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Preparation of 1-arylazulenes through regioselective photoarylation of azulene with aryl iodides[†]

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Abstract—Photoirradiation of aryl iodide in the presence of azulene has been shown to be a useful method for regioselective arylation of azulene at the electron rich 1-position. © 2001 Elsevier Science Ltd. All rights reserved.

Biaryls are useful compounds for possible applications in asymmetric catalysis, formation of liquid crystals and other novel materials. The preferred method of synthesis of biaryls via metal catalyzed coupling reactions is particularly suitable for the preparation of symmetrical biaryls.[1] The demonstration of a possible use of photolysis of diazonium salts and aryl halides to generate an reactive intermediate[2] for arylation provides a ready entry to unsymmetrical biaryls. Radical mechanism was initially suggested[2] but carbocation intermediate was subsequently suggested[3] particularly after the recent finding that the photolysis of chlorobenzene and fluorobenzene is facilitated by the presence of an electron donating group at the *para*-position appears to favor a reactive carbocation intermediate.[4] In a matrix isolation spectroscopic study, Winkler and Sander showed that photolysis of iodobenzene led to phenyl cation, characterized spectroscopically for the first time.[5] However, the method of production of the phenyl cation could not rule out prior involvement of the phenyl radical. This work is also encouraged by successful trapping of reactive intermediates produced from irradiation of aryl iodides by conventional nucleophiles such as enolates.[6]

It occurred to us that such an electron deficient intermediate might be used to effect regioselective arylation of azulenes attacking preferentially at the electron rich sites at C-1 and C-3. This could provide a ready entry to 1-arylazulenes, **1**. However, because of the highly colored nature of the azulene chromophore (possibly serving the destructive role of internal filters or a quencher of excited species), such a photochemical conversion obviously will have to be performed under controlled conditions. In this paper, we would like to report successful execution of photoarylation of azulenes resulting in respectable yields of products. Thus, the reaction has the potential of becoming a viable method for preparation of some of the unusual arylazulenes.

We found that photoirradiation of a hexane solution of azulene and an iodoarene with light between 254 and 350 nm led to the decomposition of the iodoarene and the formation of 1-arylazulene (**1**) in yields ranging 63–92%. The six aryliodides that we have used so far varied from phenyl (**2**), substituted phenyls (**3**,**4**), α-naphthyl (**5**), 2-thienyl (**6**) to 1-azulenyl (**7**) for the aryl group giving products **1a**–**f**.[7,8] In a typical run, we irradiated a 12 ml *n*-hexane solution containing 17 mmole of azulene and 34 mmole of iodobenzene with a bank of 16 (24 W) germincidal lamps in a Rayonet reactor for 24 h. From the irradiated mixture, 10 mmole of unreacted azulene was recovered (41% conversion) and 6 mmoles of 1-phenylazulene was isolated (85% yield). While the irradiation period was arbitrarily chosen, we generally detected a significant reduction of efficiency if the reaction was allowed to proceed further. We suspect the trend was due to the increasing effect of internal filtering contributed by both the azulene and the product. The results of these six cases are summarized in Table 1.

It might appear odd that while proposing a carbocation intermediate, we preferred to use a non-polar solvent (hexane) in these photo-arylation reactions. Earlier, not surprisingly, we found that irradiation of iodobenzene in methanol led to its complete disappearance within 6

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h. This rapid loss of halide is largely unaffected by the addition of azulene while only minute amounts of the arylation product was detected. Clearly, methanol not only assisted the heterolysis of iodobenzene but also efficiently trapped the resulting carbocation. This interpretation is consistent with the electrochemical work reported earlier.[9] Thus, such a polar solvent, while facilitating the photolysis, is not suitable for our arylations.

In an effort to extend similar reactions to other aryl halides, we found that irradiation of a mixture of bromobenzene or chlorobenzene with azulene failed to give any arylated azulenes. This is in contrast with reports that bromobenzene and chlorobenzene undergo similar photolysis of the C–X bond as in iodobenzene. The difference is perhaps not surprising when one considers that azulene with a low lying excited state is likely to be an efficient quencher whether of the S_1 or the T_1 state of the aryl halides. Only in the case of the weak C-I, its homolysis from the reactive excited state apparently proceeded at a rate competitive with bimolecular quenching by azulene.

The six reactions shown in Table 1 are not very sensitive to variation of excitation wavelength from 254 nm to 350 nm. The observation of minor difference in yields (or extent of conversion within the same period of irradiation) is more likely due to changing internal filtering effect rather than the difference in excitation energy. The case of 1-iodoazulene with azulene (entry 6 in Table 1) is a particularly interesting one. While excitation within the 254–350 nm window (absorbed primarily by the strong S_2-band of azulene) brought about similar conversion and yield of 1,1′-bi-azulenyl (**1f**), however we observed that irradiation with light >450 nm (absorbed selectively by the weak S_1-band of azulene) for the same period of time failed to produce any detectable of the coupled product. This negative result clearly showed that homolysis of iodoazulene can only take place from the S_2 state (or the T_2 state)[10] but not the lower S_1 (or the T_1) state. Thus, entry 6 is another rare case of chemical reaction originating from an upper state, a chemical example violating the Kasha's Rule.

We have further noticed that the reactive intermediate thus generated is sufficiently reactive toward other aryl systems. Thus, when 1-iodoazulene was irradiated in the presence of benzene as solvent, the same 1-phenylazulene (cf entry 1, Table 1) was obtained in improved 94% yield (50% conversion). And, in a preliminary experiment, we have prepared the highly crowded 1,1′-bi-guaiazulenyl (**8**) by a similar photochemical procedure. Thus, it is our intention to apply similar photochemical procedure for the preparation of other similarly crowded azulenic compounds, which are azulene anaogs of 1,1′-binaphthyl.[11]

In summary, in spite of the potential problems of internal filtering and efficient quenching, we have shown that photolysis of aryl iodides can be used as a viable entry to 1-arylazulenes.

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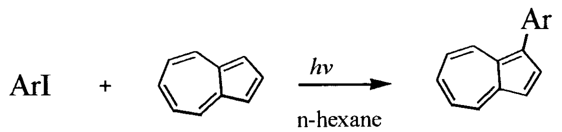

2-7 **1a-1f**

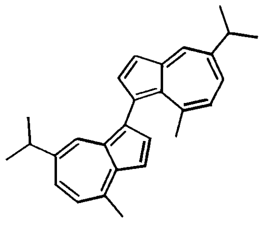

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Table 1. Photolysis of aryl iodides **2**–**7** in the presence of azulene[a]

Entry	Aryl iodide, cpd	Product	Conversion/%	Yield[b]/%
1	Phenyl, **2**	1-Phenylazulene	41	85
2	*p*-Tolyl, **3**	1-*p*-Tolylazulene	37	75
3	*m*-Tolyl, **4**	1-*m*-Tolylazulene	34	72
4	α-Naphthyl, **5**	1-α-Naphthylazulene	18	92
5	2-Thienyl, **6**	1-(2′-Thienyl)azulene	50	63
6	1-Azulenyl, **7**	1,1′-Bi-azulenyl	28	67

[a] Irradiated for approx. 24 h at 254, 300 or 350 nm. Usually the best yield was achieved with 350 nm light.

[b] Based on consumption of azulene.

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7. Compounds **1a**, **1b**, **1d** and **1f** are known compounds. Spectral characterization data can be found in: Nefedov, V. A.; German, N. A.; Lutsenko, A. I. *J. Org. Soc. Chem. USSR (Engl)*, **1987,** *23*, 154-162 (for **1a**, **b**, **d**) and Morita, T.; Yakase, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1144-1152 (for **1f**).
8. Key spectral data for compound **1c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, $J=9.8$ Hz, 1H), 8.33 (d, $J=9.2$ Hz, 1H), 7.99 (d, $J=4.0$ Hz, 1H), 7.56 (t, $J=9.8$ Hz, 1H), 7.35-7.42 (m, 4H), 7.16 (t, $J=4.8$ Hz, 1H), 7.12 (t, $J=10.0$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 138.2, 138.1, 137.6, 137.4, 137.1, 135.7, 135.3, 131.5, 130.5, 128.5, 127.1, 126.8, 123.2, 122.9, 117.4, 21.6 ppm. MS (70 ev, EI) 218 (M^+, 100), 202 (36); HR-MS calcd for $C_{17}H_{14}$: 218.1096, found: 218.1101. **1e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (d, $J=9.7$ Hz, 1H), 8.30 (d, $J=9.5$ Hz, 1H), 8.04 (d, $J=3.9$ Hz, 1H), 7.59 (t, $J=9.9$ Hz, 1H), 7.35 (dd, $J=5.1$, 1.3 Hz, 1H), 7.28 (d, $J=3.9$ Hz, 2H), 7.21-7.11 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.2, 139.7, 138.5, 137.3, 137.2, 135.7, 135.4, 135.0, 127.7, 124.5, 124.4, 123.6, 123.5, 117.7 ppm; MS (70 ev, EI) 210 (M^+, 100) 165 (23), HR-MS: calcd for $C_{14}H_{14}S$: 210.0503, found: 210.0497.
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11. By a similar photoarylation procedure, binaphthyl was obtained in 28% yield (75% conversion).