The Photochemical Decomposition of Benzenediazonium *o*-Carboxylate in Several Solvents

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The photochemical decompositions of benzenediazonium *o*-carboxylate (**1**) in water, ethanol, acetone, and dichloromethane were studied. In every case, the initial loss of molecular nitrogen to give a zwitterion (**3**) and/or a diradical (**4**) was the primary process. In the solvents which are susceptible to hydrogen abstraction by a radical (ethanol and acetone), reduction takes place to give benzoic acid, through **4**, in a good yield. In water, from which a hydrogen atom is less easily abstracted homolytically, salicylic acid was the main product (24%), while benzoic acid was the minor one (9%). In CH_2Cl_2, the reduction product (benzoic acid, 20%) and biphenylene (10%) were formed. The formation of the latter compound prompted us to study the photochemical decomposition of **1** in CH_2Cl_2 in the presence of tropone. This reaction gave cycloaddition products, (**11**) and (**12**), in 3.2 and 0.7% yields respectively.

Aromatic diazonium compounds readily lose molecular nitrogen, leaving a positive charge or an odd electron on the carbon atom which have been originally bonded to the diazonium group, when irradiated in solution.[1]

It is well known that benzenediazonium *o*-carboxylate (**1**) decomposes to 1,2-dehydrobenzene (**2**), with the simultaneous loss of N_2 and CO_2, when flash-photolyzed in a solid state.[2] Although the production of **2** in solution by the photolysis of *o*-iodophenylmercuric iodide,[3] phthaloyl peroxide,[3,4] and benzothiadiazole 1,1-dioxide[5] had been confirmed, the photochemical behavior of **1** in solution has not yet been described.

The present authors were interested in comparing the fate of **1** and the reactivities of **2** under photolysis with those under thermolysis.[6] In this article, we wish to report on the photochemical reaction of **1** in several solvents. The results are summarized in Table 1, accompanied by some data of the thermal decomposition.

The table shows that the reaction proceeds with an initial loss of molecular nitrogen, followed either by a reaction with the solvent used or by a loss of carbon dioxide.[7]

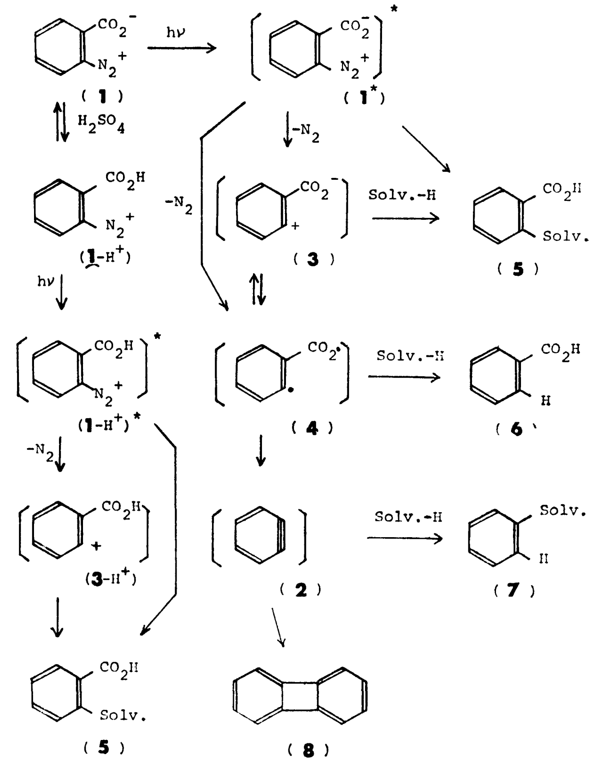
The second stage of the reaction is observed to be as follows: (i) In the solvents which are susceptible to hydrogen abstraction by radicals (No. 4 and 5), the abstraction by the diradical (**4**) occurs as the main course of the decomposition to give benzoic acid, especially in the case of ethanol as a solvent in a high yield (92%). (ii) Irradiation in water, from which the hydrogen atom is less easily abstracted homolytically, gave salicylic acid as the main product (24%), along with some benzoic acid (9%). The formation of benzoic acid in water is remarkable, since the photochemical decomposition of *p*-nitrobenzenediazonium chloride in an aqueous solution proceeds heterolytically and gives no reduction product.[1c] The formation of benzoic acid was somewhat suppressed when **1** was irradiated either in dilute sulfuric acid or in aqueous sodium chloride; instead a nucleophilic attack by water on either (**1**–H^+)* or (**3**–H^+), or by the chloride ion on either (**1***) or (**3**), may occur. (iii) Dehydrobenzene is formed in only a trace amount in the solvents other

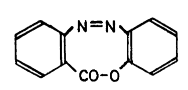
TABLE 1. PHOTOCHEMICAL AND THERMAL DECOMPOSITIONS OF BENZENEDIAZONIUM *o*-CARBOXYLATE IN SOME SOLVENTS

No.	Photochemical decomposition			Yields of the products			
	A[a] (g)	Solvents (340 ml)	Decomposition Time (hr)	Salicylic acid (%)	Benzoic acid (%)	Phenol (%)	Biphenylene (%)[14]
1	1.40	H_2O	2.0	24.4	9.2	2.6	—
2	1.40	H_2O (NaCl 40 g)	2.8	24.2 3.5[d]	2.4	—	—
3	1.40	0.1M H_2SO_4	2.0	37.0	3.5	1.9	—
4	1.40	EtOH	0.5	2.1[e]	92.5	—	—
5	1.90	Acetone	1.5	0.7	45.0	—	1
6	2.74	Acetone (LiCl 4.2 g)	4.0	3.4 2.1[d]	27.0	—	1
7	2.74	CH_2Cl_2	0.83	—	20.0	—	9.9
Thermal decomposition							
8	1.4	H_2O	1.0	88.6	—	—	—
9	1.4	EtOH	1.0	36.1[e]	18.5	2.0[f]	Trace
10	5.0	Acetone	1.0	—	15.0	—	7.0

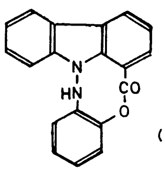
a) The amount of anthranilic acid used for preparation of **1**. b) The yields were calculated based on the amount of **1** used. c) A similar result was reported by Stiles *et al.*[13] d) *o*-Chlorobenzoic acid. e) Salicylic acid ethyl ether. f) Phenetole.

than dichloromethane, in which the photochemical decomposition proceeds to give an appreciable amount (10%) of biphenylene (**8**) through **2**. Since a nucleophilic attack by solvent is prohibited in this case, the rate of the loss of carbon dioxide from **4** is competitive with that of H-abstraction by **4**. In the photochemical decomposition of **1** in acetone, we could not detect the dehydrobenzene-adducts of **1**, **9** and **10**, reported earlier in the thermal decomposition of **1** in acetone,[8] because **4** does not lose CO_2 to give dehydrobenzene, but instead readily abstracts hydrogen from acetone to give benzoic acid under such a comparatively low temperature.

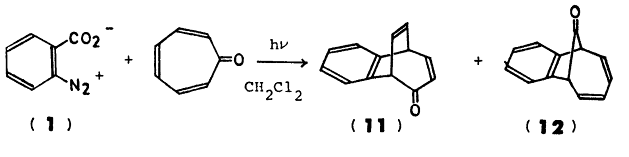


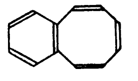


(**9**)

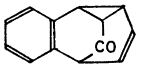


(**10**)

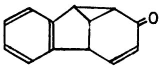




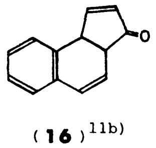
(**13**)[10a]



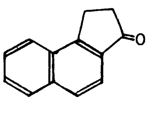
(**14**)[10b]



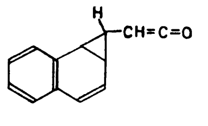
(**15**)[11c]



(**16**)[11b]



(**17**)[11b]



(**18**)[11a)11b]

In contrast to the photochemical decomposition, the thermal decomposition of **1** proceeds in preference to the nucleophilic substitution on **1** in protic solvents upon the radical reaction through **4**, but in the aprotic solvents the intermediate, **4**, readily loses CO_2 thermally to give **2**.[9]

As it was found that the photochemical decomposition of **1** in CH_2Cl_2 gave **2** as the reactive intermediate, we tried the reaction with tropone. After the irradiation of **1** and tropone (1.5 equivalent mole) in CH_2Cl_2 for 3 hr, the 1,4-adduct (**11**) and the 1,6-adduct (**12**) were obtained in 3.2 and 0.7% yields respectively. The ratios of the amounts of **12** to **11** in several runs varies from 0.1—0.3, but the value was clearly larger than that of the thermal reactions, **12**: **11**=0.06—0.08. Although **11** and **12**, the adducts, were known to be sensitive to the irradiation conditions used to produce rearranged products, (**13**)—(**18**),[10,11] we could not detect such products in the present photolysis experiments.*

Experimental

Benzenediazonium o-*Carboxylate (1)*. The starting material (**1**) was prepared as has been described before[12] and was used directly after having been washed successively with cold CH_2Cl_2 and cold ether. The purity of **1** was checked by means of its UV and IR spectra.[13] The wave lengths of the UV maxima of **1** in CH_2Cl_2 (257, 303^{infl} nm) were similar to those taken in water, but new maxima at 244 and 253 nm, due to biphenylene, appeared within a few minutes at room temperature.

Irradiation Apparatus. Irradiation was carried out internally in an immersion-type quartz vessel using an Ushio high-pressure mercury lamp (UM-452) through a Pyrex filter. During the irradiation, the vessel was cooled externally with ice–water.

General Procedure. A solution or suspension of **1** in an appropriate solvent was deoxygenated by bubbling in nitrogen gas for five minutes and then irradiated under nitrogen until the gas evolution had ceased. In the case of irradiation in an aqueous solution, the mixture was extracted with ether. In other cases, the solvents were evaporated *in vacuo* and the residues were taken up in ether or in CH_2Cl_2. These extracts were then washed with water and extracted successively with 5% aqueous $NaHCO_3$ and aqueous NaOH; finally, they were washed with water and dried (anhyd. Na_2SO_4). From this organic layer, the neutral part was obtained and separated by column chromatography (silicic acid/$CHCl_3$). From the extracts obtained with 5% aqueous $NaHCO_3$ and 1 M NaOH mentioned above, the acidic and the phenolic products were isolated respectively after acidification with 1 M HCl and extraction with ether. The acid mixture was further characterized by glc after transformation to its esters with diazomethane in ether. The identification of the products was carried out by a direct comparison of their IR, UV, and NMR data with those of authentic samples.

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* In the present stage, the reason why the ratios of **12** to **11** are different to each other between thermal and photochemical reactions is not clear.

The glc Retention Times of the Individual Compounds. The identification by glc was carried out by means of a Shimadzu GC-1A instrument using a column, 2.1 m×ϕ8 mm, packed with 20% Apiezon L on Chromosorb E at 183 °C and a H_2 flow rate of 80 ml/min; retention times (min), methyl benzoate, 3.3; methyl salicylate, 5.4; methyl *o*-chlorobenzoate, 6.9; methyl *o*-ethoxybenzoate, 10.7.

Irradiation of 1 in CH_2Cl_2 in the Presence of Tropone. **1**, prepared from anthranilic acid (3.0 g, 22 mM) and suspended in CH_2Cl_2 (340 ml) containing tropone (4.5 g, 42 mM), was irradiated at 15 °C for 3 hr using the abovementioned apparatus. After washing with 1 M NaOH and drying (anhyd. Na_2SO_4), the CH_2Cl_2-solution was concentrated to dryness to give a brown liquid, which was then chromatographed (benzene) on silicic acid (100 g). Fractions were collected every 100 ml; Fractions 3—4 gave a 1,6-cycloaddition product (**12**) (97 mg), and Fractions 5—6, a 1,4-cycloaddition product (**11**) (151 mg). The repeated chromatography and sublimation of each product gave: **11**, 91 °C/4 mmHg, 138 mg (3.2%), mp 84—84.5 °C, tlc (silica gel/benzene) R_f-value 0.29; **12**, 80 °C/4 mmHg, 28 mg (0.7%), mp 79.5—80 °C, R_f-value 0.38. These substances were identified by direct comparison with an authentic sample reported earlier.[10]

Similar results were obtained in acetonitrile as the solvent; **11**, 3.5% yield; **12**, 0.3% yield.

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