

$$PtBr_6^{-2} \longrightarrow [PtBr_4^{-2}] + Br_2 \qquad (2)$$
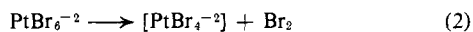
Reaction 2 is a two-electron oxidation–reduction step which although new is not implausible. From the structure of H_2PtBr_6,[8] the Br–Br distance is 3.41 Å., or less than the van der Waals distance of 3.90 Å.[9] We are thus supposing that the concerted departure of two bromine atoms with conmitant development of a Br–Br bond is easier than for process 1 to occur.

It also appears that the $[PtBr_4^{-2}]$ formed has a geometry which allows it to react rapidly with bromine to form $PtBr_6^{-2}$. The planar form will not do this either in the presence or the absence of added bromide ion. A likely configuration is a trigonal pyramid, or, in the presence of bromide, a trigonal bipyramid; these must live long enough to serve as chain carriers in

the exchange of bromide ion with $PtBr_6^{-2}$ and to react with some bromine derivative (Br_3^- or BrOH) to give the net reaction noted under a above. Conformational isomers in tetracoordinated systems are, of course, known, but it seems generally assumed that their interconversion is rapid.[10] In fact, the 0.1-sec. half-time species observed with PtI_6^{-2} may be the analog of our $[PtBr_4^{-2}]$ isomer. We are in the process of obtaining more complete data so as to be able to decide on this interesting possibility.

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The Radical Fragmentation Route on Photolysis of 2,5-Cyclohexadienones. 4-Methyl-4-trichloromethyl-2,5-cyclohexadienone[1,2]

Sir:

Considerable attention has been given recently to the mechanisms of phototransformations of unsaturated ketones in solution, particularly of 2,5-cyclohexadienones.[3] In almost all the reactions studied[3] the product-determining intermediates are best understood as being ionic in character, and Chapman[3c] has proposed that consideration of "polar state intermediates" II derived from dienones I allows for rationalization of the structures of the various products of these reactions.

Chart I
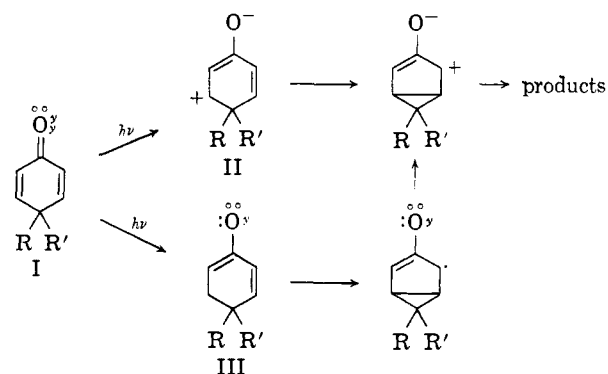
The mode of formation of the "polar state" II has not been explicitly outlined, although it has been suggested[4] that II may be an adequate representation of the excited state. Zimmerman has proposed[3a,b,d] an

(1) Part V. Photochemistry of Unsaturated Ketones. Part IV: D. I. Schuster, F.-T. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, in press.
(2) Supported in part by Grant No. DA-ARO(D)-31-124-G425 from the Army Research Office (Durham).
(3) For reviews of recent studies, see (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962); (b) H. E. Zimmerman, *Advan. Photochem.*, 1, 183 (1963); (c) O. L. Chapman, *ibid.*, 1, 323 (1963); (d) H. E. Zimmerman, *Tetrahedron Suppl.*, 2, 393 (1963); (e) P. J. Kropp, *J. Am. Chem, Soc.*, **86**, 4053 (1964).
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