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Photolysis of *N*-[(4-benzoyl)benzenesulfonyl]benzenesulfonamide

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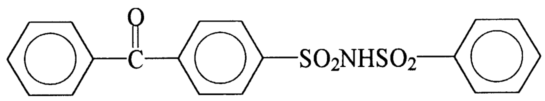
Abstract

The photodecomposition of *N*-[(4-benzoyl)benzenesulfonyl]benzenesulfonamide (**1**) in an aqueous solution was investigated. The primary process of the irradiation of **1** in water involves two competitive modes of fragmentation of the excited **1**. However, the resulting products indicate that the cleavage of S–N bond is not equivalent. The photodecomposition products consists of four main organic compounds and trace amounts of unidentified substances.

Keywords: Photolysis; Arylsulfonamides

1. Introduction

It was shown that *N*-[(4-benzoyl)benzenesulfonyl]-benzenesulfonamide (**1**) is an efficient photoinitiator of free-radical polymerization of styrene in water Triton X-100 emulsion [1], 2-hydroxyethyl methacrylate in aqueous solution [2] and methyl methacrylate in bulk [3].

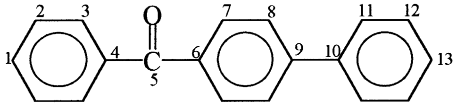


It was assumed that radicals formed by homolytic cleavage of an S–N bond of photoinitiator, initiates polymerization. It is known from literature that a S–N bond is the weakest one in the molecule of the tested compound **1** [4]. While the photolysis of sulfonamides has been a subject of numerous studies [5–9] to the best of the authors' knowledge this is the first report on the photolysis of the compound containing different two sulfonyl groups bonded to the same nitrogen atom. The purpose of these studies was to show which route of the S–N bond cleavage dominates in the process.

2. Results and discussion

The photoreaction was monitored at internals by TLC. After several minutes of the irradiation of an aqueous solution of **1** a solid was precipitated and after 1 h all the substrate completely disappeared. Then water was removed by evaporation and the residue was separated by TLC preparative chromatography (eluent chloroform–ethyl acetate, 6:1 v/v). The products of the reaction were identified by spectroscopic methods (^{1}H, ^{13}C NMR, and MS) and melting points. The results are summarized in Tables 1 and 2.

The analysis of Tables 1 and 2 shows that the main photoproduct (95%) consists of four main products: 4-benzoylbiphenyl (**2**), 2-hydroxy-4′-benzoylbiphenyl (**3**), 3-(2-phenyl-benzoyl)-7-thia-8-aza-bicyclo[4.2.0]octa-1(6), 2,4-triene-7,7-dioxide (**4**), 4-(2-phenyl-benzoyl)-benzenesulfonic acid amide (**5**) and trace amounts (5%) of unidentified material, which consists of seven compounds.



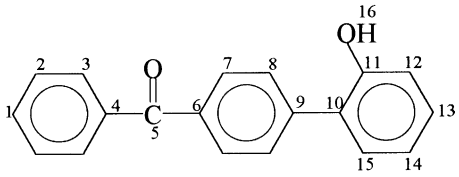


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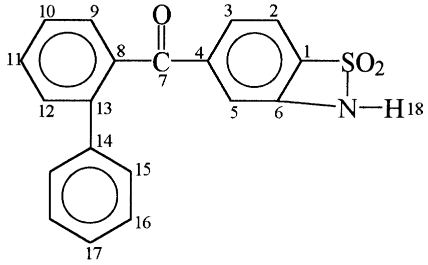
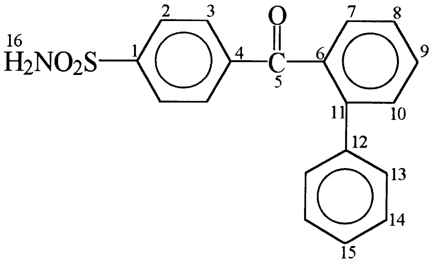
Table 1
^{1}H (ppm) and ^{13}C (ppm) chemical shifts for compounds **2**–**5**

No.	$CDCl_3$, 293 K (**2**)		$CDCl_3$, 293 K (**3**)		Acetone-d_6, 300 K (**4**)		Acetone-d_6, 300 K (**5**)	
	^{1}H	^{13}C [11]	^{1}H	^{13}C [12]	^{1}H	^{13}C	^{1}H	^{13}C
1	7.61	132.28	7.60	132.43	–	126.6	–	137.25
2	7.48	128.85	7.51	128.27	8.41	126.6	7.63	130.20
3	7.84	129.89	7.85	129.94	7.63	126.1	7.83	129.88
4	–	137.61	–	137.38	–	137.8	–	144.94
5	–	196.15	–	196.00	7.73	122.0	–	195.92
6	–	136.08	–	136.58	–	139.8	–	142.76
7	7.90	130.62	7.93	130.72	–	195.3	8.17	128.35
8	7.71	126.86	7.63	128.95	–	132.4	7.61	128.75
9	–	145.01	–	141.53	8.35	127.3	7.69	132.38
10	–	139.84	–	128.74	7.91	133.6	7.41	132.76
11	7.65	127.19	–	152.24	7.78	130.4	–	140.17
12	7.51	128.20	6.99	116.15	8.05	122.6	–	138.25
13	7.41	128.07	7.30	129.68	–	136.9	7.84	130.36
14			7.04	121.13	–	138.2	7.58	129.05
15			7.31	130.25	7.86	130.7	7.68	133.06
16			5.12	–	7.60	129.5	6.26	–
17					7.71	133.7		
18					11.5	–		

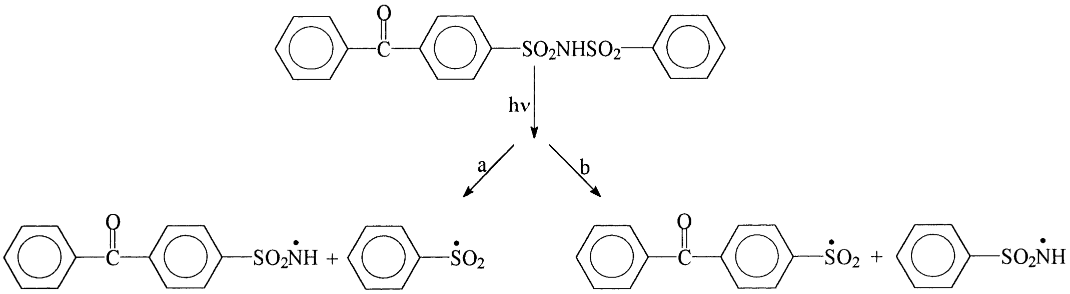




The primary process appears to involve the homolytic fission of the S–N bond to form arylsulfonylamino and arylsulfonyl radicals (Scheme 1).

In the secondary process (route ‘a’), 4-benzoylphenylsulfamidyl radicals abstract hydrogen to form 4-benzoylphenylsulfonylamide and a small amount cyclise with the loss of hydrogen atom to give 3-benzoyl-7-thia-8-aza-bicyclo-[4.2.0]octa-1(6),2,4-triene-7,7-dioxide. Phenylsulfonyl radicals in turn extrude sulfur dioxide forming phenyl radicals that couple with 4-benzoyl-phenylsulfonyl-amide to give **5** (Scheme 2). Great yield of **5** indicates that route ‘a’ dominates in the photodissociation process.

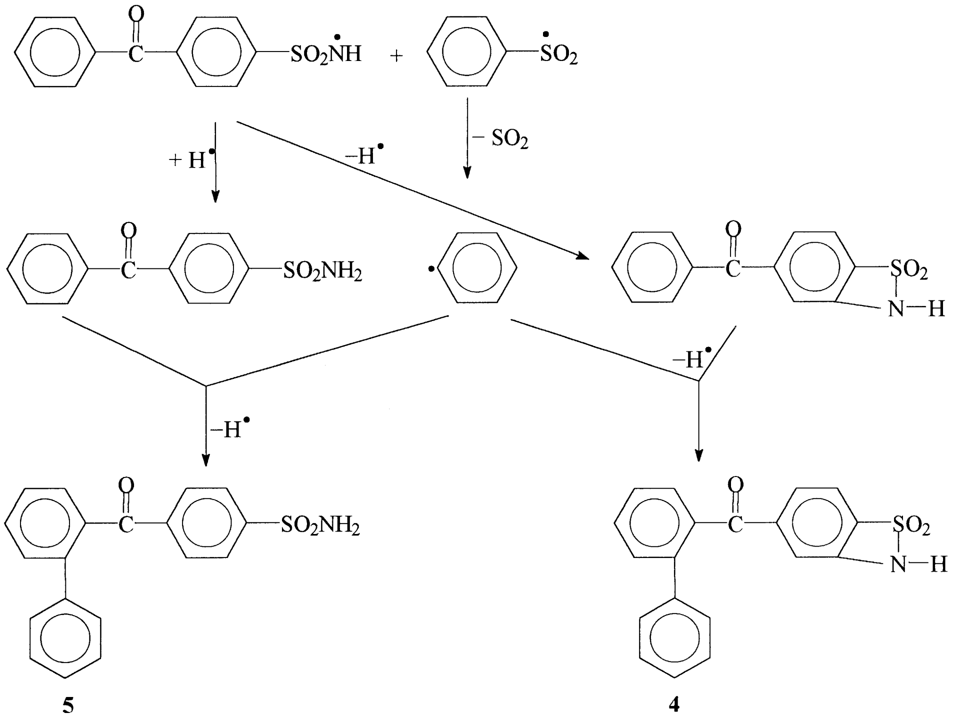
A small amount of 3-benzoyl-7-thia-8-aza-bicyclo[4.2.0] octa-1(6),2,4-triene-7,7-dioxide couples with phenyl radicals to yield **4**. Route ‘b’ of photodecomposition also involves the S–N bond cleavage but the process is less effective than that of route ‘a’. As a result benzoyl phenyl-sulfonyl and benzenesulfamidyl radicals are the product of photodecomposition. The former extrudes sulfur dioxide forming benzoylphenyl radicals and the latter extrudes SO_2NH to give phenyl radicals (Scheme 3). Benzoylbenzene radicals couple with phenyl ones forming 4-benzoylbiphenyl (**2**). The



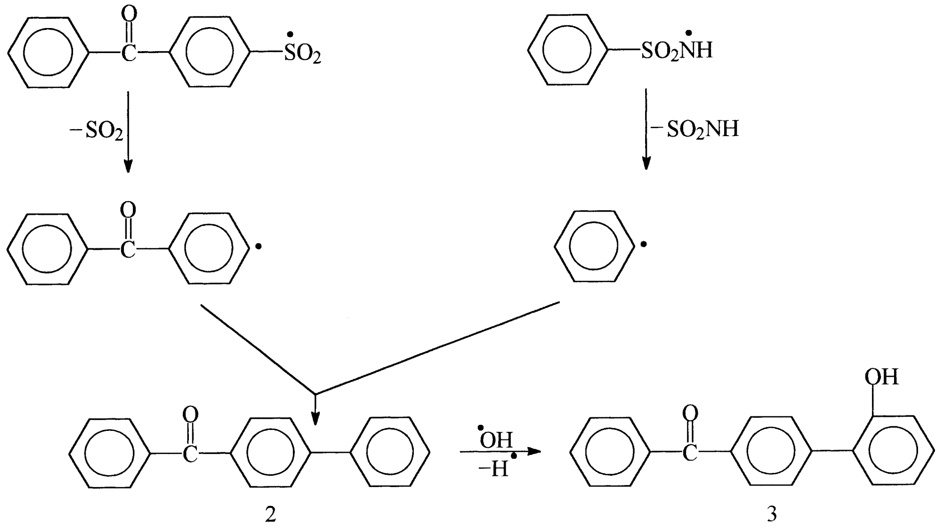
Scheme 1.

Table 2
Synthetic and physical data for compounds **2**–**5**

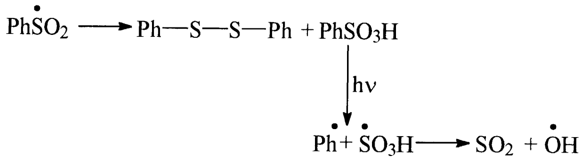
Product	Yield (%)	Melting point (°C)	R_f	Molecular formula	*m*/*z* (relative intensity)
2	3	101–102	0.88	$C_{19}H_{14}O$ (258.30)	259 (18), 258 (85), 182 (15), 181 (100), 153 (21), 152 (40), 151 (10), 149 (16), 105 (16), 77 (19)
3	5	114–116	0.71	$C_{19}H_{14}O_2$ (274.32)	275 (19), 274 (88), 258 (19), 198 (14), 197 (100), 181 (27), 169 (21), 168 (11), 152 (14), 149 (24), 141 (21), 139 (17), 115 (25), 105 (56), 77 (49)
4	7	228–230	0.55	$C_{19}H_{13}NO_3S$ (335.38)	337 (11), 336 (23), 335 (100), 270 (11), 258 (53), 166 (10), 139 (13), 105 (24), 77 (24)
5	80	131–133	0.33	$C_{19}H_{15}NO_3S$ (337.40)	338 (12), 337 (55), 261 (15), 260 (100), 256 (14), 152 (10), 105 (26), 77 (24)



Scheme 2.



Scheme 3.



Scheme 4.

small amount of the compound **2** reacts with hydroxyl radicals to form 2-hydroxy-4′-benzoylbiphenyl (**3**). Hydroxyl radicals may arise from the disproportionation of phenylsulfonyl radicals [10] (Scheme 4).

In conclusion it should be pointed out that *N*-[(4-benzoyl)-benzenesulfonyl]benzenesulfonamide undergoes effectively S–N bond cleavage but the process is not into equal part and it depends on the nature of the bond in the molecule.

3. Experimental

3.1. Synthesis

Synthesis of *N*-[(4-benzoyl)benzenesulfonyl]benzenesulfonamide (**1**) was described elsewhere [3].

3.2. Irradiation

A solution of **1** (0.17 g) in distilled water (400 cm^3) was irradiated under helium for 1 h in a photochemical reactor type RQ 400, equipped with a 254 nm low pressure lamp.

3.3. Identification of the product

The molecular weight determination of some reaction products was carried out on a mass spectrophotometer, Model AMD 402. The ^1H and ^{13}C NMR spectra were recorded on a Bruker 600 MHz (**4**, **5**) and Varian Mercury 300 MHz (**2**, **3**) spectrometer, using tetramethylsilane as internal standard. All the products of the irradiation were separated by the preparative TLC method (Kiselgel 60 F 254, Merck), eluent chloroform–ethyl acetate, 6:1 v/v, and were further purified by crystallization from chloroform. Melting points (determined on a Boetius apparatus) are uncorrected.

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