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Iodine-Promoted Decomposition of 1-Aryl-3,3-dialkyltriazenes: A Mild Method for the Synthesis of Aryl Iodides

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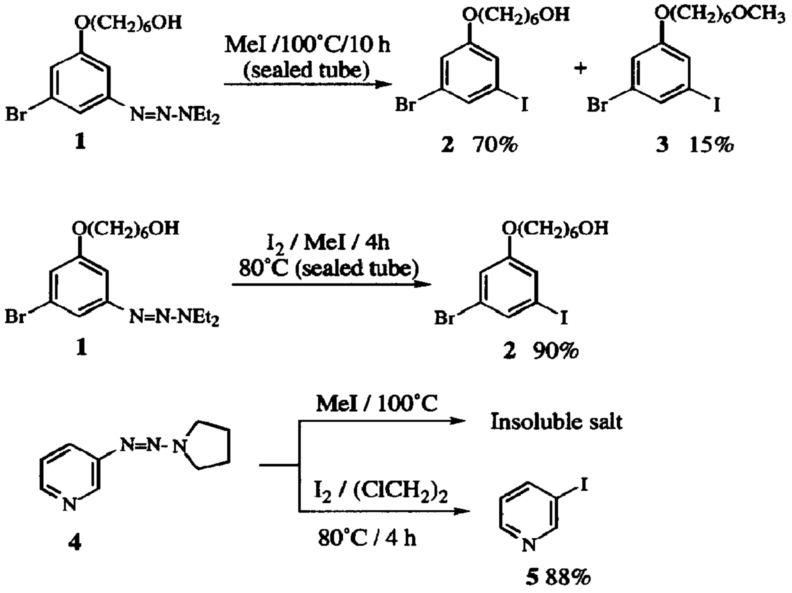
Abstract: Iodine promoted decomposition of 1-aryl-3,3-dialkyltriazenes in organic solvents is shown to give high yields of the corresponding aryl iodides under extremely mild conditions. The presence of iodine greatly accelerates the reaction in both iodoalkanes as well as in non-iodinated solvents.

1-Aryl-3,3-dialkyltriazenes are stable forms of aryl diazonium ions and have advantages in various synthetic transformations compared to their diazonium counterparts, especially in the role of a haloarene source.[1] Most aryltriazenes are crystalline solids or liquids that can easily be purified by recrystallization or distillation. They are stable to air, various bases and nucleophiles including organolithium reagents, as well as many common oxidants and reducing reagents; therefore, they are well-suited as a masking group for aryl halides. Reports on the preparation of aryl halides from aryltriazenes have typically used acid catalyzed decomposition of triazenes in the presence of halide ions as nucleophiles.[2] These conditions generate protonated by-products and are unsuitable for acid liable functional groups. Barrio and coworkers have described the conversion of aryltriazenes to aryl iodides using trimethylsilyl iodides in acetonitrile;[3] however, functional groups such as ethers or esters are cleaved under such conditions. We[4] and others[5] have successfully employed the triazene group to mask aryl iodide substrates in schemes for sequential oligomer syntheses based on palladium-catalyzed cross-coupling reactions. Frequently we encounter situations for which the known methods of transforming the triazene to iodide are unsuitable. Here we describe relatively mild conditions for carrying out this transformation involving the treatment of aryltriazenes with iodine at or below 100°C.

Previously we reported a procedure for the thermal decomposition of aryltriazenes to aryl iodides in neat iodomethane at 100-120°C.[6] Although these neutral conditions can tolerate a wide range of functional groups, the required temperature is high, especially with aryltriazenes containing electron withdrawing substituents. For example, the decomposition of 1-(4'-nitrophenyl)-3,3-diethyltriazene requires temperature as high as 150°C. Another disadvantage of our previous method is that some functional groups are methylated under these conditions (Scheme 1). For example, alcohol **2** was isolated in 70% along with the methylated compound **3** (15%). Moreover, pyridine **4** immediately formed an insoluble salt in iodomethane that decomposed to an intractable mixture on further heating. Attempts to assist the reaction by addition of iodide salts to iodomethane had no effect. We then discovered that addition of iodine greatly accelerated the reaction rate and eliminated the methylated products. Scheme I shows that both triazenes **1** and **4** are successfully converted to the corresponding aryl iodide in high yield using these modified conditions. For example, the addition of one equivalent of iodine to an iodomethane solution of compound **1** lowered the reaction temperature from 100°C to 80°C and shortened the reaction time from 10 h to 4 h. Alcohol **2** was isolated in 90% yield without methylation of the hydroxyl group, thereby avoiding the need for a protecting group. Using solvents other than iodomethane, transformations of less soluble or salt forming substrates can be accomplished. For example, we found that the triazene group of pyridine **4** could be transformed to iodide **5** in 88% upon treatment with iodine in 1,2-dichloroethane at 80°C. It is interesting to note that in this case molecular iodine serves as the sole source of iodide.

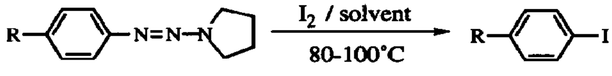


Scheme I

Further studies showed these conditions to be quite general. Treatment of various 1-aryl-3,3-dialkyltriazenes with iodine in common organic solvents at 80-100°C gave aryl iodides in high yields. Examples of various conditions and substrates are summarized in Table 1. Thus, a wide range of substituted aryltriazenes can be thermally decomposed to the corresponding aryl iodides by iodine with or without iodoalkane solvents. Significantly, even for aryltriazenes containing strongly electron withdrawing substituents such as 4-cyano and 4-nitro, the reactions are complete in less than 12 h at 100°C. It should be noted that when chloroform, benzene, or toluene was used as the solvent, protonated and/or biaryl compounds were isolated along with the desired iodide (data not shown). These results, and the observation that the reactions are strongly inhibited by molecular oxygen, suggest the radical character of the reaction. Further studies on the mechanism and other reactions using aryltriazenes as aryl radical sources are currently under investigation.

In summary, molecular iodine serves to greatly accelerate the decomposition of aryltriazenes in the presence of iodoalkanes. Interestingly, the reaction proceeds smoothly even in non-iodinated solvents, albeit with slightly lower yields.

Table 1. Yield Data for the Transformation of Aryltriazenes to Aryl Iodides



-R	solvent	temp. (time)[a]	yield[b] (%)
-H	diiodomethane	80°C (4 h)	>98
	1,2-dichloroethane		83
$-OCH_3$	diiodomethane	80°C (4 h)	>98
	1,2-dichloroethane		87
	acetonitrile		91
-I	hexane	100°C (4 h)	84
	1,2-dichloroethane		85
	acetonitrile		89
-CN	iodomethane	100°C (9 h)	88
	diiodomethane		92
$-CO_2CH_3$	diiodomethane	100°C (9 h)	97
	1,2-dichloroethane		86
	acetonitrile		89
$-NO_2$	diiodomethane	100°C (12 h)	>98
	1,2-dichloroethane		90
	acetonitrile		85

[a] Preliminary kinetic experiments indicate that the reaction rate is proportional to the concentration of iodine. However, yields diminish as the iodine concentration increases. One equivalent of iodine was used for all the reactions shown in Table 1. [b] Yields were determined by gas chromatography using an internal standard.

EXPERIMENTAL PROCEDURE

A sealable flask was charged with 1-(4-bromophenyl)-3,3-butanediyltriazene (0.51 g, 2.0 mmol), iodine (0.51 g, 2.0 mmol) and 1,2-dichloroethane (10 mL). The solution was degassed, back filled with nitrogen, sealed and stirred at 80°C for 4 h. The solvent was removed under reduced pressure and the residue was filtered through a short plug of silica gel eluting with hexane. The hexane solution was washed with saturated $Na_2S_2O_3$ solution, water and then dried over $MgSO_4$. Removal of the solvent gave pure 4-bromophenyl iodide (0.45 g, 80% yield).[7]

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