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# THE INTERCEPTION OF HYDRAZINO RADICALS IN THE OXIDATION OF ARYLHYDRAZINES

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The oxidation of arylhydrazines can involve diimides (1) or aryl radicals (2) as reactive intermediates thus

$$ArNHNH_2 \longrightarrow ArNHNH \longrightarrow Ar\text{-}N{=}N\text{-}H \longrightarrow ArN{=}N^{\bullet} \longrightarrow Ar^{\bullet}$$

We have succeeded in intercepting the first of the radicals in this sequence. The technique we used may be illustrated as follows. Sulphur dioxide gas was passed into a stirred solution of phenylhydrazine (46 m.moles) in 150 ml. of dry benzene at 5°. Silver oxide (23 m.moles) was then slowly added. After 1 hour stirring was discontinued and the addition of sulphur dioxide which had been maintained throughout was stopped. The stoppered reaction mixture was allowed to stand for 24 hours at room temperature. The resulting solution, on work-up gave 19.8 m.moles(86%) of N-phenyl-N-benzenesulphonhydrazide, m.p. 156°. This was identical with a sample prepared unambiguously by the reaction of benzene sulphonyl chloride and phenylhydrazine. One sequence to explain the reaction with sulphur dioxide is as follows:

1. $C_6H_5NHNH_2 \longrightarrow C_6H_5NHNH^{\bullet} \longrightarrow C_6H_5$
2. $C_6H_5^{\bullet} + SO_2 \longrightarrow C_6H_5SO_2^{\bullet}$ (3)
3. $C_6H_5SO_2^{\bullet} + C_6H_5NHNH^{\bullet} \longrightarrow C_6H_5SO_2NHNHC_6H_5$

i.e. both phenyl radicals and phenyl hydrazino radicals appear to survive long enough to interact with sulphur dioxide. (4)

We have prepared a series of analogous sulphonylhydrazides by extending the above procedure to a number of other arylhydrazines. The results obtained are summarized below. All the products were also synthesised unambiguously by reaction of the corresponding aryl hydrazine and aryl sulphonyl chloride.

Two efforts were made to determine the extent to which the radicals involved were free. In the first of these the oxidation of phenylhydrazine described above was repeated using as solvent dry benzene containing 0.5 mc. of $\mu$-$C^{14}$-labelled benzene. None of the N-phenyl-benzenesulphonhydrazide

TABLE I . HYDRAZIDE PREPARATIONS

| Hydrazine | Product | Yield % | m.p. |
|---|---|---|---|
| p-$ClC_6H_4NHNH_2$ | p-$ClC_6H_4SO_2NHNHC_6H_4Cl$-p | 88 | 152° |
| p-$BrC_6H_4NHNH_2$ | p-$BrC_6H_4SO_2NHNHC_6H_4Br$-p | 80 | 164° |
| p-$MeC_6H_4NHNH_2$ | p-$MeC_6H_4SO_2NHNHC_6H_4Me$-p | 61 | 154° |
| 2-$C_{10}H_7NHNH_2$[a] | 2-$C_{10}H_7SO_2NHNHC_{10}H_7$-2 | 37 | 165° |
| p-$NO_2C_6H_4NHNH_2$ | p-$NO_2C_6H_4SO_2NHNHC_6H_4NO_2$-p | 24 | 180°[b] |

[a] $C_{10}H_7$ represents naphthyl. [b] The m.p. of N-p-nitrophenyl-p-nitrobenzenesulphonhydrazide has been reported as 160° (H. Limpricht, Ber., 20, 1238 (1887) )and 174° (H. Brintzinger, K. Pfannstiel and H. Noeske, Farben, Lacke, Anstrichstoffe 4, 78 (1950) : Chem. Abs., 44, 5142 (1950).)

isolated (83% yield) was radiolabelled. Thus, no scrambling between the phenyl radicals and any radicals derived from solvent took place. In the second of these experiments, the oxidation of p-bromophenylhydrazine was effected using chlorobenzene as solvent and again no product derived from solvent attack was isolated,the reaction product being N-p-bromophenyl-p-bromobenzenesulphonhydrazide, in 80% yield, a result identical with that obtained using benzene as solvent. Thus, despite the ease with which externally added sulphur dioxide can be introduced into the radical sequence, no solvent based radicals appear to become involved.

## REFERENCES

(1) P.C. Huang and E. M. Kosower, J.Am.Chem.Soc., 89, 3911 (1967).

(2) (a) R. L. Hardie and R. H. Thomson, J.Chem.Soc., 2512 (1957);

(b) H.-H. Stroh and L. Ebert, Chem.Ber., 97, 2335 (1964).

(3) The $SO_2$ could also react with the $C_6H_5NHNH^{\bullet}$ first, instead of as written.

(4) This sequence confirms one we proposed as being involved in the reaction of phenylhydrazine with dimethylsulphamyl chloride, F. L. Scott and J. A. Barry, Tetrahedron Letters, xx (1968).