4,4-Dimethylcyclohexanone.[15]—A mixture of 15.4 g of 4,4-dimethyl-2-cyclohexen-1-one, 50 ml of ether, and 1 g of platinum black was hydrogenated at room temperature using an initial hydrogen pressure of 24 psi. The mixture was allowed to react for 14 hr, filtered, and evaporatively distilled. The ir showed an absorption at 1710 cm^{-1} (C=O) (lit.[15] 1710 cm^{-1}). Another absorption was observed at 3390 cm^{-1} (OH) indicating that a part of the ketone had been reduced to the corresponding alcohol. To reoxidize the alcohol to the ketone, the procedure of Auwers and Lange was used.[16] A solution consisting of 10 g of potassium dichromate and 8.5 g of concentrated sulfuric acid in 50 ml of water was prepared and the crude reaction mixture containing both alcohol and ketone was added. This mixture was stirred for 0.5 hr, heated on a steam bath for 10 min, and steam distilled. The distillate was saturated with sodium chloride, extracted with ether, dried over anhydrous magnesium sulfate, and evaporatively distilled, resulting in the recovery of 12.1 g of white needle crystals: uv λ_{max} (EtOH) 281.0 mμ (ϵ 31) [lit.[15] λ_{max} (EtOH) 281.0 mμ (ϵ 32)].

1,1′-Hydrazobis-1-cyano-4,4-dimethylcyclohexane.—A solution of 19.0 g (0.15 mol) of 4,4-dimethylcyclohexanone, 7.4 g (0.15 mol) of sodium cyanide, 9.8 g (0.075 mol) of hydrazine sulfate, and 15 ml of dioxane in 100 ml of water was stirred for 50 hr at room temperature. The resulting solid was filtered and recrystallized from 95% ethanol, 2.19 g (97% yield), mp 148–149°.

1,1′-Azobis-1-cyano-4,4-dimethylcyclohexane (ACDC) (11).—A 15.1-g (0.05 mol) sample of the hydrazo compound was stirred with 25 ml of 2 *N* HCl, and bromine was added in 0.5-ml portions to the resulting slurry with cooling until the mixture retained a yellowish color. A total of 2.58 ml of bromine was added (94.5% of theoretical). The yellowish, fluffy solid was removed by filtration, recrystallized first from methanol, and then from low-boiling petroleum ether (bp 30–60°). The azo compound was obtained in 79% yield: mp 132–133° dec; uv λ_{max} (95% EtOH) 351.0 mμ (ϵ 18.3). *Anal.* Calcd for $C_{18}H_{28}N_4$: C, 71.96; H, 9.39; N, 18.65. Found: C, 71.75; H, 9.38; N, 18.24. The yield of nitrogen gas on thermal decomposition was *ca.* 100% of theoretical.

1,1′-Azobis-1-cyanocyclohexane (ACC) (10).—This compound was synthesized by Mr. M. Amrich according to the procedure reported by Overberger (see Hammond)[12] and recrystallized from methanol: mp 113–115° dec (lit.[12] 113–114°, 114–115°); uv ϵ at 350.0 mμ (95% ethanol), 18.2 (lit.[12] 17.9, ethanol; 19.4, chlorobenzene).

Kinetic Studies.—Nitrogen evolution was monitored using a constant-pressure gas apparatus based on a design by Professor T. Traylor.[9]

Efficiency Studies.—Oxygen uptake was monitored using the gas apparatus employed in the kinetic studies.

Registry No.—**5**, 32174-90-6; **8**, 32174-91-7; **8** nitrate, 32174-92-8; **9**, 32174-93-9; **9** dinitrate, 32256-09-0; **9** diiodide, 32174-94-0; **11**, 32174-95-1; 1,1′-hydrazobis-1-cyano-4,4-dimethylcyclohexane, 32174-96-2.

[16] K. v. Auwers and E. Lange, *Justus Liebigs Ann. Chem.*, **401**, 303 (1913).

Ion Radicals. XXIII. Some Reactions of the Perylene Cation Radical[1,2]

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Solid perylene cation radical perchlorate has been prepared (a) in admixture with perylene by anodic oxidation of perylene, and (b) in admixture with silver iodide by oxidation of perylene with iodine–silver perchlorate. Each of these preparations is usable for studying reactions of the cation radical. Reaction with water led to perylene and 3,10-perylenequinone (**3**). The stoichiometry of this reaction is $6C_{20}H_{12}\cdot^{+} + 2H_2O \rightarrow 5C_{20}H_{12} + C_{20}H_{10}O_2 + 6H^{+}$. Reaction with pyridine gave *N*-(3-perylenyl)pyridinium perchlorate (**9**), degradation of which by the Zincke method gave 3-aminoperylene. Compound **9** was also obtained easily by the direct reaction of perylene, iodine, silver perchlorate, and pyridine. Perylene cation radical was reduced quantitatively by iodide ion. Reduction by bromide ion also appeared to be quantitative. Reaction with chloride ion also led mostly to perylene. Reaction with fluoride ion did not occur; reaction with unremoved small amounts of water occurred slowly instead. Reaction with acetate and benzoate ion led to the 3-perylenyl esters. The overall picture is that nucleophilic substitution occurs where the nucleophile is not easily oxidized, and substitution occurs at the position in the cation radical which has the highest positive charge density according to simple HMO calculations.

Although the perylene cation radical has been known for some time and has been well characterized spectroscopically,[4] hardly anything is known about its chemistry. Some years ago it was found that perylene was recovered from dilution of a solution of the cation radical in 96% sulfuric acid with water.[5] Since conversion of perylene into the cation radical in 96% sulfuric acid is high,[5] the re-formation of perylene by dilution with water was, apparently, a chemical rather than physical reaction.

Cation radicals are frequently made in strong acid solutions. Chemical studies in such cases are almost impossible. Antimony pentachloride is also frequently used, both for spectroscopic, solution studies[4] and for precipitating cation radicals as antimony halide salts.[6] The composition of the perylene cation radical salt has been reported as $C_{20}H_{12}SbCl_5$, for example.[6] The use of antimony pentachloride systems for chemical studies, however, does not seem to be suitable. Complications are caused by the antimony halide, and, in reaction with nucleophiles, organoantimony compounds or complexes are formed.[7]

Recently, the perylene cation radical was prepared in the solid state by two methods which we have adapted fruitfully to chemical studies. Williams prepared a 1:1 complex of perylene and perylene perchlorate by anodic oxidation,[8] while Sato and coworkers[6] precipitated the perchlorate in admixture with silver iodide by treating perylene with iodine and silver perchlorate. We have already shown that the cation radical isolable by each of these methods can be used

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[1] Part XXII: J. J. Silber and H. J. Shine, *J. Org. Chem.*, **36**, 2923 (1971).

[2] Supported by the National Science Foundation Grant No. GP-25989X.

[3] Postdoctoral fellow.

[4] I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

[5] W. I. J. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, 3049 (1959).

[6] Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, *Bull. Chem. Soc. Jap.*, **42**, 3051 (1969).

[7] Unpublished work in these laboratories by T. Okuyama.

[8] D. F. Williams, Abstracts, Fourth Molecular Crystal Symposium, Enschede, Holland, July 1968. We thank Dr. Williams for further details by private communications. T. C. Chiang, A. H. Reddoch, and D. F. Williams, *J. Chem. Phys.*, **54**, 2051 (1971).

for a convenient, new preparation of 3-nitroperylene.[9] We now report a number of other studies.

Results

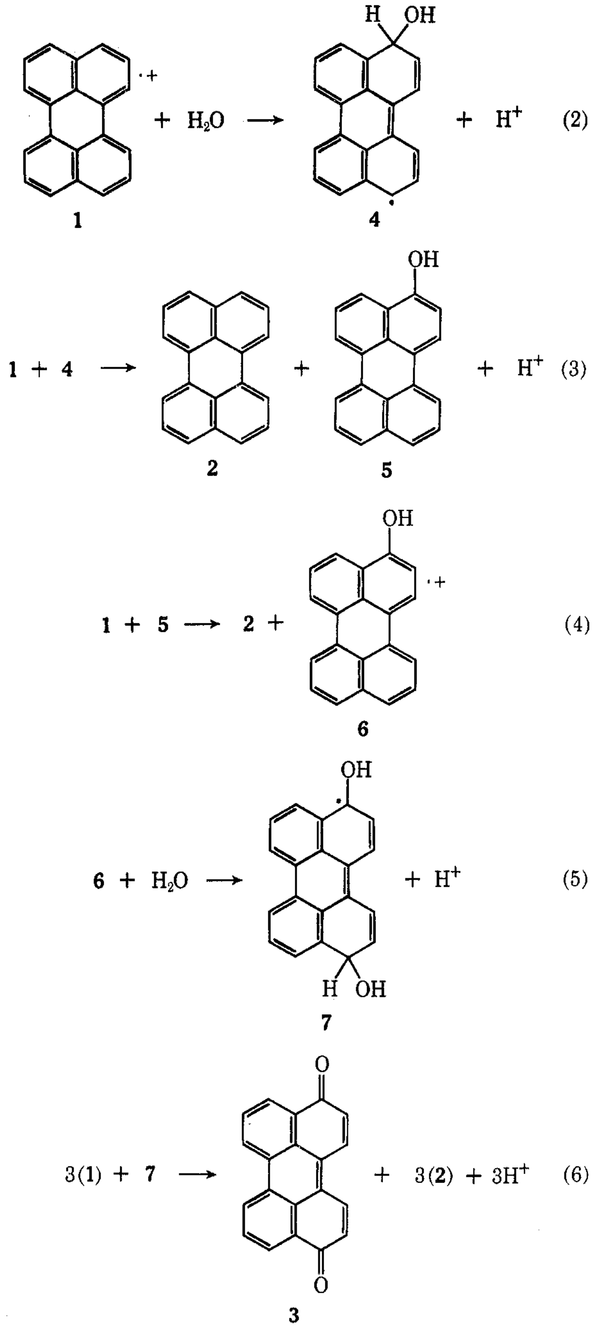
Electrochemical Preparation.—We have not been able to grow large, well-defined crystals of perylene–perylene perchlorate complex.[8] In our hands, anodic oxidation of perylene gave deposits of small crystals containing both perylene and its cation radical perchlorate, but in varying proportions. Both elemental and iodimetric analysis showed the cation-radical content to be between 60–70%. A 1:1 complex requires 58% by weight. Repeated washing of the solid mixture removed perylene. Attempts to remove all of the perylene only resulted in eventual decomposition of the cation radical. In spite of its composition, the electrochemically prepared product was easily usable for chemical studies. In most reactions of the perylene cation radical perylene itself is one of the products. Therefore, in using the electrochemical preparation for quantitative chemical studies it is necessary to know its perylene content. We have found that iodimetric analysis is very easy and reliable. Electron transfer between the cation radical and iodide ion is quantitative, and potentiometric titration of the iodine gives a quick assay of cation-radical content.

Chemical Preparation with Iodine–Silver Perchlorate.—By mixing a concentrated solution of perylene and silver perchlorate with one of iodine a well-dispersed mixture of silver iodide and cation radical perchlorate precipitates.[6] The solid mixture is easily analyzed iodimetrically, and has been found to contain at least 95% of the required cation radical perchlorate. This method of preparing cation-radical salts has also been used for heterocyclic and amino compounds by Ledwith,[10] who was able to extract the cation radical with solvent. We have found that perylene cation radical perchlorate can be extracted from admixture with silver iodide, but losses occur because of the impossibility of having perfectly dry solvents. Instead of extracting the cation radical for later use we have found that the mixed solids can be used for many preparative chemical reactions. We have also found that in some cases reaction of the cation radical can be achieved in one step by mixing a solution of perylene, silver perchlorate, and reactant with a solution of iodine. Reaction with nitrite ion is a case in point, and in that we have also achieved reaction by using only perylene, silver nitrite, and iodine.[9]

Reaction with Water.—Reactions of cation radicals with water are not well documented and are still not well understood. It has been thought in some instances that one-electron exchange occurred.[11,12] More recently, the water molecule has been represented as a nucleophile attacking a cationic rather than a radical center, but there is no general agreement on mechanistic details. Reaction of water with thianthrene cation radical is second order in cation radical, and has been interpreted as involving the thianthrene dication rather than the cation radical directly.[13] The role of the dication in this reaction has also been examined electrochemically.[14,15] Reaction of the 9,10-diphenylanthracene cation radical is first order in cation radical and has been interpreted as occurring by direct attack of water on the cationic 9 position of the cation radical.[16]

$$\underset{1}{6\mathrm{C_{20}H_{12}}\cdot^{+}} + 2\mathrm{H_2O} \longrightarrow \underset{2}{5\mathrm{C_{20}H_{12}}} + \underset{3}{\mathrm{C_{20}H_{10}O_2}} + 6\mathrm{H^{+}} \qquad (1)$$

SCHEME I



Several other examples of *in situ* reaction of water with a cation radical formed at an anode have been interpreted analogously as ECE reactions.[17]

No detailed chemical study of the reaction of a hydrocarbon cation radical with water has been reported.

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[9] C. V. Ristagno and H. J. Shine, *J. Amer. Chem. Soc.*, **93**, 1811 (1971).

[10] F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. B*, 2719 (1969).

[11] G. Cauquis, *Bull. Soc. Chim. Fr.*, 1618 (1968).

[12] H. J. Shine and L. Piette, *J. Amer. Chem. Soc.*, **84**, 4798 (1962).

[13] Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969).

[14] V. D. Parker and L. Eberson, *J. Amer. Chem. Soc.*, **92**, 7488 (1970).

[15] L. S. Marcoux, personal communication.

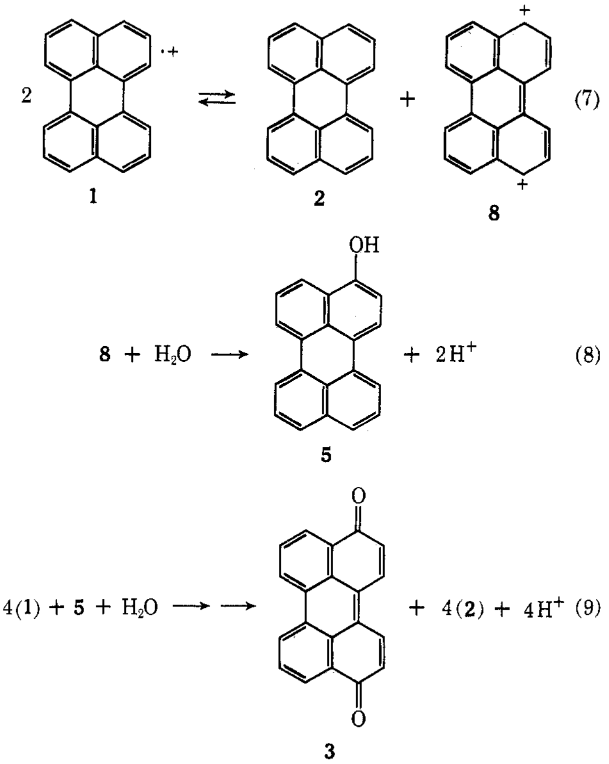
[16] R. Sioda, *J. Phys. Chem.*, **72**, 2322 (1968).

[17] (a) L. Jeftic and R. N. Adams, *J. Amer. Chem. Soc.*, **92**, 1332 (1970); (b) E. J. Majeski, J. D. Stuart, and W. E. Ohnesorge, *ibid.*, **90**, 633 (1968).

Anodic oxidation studies ordinarily rely on electrochemical data without isolation of products. Sioda isolated one of the products (9,10-dihydroxy-9,10-diphenylanthracene) but not the other (the original hydrocarbon).[16] In our present work we have isolated the final products quantitatively and can write the overall stoichiometry for the reaction of the perylene cation radical (**1**) with water (eq 1). We have not attempted kinetic work yet. According to eq 1, 82 mol % of cation radical reverts to perylene (**2**). It is not surprising, therefore, that perylene was recovered by previous workers.[5] The only other product obtained by us was 3,10-perylenequinone (**3**). Our results with electrochemically prepared cation radical gave 91% of the perylene and 86% of the quinone required by eq **1**. Analogous results with the silver iodide mixture were 87 and 70%.

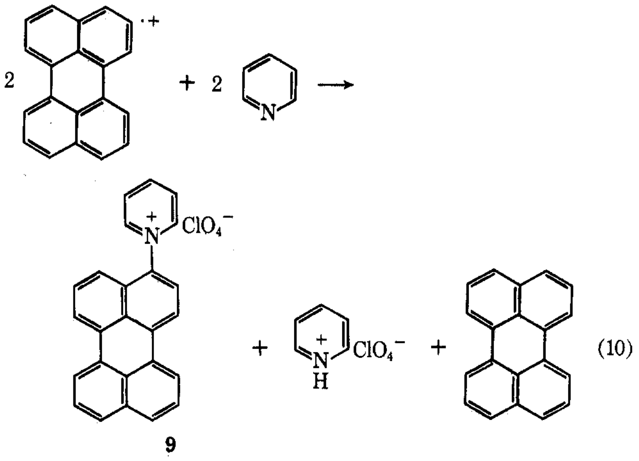
It is possible to explain the results in two ways (Schemes I and II), and a distinction cannot be made until, possibly, kinetic data for the series of reactions are obtained. Each of these schemes has 3-hydroxyperylene (**5**) as an intermediate. We have written the schemes in this way rather than having the initial formation of 3,10-dihydroxyperylene (or 3,10-dihydro-3,10-dihydroxyperylene) on the basis of our work with **1** and pyridine. Only one pyridine unit is introduced into the perylene nucleus (see later) in a very rapid reaction. It does not seem reasonable that, in contrast, reaction with water, a poorer nucleophile, would go directly to the dihydroxy compound.

SCHEME II



In Scheme I, attack of water (eq 2) occurs at the position in the cation radical which simple HMO calculations[18] show as having the highest positive charge density. It is to be expected that 3-hydroxyperylene would be oxidized by the perylene cation radical (eq 4), and under our experimental conditions, therefore, would not survive. The possibilities that 3-hydroxyperylene is further oxidized by air to the quinone, or that either 3,10-dihydroxyperylene or 3,10-dihydro-3,10-dihydroxyperylene are formed and similarly oxidized do not seem to be serious, since our quantities of isolated perylene would not fit large-scale incursions of those oxidation reactions.

Reaction with Pyridine.—Reaction of perylene cation radical with pyridine is fast and clean, and has the stoichiometry of eq 10. On the basis of this stoichiometry, reaction with the electrochemically prepared cation radical gave 92% of the required perylene and 87% of the required substitution product (**9**). Reaction with the silver iodide mixture gave 98% of the required perylene and 84% of **9**.



Compound **9** was identified by elemental analysis and by Zincke degradation to 3-aminoperylene.

The difference between the pyridine and water reactions is probably attributable to the difficulty one might expect of oxidizing **9**, which bears an electron-withdrawing group, as compared with oxidizing **5** (eq 4) which bears an electron-donating substituent. Rochlitz[19] has isolated monopyridinium substitution products from reaction of polynuclear aromatic hydrocarbons with iodine and pyridine, while Lund obtained 9,10-dihydroanthracenyldipyridinium diperchlorate from anthracene.[20]

Reaction with Acetate and Benzoate Ions.—The reactions of perylene cation radical with sodium acetate and sodium benzoate are fast and give relatively low yields of the corresponding esters. Reaction of the cation radical with sodium acetate and sodium benzoate gave 26 and 33% of the corresponding 3-perylenyl esters, **10** and **11**, and 105 and 113% of perylene based on the stoichiometry in eq 11. It is believed that the relatively low yields of the esters can be attributed in part to hydrolysis in the presence of the perchloric acid which is generated. The hydrolysis product, 3-hydroxyperylene, was not identified positively, but is thought, from spectroscopic evidence, to have comprised one of the fractions removed from the chromatography col-

$$2C_{20}H_{12}\cdot^{+} + RCO_2^{-} \longrightarrow \underset{\substack{\mathbf{10},\ R = Me \\ \mathbf{11},\ R = C_6H_5}}{C_{20}H_{11}O_2CR} + C_{20}H_{12} + H^{+} \qquad (11)$$

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[18] C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press, New York, N. Y., 1965.

[19] J. Rochlitz, *Tetrahedron*, **23**, 3043 (1967).

[20] H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

umn. Some 3,10-perylenequinone was formed also, and this might account for the high yield of perylene (see stoichiometry for the formation of the quinone by reaction of $P\cdot^{+}ClO_4^{-}$ with water). The acetate and benzoate esters are rapidly hydrolyzed by base.

Electron Exchange Reactions.—Perylene cation radical is reduced quantitatively by iodide ion. The reaction is a good way of assaying cation-radical purity. Reduction by bromide ion also occurs. Anodic bromination of anthracene has been reported by Millington.[21] We had thought that reaction between perylene cation radical and bromide ion might give 3-bromoperylene, but none could be detected by tlc. Bromine formed in reaction was determined iodimetrically. The quantities of perylene and bromine formed (eq 12, X =

$$2C_{20}H_{12}\cdot^{+} + 2X^{-} \longrightarrow 2C_{20}H_{12} + X_2 \qquad (12)$$

Br) from both the electrochemical product and the silver iodide mixture gave results consistent with eq 12, that is, 92 and 84% of the anticipated perylene and 87 and 90% of the bromine.

The facts that the color of both preparations of cation radical was discharged by addition of bromide ion and both preparations gave similar analytical results establish reliability in the results. It is possible with the use of the silver iodide mixture and a nucleophile X^- that, if the solubility product of AgX were significantly smaller than or comparable with that of AgI ($K_{sp} = 8.5 \times 10^{-17}$), exchange between X^- and I^- may occur. In that case reduction of cation radical by iodide ion would follow. This does not seem to be the case when bromide ion (K_{sp} AgBr $= 5.0 \times 10^{-13}$) is used. Reaction between chloride ion (K_{sp} AgCl $= 1.7 \times 10^{-10}$) and the silver iodide mixture led to 84% of the anticipated perylene and 90% of the anticipated halogen (eq 11), while the electrochemically produced cation radical gave 95% of the anticipated perylene and 84% of the anticipated halogen.

Reaction with cyanide ion remains unsettled. Use of potassium cyanide with the silver iodide mixture was accompanied by almost total reduction of the cation radical to perylene. Use of electrochemical product, however, gave a mixture of perylene and a green, fluorescent compound which has not as yet been characterized. It appears that the use of the silver iodide mixture and cyanide may lead to halide exchange (K_{sp} AgCN $= 1.6 \times 10^{-14}$) through the complex $Ag(CN)_2^-$.

It is recognized, of course, that data on solubility products and complex formation relate to aqueous solutions and may have limited validity in the reactions we have examined.

Reaction with fluoride ion failed to occur. We had hoped that since electron transfer was not to be expected, nucleophilic substitution by fluoride ion would occur. However in none of the many attempts with various fluorides was an organic fluoride formed. The only products isolated were perylene and its 3,10-quinone, and these are presumed to have been formed from slow reaction with small amounts of water remaining in the reactants or finding ingress from the atmosphere. We conclude that fluoride ion is too weakly nucleophilic to react with perylene cation radical.

Summary

Perylene cation radical reacts with certain nucleophiles at the 3 position. Other nucleophiles, *e.g.*, iodide and bromide ion, usually acknowledged as "good" nucleophiles do not attack at carbon but donate an electron to perylene cation radical. Earlier work showed that pyrene cation radical is "nitrated" by nitrite ion in the 1 position.[9] The overall picture is that a cation radical will undergo nucleophilic substitution at the position of highest positive charge density provided that the nucleophile is itself not easily oxidized by the cation radical. Thus, in their reactions with cation radicals, nucleophiles are controlled by their nucleophilicity and oxidation potentials. It is hoped that further work will bring out the relationships more quantitatively.

Experimental Section

Perylene was purified by chromatography on an alumina column followed by crystallization from benzene. Tetrahydrofuran (THF) was dried by distilling over lithium aluminum hydride.

Electrochemical Preparations.—Controlled potential oxidations were performed with a Princeton Applied Research Electrochemistry System, Model 170. An H cell with compartments separated by a fritted glass disk, and with a platinum gauze anode and a copper wire cathode, was used. In a typical procedure about 25 ml of THF containing 1.2 g of dried tetrabutylammonium perchlorate (TBAP) (an approximately 0.2 *M* solution) was placed in each compartment of the cell. Perylene was then added to the anode compartment to saturate the solution. Electrolysis was carried out at 1.25 V (*vs.* sce) while the anolyte was stirred continuously magnetically. A black solid began depositing on the anode as soon as electrolysis was begun. Electrolysis was interrupted at 15-min intervals and the anode deposit was carefully scraped off. Perylene was added to the anode compartment at each interval. In this way it was possible to collect quantities of deposit of the order of 1 g in 5 hr. The deposit was washed with 10-ml portions of THF and dried under vacuum. Washing removed perylene from the deposit, but perylene removal was never complete. Attempts to completely extract perylene ended only in slow decomposition of the cation radical salt. As a typical example, 563 mg of deposit was washed with ten 10-ml portions of THF, leaving 475 mg of solid.

Anal. Calcd for $C_{20}H_{12}ClO_4$: C, 68.2; H, 3.41; Cl, 10.10. Found: C, 70.15; H, 4.36; Cl, 7.10.

Analysis indicated that the composition of the solid was 70% $C_{20}H_{12}ClO_4$ and 30% $C_{20}H_{12}$. This was confirmed by potentiometric iodimetric titration, as follows. A solution of the solid in 100 ml of dry acetonitrile was deaerated by nitrogen bubbling for 5 min. Addition of 100 mg of tetrabutylammonium iodide immediately discharged the purple color of the ion radical. The yellow iodine solution was titrated potentiometrically with thiosulfate, using the PAR instrument. Two analyses, beginning with 55 and 57 mg of solid, respectively, showed the solid to contain 68 and 71% of its weight as cation radical perchlorate. In the latter case perylene was extracted from the solution with benzene after titration was complete. The perylene was placed on a silica gel column and eluted with benzene, a solvent capable of separating perylene and its 3,10-quinone. The amount of perylene recovered was 41 mg. If the electrochemical solid was a mixture of 70% cation radical perchlorate and 30% perylene, the amount of perylene anticipated after reduction with iodide ion is 45.8 mg. Stripping of the silica gel column with benzene–methanol (3:1) gave a solution whose visible spectrum indicated the presence of some perylene-3,10-quinone (**3**).

Chemical Preparation ($P\cdot^{+}ClO_4^{-}$, AgI).—To a solution of 504 mg of perylene in a minimum of dry methylene chloride was added a solution of 414 mg of dry silver perchlorate in a minimum of acetonitrile. To this mixture was added a solution of 203 mg of iodine in a minimum of methylene chloride. All operations were carried out under nitrogen to exclude moisture. A dark precipitate formed immediately. After stirring for 3 min the mixture was filtered and dried under vacuum, giving 912 mg

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[21] J. P. Millington, *J. Chem. Soc. B*, 982 (1969).

(97%) of $P\cdot^+ClO_4^-$, AgI. Potentiometric iodimetry showed the solid to contain 95% of the required amount of $P\cdot^+ClO_4^-$.

Reaction with Water. A. Electrochemical Product.—To 75 mg of solid product was added 150 ml of acetonitrile containing 0.1 ml of water. The mixture was stirred under a nitrogen bubbler for 7 hr. Five grams of silica gel was added and the solvent was evaporated. The silica gel was placed on the top of a column of silica gel for chromatography. Perylene was removed with benzene, and the column was next eluted with benzene–methanol (3:1). Evaporation of the benzene solutions gave 51 mg (96%) of solid, found to be perylene by ultraviolet and visible spectroscopy. Evaporation of the benzene–methanol solution gave 6 mg (86%) of solid identified by visible spectrum as perylene-3,10-quinone. On the basis that the electrochemical product was 70% cation radical perchlorate and 30% perylene, the anticipated products from reaction with water are 53 mg of perylene and 7 mg of quinone (see discussion for stoichiometry).

B. $P\cdot^+ClO_4^-$, AgI.—A suspension of 151 mg of solid in 60 ml of acetonitrile containing 0.5 ml of water was stirred for 3 hr under nitrogen. Filtration gave 44 mg (73%) of silver iodide. The acetonitrile was evaporated and the residue was chromatographed on alumina, using benzene to remove perylene, and 3:1 benzene–methanol to remove the 3,10-quinone. Isolation of solutes gave 47 mg (87%) of perylene and 8.5 mg (70%) of the quinone.

Reaction with Pyridine. A. Electrochemical Product.—A solution of 0.1 ml of pyridine in 150 ml of acetonitrile was added to 75 mg of electrochemical product under nitrogen. The reaction mixture turned yellow immediately. After 30 min of stirring, the solvent was pumped off and the residue was extracted with 50 ml of hot benzene. Evaporation of the benzene gave 38 mg (92%) of perylene, identified and assayed by its absorption spectrum. The benzene-insoluble portion was 39 mg of yellow solid. This was washed with 100 ml of water to remove pyridinium perchlorate, leaving 28 mg (87%) of yellow-brown solid, which was identified as *N*-(3-perylenyl)pyridinium perchlorate (**9**) as described later.

On the basis that the electrochemical product contained only 52.5 mg (70%) of cation radical perchlorate, reaction with pyridine should have given 32.2 mg of *N*-(3-perylenyl)pyridinium perchlorate and a total of 41.4 mg of perylene.

B. $P\cdot^+ClO_4^-$, AgI.—A solution of 0.1 ml of pyridine in 100 ml of acetonitrile was added to 123 mg of the mixture of salts. After stirring, a yellow solution and a yellow precipitate (silver iodide) were obtained. Filtration gave 48.7 mg (99%) of silver iodide. Evaporation of the acetonitrile solution and benzene extraction gave 30 mg of benzene-soluble and 59 mg of benzene-insoluble material. Chromatography of the benzene-soluble solid on silica gel column gave 26 mg (98%) of perylene.

C. By Direct, Iodine–Silver Ion Initiated Reaction.—To a mixture of 300 mg (1.2 mmol) of perylene, 606 mg (2.4 mmol) of iodine, and 1.0 g (4.8 mmol) of silver perchlorate in 200 ml of acetonitrile was added 2 ml (26 mmol) of pyridine. The mixture turned yellow immediately. Work-up as above gave 125 mg (32%) of *N*-(3-perylenyl)pyridinium perchlorate (**9**). A sample of **9** was crystallized from benzene–methanol: mp 309° dec; λ_{max} (methanol) 442, 419, 400 (s), 252, 247 nm (s).

Anal. Calcd for $C_{25}H_{16}ClNO_4$: C, 70.0; H, 3.73; N, 3.26; Cl, 8.25. Found: C, 70.1; H, 4.24; N, 3.22; Cl, 7.73.

Degradation of 50 mg (0.12 mmol) of **9** to 3-aminoperylene was carried out by Zincke's method.[22] The organic product was extracted with benzene and chromatographed on silica gel with 50:50 benzene–ether as eluent, giving 8 mg (26%) of 3-aminoperylene, mp 218° dec, shown to be identical with an authentic sample.

3-Aminoperylene.—3-Nitroperylene was prepared by the reaction of perylene cation radical with nitrite ion,[9] and reduced with hydrazine and a palladium/charcoal catalyst,[23] mp 222° dec (lit. mp 220–230° dec.)[23]

Reaction with Sodium Acetate.—A solution of 328 mg (4 mmol) of sodium acetate in 100 ml of acetonitrile was deaerated by nitrogen bubbler. To this was added 401 mg (0.68 mmol) of $P\cdot^+ClO_4^-$, AgI. Immediately the reaction mixture turned yellow. The mixture was stirred for 15 min under nitrogen, filtered, and chromatographed on silica gel. Perylene was removed with benzene–petroleum ether (1:1) and the blue-fluorescent ester was removed with benzene. Evaporation of the benzene–petroleum ether fraction gave 111 mg (105%) of perylene. Evaporation of the benzene solution gave 22 mg (26%) of a bright yellow solid, mp 182–187°, which was identified as 3-perylenyl acetate (**10**). A sample was recrystallized from ethanol: mp 193–194°; λ_{max} (methanol) 438, 412, 390 (s), 253, 246 nm.

Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.16; H, 4.52. Found: C, 84.92; H, 4.41

The ester bands on the column were followed by a small yellow band having a strong green fluorescence. This was eluted and had ultraviolet and visible spectra identical with those attributed to 3-hydroxyperylene (see below). Continued elution with benzene–methanol (3:1) gave some 3,10-perylenequinone.

Reaction with Sodium Benzoate.—A mixture of 331 mg (0.56 mmol) of $P\cdot^+ClO_4^-$, AgI, and sodium benzoate was treated as described above; 80 mg (113%) of perylene and 34 mg (33%) of 3-perylenyl benzoate (**11**) were obtained. A sample of the benzoate was recrystallized from ethanol: mp 209–210°; λ_{max} (methanol) 439, 412, 391 (s), 253, 247 nm.

Anal. Calcd for $C_{27}H_{16}O_2$: C, 87.09; H, 4.30. Found: C, 86.89; H, 4.14.

Treatment of either **10** or **11** with 5% sodium hydroxide in methanol caused a rapid change in the ultraviolet spectrum resulting, we believe, from hydrolysis to the anion of 3-hydroxyperylene, λ_{max} (methanol) 488, 345, 330, 300 (s), 270 (s), 264 nm. Acidification of the basic solution gave, we believe, 3-hydroxyperylene, λ_{max} (methanol) 448, 426, 258, 252 nm (s).

Reaction with Bromide Ion. A. Electrochemical Product.—The electrochemical product was found to be 60% cation radical perchlorate by iodimetry. Of this, 49.8 mg in 50 ml of acetonitrile was deaerated by nitrogen bubbler and capped with a serum cap. A solution of 100 mg of tetrabutylammonium bromide in acetonitrile was injected. The solution turned yellow. After 5 min a solution of tetrabutylammonium iodide in acetonitrile was injected. The yellow-orange solution was removed for potentiometric titration with thiosulfate, and found to contain 87% of theoretical iodine. The titrated solution was extracted with benzene and gave 38 mg (92%) of perylene. Based on electron exchange between bromide ion and 29.9 mg of cation radical perchlorate (60% of the solid used), the expected yield of perylene was 41.4 mg.

B. With $P\cdot^+ClO_4^-$, AgI.—A sample of 109 mg of salt was treated as above. Titration gave 90% of theoretical iodine. Extraction gave 39 mg (84%) of perylene.

Reaction with Chloride Ion. A. Electrochemical Product.—The electrochemical product was found to be 63% cation radical perchlorate by iodimetry; 75 mg of the cation radical salt and 144 mg of tetrabutylammonium chloride were placed in a one-neck, 100-ml round-bottom flask under nitrogen and sealed with a serum cap; and 40 ml of CH_3CN was injected. The solution turned yellow. After 5 min a solution of tetrabutylammonium iodide in acetonitrile was injected. The solution turned yellow-orange. The solution was removed for potentiometric titration with thiosulfate and found to contain 84% of theoretical iodine. The titrated solution was extracted with benzene and chromatographed on silica gel to give 58 mg (95%) of perylene.

B. With $P\cdot^+ClO_4^-$, AgI.—A sample of 103 mg of salt was treated as above. Titration gave 90% of theoretical iodine. Extraction gave 37 mg (84%) of perylene.

Attempted Reaction with Fluoride Ion.—$P\cdot^+ClO_4^-$, AgI was used in all attempts. The cation radical salt was added to the fluoride salt, which was either dissolved or suspended in acetonitrile. The mixture was stirred under nitrogen until the color of the cation radical either disappeared or failed to disappear over a period of 36 hr. In the latter case reaction was presumed not to have occurred. When hydrogen fluoride was used at room temperature the gas was bubbled through the acetonitrile solution. Liquid hydrogen fluoride was used at 0°. A reaction mixture was worked up by first evaporating the solution and next chromatographing on a column of silica gel, using benzene and 3:1 benzene–methanol for elution as described earlier. These solvents were chosen for separating perylene and its 3,10-quinone when considerable exploratory work showed that these two compounds were the only ones formed. In no case was any evidence found by tlc for the presence of any other compound than these two. Further search for the presence of an organic fluoride was made by subjecting each organic fraction isolated from the silica gel column to sodium fusion and the zirconium–alizarin

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[22] T. Zincke, *Justus Liebigs Ann. Chem.*, **330**, 361 (1903); **333**, 296 (1904).

[23] M. J. Dewar and T. Mole, *J. Chem. Soc.*, 1441 (1956).

test for fluoride ion.[24] This method was successful when applied to small amounts of 1-fluoronaphthalene. All of the isolated organic fractions failed to show the presence of a fluoride.

Perylene and its 3,10-quinone were isolated from attempted reaction with AgF (97%, 46%); AgF, HF (gas) (90%, 47%); and KF (97%, 50%). The figures in parentheses refer to products formed in reaction with unremoved water according to the stoichiometry of eq 1. The use of HF (gas), KF, HF (gas), KF, HF (liquid), and $(n\text{-}C_4H_9)_4NF$ failed to discharge the color of the cation radical during a 36-hr period.

Iodimetric Assay.—In a typical iodimetric analysis, 124.8 mg of $P\cdot^{+}ClO_4$, AgI (2.13×10^{-4} equiv) was placed in 150 ml of deaerated, dry acetonitrile and 200 mg (5.42×10^{-4} equiv) of tetra-*n*-butylammonium iodide was added. The purple reaction mixture *immediately* turned yellow. The reaction mixture was then titrated potentiometrically using a 0.0566 *N* sodium thiosulfate solution. An end point corresponding to 2.13×10^{-4} equiv of I_2 was obtained. The titrated solution was then poured into water and extracted with benzene. The benzene extract was chromatographed on silica gel giving 48 mg of perylene (89.6% of theory).

Registry No. 1, 12576-62-4; 1 perchlorate, 12576-63-5: **9**, 32174-97-3; **10**, 32174-98-4; **11**, 32174-99-5.

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(24) A. I. Vogel, "Practical Organic Chemistry," Wiley, New York, N. Y., 1956, p 1043.

Electrophilic and Homolytic Cleavage of 5-Aryl-5*H*-dibenziodoles[1]

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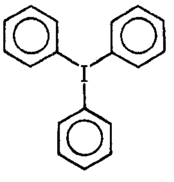
The organometallic character of triaryliodine compounds has been demonstrated by the reactivity of 5-phenyl-5*H*-dibenziodole toward water, protonic acids, and Lewis acids. Cleavage of 5-phenyl-5*H*-dibenziodole by electrophilic reagents is rapid and gives both cyclic dibenziodolium and acyclic 2-biphenylylphenyliodonium salts. The product ratio was found to be dependent on the electrophile used. Thermal decomposition and rearrangement of 5-phenyl-5*H*-dibenziodole have also been studied. A free-radical mechanism is suggested to account for the complexity of the products in the presence of alkyl and acyl halides. In contract, heating in hexane gives 2-iodo-*o*-terphenyl in good yield and suggests a molecular rearrangement. Various new 5*H*-dibenziodoles have been prepared with aryl groups attached to iodine: *p*-tolyl, *m*- and *p*-chlorophenyl, and 1-naphthyl. Cleavage of these species with ethereal hydrogen chloride has also been studied.

Since the first isolation of triphenyliodine (**1**) by Wittig[2] in 1952, little work has been reported on the relatively unstable triorganoiodine compounds. In 1955, Clauss[3] prepared from dibenziodolium iodide and phenyllithium the first triaryliodine, 5-phenyl-5*H*-dibenziodole (**2**) that is stable at room temperature.



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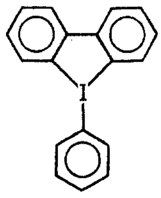
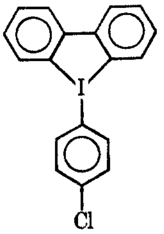


2

Using the method of Clauss, we have successfully prepared three previously unknown 5-aryl-5*H*-dibenziodoles, *i.e.*, 5-(*p*-chlorophenyl)-5*H*-dibenziodole (**3**), 5-(*p*-tolyl)-5*H*-dibenziodole (**4**), and 5-(1-naphthyl)-5*H*-dibenziodole (**5**), in 75–85% yield. Attempts to isolate 5-(*m*-chlorophenyl)-5*H*-dibenziodole (**6**) from the reaction mixture of dibenziodolium chloride and *m*-chlorophenyllithium solution were unsuccessful because of its high solubility in the reaction medium. Therefore, **6** was often used immediately without isolation for further reaction. 5-Phenyl-5*H*-dibenziodole was also successfully prepared by the present authors from dibenziodolium chloride and phenylmagnesium bromide in 90% yield.



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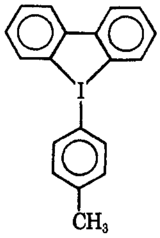

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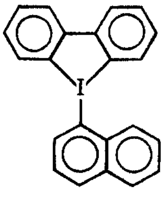

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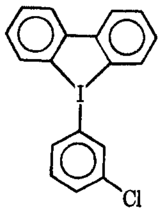

6

Thermal Decomposition and Rearrangement.—It has been long known that trisubstituted organoiodine compounds on heating decompose homolytically to complex products.[4–6] When a suspension of 5-phenyl-5*H*-dibenziodole (**2**) in hexane was decomposed gradually at room temperature, the products were benzene, iodobenzene, biphenyl, 2-iodobiphenyl, and 2,2′-diiodobiphenyl, all in 10–15% yield, and 2-iodo-*o*-terphenyl in about 10% yield. At higher temperature (refluxing hexane), 2-iodo-*o*-terphenyl was formed as the major product (*ca.* 80%). Adapting the radical mechanism proposed previously[4,5] for the thermal cleavage of Ph_2IR[6] and Ph_2ISR, one can envision free-radical sequences initiated by homolysis to account for the complexity of the products from **2**. Path L, in-

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(1) (a) Taken from the dissertation of L. L. Chang submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry), 1971. (b) Supported by National Institutes of Health, 1968–1969, through Grant No. 5-SO5-FR-07063-04.

(2) G. Wittig and K. Clauss, *Justus Liebigs Ann. Chem.*, **578**, 136 (1952).

(3) K. Clauss, *Chem. Ber.*, **88**, 268 (1955).

(4) F. M. Beringer, J. W. Dehn, Jr., and M. Winicov, *J. Amer. Chem. Soc.*, **82**, 2948 (1960).

(5) J. W. Greidanus, W. J. Rebel, and R. B. Sandin, *ibid.*, **84**, 1504 (1962).

(6) M. C. Caserio, D. L. Glusker, and J. D. Roberts, *ibid.*, **81**, 336 (1959).