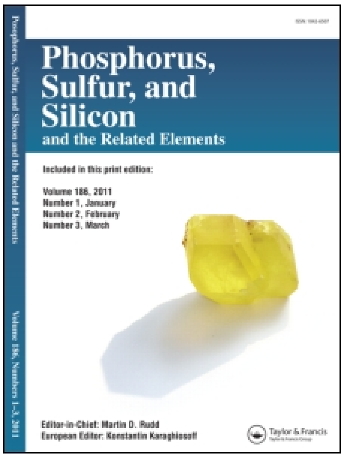

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PHENYLATION OF PYRIDINE BY PHOTOLYSIS OF DIPHENYL SULFONE

by

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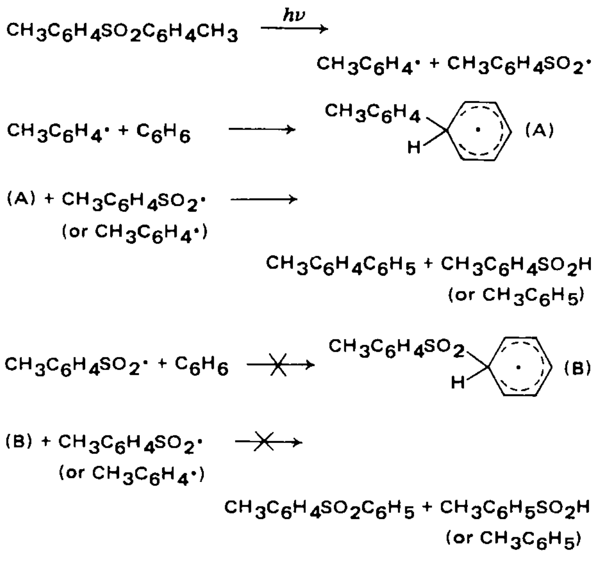
ABSTRACT

The photolysis of diphenyl sulfone in neat pyridine or pyridine diluted with the organic solvent, with a high-pressure mercury arc lamp, was studied. The presence of acetone in the reaction system remarkably promoted photochemical conversion of the sulfone. The isomer distribution ratios ($\beta > \alpha > \gamma$) of phenylpyridines produced during the reaction were clearly different from those ($\alpha > \beta > \gamma$) so far reported for a free-radical phenylation of pyridine. Benzenesulfinic acid produced in the reaction was separated from the product mixture and identified as its S-benzylthiuronium derivative.

In 1967 Kharasch and Khodair[1] reported that the photolysis of aromatic sulfones (diphenyl and di-*p*-tolyl) in benzene produces aryl radicals which give rise to the corresponding biphenyls in good yields. They proposed the following intermolecular mechanism since the photolysis of di-*p*-tolyl sulfone in benzene gave only *p*-methylbiphenyl and no *p,p*′-dimethylbiphenyl.



This mechanism (under similar conditions as in ref. 1) was confirmed recently by Oae and coworkers[2] in the photolysis of a benzene solution of diphenyl sulfone specifically labeled with ^{14}C at 1-position of diphenyl sulfone. More recently, Khodair and coworkers[3] reported that the photolysis of a series of symmetrical and unsymmetrical aromatic sulfones in dilute benzene solutions gives rise to the corresponding monosubstituted biphenyl derivatives.

We also demonstrated in our previous paper[4] that diphenyl sulfone in selected aromatic solvents undergoes photolysis to afford the corresponding isomeric biphenyls (*o*-, *p*-, and *m*-). In an extension of these studies we have examined the photolysis of diphenyl sulfone in pyridine. Most of the present work was carried out using pyridine containing the organic solvents such as acetone, acetonitrile, and *i*-propanol, because the photolysis of diphenyl sulfone in neat pyridine was extremely slow.

Results and Discussion

Diphenyl sulfone (1.5 mmol, 327.4 mg) in 100 ml of pyridine or pyridine diluted with the organic solvent was irradiated for various periods at room temperature, with a 400-W high-pressure mercury arc lamp. After the irradiation, the unchanged sulfone and the isomeric phenylpyridines produced during the reaction were identified and estimated by glc. The results are summarized in Table I. Table I indicates that the presence of acetone in the reaction system enhances remarkably the photochemical conversion of the sulfone. However, supplementary work showed that when a low-pressure mercury arc lamp was employed the presence of acetone did not enhance the photochemical conversion of the sulfone. Table I also shows that yields of phenylpyridines produced in the presence of acetonitrile or *i*-propanol (Runs 6 and 7) were low compared with those obtained in the cases of neat pyridine (Run 1) and acetone-pyridine (Runs 2, 3, 4, and 5). In Runs 1,

TABLE I

Phenylation of Pyridine by Photolysis of Diphenyl Sulfone[a]

Run	Pyridine used, ml	Solvent used, ml	Irrad. time, hr	Photolysis, %	Yield[b] of phenylpyridines, %	Isomer ratios of phenylpyridines, %		
						α-	β-	γ-
1	100	0	30	9.3	115.0	28.1	66.1	5.8
2	50	$(CH_3)_2CO$, 50	5	27.6	92.5	26.4	65.5	8.1
3	50	$(CH_3)_2CO$, 50	20	44.1	99.0	27.0	65.1	7.9
4	25	$(CH_3)_2CO$, 75	20	34.1	105.0	29.7	62.7	7.6
5	90	$(CH_3)_2CO$, 10	20	28.5	121.5	29.1	65.0	5.9
6	50	CH_3CN, 50	20	13.0	86.8	20.2	71.8	8.0
7	50	$(CH_3)_2CHOH$, 50	20	6.9	73.1	23.9	67.5	8.5

[a] In all runs, about 100 ml of 0.015 *M* solution was photolyzed at room temperature using a high-pressure mercury arc lamp.

[b] The yield recorded is based on the amount which actually underwent photolysis and on the assumption that one mole of the sulfone yielded one mole of phenylation product.

4, and 5, the yields of the phenylpyridines were greater than 100%. These results seem reasonable by assuming that benzenesulfinic acid produced in the course of the reaction reacts with pyridine to give its pyridinium salt. Then the salt is photodecomposed gradually in pyridine to afford the phenylpyridines.

From this point of view, further work was carried out; authentic benzenesulfinic acid (1.5 mmol, 213.3 mg) in 100 ml of 1 : 1 pyridine-acetone was photolyzed for 20 hr in the same manner as for the sulfone, yielding small amounts (α, 9.5 mg; β, 5.64 mg; γ, 2.76 mg) of the phenylpyridines. In Run 2, besides the isomeric phenylpyridines, benzenesulfinic acid could be isolated from the product mixture and identified as its S-benzylthiuronium derivative.[5]

The isomer distribution ratios of the phenylpyridines in Table I are in the order of $\beta > \alpha > \gamma$ regardless of the presence or absence of the organic solvent in the reaction system. In order to examine whether or not phenylpyridines undergo mutual isomerization under our conditions, authentic specimens in acetone were irradiated separately in the same way as for the sulfone. Glc analyses of the irradiated solutions showed that all the phenylpyridines were recovered unchanged. The results indicated in Table I are inconsistent with the fact that the isomeric distribution ratios[6–9] reported for a free-radical phenylation of pyridine is generally in the order of $\alpha > \beta > \gamma$, irrespective of the sources of phenyl radical. This discrepancy may be interpreted either way as mentioned below. First, (a) the behavior

TABLE II

Phenylation of Pyridine by Radicals Generated from Benzoyl Peroxide and Iodobenzene

Radical source	Reaction condition	Isomer ratios of phenylpyridines		
		α-	β-	γ-
Benzoyl peroxide[a]	irradiated for 20 hr at room temp. with a 400-W high-press. Hg lamp	51.1	32.5	15.4
Iodobenzene[a]	irradiated for 20 hr at room temp. with a 400-W high-press. Hg lamp	48.3	34.9	16.8
Benzoyl peroxide[b]	refluxed for 24 hr	48.5	32.5	19.0

[a] In these runs, 100 ml of 0.015 *M* 1 : 1 acetone/pyridine solution was used.

[b] In this run, 650 mg of benzoyl peroxide in 25 ml of pyridine was used.

of radicals photochemically generated and that of radicals thermally generated are slightly different due to the difference of the solvation. In order to explore this possibility, isomer distribution ratios of the phenylpyridines obtained from the photolysis of the sulfone were compared with those obtained from the thermolysis of the sulfone. However, since no detectable thermal decomposition of the sulfone in pyridine was noted in about 200 hr at 300° using an autoclave, benzoyl peroxide was chosen in place of the sulfone and employed for comparison of the results from the photolysis and thermolysis. The reaction conditions and results obtained are summarized in Table II, which also contains the results from the photolysis of iodobenzene in pyridine. The isomer distribution ratios of the phenylpyridines shown in Table II are in agreement with those in the literature and independent of such reaction conditions as photolysis and thermolysis. Accordingly, the first possibility (a) can be ruled out. Next, (b) an intermediate species is formed under the uv-irradiation between the sulfone and pyridine. Then the intermediate species undergo photodecomposition to produce isomeric phenyldihydropyridyl radicals, resulting in the isomer distribution ratios of the phenylpyridines as shown in Table I. Although the reaction pathways *via* (b) seem plausible for the present reaction, no clear evidence is found for this possibility at this time. Therefore, the present reaction can be formulated only by the following overall reaction equation.

$$C_6H_5SO_2C_6H_5 + C_5H_5N \xrightarrow{h\nu} \underset{(\alpha,\ \beta,\ \text{and}\ \gamma)}{C_6H_5C_5H_4N} + C_6H_5SO_2H$$

In the presence of hydrogen-atom donating solvents such as acetonitrile and *i*-propanol benzene would be produced at the expense of the phenylpyridines. Also, details concerning the photosensitization process of acetone indicated in the present study remain to be established.

Experimental Section

Materials

Commerical diphenyl sulfone was recrystallized from benzene three times, mp 122–124°. Pyridine, acetone, acetonitrile, and *i*-propanol were commercial spectroscopic grade and used without further purification. Authentic isomeric phenylpyridines (α, β, and γ) were prepared from benzenediazonium chloride and pyridine by the Gomberg-Hey reaction.[10] All the authentic specimens were purified, by recrystallizations (γ) to constant melting point or preparative glc (α and β) on a $\frac{3}{8}$ in x10 ft column packed with 30% SE-30 on Celite 545, using a Varian Aerograph Series 1700 Gas Chromatograph. The purity of each authentic compound was checked by glc; single peaks were observed in each case.

General Procedure for the Photolysis of Diphenyl Sulfone

A solution of diphenyl sulfone (1.5 mmol, 327.4 mg) in 100 ml of pyridine or pyridine-organic solvent (acetone, acetonitrile, or *i*-propanol) was placed in a quartz cylinder. The solution was irradiated for various lengths of time at room temperature, with a high-pressure mercury arc lamp. After irradiation, the photolysate was transferred to a round-bottomed flask, and the solvent and excess pyridine were removed by means of a rotary evaporator. The residue was triturated with benzene several times. The benzene solution was washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was placed in a volumetric flask, adjusted to an appropriate volume with acetone, and subjected to glc analysis by a Shimazu Gas Chromatograph GC-3AF with a flame-ionization detector.

The isomeric phenylpyridines (α, β, and γ) produced in the reaction were identified by comparison of their retention times with those of authentic specimens, and their amounts were estimated by use of calibration curves. Columns employed in glc analyses were as follows; a 1 m x 3 mm column packed with 5% SE-30 on chromosorb W for diphenyl sulfone and a 3 m x 3 mm column packed with 5% OV-210 on Shimalite W (201 D) for isomeric phenylpyridines.

Identification of Benzenesulfinic Acid Produced in the Reaction

In all runs, some water-soluble product was also obtained, but not investigated except in Run 2. In Run 2, after irradiation during 5 hr, acetone and excess pyridine were removed under reduced pressure. The residue was dissolved in benzene; the solution was washed several times with small amounts of water to obtain a water-soluble material from the reaction products. After the aqueous solution was filtered, to the filterate was added a warm saturated aqueous solution of S-benzylthiuronium chloride (0.1 g). A small amount of a crystalline precipitate was separated from the solution after being kept overnight at room temperature. It was identified by mixed melting point with authentic S-benzylthiuronium benzenesulfinate.[5]

Phenylation of Pyridine by Radicals generated from Benzoyl Peroxide and Iodobenzene

A pyridine solution of benzoyl peroxide or iodobenzene was conducted under the conditions as mentioned in Table II. At the end of the reaction period, pyridine or acetone was removed *in vacuo*. The residue was triturated several times with benzene, and the solution was washed with water or 10% aqueous sodium thiosulfate to remove iodine produced in the reaction in the case of iodobenzene. The solution was dried over anhydrous soidum sulfate, and then benzene was removed under reduced pressure. The residue which contains the unchanged starting compound and isomeric phenylpyridines produced in the reaction was subjected to glc analysis.

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