CHEMISTRY LETTERS, pp. 393-396, 1972. Published by the Chemical Society of Japan

AROMATIC SUBSTITUTION WITH ARENESULFONYLOXY FREE RADICAL [1)]

Michio KOBAYASHI, Masatsugu SEKIGUCHI, and Hiroshi MINATO
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

m-Nitrobenzenesulfonyl peroxide has been photolyzed in nitrobenzene and benzonitrile. On the basis of the product analyses, the reactivity of the sulfonyloxy radical is discussed.

Various S-containing free radicals have been reported in the literature, but concerning the reactions of sulfonyloxy radicals very little is known. In an attempt to generate a sulfonyloxy radical, m-nitrobenzenesulfonyl peroxide in aromatic solvents has been irradiated with UV light, and it has been found that aromatic substitution with the sulfonyloxy free radical occurs producing aryl m-nitrobenzenesulfonates. The results will be described in this communication.

m-Nitrobenzenesulfonyl peroxide (I) is fairly stable at room temperature, and no change is observed for several months when stored at -20°C. It reacts very rapidly with benzene or toluene at room temperature, producing aryl m-nitrobenzenesulfonates and m-nitrobenzenesulfonic acid in high yield.[2)] With nitrobenzene the reaction is much slower, and m-nitrophenyl m-nitrobenzenesulfonate and m-nitrobenzenesulfonic acid are produced. A Hammett equation holds for relative rates of reaction of this peroxide with various arenes.[3)] These findings together with the results of an oxygen-18 study [3)] suggest that the thermal reactions of (I) with arenes are electrophilic substitution reactions.[3,4)]

When a nitrobenzene (or benzonitrile) solution (300 ml) of (I) (3.0 mmol) was irradiated by use of a high-pressure mercury lamp under nitrogen at room temperature, fairly rapid decomposition took place. Decomposition was followed by iodometric titrations of the remaining (I). As shown in Table, the rates of photolyses are much greater than those of thermolyses, especially in benzonitrile. Yields of aryl m-nitrobenzenesulfonates were determined by glc (Silicone SE 30 column).

TABLE

Photolyses and Thermolyses of (I) in $PhNO_2$ and PhCN

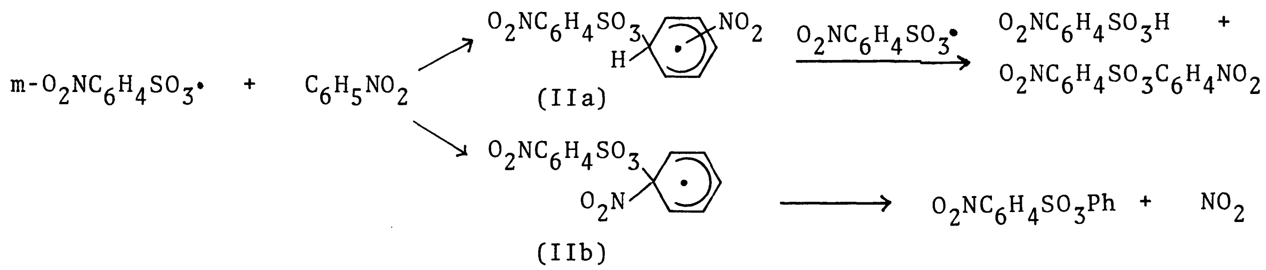
	in $PhNO_2$		in PhCN	
	Photolysis	Thermolysis	Photolysis	Thermolysis
Reaction Temperature (°C)	13 ± 2	20	11 ± 2	18
10^5 k_1 (sec^{-1})	3.9	1.4	32	3.6
Products (mol/mol(I))				
m-$O_2NC_6H_4SO_3H$	1.5	0.9	1.5	1.2
m-$O_2NC_6H_4SO_3C_6H_5$	0.28	0	0	0
m-$O_2NC_6H_4SO_3C_6H_4X$	X = NO_2		X = CN	
	0.047	0.72	0.35	0.43
	o 21%	o 0%	o 43%	o 39%
	m 58%	m 100%	m 35%	m 42%
	p 21%	p 0%	p 22%	p 19%

In nitrobenzene, the thermolysis gave only the m-nitrophenyl sulfonate, whereas the photolysis gave a mixture of the o-, m- and p-isomers. This finding shows that the photolytic sulfonyloxylation involves m-nitrobenzenesulfonyloxy free radical. In benzonitrile, o- and p-cyanophenyl sulfonates were formed in addition to the meta isomer in the thermolysis because of the weaker electron-withdrawing character of the cyano group in comparison with the nitro group. However, the isomer distributions are different; in the thermolysis the yield of the meta isomer is large whereas in the photolysis the yields of the ortho and para isomers are large.

The percentage of the meta-substitution of nitrobenzene with sulfonyloxy radical is much greater than that with phenyl radical (m-, 5-10%, o-, 60-70%, p-, 10-30%). These data show the electrophilic nature of sulfonyloxy radical. Benzoyloxy radical is a similar acyloxy radical of electrophilic nature, and is known to give no nitrophenyl benzoate upon reaction with nitrobenzene.5) Recently it was shown by CIDNP that pentafluorobenzoyloxy radical attacks only the meta position of nitrobenzene.6) Since the σ value of the benzenesulfonyl group is greater than that of the benzoyl group, the electrophilicity of a benzenesulfonyloxy radical is expected to be greater than that of benzoyloxy radical. It is interesting that the results of the aromatic substitution of these radicals are the opposite to what is expected.

The fact that phenyl m-nitrobenzenesulfonate was found in the photolysis of (I) in nitrobenzene is very interesting. This can be explained in terms of the attack of m-nitrobenzenesulfonyloxy radical to nitrobenzene at the carbon atom connected with the nitro group. The reactions of m-nitrobenzenesulfonyloxy radical with nitrobenzene can be summarized in the following scheme.

$$(\text{m-}O_2NC_6H_4SO_2\text{-}O\text{-})_2 \xrightarrow{h\nu} 2\ \text{m-}O_2NC_6H_4SO_2\text{-}O\bullet$$



Since the addition of sulfonyloxy radicals to arene is probably reversible like the addition of benzoyloxy radicals,[5,7] cyclohexadienyl radical (IIa) will dissociate back to the sulfonyloxy radical and nitrobenzene when abstraction of hydrogen from (IIa) is slow. It is likely that abstraction of hydrogen from bulky sulfonyloxycyclohexadienyl radical (IIa) with the bulky and electrophilic sulfonyloxy radical is slow. On the other hand, help of the hydrogen-abstracting agents is not necessary for the formation of phenyl m-nitrobenzenesulfonate from another cyclohexadienyl radical (IIb). Consequently the yield of the phenyl ester is greater than that of the m-nitrophenyl ester.

Displacement of nitro group on arenes with carbon radicals has not been reported in the literature. This is probably because the cyclohexadienyl radicals formed do not tend to regenerate the original carbon radicals and arenes, and because some carbon radicals attack the oxygen atom of the nitro group, producing nitrosobenzene derivatives.[8] Sulfonyloxy radical, being the oxygen radical, is not likely to attack the oxygen atom of nitro groups. Free radical displacement of a nitro group on arenes by sulfonyloxy radicals is unique and interesting.

References

1) Organic Sulfur Compounds. XXXV.

2) R. L. Dannley and G. E. Corbett, J. Org. Chem., 31, 153 (1966).

3) Y. Yokoyama, H. Wada, M. Kobayashi, and H. Minato, Bull. Chem. Soc. Japan, 44, 2479 (1971).

4) R. L. Dannley, J. E. Gagen, and O. J. Stewart, J. Org. Chem., 35, 3076 (1970).

5) T. Nakata, K. Tokumaru, and O. Simamura, Tetrahedron Lett., 1967, 3303.

6) J. Bargon, J. Amer. Chem. Soc., 93, 4630 (1971).

7) J. Satiel and H. C. Curtis, ibid., 93, 2056 (1971).

8) N. Inamoto and O. Simamura, J. Org. Chem., 23, 408 (1958).

(Received March 24, 1972)