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Photochemical Reaction of Diaryliodonium Salts with Dimethylaniline

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Key Words: 4,4'-dimethyldiphenyl iodonium salt; N,N-dimethylaniline; 4,4'-methylenebis(N,N-dimethylaniline); crystal violet; methyl violet.

Abstract: *A solution of 4,4'-dimethyldiphenyl iodonium tetrafluoroborate and N,N-dimethylaniline in acetonitrile is irradiated by UV light to give iodotoluene, toluene, 4,4'-methylenebis(N,N-dimethylaniline), crystal violet, methyl violet.*

The photochemistry of diphenyliodonium salts in alcohol solution was studied originally by Knapczyk, Lubinkowski and McEwen,[2] and more recently, owing to the increased application of the onium salts as photoinitiators for acid-catalyzed reactions in polymer systems[3] by Dektar and Hacker.[4] Strong Lewis acid salts of diphenyliodonium form photolysis products not only by homolysis to phenyl radical and iodobenzene radical cation but also by heterolysis to phenyl cation and iodobenzene. The interconversion between the phenyl cation pair and the phenyl radical pair may also result from electron transfer.[4] Iodobenzene radical cation abstracts a hydrogen from donor to produce iodobenzene and a strong Lewis acid. The photochemistry of iodonium salts with more efficient hydrogen donors[5] has not been reported. Recently, it has been reported that a diphenyliodonium salt and an amine can be used as an effective photoinitiating system for radical polymerization.[6,7] We have found that N,N-dimethylaniline (DMA) is an efficient coinitiator for the cationic photopolymerization of epoxides in the visible region.[8] We report on the photoproducts derived from bis(4-methylphenyl)iodonium hexafluorophosphate(BMPI) and DMA.

An argon purged solution of BMPI and DMA (1:4) in acetonitrile was irradiated[9] for 6 hours. The solution first became ocean blue (λ_{max} 604nm) then brownish yellow; The same solution saturated with oxygen first became blue, then deep violet (λ_{max} 586nm). Both the irradiated argon purged and oxygen saturated solutions were extracted with hexane. Nine (9) products can be isolated and quantitated by GC using hexadecane as an internal standard. These are 1,4-iodotoluene, **2**, toluene **3**, N-methylaniline **4**, 4,4'-methylenebis(N,N-dimethylaniline) **5**, N,N,N'-trimethyl-4,4'-methylenebisaniline **6**, 4-(*p*-tolyl)-N,N-dimethylaniline **7**, 2-(*p*-tolyl)-N,N-dimethylaniline **8**, N-(*p*-methylbenzyl)-N-methylaniline **9** N-(*p*-dimethylaminobenzyl)-N-methylaniline, **10** crystal violet, and **11** methyl violet. All these are identified by GC-MS and structures confirmed by comparison of the retention times with authentic samples.The relative amounts of the products are listed in table 1. Two bands very close in color (λ_{max} 588nm) and (λ_{max} 582nm) can be isolated by TLC [Alumina; DME:chloroform (70:30]. These are identified as crystal violet **10**(61 parts) and methyl violet **11**(39 parts).[10]

There is no evidence of complexation of BMPI and DMA in the ground state. Unlike the diphenyliodonium chloride/triethylamine system in acetonitrile[11] in which a new absorption band is formed at longer wavelength and diphenyliodonium tetrafluoroborate/aniline system in acetone[12] in which a yellow color is formed, the composite absorption spectrum of BMPI and DMA is exactly same as the spectrum of their solution up to 4×10^{-4}M. BMPI does quench the fluorescence of DMA, with a quenching constant $4.0\text{x}10^{10}$ $M^{-1}S^{-1}$.[13] This is close to the diffusion controlled quenching constant $2.9\text{x}10^{10}$ $M^{-1}S^{-1}$[14], and does not indicate the complex formation.

Table 1

Photoreaction Products from BMPI and Dimethylanaline

	A,a	A,b	B,a	B,b	B,a,c
1,4-iodotoluene [x 10^{-3}]	3.0	4.2	1.9	3.5	1.8
2, toluene [x 10^{-3}]	3.8	0.6	4.7	0.7	4.6
3,N-methylaniline [x 10^{-4}]	3.2	0.4	-	0.3	-
4, 4,4'-methylenebis(N,N-dimethylaniline) [x 10^{-3}]	1.7	2.2	1.8	2.4	2.2
5, N,N,N'-trimethyl-4,4'methylenebisaniline [x 10^{-3}]	1.7	2.2	1.8	2.4	2.2
6, 4-(*p*-tolyl)-N,N-dimethylaniline [x 10^{-4}]	4.4	2.4	4.7	3.4	3.4
7, 2-(*p*-tolyl)-N,N-dimethylaniline [x 10^{-4}]	1.8	2.3	0.7	2.0	0.7
8, N-(*p*-methylbenzyl)-N-methylaniline					
9, N-(*p*-dimethylaminobenzyl)-N-methylaniline					
10 crystal violet [x 10^{-4}]	-	3.1	-	1.4	-
11 methyl violet [x 10^{-4}]	-	2.0	-	0.7	-

* Concentration: [DMPI] $=1.0\text{x}10^{-2}$M, [DMA] = $4.0\text{ x}10^{-2}$M, **A: acetonitrile; B: acetonitrile/water=19/1, *** a: argon purged; b: oxygen saturated; c: [CH_2O]= $2.0 \text{ x } 10^{-2}$M.

DMA absorbs at a longer wavelength than BMPI but undergoes no decomposition upon prolonged irradiation alone. Diaryliodonium salts (λ_{max} 230nm) are highly photosensitive, even at wavelengths as high 365nm.[3] It is reasonable to assume that the dissociation of BMPI first initiates the photochemical reaction.

The heterolytic cleavage of BMPI leads to **1** and 4-methylphenyl cation. The electrophilic attack of the aryl cation on the ortho and para position of DMA gives products **6** and **7**.

$$\text{BMPI} \longrightarrow CH_3Ph^+ + \mathbf{1} \qquad (1)$$

$$CH_3Ph^+ + \text{DMA} \longrightarrow \mathbf{6} + \mathbf{7} + H^+ \qquad (2)$$

Homolytic cleavage of BMPI gives tolyl radical and the iodotoluene radical cation. Hydrogen abstraction by tolyl from DMA gives **2** and radical **12** and electron transfer from **12** to the iodotoluene gives **1** and a carbocation **13**.

$$\text{BMPI} \longrightarrow CH_3Ph\cdot + CH_3PhI^{+\cdot} \qquad (3)$$

$$CH_3Ph\cdot + \text{DME} \longrightarrow \mathbf{2} + \underset{\mathbf{12}}{PhN(CH_3)CH_2\cdot} \qquad (4)$$

$$\mathbf{12} + CH_3PhI^{+\cdot} \longrightarrow \mathbf{1} + \underset{\mathbf{13}}{PhN(CH_3)CH_2^+} \qquad (5)$$

Products **8** and **9** clearly indicate the existence of the two intermediates. Radical **12** may couple with another toluene radical to form **8**, and carbocation **13**, which acts as electrophile, attacks ground state DMA to give product **9**.

$$\mathbf{12} + CH_3Ph\cdot \text{------------}> \mathbf{8} \qquad (6)$$

$$\mathbf{13} + DME \text{------------}> \mathbf{9} + H \qquad (7)$$

Owing to the formation of an appreciable amount of **3** and **5**, we conclude that the central methylene carbon in products **4** and **5** is derived from a methyl group in DMA. There are two possible ways for the formation of **4**: Path 1 is:

$$\mathbf{13} + H_2O \text{———————}> PhN(CH_3)CH_2OH + H^+ \qquad (8)$$

$$PhN(CH_3)CH_2OH \text{———————}> PhNH(CH_3) + CH_2O \qquad (9)$$

$$CH_2O + 2DMA \text{———————}> \mathbf{4} + H_2O \qquad (10)$$

This path requires water and produces formaldehyde as an intermediate. The addition of water and formaldehyde to the reaction system should increase the yields of **4** and **5** formation. They do not.

Path 2 is based on the instability of **9** in acid.[9] Retro-Mannich reaction would give **3** and a benzylic cation **14**, which would attack DMA in the para-position to yield **4** or attack **3** leading to **5**.

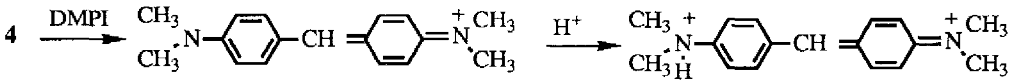
$$\mathbf{9} + H^+ \text{———}>PhN^+H(CH_3)CH_2PhN(CH_3)_2 \text{————}> \underset{\mathbf{3}}{PhNH(CH_3)} + \underset{\mathbf{14}}{{}^+CH_2PhN(CH_3)_2} \qquad (11)$$

$$\mathbf{14} + DMA \text{----------}> \mathbf{4} + H^+ \qquad (12)$$

$$\mathbf{14} + \mathbf{3} \text{----------}> \mathbf{5} + H^+ \qquad (13)$$

Authentic **9** upon the addition of tetrafluoroboric acid to the acetonitrile solution (0.05M) shows 99% decompsition at 50°. Owing to the fact that we have detected **9** in our reaction mixture, we suggest **4** an **5** are formed mainly thru path 2.

Irradiation of the mixture of **4** with BMPI in acetonitrile produces a blue species (λ_{max} 604nm). The addition of iodine to **4** in acetonitrile produces the same color.[15] It is the quinone-immonium cation of **4**.



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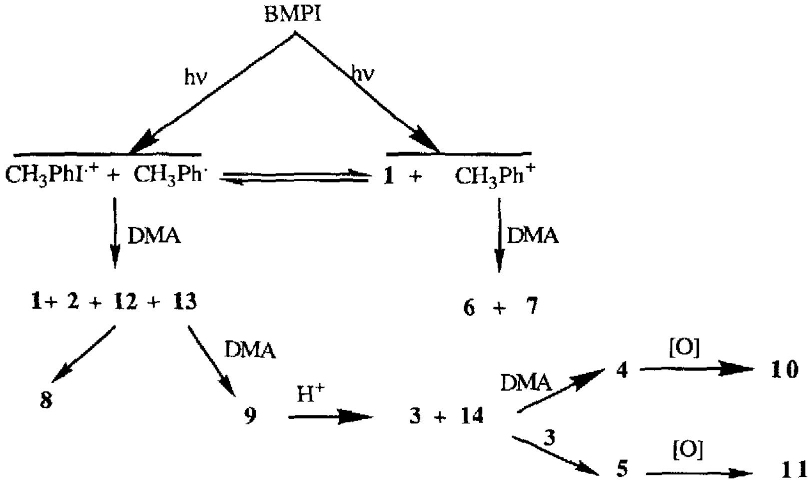
Upon addition of tetrafluoroboric acid to the blue color disappeared, and left a brownish yellow solution, probably due to the protonation of the dimethyl amino group in the cation. This color change also occured upon irradiation in argon.

Irradiation of the solution of **4**, DMA, and BMPI (1:1:1) in air gives exclusively crystal violet. This shows that the quinone immonium cation plays a decisive role in its formation. Probably the quino immonium cation attacks the para-position of DMA and to form the leuco dye. Continued hydrogen abstraction and electron transfer with the assistance of oxygen leads to crystal violet and methyl violet.

A simple mechanism for the formation of the products is depicted as follows:



The photochemical reaction of BMPI and DMA not only produce protonic acid but also carbocation **13** and **14** as an intermediates. These positively charged intermediates with nonelectrophilic counter anions likely initiate cationic polymerization.

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[9] 253.7 nm in a Rayonet reactor.

[10] MW; MS Leuco form; **10** = 373.25; Leuco form; **11** = 359.25; Structures confirmed by nmr.

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