View Article Online / Journal Homepage / Table of Contents for this issue

Formation of Crossed Phenazine from the Reaction between Tetra-*p*-anisyland Tetra-*p*-tolyl-hydrazines in Liquid Sulphur Dioxide

By Takao Ando, Masatomo Nojima, and Niichiro Tokura*

(Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan)

Summary On dissolving tetra-p-anisyl- and tetra-p-tolylhydrazines in liquid sulphur dioxide in the dark in the absence of oxygen, the tetra-p-anisylhydrazine cation radical was formed and 2-methoxy-7-methyl-5-p-anisyl-10-p-tolyl-5,10-dihydrophenazine was isolated from the reaction mixture.

RECENTLY the cation radicals of tetra-p-anisylhydrazine (1) and tetra-p-tolylhydrazine (2) prepared by anodic oxidation, were found to give 5,10-dihydrophenazines.¹ Considering the stability of the di-p-anisylaminyl cation,² it is probable that the cation radical of (1) dissociates into the di-p-anisylaminyl radical and the di-p-anisylaminyl cation, which then attacks excess hydrazine to give the phenazine intermolecularly.

In the light of these reactions we expected the formation of a 'crossed' phenazine from the reaction of (1) and (2) in liquid sulphur dioxide. Liquid sulphur dioxide is well known to be a mild oxidant.³ The reaction path is expected to be simple because of the absence of a proton source. When (1) was treated with sulphur dioxide, the formation of



J.C.S. Снем. Сомм., 1975

its cation radical¹ was observed in the first stage of the reaction by the periodical measurement of e.s.r. and u.v. spectra, and then the cation radical of 2,7-dimethoxy-5, 10-di-p-anisyl-5,10-dihydrophenazine (3)¹ started to form and the intensity of this absorption increased during the reaction. After 24 h (3) and di-p-anisylamine (4) were obtained in yields of 10 and 40% respectively. The same behaviour was observed in the reaction of (2) with sulphur dioxide, although the reaction rate was slower than that of (1). After 48 h 2,7-dimethyl-5,10-di-p-tolyl-5,10-dihydrophenazine (5) (15% yield), and di-p-tolylamine (6) (65%) yield), were isolated after work-up.

When the appropriate amount of degassed sulphur dioxide was added to a mixture of (1) and (2), the tetra-panisylhydrazine cation radical was formed immediately; u.v. and e.s.r. spectra very similar to those of the cation radical of (3) were then seen, and the reaction was continued for 24 h. Careful investigation of the mass spectrum of the crude products suggested the formation of (3), 2methoxy-7-methyl-5-p-anisyl-10-p-tolyl-5,10-dihydrophenazine (7), and (4) and (6). The diphenylamines were separated from the dihydrophenazines by extracting with petroleum ether. Column chromatography on silica gel gave di-p-anisylamine and di-p-tolylamine in yields of 20 and 40% respectively. Compounds (7) $[m/e 422; \delta 2.18]$ (6H), 3.66 (6H)] and (3) were also obtained in 4 and 5%yields respectively using column chromatography on silica gel.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan.

(Received, 12th September 1975; Com. 1042.)

 ¹ G. Cauquis, H. Delhomme, and D. Serve, Tetrahedron Letters, 1971, 4649.
² U. Svanholm and V. D. Parker, J. Amer. Chem. Soc., 1974, 96, 1234.
³ J. M. Sichel, Canad. J. Chem., 1973, 51, 2124; T. Nagai, K. Katayama, and N. Tokura, Chem. Letters, 1973, 919; T. Nagai, T. Miyazaki, Y. Sonoyama, and N. Tokura, J. Polymer Sci., Part A-1, 1968, 6, 3087.