Intramolecular Aromatic *ipso*-Substitution in the Photolysis of 2-Iodoazobenzenes

By Luisa Benati,* Piero Spagnolo, Antonio Tundo,* and Giuseppe Zanardi
(*Istituto di Chimica Organica dell'Università, Viale Risorgimento* 4, 40136 *Bologna, Italy*)

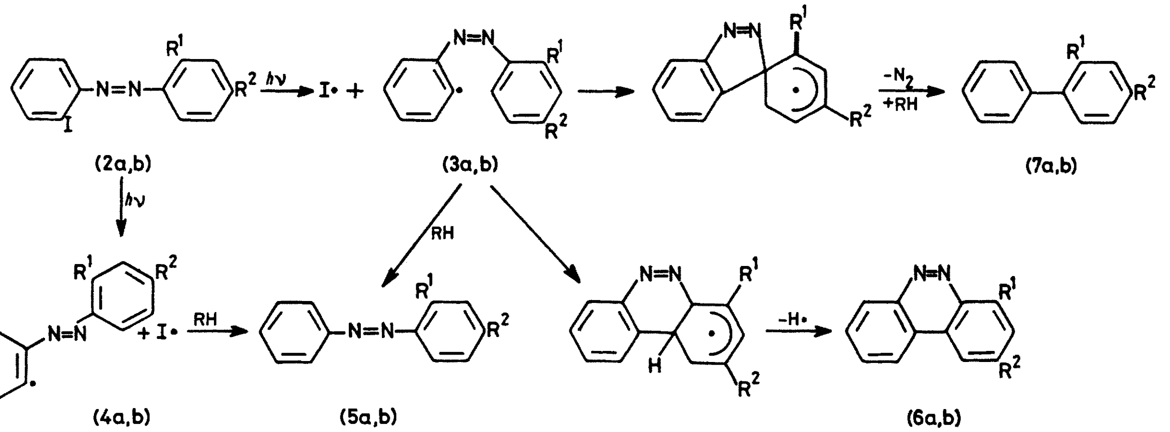
Summary Photolysis of 2-iodoazobenzene (**2a**) and 4′-chloro-2-iodoazobenzene (**2b**) affords the corresponding 2-arylazophenyl radicals which undergo hydrogen abstraction to give the azobenzenes (**5a,b**), intramolecular 1,6-cyclization to give the benzo[*c*]cinnolines (**6a,b**), and intramolecular *ipso*-substitution leading ultimately to the biphenyls (**7a,b**); photolysis of 2-(*o*-iodophenylazo)biphenyl (**2**; $R^1 = Ph$, $R^2 = H$) affords 2-(phenylazo)biphenyl (**5**; $R^1 = Ph$, $R^2 = H$) and triphenylene (**8**) as the only identifiable products.

Recently we have reported examples of addition of aryl radicals to the azo-group; we have observed that 2′-arylazobiphenyl-2-yl radicals lead to the formation of *N*-(carbazol-9-yl)arylaminyls by intramolecular 1,5-addition to the azo-group.[1] In arylazo systems homolytic displacement of the azo function is an additional possibility. Although several examples of homolytic aromatic *ipso*-attack by carbon radicals, leading to displacement of a variety of groups, have been observed,[2] the only report of azo function displacement appears to be that of the reaction of phenyl radicals with γ-(*p*-nitrophenylazo)-γ-valerolactone (**1**) afford-

$$p\text{-}O_2NC_6H_4N{=}N\overline{CMeCH_2CH_2C(:O)O}$$

(**1**)

ing *p*-nitroazobenzene as the major product.[3] Herein we present preliminary results of a study of the photolysis of the 2-iodoazobenzenes (**2**), which appears to provide an additional example of azo function displacement by aryl radicals.



Scheme 1. **a**, $R^1 = R^2 = H$; **b**, $R^1 = H$, $R^2 = Cl$

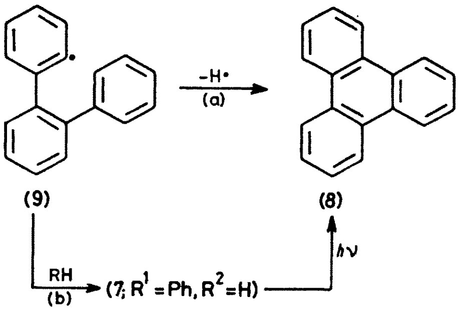
Irradiation of a degassed solution of 2-iodoazobenzene (**2a**) in cyclohexane (*ca.* 0·01 M) with a 100 W high-pressure mercury lamp for 48 h gave unchanged (**2a**) (10%), biphenyl (**7a**) (32%),† azobenzene (**5a**) (24%),† and benzo[*c*]cinnoline (**6a**) (11%)† as well as trace amounts of azoxybenzene and 2-hydroxyazobenzene as the only identifiable products after column chromatography. The formation of these photolysis products could be most reasonably rationalized by assuming photochemical *trans–cis* isomerization of (**2a**) and homolytic fission of the carbon–iodine bond[4] affording the aryl radicals (**3a**) and (**4a**); hydrogen abstraction by (**3a**) and (**4a**) would lead to (**5a**) and products (**6a**) and (**7a**) would arise by intramolecular 1,6-cyclization and *ipso* 1,5-substitution of radical (**3a**) respectively (Scheme 1).

The presence of trace amounts of azoxybenzene and 2-hydroxyazobenzene appears to be due to a photochemical reaction of (**5a**) [or (**2a**)] with oxygen, affording azoxybenzene, from which 2-hydroxyazobenzene can be formed by photorearrangement.[5] Control experiments showed that irradiation of azobenzene (**5a**) under the same conditions as employed in the photolysis of (**2a**) brought about *trans–cis* isomerization of (**5a**) as well as formation of traces of azoxybenzene and 2-hydroxyazobenzene. These two latter compounds were formed in greater amounts on irradiation of (**5a**) in the presence of oxygen.

Analogous results were obtained from photolysis of 4′-chloro-2-iodoazobenzene‡ (**2b**). Chromatography gave the starting material (**2b**) (5%), 4-chlorobiphenyl (**7b**) (29%),† 4-chloroazobenzene (**5b**) (31%),† and 2-chlorobenzo[*c*]cinnoline[6] (**6b**) (16%).†

Finally, photolysis of 2-(*o*-iodophenylazo)biphenyl‡ (**2**; $R^1 = Ph$, $R^2 = H$) for 48 h afforded unchanged (**2**; $R^1 = Ph$, $R^2 = H$) (50%), triphenylene[7] (**8**) (46%),† and 2-(phenylazo)biphenyl[8] (**5**; $R^1 = Ph$, $R^2 = H$) (24%)† together with a complex mixture from which no evidence of formation of 2-phenylbenzo[*c*]cinnoline (**6**; $R^1 = Ph$, $R^2 = H$) could be obtained. Attempts to prepare the unknown 2-phenylbenzo[*c*]cinnoline (**6**; $R^1 = Ph$, $R^2 = H$) by photocyclization of 2-(phenylazo)biphenyl (**5**; $R^1 = Ph$, $R^2 = H$) in an acidic medium[9] were unsuccessful.

Formation of triphenylene (**8**) can be most reasonably attributed to intramolecular homolytic substitution of the aryl radical (**9**) derived from intramolecular *ipso* 1,5-substitution of the radical (**3**; $R^1 = Ph$, $R^2 = H$) and subsequent loss of nitrogen (path a). Triphenylene (**8**) could be also formed by photocyclodehydrogenation[7] of



Scheme 2

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† Yields are based on consumed (**2a**), (**2b**), and (**2**; $R^1 = Ph$, $R^2 = H$) respectively.

‡ All new compounds gave satisfactory spectral data and elemental analysis.

o-terphenyl (**7**; $R^1 = Ph$, $R^2 = H$) arising from the radical (**9**) by hydrogen abstraction (path b). However, no evidence for the presence of *o*-terphenyl (**7**; $R^1 = Ph$, $R^2 = H$) was obtained (Scheme 2).

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