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Photochemical Coupling between Indene and Nitroarenes

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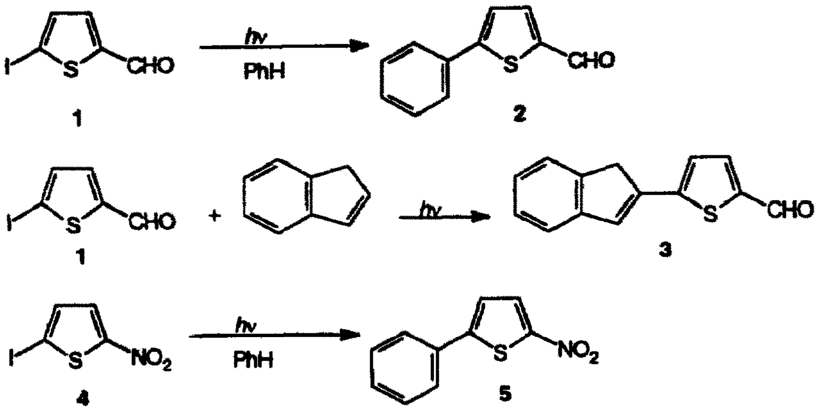
Abstract - The photochemical reaction between indene and nitroarenes gave an unusual reaction performing the substitution of the nitro group.

In our previous work we have found that haloheterocyclic derivatives such as **1** and **4**, when irradiated in the presence of an aromatic compound, gave the corresponding photoarylation product in high yields (Scheme 1).[1,2] Furthermore, we have found that 5-iodothiophene-2-carbaldehyde (**1**) reacts with indene to give the corresponding substitution product **3** (Scheme 1).[3] The coupling products of type **3** showed both interesting photophysical properties as singlet oxygen sensitizers,[4] and photobiological properties with activity against erythrocytes, insect larvae, fishes and supercoiled DNA.[5]

Scheme 1



In order to test photophysical and photobiological properties of nitroindenylthiophenes we have tested the reaction of 5-iodo-2-nitrothiophene (**4**)[6] with indene. Surprisingly, we found that the reaction did not give the expected coupling product but gave a mixture of two products (**6** and **7**) deriving from photosubstitution of nitro group (Scheme 2). Clearly compound **7** derived from **6** through homolytic cleavage of the C-I bond.

Scheme 2

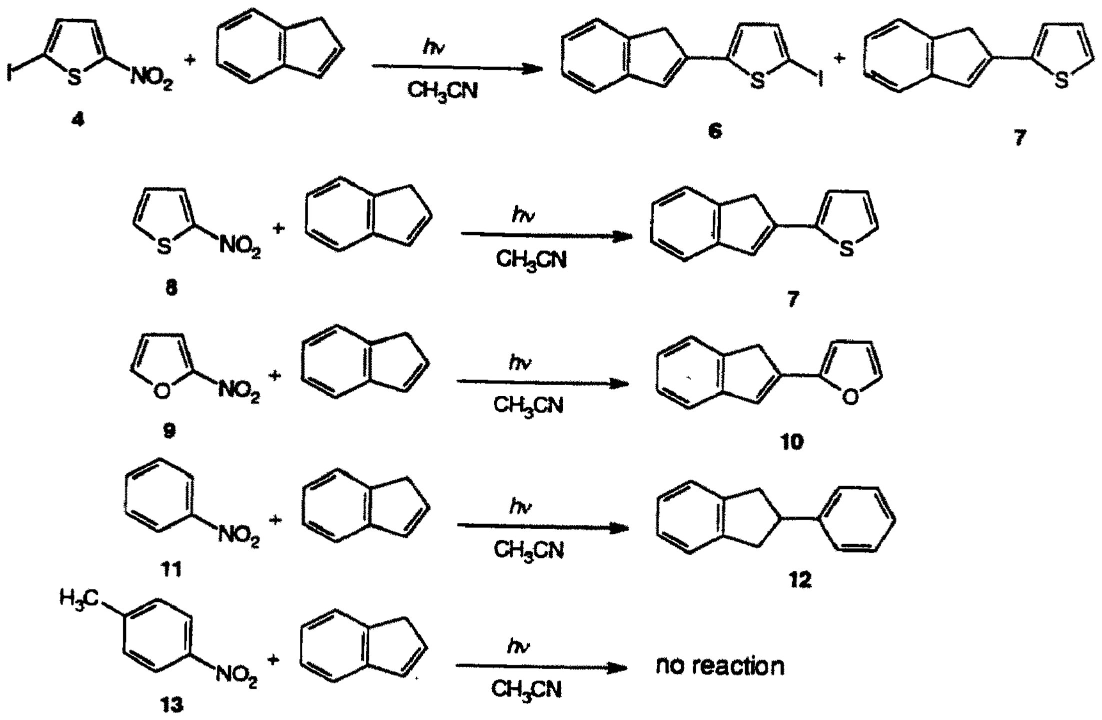


Table 1 - Photochemical behaviour of nitroarenes

Starting Compound	Irradiation Time (h)	Product	Yield (%)[a]
4	1	**6**	75
		7	25
8	1	**7**	66
9	1	**10**	52
11	4	**12**	37
13	8	-	-

a) All the yields refer to isolated chromatographically pure compounds.

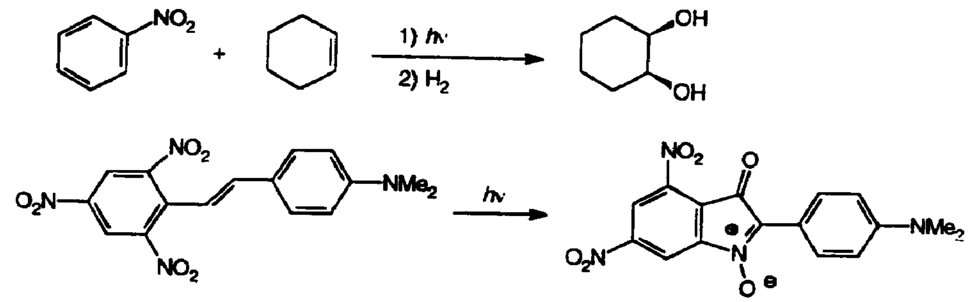
Compounds **6** and **7** was obtained in quantitative yields in a 3:1 ratio (Table 1). This type of reaction was then tested with other nitroarenes. 2-nitrothiophene (**8**) and 2-nitrofuran (**9**) gave the corresponding indenyl derivatives **7** and **10** (Scheme 2) in excellent yields (Table 1). On the contrary nitrobenzene (**11**) gave the indane **12** in only 37% yield (Scheme 2, Table 1), while *p*-nitrotoluene was completely unreactive. It is noteworthy that **11** gave the reduction product instead of the substitution one.

In conclusion, considering that **11** and **13** did not give substitution products, the photosubstitution reaction seems to be a feature of heterocyclic compounds.

In a typical experimental procedure 2-nitrothiophene (197 mg) was dissolved in acetonitrile (70 ml) in the presence of indene (5 ml). The reaction mixture was irradiated for 1 h with a 250 W high-pressure mercury arc (Helios-Italquartz). At the end of the reaction (GC-MS) the solvent was evaporated and excess indene distilled under reduced pressure. The residue was chromatographed on SiO_2. Elution with *n*-hexane gave 200 mg of pure **7**.[7,8]

It is noteworthy that to our knowledge this is the first example of this type of reactivity in photochemical reactions of nitroarenes with alkenes. In fact, the addition of nitroarenes to alkenes to give the corresponding 1,2-diols after hydrogenation is a well-known reaction[9-11] as well as photochemical transposition of nitrostilbenes to give isatogens and isatogen-like compounds[12,13] (Scheme 3). Nevertheless, no photochemical replacement reaction of nitro group when nitrocompounds were irradiated in the presence of arylalkenes was described.

Scheme 3



Recently we have shown that the photochemical reaction of *trans*-α,α'-dimethylstilbene with oxygen can be an interesting method to establish whether a compound shows a type I or II photodynamic properties.[14,15] We tested this reaction on compounds **7** and **10**. The results showed that these compounds were singlet oxygen sensitizers. Then, photochemical properties of indenylthiophene derivatives did not need the presence of the carbonyl group as in compound **3**. Furthermore, in the literature dithienylethylene, a compound strictly related to **7**, was described as a compound with no photobiological properties.[16] Then, on the basis of the present results, the lack of photobiological behaviour of this compound can be explained considering that probably *cis-trans* isomerization in the excited singlet state inhibits the formation of the excited triplet state that could react with oxygen.

In conclusion, the photochemical reaction of nitroarenes with indene gave a new photochemical reaction that allowed us to obtain compounds showing interesting photophysical properties.

References and Notes

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7. In the reaction of **4** with indene the reaction mixture was concentrated, diluted with EtOAc, washed with 0.1 *M* $Na_2S_2O_3$, and dried (Na_2SO_4).
8. **6**: ^{1}H NMR ($CHCl_3$) δ: 7.65 (d, 1 H, *J* = 7 Hz), 7.47 (d, 1 H, *J* = 7 Hz), 7.23 (s, 1 H), 7.21 (m, 4 H), 3.39 (s, 2 H); MS (*m/z*): 326 (5%), 325 (15), 324 (100), 323 (5), 198 (32), 165 (9), 153 (11), 152 (15), 151 (5), 139 (8). **7**: ^{1}H NMR ($CDCl_3$) δ: 7.38 (m, 1 H), 7.24 (s, 1 H), 7.20 (m, 5 H), 7.02 (m, 1 H), 3.78 (s, 2 H); MS (*m/z*): 200 (6%), 199 (18), 198 (100), 197 (65), 195 (4), 171 (7), 166 (8), 165 (4), 163 (4), 153 (7), 152 (15), 151 (5), 139 (7), 125 (6), 97 (6), 63 (5). **10**: ^{1}H NMR ($CDCl_3$) δ: 7.38 (m, 1 H), 7.24 (s, 1 H), 7.21 (m, 5 H), 7.16 (m, 1 H), 3.69 (s, 2 H): MS (*m/z*): 183 (18%), 182 (100), 181 (35), 169 (4), 154 (17), 153 (86), 152 (52), 151 (17), 150 (6), 141 (6), 128 (8), 127 (6), 116 (5), 115 (13), 91 (9), 77 (5), 76 (16), 75 (5), 63 (9), 51 (5). **12**: ^{1}H NMR ($CDCl_3$) δ: 7.30 (m, 9 H), 4.13 (d, 4 H, *J* = 7 Hz), 3.50 (t, 1 H, *J* = 7 Hz); MS (*m/z*): 196 (11%), 195 (75), 194 (96), 193 (15), 180 (15), 179 (25), 178 (100), 177 (5), 167 (4), 165 (7), 152 (4), 118 (22), 117 (7), 116 (12), 104 (5), 91 (11), 90 (4), 89 (6), 78 (5), 77 (35), 65 (5), 63 (4), 51 (11).
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