by conversion to homoisocarbacyclin.[12] It should be mentioned that these results are in full accord with MM2 calculations[13] (Scheme II, Table I).

Encouraged by this excellent result, we then turned our attention to the stereocontrolled construction of trans angularly methylated hydrindans, which are known to be very important as steroidal intermediates. Bromo esters **13a** and **13b** were efficiently prepared as shown in Scheme II.[18] MM2 calculations show that *trans*-hydrindans **14a** and **14b** would be produced under the thermodynamically controlled conditions (*trans*-**14a′** (R^3 = H, R^4 = $OSiMe_3$) and **14b′** (R^3 = $OSiMe_3$, R^4 = H) are 1.3 and 0.7 kcal/mol more stable than the cis isomers, respectively). As expected, treatment of **13a** (*E*:*Z* = 1:7) with Bu_3SnH in toluene (4.0×10^{-3} M) at −30 °C for 1.5 h produced the desired *trans*-hydrindan **14a** stereoselectively (87%, trans:cis = 95:5),[19] a potential intermediate for various steroids such as adrenosterone, together with the reduced product (<8%) and the 5-*exo* cyclized product (<2%) (run 6, Table I). The previous reaction when carried out at −70 °C and at much higher concentration (2.0×10^{-1} M) gave the same three cyclization products (6-endo-trans, 6-endo-cis, and 5-exo) in a similar ratio (run 7, Table I).[20] This result appears to indicate that the alkenyl radical produces the hydrindan radical directly owing to steric factors. The stereochemistry of *trans*-**14a** and *cis*-**14a** was unequivocally determined by conversion to the known diketone **15** in six steps (i. Pd/C, H_2, ii. LDA, O_2, iii. $LiAlH_4$, iv. $NaIO_4$, v. TBAF, vi. PCC-MS4A, 26% overall yield).[1a] On the other hand, exposure of **13b** (*E*:*Z* = 1:4) to Bu_3SnH at −30 °C (run 9, Table I) gave hydrindans **14b** with much lower stereoselectivity (trans:cis = 57:43), indicating that there is severe steric repulsion between the (*tert*-butyldimethylsilyl)oxy group and Bu_3SnH in the transition state **16**.[21]

In conclusion, a conceptually new synthetic route to *trans*-hydrindans has been developed by a novel type of radical cyclization. The present methodology should be useful for construction of other ring systems. In addition, it has been successfully demonstrated that MM2 calculations are useful for the design of radical cyclization substrates.

Supplementary Material Available: Experimental procedures for the preparation of compounds **7b**, **8b**, **12a**, **13a**, and **14a** (7 pages). Ordering information is given on any current masthead page.

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(19) Use of the syringe pump technique did not improve the result.

(20) In general, slightly lower stereoselectivity was obtained at lower reaction temperature. The reason is not clear at present.

(21) Although the reason is not clear at present, treatment of **13b** with Bu_3SnH at −60 °C produced **14b** in a trans–cis (30:70) ratio.

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The Photochemistry of Diphenyliodonium Halides: Evidence for Reactions from Solvent-Separated and Tight Ion Pairs

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Summary: Diphenyliodonium halides exist as tight ion pairs in acetonitrile, and photolysis gives almost exclusively iodobenzene by a homolytic cleavage reaction from a charge transfer excited state, whereas in aqueous acetonitrile the ion pairs are solvent separated and photolysis gives substantial amounts of 2-, 3-, and 4-iodobiphenyls, in addition to iodobenzene, by an initial heterolytic cleavage.

Onium salts have found important applications as photoinitiators for acid-catalyzed processes in polymers.[1] Recent mechanistic studies have found that onium salt photolysis produces acid by both in-cage recombination reactions and cage-escape reactions with solvent.[2-7] We have recently reported that direct photolysis of diaryliodonium salts produces 2-, 3-, and 4-iodobiphenyls, io-

Scheme I. Products from Photolysis of Diphenyliodonium Salts in Acetonitrile and Aqueous Acetonitrile

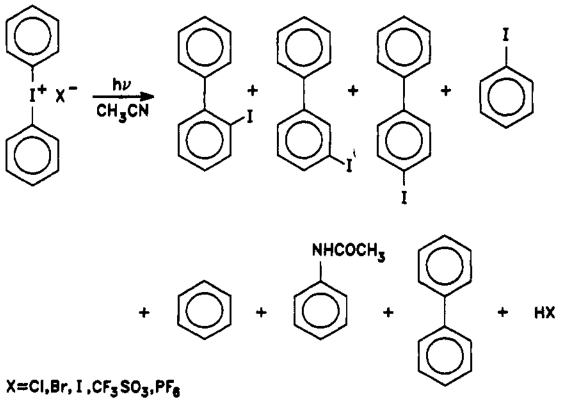

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Table I. Photoproduct Distribution from Irradiation of Diphenyliodonium Salts (Concentration × 10^5 M)

X	PhX	PhI	Ph-PhI	Ph-Ph	PhX/PhI	Ph-Ph/PhI	other products
				CH_3CN			
Cl	8.0	30.5	0.58	0.64	0.26	0.019	PhH, $ClCH_2CN$
Br	9.7	30.3	0.43	0.48	0.32	0.014	PhH, $BrCH_2CN$
I	-	44.5	0.90	0.74	-	0.021	PhH, ICH_2CN
CF_3SO_3	-	15.4	4.4	2.5	-	0.29	$PhNHCOCH_3$, PhH
PF_6	-	15.8	4.5	2.5	-	0.29	$PhNHCOCH_3$, PhH
				CH_3CN/25% H_2O			
Cl	0.54	14.6	4.3	1.7	0.037	0.29	$PhNHCOCH_3$, PhOH, PhH
Br	0.93	17.0	4.6	1.8	0.055	0.27	$PhNHCOCH_3$, PhOH, PhH
I	-	17.6	3.7	1.5	-	0.21	$PhNHCOCH_3$, PhOH, PhH
CF_3SO_3	-	16.5	5.7	1.7	-	0.35	$PhNHCOCH_3$, PhOH, PhH
PF_6	-	15.8	5.8	1.6	-	0.38	$PhNHCOCH_3$, PhOH, PhH

dobenzene, acetanilide, benzene, and acid by an initial heterolytic cleavage pathway (Scheme I).[7] The initially formed in-cage fragments from heterolysis of the excited state, phenyl cation and iodobenzene, can interconvert with the singlet and triplet phenyl radical–iodobenzene radical pairs and subsequent in-cage reactions of these intermediates give 2-, 3-, and 4-iodobiphenyls, whereas reaction of these intermediates with the solvent gives the escape products iodobenzene, acetanilide, and benzene. To date, all of the studies on the direct photolysis of onium salts in solution have found that the same products and product distribution are observed regardless of which anion is associated with the onium cation.[8] Here we report the photochemistry of diphenyliodonium halides and the first observation of a remarkable anion dependence on product formation in solution which shows strong evidence for reaction of tight ion pairs in organic solution and solvent separated ions in aqueous solutions.

Photolysis (λ = 245 nm) of 0.001 M diphenyliodonium chloride (1-Cl) in acetonitrile gave chlorobenzene, iodobenzene, biphenyl, and trace amounts (<1%) of 2-iodobiphenyl.[9] The detection of only traces of iodobiphenyl in acetonitrile stands in contrast to our previous studies on photolysis of 0.01 M solutions of 1-PF_6 and 1-CF_3SO_3, which give substantial quantities (up to 30%) of all three iodobiphenyl isomers.[7] The change in product distribution was not due to a dilution effect as 0.001 M solutions of 1-PF_6 and 1-CF_3SO_3, irradiated under identical conditions, gave essentially the same product distributions as those observed at higher concentrations, i.e. the ratio of iodobiphenyls:iodobenzene is 0.29 (Table I). The lack of iodobiphenyls was also observed from photolysis of the other diphenyliodonium halides 1-Br and 1-I. Table I also shows that substantial amounts of chlorobenzene and bromobenzene are formed from photolysis of 1-Cl and 1-Br. Chlorobenzene represents 26% and bromobenzene represents 32% of the iodobenzene formed, whereas bromobenzene represented only 9% of the diphenyl sulfide formed from triphenylsulfonium bromide photolysis.[2e] The observation of larger amounts of chlorobenzene and bromobenzene indicates efficient trapping of the initially formed phenyl fragment by halide in the solvent cage. In addition, the yield of iodobenzene is nearly 50% higher for 1-I than for 1-Cl and 1-Br, which suggests that a mechanism analogous to that for chlorobenzene and bromobenzene formation from 1-Cl and 1-Br, respectively, also forms iodobenzene from 1-I.

Photolyses of diphenyliodonium halides were usually run in aqueous acetonitrile; the water was added to improve the solubility of the salt.[4,5,7] In these studies the iodobiphenyl isomers were always significant products. To determine if the change in product distribution was due to a solvent effect, the 0.001 M solutions were irradiated in 25% aqueous acetonitrile under identical conditions to those used for the anhydrous solvent. In the aqueous solvent mixture, all three iodobiphenyl isomers are observed from all the iodonium halides studied. The ratio of iodobiphenyls:iodobenzene increases by more than 1 order of magnitude from 0.014–0.021:1 to 0.21–0.38:1 (Table I). Accompanying the increase in iodobiphenyl formation in the aqueous solvent mixture is a decrease in the formation of chlorobenzene and bromobenzene, also by more than 1 order of magnitude, from their respective iodonium salts.

It is well established that phenyl cation reacts with acetonitrile to give acetanilide and that phenyl radical reacts with solvent to give benzene, from photolysis of onium salts.[2,7] Thus analysis for acetanilide and benzene from photolysis of the iodonium salts should help determine the identity of the initially formed phenyl fragments. Actually detected from direct photolysis of the iodonium halides were chlorobenzene (bromobenzene), chloroacetonitrile (bromoacetonitrile, iodoacetonitrile), acetanilide, phenol, biphenyl, and iodobiphenyls (Table I). Acetanilide is not detected from photolysis of the iodonium halides in acetonitrile whereas benzene and halobenzene account for all of the initially formed phenyl moiety. In contrast the iodonium triflate photolysis gives a 50:50 mixture of acetanilide and benzene, along with 2-iodobiphenyl. However in aqueous acetonitrile photolysis of the iodonium halides and the triflate, gives the phenyl cation trapped products, acetanilide and phenol, in addition to benzene. In all cases where acetanilide and phenol (heterolysis products) are formed, the ratio of iodobiphenyl isomers:iodobenzene increases by 1 order of magnitude. Whereas when haloacetonitrile and benzene (homolysis products) are formed, only traces of iodobiphenyls are detected. These results indicate that the iodonium halides photodecompose exclusively via a radical process in nonaqueous solvent and can cleave by heterolysis in aqueous solvent, whereas photolysis of iodonium triflate and other salts proceeds mainly by heterolysis, and partially by homolysis, in both aqueous and nonaqueous solvents.

The photodecomposition of the iodonium halides in acetonitrile is remarkably efficient. The quantum yield of diphenyliodonium triflate at 248 nm is 0.54 in acetonitrile;[7] thus from the conversions in Table I, the quantum yields for the diphenyliodonium halides are estimated to be 0.8–1.0 in acetonitrile and decrease to about 0.5 in

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(9) Diphenyliodonium salt solutions (0.001 M) were irradiated in a Rayonet reactor. The quenched reaction mixtures were extracted with hexanes or dichloromethane containing *n*-tetradecane internal standard and the photoproducts were identified by GC retention times (see ref 7 for details).

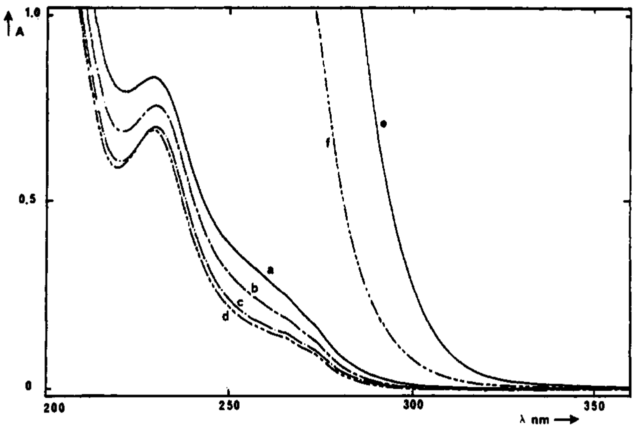
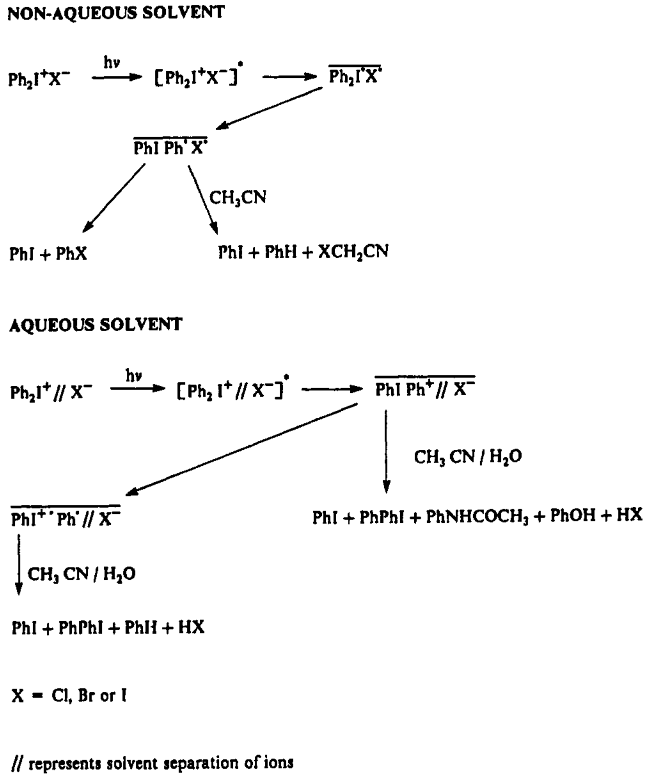


Figure 1. UV absorption spectra of diphenyliodonium chloride at 5 × 10^{-5} M in 0, 1, 5, and 25% aqueous acetonitrile (a–d) and at 5 × 10^{-4} M in 0 and 25% aqueous acetonitrile (e, f).

aqueous acetonitrile. These dramatic changes in product distribution and yield from photolysis of diphenyliodonium halides in acetonitrile and aqueous acetonitrile clearly demonstrates the difference in reactivity of a tight ion pair and solvent-separated ion pair. The diphenyliodonium halides are not very soluble in acetonitrile, likely due to the solvent being incapable of separating the ion pair. In contrast diphenyliodonium triflate and hexafluorophosphate are readily solubilized by acetonitrile. UV absorption spectra were measured for the aqueous and nonaqueous solutions. For the iodonium halides, the nonaqueous solutions exhibited UV absorption bands which were red-shifted from those observed in the aqueous solutions (e.g. Figure 1). This red shift may be due to a charge transfer absorption.[10] Indeed the UV absorption spectra of the 25% aqueous solutions of iodonium halides were similar to the spectra of other iodonium salts in anhydrous solvent. If the charge-transfer absorption is responsible for the photochemistry observed in the nonaqueous solutions, then the initial products would be diphenyliodine radical and halogen radical, which would decompose to the triad of iodobenzene, phenyl radical, and halogen radical. This differs from other iodonium salt photolyses where reactivity from both heterolytic and homolytic cleavage reactions are observed.[7] In addition to our results, recent picosecond flash photolysis experiments and conductance measurements on 1-PF_6 and 1-Cl in dichloromethane also show different reactivities from solvent separated and tight ion pairs.[11]

Scheme II. Mechanism for Product Formation from Photolysis of Diphenyliodonium Halides in Acetonitrile and Aqueous Acetonitrile



X = Cl, Br or I

// represents solvent separation of ions

The mechanism for product formation from diphenyliodonium halides in acetonitrile and aqueous acetonitrile is shown in Scheme II. In acetonitrile the tight ion pair of diphenyliodonium halide gives a charge-transfer excited state which decomposes via the diphenyliodine radical and halogen radical pair to give an in-cage triad of iodobenzene, phenyl radical, and halogen radical. The latter two intermediates can combine in the solvent cage to give halobenzene, whereas reaction with the solvent gives benzene and cyanomethyl radical which combines with halogen radical to yield haloacetonitrile. Abstraction of hydrogen from solvent by the halogen radical to generate cyanomethyl radical or dimerization of cyanomethyl radical does not occur, as benzylcyanide and succinonitrile are not detected among the photoproducts. In aqueous solutions, the diphenyliodonium halides are solvent separated and charge transfer is less favored. Thus photodecomposition occurs via initial heterolysis of the excited state as previously reported for other iodonium salts.

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4-Piperidinylimino: A Nearly Linear Head-to-Tail Linking Group for Dipolar Chromophores

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Summary: Linkage of the *p*-aminobenzaldimine and *p*-nitroaniline chromophores through a piperidine ring gives a compound whose dipole moment is almost exactly the sum of the moments of the constituent chromophores.

Oligomers consisting of head-to-tail-linked, dipolar, π-conjugated monomers are of interest as electrically

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