Photochemistry of *β*-Methoxystyrene in the Presence of Nitroarenes. Unusual Products Formation

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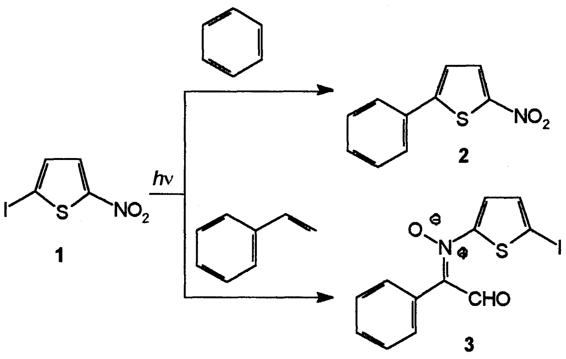
The irradiation of β-methoxystyrene in the presence of nitroarenes gave un unusual product deriving from dimerization and oxidation of the starting material. In the reaction mixture also an amide was identified.

The photochemistry of nitroarenes when they are irradiated in the presence of alkenes was an interesting research field and numerous investigations covered it. In fact, the addition of nitroarenes to alkenes to give the corresponding 1,2-diols after hydrogenation is a well-known reaction[1-3] as well as photochemical transposition of both *o*-nitrostilbenes and 1-(*o*-nitrophenyl)-4-phenyl-1,3-butadienes to give isatogens and isatogen-like compounds.[4,5] Recently we have reported that 5-iodo-2-nitrothiophene (**1**) reacted with arenes to give the corresponding substitution product **2** (Scheme 1).[6] Following the same approach used with halogenothienyl carbonyl derivatives[7] we tested the photochemical behavior of **1** in the presence of styrene showing that nitrone **3** can be obtained (Scheme 1).[8]

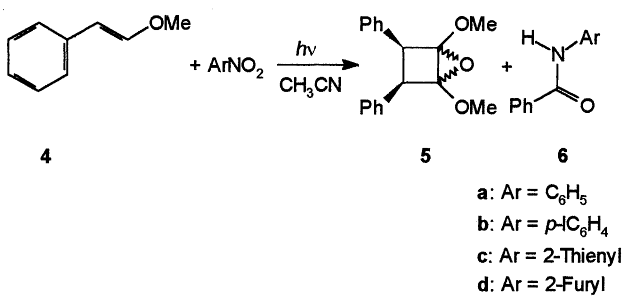


Scheme 1.

In order to test the general character of this conversion, we tested the reactivity of β-methoxystyrene. In this communication we want to report our data on the reactivity of this substrate in the presence of nitroarenes. Our results show that β-methoxystyrene gave completely different reaction products opening a new research field.

In a typical experiment β-methoxystyrene (3.5 g) was dissolved in acetonitrile in the presence of nitrobenzene (265 mg) and irradiated with a 250 W high-pressure mercury arc (Helios-Italquartz) surrounded by a Pyrex water-jacket. After 2 h, the solvent was evaporated and the crude product was chromatographed on silica gel. Elution with *n*-hexane/Et_2O 9:1 gave **5** (47%)[9] while elution with *n*-hexane/Et_2O 2:1 gave **6a** (36%) (Scheme 2, Table 1).

To confirm this behavior we performed the photochemical reaction using some other nitroarenes (Scheme 2, Table 1) giving the corresponding products. By using *p*-iodonitrobenzene, 2-nitrothiophene, and 2-nitrofuran as substrates, we obtained **5** in quite similar yields. It is noteworthy that, when *p*-iodonitrobenzene was used, we did not observe any product deriving from homolytic cleavage of carbon-iodine bond. In fact, the photochemical arylation of *p*-iodonitrobenzene is reported when this substrate was irradiated in benzene.[10] In our hands, only 48% of the corresponding phenyl derivative was observed after 48 h irradiation in benzene, while the irradiation of this substrate in acetonitrile in the presence of excess benzene did not give any reaction after a prolonged irradiation time. Then, in acetonitrile, the homolytic cleavage of carbon-iodine bond is not a favorable process. This evidence is in agreement with literature data showing that *p*-iodonitrobenzene anion radical gave no dehalogenation reaction at all,[11] or gave this reaction in very slow rate.[12] Using heterocyclic nitro compounds we obtained contrasting results: with 2-nitrothiophene as starting material the usual mixture of two products was obtained. Nevertheless, the



Scheme 2.

Table 1. Reaction of β-methoxystyrene with nitroarenes

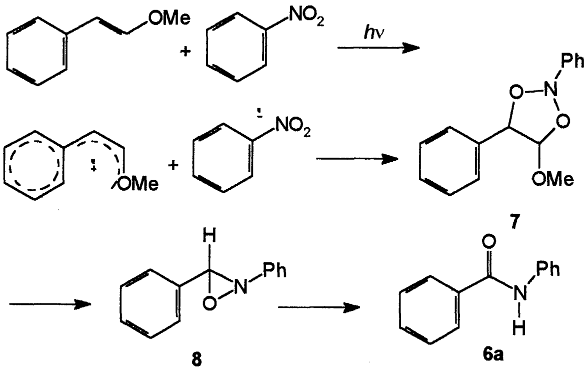
Nitroarene	Irradiation time h	Product	Yields/%[a,b]
-	4	-	-
nitrobenzene	2	**5**	47
		6a	3
p-iodonitrobenzene	2	**5**	60
		6b	23
2-nitrothiophene	4	**5**	54
		6c	16
2-nitrofuran	2	**5**	51

[a]All the yields refer to isolated chromatographically pure compounds. [b]Yields calculated on the basis of the amount of nitroarene.

yields of the formation of the amide **6c** were lower than in the other cases. Using 2-nitrofuran only compound **5** was obtained while no amide was recovered in the reaction mixture.

In our previous work in this field,[8] the obtained results were in agreement with the mechanism proposed by Splitter and Calvin for this type of reaction.[4] In that work electron transfer between nitroarene (acceptor) and arylalkene (donor) allowed to obtain the addition intermediate **7**. A transposition reaction followed by a dark oxidation accounted of the obtained products.

In this work the formation of **5** can not be explained on the basis of the same mechanism. However, our data can not allowed us to formulate a mechanism hypothesis. On the contrary, the formation of the amide can be explained considering that, during the usual transposition of **7**, methyl formate can be eliminated to give **8** and then the product (Scheme 3).



Scheme 3.

It is noteworthy that the above reported results begin to cover the large lack of knowledge on the photochemical behavior of β-methoxystyrene. In fact, only photooxidation of **4** has been studied.[13-17]

In conclusion, we have seen that the presence of a methoxy group an arylalkenes can modify the reactivity of the substrate giving a dimeric product and an amide.

References and Notes

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9 Compound **5**: ^{1}H NMR ($CDCl_3$) δ: 7.97 (1 H, m), 7.5 (1 H, m), 7.46 (1 H, m), 7.30 (2 H, m), 3.34 (1.5 H, s), 2.92 (1 H, m), and 2.60 ppm (1.5 H, s); ^{13}C NMR ($CDCl_3$) δ: 132.93, 129.32, 128.45, 128.20, 105.37, 53.24, 39.67, and 26.36 ppm; IR (film, ν_{max}): 1600, 1580, 1500, 1450, 1360, 1345, 1265, 1180, 1125, 1060, 960, 765, 685, and 590 cm^{-1}.

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