

The 'atomic' chlorination of *cyclo*-hexene to  $\Delta^2$ *cyclo*-hexenyl chloride by benzene diazonium chloride was reported by me in 1939<sup>4</sup>, and in 1937 I had suggested tentatively that compounds containing the so-called 'positive halogens', as, for example, the N-halogeno-imides, were molecules which underwent neutral or 'atomic' bond fission in preference to ionic bond fission<sup>5</sup>. The work of Ziegler should be regarded as a definite confirmation of this hypothesis.

Reaction mechanisms involving the neutral bond fission of 'positive halogen' compounds should, however, be applied with caution, since chemical changes of this type are in general chain processes very much dependent for their success on the concentrations and energy-levels of the transient radicals<sup>6</sup>, and on the non-polar character of the solvent used. Thus Kharasch and Priestley<sup>7</sup> have reported the occurrence of two distinct types of addition reactions between N-halogeno-imides and olefines, and the regular use by Ziegler of carbon tetrachloride as solvent may well be an essential factor in contributing to the success of the  $\alpha$ -methylene substitution<sup>8</sup>.

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<sup>1</sup> "Annual Reports of the Chemical Society", **40**, 101 (1943).

<sup>2</sup> *Annalen der Chemie*, **551**, 80 (1942).

<sup>3</sup> *Trans. Faraday Soc.*, **38**, 340 (1942).

<sup>4</sup> *J. Chem. Soc.*, 1805 (1939).

<sup>5</sup> *J. Chem. Soc.*, 2007 (1937).

<sup>6</sup> Waters, *Trans. Faraday Soc.*, **37**, 770 (1941).

<sup>7</sup> *J. Amer. Chem. Soc.*, **61**, 3425 (1939).

acetamidine give a pale yellow colour. Guanidines, biguanides, amines or aliphatic amidines do not react.

The reaction products from some aromatic amidines fluoresce in ultra-violet light down to dilutions of 1 in 100 millions. Those from the diamidine series (for example, propamidine) are sparingly soluble, show no colour change with variation of pH, and do not fluoresce.

When the method had been in use for some time, Devine<sup>3</sup> published a process of estimation using the brown colour produced when an amidine is heated with a large excess of glyoxal in strong caustic soda. This has the disadvantages that the glyoxal reagent is unstable and must be made up daily; that the conditions of heating are difficult to reproduce exactly; and that the colour is unstable and must be estimated immediately. It is, however, not so sensitive to variations in the amount of glyoxal used as is the present method.

I wish to thank Dr. H. King and Dr. J. Walker for supplying the compounds.

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<sup>1</sup> Ekeley, J. B., and Ronzio, A. R., *J. Amer. Chem. Soc.*, **57**, 1355 (1935).

<sup>2</sup> Evans, D. G., Fuller, A. T., and Walker, J., *Lancet*, ii, 523 (1944).

<sup>3</sup> Devine, J., *Ann. Trop. Med. and Parasitol.*, **38**, 35 (1944).

## David Forbes and Guano Archæology

In a footnote to a brief communication made by Virchow in 1873<sup>1</sup> is a statement transmitted to him through Jagor and A. W. Franks, which seems to imply that David Forbes, the well-known geologist, owned or knew of wooden statuettes taken from the guano deposits of the Peruvian coast, depicting a man being bitten in the penis by a snake. This *motif* is known on certain Mochica ceramics<sup>2</sup>, but otherwise appears to be absent from Peruvian iconography.

We are engaged in the collection of all available data on the archæology of the now exhausted Peruvian guano deposits. The available information strongly indicates that important chronological and climatological results may be expected from this neglected field. We are therefore anxious to trace any further references to the material known to Forbes, as no published figure of an object from the guano, exemplifying the *motif* in question, is known to us. If the objects could be identified and were accompanied by indications of locality and depth, they would probably provide an important addition to the very restricted series of authenticated finds of early Peruvian cultures in guano. David Forbes is known to have made extensive mineralogical, geological and ethnographic collections; but the fate of these and of his extensive manuscript notes, not mentioned in his will, are unknown to us. We should be most grateful for any information that would lead to the discovery of this or of any other guano finds.

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<sup>1</sup> *Verhandl. Berliner Ges. f. Anthropol. Ethnol. u. Urgeschichte*, 154 (1873) in *Z. Ethnol.*, **5** (1873).

<sup>2</sup> For example, "Cerámicas del antiguo Perú, coll. Wassermann-San Blas", privately printed (Buenos Aires, 1938), 272-73, Figs. 471, 742.

## A Colour Reaction for Aromatic Amidines

Ekeley and Ronzio<sup>1</sup> have described a series of colored compounds which are obtained when aromatic amidines are heated with glyoxal in alkaline solution. The reaction is complex, and the results are uncertain and dependent on the conditions employed. By heating with a very small amount of glyoxal at pH 9 in the presence of a borate buffer, the reaction is made much more sensitive and reliable, and is suitable for the quantitative estimation of amidines down to 1 in 100,000<sup>2</sup>. The buffer is made up from 4 gm. of boric acid neutralized in hot solution with caustic soda to pH 9, and diluted to 100 ml. The glyoxal reagent is a 0.5 per cent aqueous solution of glyoxal sodium bisulphite.

To a few millilitres of the suspected amidine solution (containing a few milligrams of amidine and roughly neutralized if necessary) is added about a millilitre each of buffer and glyoxal reagent, and the mixture is heated almost to boiling for a few minutes, or for ten minutes in a boiling water bath. A pink or magenta colour appears, which usually becomes redder in acid and bluer in alkaline solution. Maximum colour is obtained with about two molecules to one of amidine, and excess of glyoxal inhibits the reaction.

The reaction appears to be sharply specific for an unsubstituted aromatic amidine group. It is given by C-substituted benzamidines, naphthalene diamidine and nicotinamidine. Nearly fifty aromatic amidines have been tested and found to give the reaction. It is not given by aromatic amidines with one or two methyl groups on the nitrogen atoms of the amidine group. Benzamidrazone and phenyl