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Para Tolylation of Pyridine by Photolysis of Di-*p*-Tolyl Sulfone and Related Compounds

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Synopsis. Di-*p*-tolyl sulfone, sulfoxide and sulfide, *p*-toluoyl peroxide, and *p*-iodotoluene were respectively photolyzed in pyridine with a mercury arc lamp. It was found that all the compounds decompose photochemically to yield the isomeric *p*-tolylpyridines (α, β, and γ). The isomer distribution ratios ($\beta>\alpha>\gamma$) obtained with the sulfone differ from those ($\alpha>\beta>\gamma$) with the other compounds. The presence of acetone in the reaction system remarkably promoted the photochemical conversion of both the sulfone and sulfoxide.

Kharasch and Khodair¹⁾ first reported that the photolysis of diaryl sulfone, sulfoxide, and sulfide in benzene produces aryl radicals which afford the corresponding biphenyl derivatives in good yields. They proposed the following intermolecular mechanism: the photolytic cleavage of the C–S bond of the sulfone, sulfoxide, or sulfide gives the aryl radical which, in turn, reacts with benzene to form the intermediate arylcyclohexadienyl radical, and finally the corresponding biphenyls are produced by the hydrogen atom abstraction from the intermediate. The mechanism was confirmed by Nakai *et al.*²⁾ in the photolysis of a benzene solution of diphenyl-$1,1'$-$^{14}C_2$ sulfone. Khodair *et al.*³⁾ reported that the photolysis of a series of symmetrical and unsymmetrical aromatic sulfones in benzene solutions gives rise to only the corresponding monosubstituted biphenyls but no disubstituted biphenyls. Diphenyl sulfone in selected aromatic solvents undergoes photolysis to afford the corresponding isomeric biphenyl derivatives (*o*-, *p*-, and *m*-).⁴⁾ This also supports the above mechanism involving the attack of aryl radical on aromatics used as the solvent. In the course of studies on the photolysis of aromatic sulfones, it was found⁵⁾ that the photolysis of diphenyl sulfone in a pyridine solution gives rise to three isomeric phenylpyridines whose isomer distribution ratios ($\beta>\alpha>\gamma$) differ from those ($\alpha>\beta>\gamma$) for a free-radical phenylation of pyridine. The purpose of the present work is to examine whether or not the order of the isomer distribution ratios of *p*-tolylpyridines produced by the photolysis of di-*p*-tolyl sulfone in pyridine coincides with that obtained with the diphenyl sulfone.

Di-*p*-tolyl sulfone (1.5 mmol, 369.5 mg) in 100 ml of pyridine or pyridine–acetone (1 : 1 in volume) was irradiated for 20 h or 50 h at room temperature, with a 400-W medium pressure mercury arc lamp. After irradiation, the unchanged sulfone and isomeric *p*-tolylpyridines produced in the reaction mixture were identified and estimated by gas chromatography. For the sake of comparison, di-*p*-tolyl sulfoxide and sulfide, *p*-toluoyl peroxide, and *p*-iodotoluene were photolyzed in the same way as for the sulfone. The results are summarized in Table 1. We see that acetone photosensitized the degradation of both sulfone and sulfoxide in pyridine solutions, but decreased markedly the yield of the isomeric *p*-tolylpyridines with sulfoxide. The isomer distribution ratios of the *p*-tolylpyridines were hardly or not at all affected by the acetone present in the reaction mixture. Either di-*p*-tolyl sulfoxide or sulfide was photolyzed in acetone to give *p*-tolyl radical which abstracts a hydrogen atom from acetone affording toluene in a good yield. Accordingly, the low yields of the *p*-tolylpyridines both with the sulfoxide and sulfide in the presence of acetone seem to be ascribed to the competitive formation of toluene with the *p*-tolylpyridines. The isomer distribution ratios ($\beta>\alpha>\gamma$) with the sulfone differ from those ($\alpha>\beta>\gamma$) obtained with the other compounds (Table 1), being comparable to those with diphenyl sulfone.⁵⁾ The gross isomer distribution ratios

Table 1. Para tolylation of pyridine by photolyses of di-*p*-tolyl sulfone and related compounds

Compound	Irrad. time (h)	Pyridine (ml)	Acetone (ml)	Photolysis^a)^ (%)	Yield^b)^ of *p*-tolylpyridines (%)	Isomer ratios^c)^ of *p*-tolylpyridines (%)		
						α	β	γ
$(p\text{-}CH_3C_6H_4\text{-})_2SO_2$	50	100	0	15.6	104.0	21.7	66.4	11.9
$(p\text{-}CH_3C_6H_4\text{-})_2SO_2$	20	50	50	50.8	92.4	26.3	64.9	8.8
$(p\text{-}CH_3C_6H_4\text{-})_2SO$	20	100	0	19.6	99.1	47.2	35.4	17.4
$(p\text{-}CH_3C_6H_4\text{-})_2SO$	20	50	50	100.0	51.2	51.9	29.9	18.2
$(p\text{-}CH_3C_6H_4\text{-})_2S$	20	100	0	65.5	58.2	50.3	31.7	18.0
$(p\text{-}CH_3C_6H_4\text{-})_2S$	20	50	50	54.0	35.2	50.7	27.5	21.7
$(p\text{-}CH_3C_6H_4COO\text{-})_2$	20	100	0	d)	d)	46.8	32.0	21.2
$p\text{-}IC_6H_4CH_3$	20	100	0	d)	d)	44.2	38.4	17.5

a) Determined by estimation of the unchanged starting compounds. b) Based on the amount which actually underwent photolysis and on the assumption that 1 mole of the starting compound gives 1 mole of *p*-tolylpyridines. c) Preliminary work indicated that authentic *p*-tolylpyridines do not isomerize mutually under our reaction conditions. d) Not determined.

in a free-radical phenylation of pyridine are essentially independent of the source of phenyl radicals.[6,7] Abramovitch and Saha[8] reported that in the reaction with *p*-tolyl radical generated by the Gomberg-Hey reaction, the isomer distribution ratios of *p*-tolylpyridines are $\alpha=58.0\%$, $\beta=26.2\%$, and $\gamma=15.7\%$. This suggests that the *p*-tolylation of pyridine with compounds other than the sulfone proceeds *via* simple *p*-tolyl radical generated from the radical sources themselves under UV irradiation. Although the reason for the characteristic result obtained with the sulfone is ambiguous, we propose the following mechanism based on the fact that the yield of the *p*-tolylpyridines with the sulfone does not decrease substantially even in the presence of acetone : the sulfone in pyridine interacts on UV irradiation with pyridine to form a sulfone-pyridine complex[9] which decomposes exclusively into the *p*-tolylpyridines giving the isomer distribution ratios of $\beta>\alpha>\gamma$.

Experimental

Materials. Commercial di-*p*-tolyl sulfone (mp 160 °C), di-*p*-tolyl sulfoxide (mp 96—97 °C), and *p*-iodotoluene were purified by recrystallization or preparative gas chromatography. *p*-Toluoyl peroxide (mp 134—135 °C, dec : lit[10] 136—137 °C, dec) was prepared by the method given in literature from the reaction of *p*-toluoyl chloride with sodium peroxide and purified by recrystallization from ethanol. Di-*p*-tolyl sulfide (mp 56—57.5 °C) was supplied by Dr. S. Tamagaki, Osaka City University. Pyridine and acetone were of spectroscopic grade and used without further purification. Authentic α-*p*-tolylpyridine was prepared from the corresponding bromopyridine according to the procedure of Abramovitch and Saha.[11] Authentic β-*p*-tolylpyridine was prepared by a slight modification of the procedure since it was found that a mixture of β-*p*-tolylpyridine and 4-methyl-1-(3-pyridyl)-1-cyclohexene was produced by the procedure; additional dehydrogenation of the above mixture was carried out with elemental sulfur at 200 °C. The two *p*-tolylpyridines thus obtained were purified by preparative gas chromatography on a 5 m × 3 mm column packed with 20% OV-210 on Shimalite W (210 D), using a JEOL Chromatograph, JGC-650. Authentic γ-*p*-tolylpyridine was prepared by the dehydrogenation of γ-*p*-tolyl-1,2,3,6-tetrahydropyridine obtained from *p*-α-dimethylstyrene, ammonium chloride, and formaldehyde.[12] The compound was purified by recrystallization twice from hexane (mp 90—91 °C, lit,[12] 90—91 °C).

*General Procedure for the Photolysis of Di-*p*-Tolyl Sulfone and Related Compounds.* The procedure for the sulfone is described here as a typical run. A 0.015 M-solution of di-*p*-tolyl sulfone in 100 ml of pyridine or pyridine-acetone (1 : 1 in volume) was placed in a quartz cylinder. The solution was irradiated for 50 h or 20 h at room temperature, with a 400 W-medium pressure mercury arc lamp. After the irradiation, the photolysate was transferred to a round-bottomed flask, acetone or pyridine being removed by means of a rotary evaporator. The residue was treated with benzene in order to remove benzene-insoluble materials. The benzene solution was washed with water and dried over anhydrous sodium sulfate. After most of the solvent had been evaporated, the oily residue was placed in a volumetric flask, adjusted to an appropriate volume with acetone, and subjected to GLC analysis to determine the unchanged sulfone and isomeric *p*-tolylpyridines produced in the reaction. All the GLC analyses were carried out with use of a Shimadzu Gas Chromatograph GC-3AF equipped with a flame ionization detector. The unchanged sulfone and isomeric *p*-tolylpyridines obtained were identified by comparison of their retention times with those of authentic specimens, their amounts being estimated by use of calibration curves for the authentic compounds. A 3 m × 3 mm column packed with 5% OV-210 on Shimalite W (210 D) was employed in the GLC analyses.

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