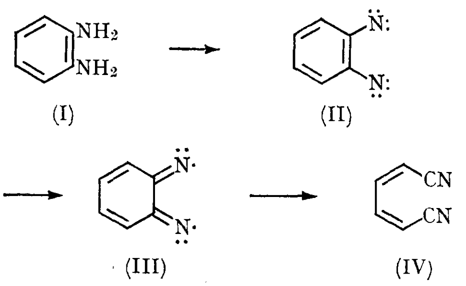
Oxidation of o-Phenylenediamines with Lead Tetra-acetate

By KUNIO NAKAGAWA and HIROSHI ONOUE
(*Shionogi Research Laboratory, Shionogi and Co., Ltd., Fukushima-ku, Osaka, Japan*)

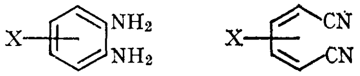
RECENTLY the thermal decomposition of *o*-diazidobenzene[1] and the lead tetra-acetate oxidation of 2-aminobenzotriazole[2] were reported to yield *cis,cis*-mucononitrile (IV), presumably by way of the dinitrene (II) and (III).

We report here that the lead tetra-acetate oxidation of *o*-phenylenediamine (I) and its derivatives also proceeds with the formation of the same product (IV) and presumably the same intermediates.



A mixture of *o*-phenylenediamine (0·02 mole), lead tetra-acetate (0·052 mole), and ether (200 ml.) was stirred for 3 hr. at room temperature under nitrogen atmosphere. After removal of the inorganic precipitate, the ether solution was washed with aqueous sodium bicarbonate and concentrated. Purification of the residue by sublimation or chromatography on alumina furnished (IV). The *cis,cis*-configuration of (IV) was determined by mixed melting point and comparison of spectra (infrared, ultraviolet, and n.m.r.) with an authentic sample. The yields and properties of *cis,cis*-muconitrile derivatives prepared by this reaction are listed in the following table.

TABLE



	Product	
o-*Phenylenediamine*	*Yield* (%)	*m.p.* (° c)
o-Phenylenediamine ..	50·5	128—129
4-Methyl	39·6	56·5—57·5
4,5-Dimethyl	39·2	107—108
4-Chloro	35·9	89—90
4,5-Dichloro	35·7	50·0—51·5
1,2-Diaminonaphthalene ..	39·7	70·0—70·5

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[1] J. H. Hall, *J. Amer. Chem. Soc.*, 1965, **87**, 1147.
[2] C. D. Campbell and C. W. Rees, *Chem. Comm.*, 1965, 192.