CIX.—*Azo-benzene Derivatives of Phloroglucinol.*

By ARTHUR GEORGE PERKIN, F.R.S.E.

ALTHOUGH the behaviour of resorcinol towards diazobenzene and allied substances has received considerable attention, the reactions of phloroglucinol in this respect have been but little studied. Previous work in this direction has shown that the latter yields azo- and disazo-derivatives although with the same reagent both azo- and disazo-derivatives have not as yet been obtained. For instance, by treatment with diazobenzene sulphate in aqueous solution (Weselsky and Benedikt, *Ber.*, 12, 226) preferably in the presence of sodium acetate, phloroglucinol-disazobenzene is formed, but no corresponding monazo-compound appears to be capable of production in this way. Phloroglucinol-disazobenzene corresponds therefore to the isomeric azobenzene-resorcinols in that they respectively represent the simplest products obtainable from these phenols under similar conditions. As is well known, resorcinol also forms isomeric disazobenzene derivatives, and considering the constitution of phloroglucinol, it seemed reasonable to expect that the latter would yield a higher or trisazo-derivative. The study of this subject suggested itself during the investigation of disazobenzenemaclurin (*Trans.*, 1895, 933), and the main results of this paper were worked out at that time. As was to be expected, the reactive capacity of various substituted diazobenzenes with phloroglucinol showed considerable dissimilarity, and further work in this direction seemed desirable. No convenient opportunity has as yet been found for this purpose, but as the presence of a free hydroxyl group in phloroglucinol-disazobenzene (*Trans.*, 1897, 187) has rendered the capacity of this phenol to form trisazo-derivatives more obvious, it was felt that it would be better to communicate the results already obtained to the Society.

Phloroglucinol-trisazobenzene.—To a solution of phloroglucinol in dilute sodium carbonate, excess of a solution of diazobenzene sulphate was added; the deep-red precipitate thus obtained was insoluble in dilute alkali, and it could not, therefore, be the disazo-compound.

After being collected, washed, and dried, it was purified by cautiously diluting a hot nitrobenzene solution with boiling alcohol, the crystals which separated on cooling being collected and washed with alcohol.

0.1339 gave 0.3217 CO_2 and 0.0517 H_2O . $\text{C} = 65.52$; $\text{H} = 4.29$.

0.1230 ,, 21.2 c.c. nitrogen at 24° and 762 mm. $\text{N} = 19.46$.

$\text{C}_6\text{H}_3\text{O}_3(\text{C}_6\text{H}_5\text{N}_2)_3$ requires $\text{C} = 65.75$; $\text{H} = 4.11$, $\text{N} = 19.17$ per cent.

The formation of this substance from phloroglucinol in the presence of aqueous sodium carbonate is apparently not dependent on the quantity of diazobenzene sulphate present, for if this be added in the proportion of only one or two molecules to one molecule of phloroglucinol, the trisazo-compound is formed, a portion of the phloroglucinol being unacted on. As is to be expected, the trisazo-compound also results from the action of diazobenzene sulphate on an alkaline solution of phloroglucinol-disazobenzene.

0.2900 gave 49 c.c. nitrogen at 16° and 740 mm. $\text{N} = 19.17$.

Theory requires $\text{N} = 19.17$ per cent.

It is obtained as a glistening mass of fine needles, having usually a beetle-green lustre; it does not melt below 300° , but when rapidly heated above this temperature, decomposes with evolution of a cloud of black vapour. Its crystallisation is facilitated by the addition of a trace of acetic acid to the hot nitrobenzene solution before dilution with alcohol. As stated above, it is insoluble in cold alkali solutions and contains no hydroxyl groups, those originally present in the phloroglucinol having assumed the ketonic form from their ortho-position relatively to the azo-groups. Sulphuric acid dissolves it with a deep crimson coloration.

Phloroglucinol-orthotrisazoanisol, prepared in a similar manner from phloroglucinol and orthodiazoisol, was purified by crystallisation from nitrobenzene.

0.1513 gave 0.3386 CO_2 and 0.0593 H_2O . $\text{C} = 61.03$; $\text{H} = 4.35$.

0.1445 ,, 20.2 c.c. nitrogen at 18° and 762 mm. $\text{N} = 16.19$.

$\text{C}_6\text{H}_3\text{O}_3(\text{C}_6\text{H}_4\text{N}_2 \cdot \text{OCH}_3)_3$ requires $\text{C} = 61.36$; $\text{H} = 4.54$; $\text{N} = 15.90$ per cent.

Attempts were made to prepare from phloroglucinol the corresponding disazo-compound by the substitution of sodium acetate for sodium carbonate solution. The product in each case was, however, the above trisazo-derivative, although analysis indicated its contamination with a trace of a lower azo-compound.

0.1420 gave 18.8 c.c. nitrogen at 17° and 758 mm. $\text{N} = 15.32$.

Theory requires $\text{N} = 15.90$ per cent.

Phloroglucinol-trisazoanisol crystallises from nitrobenzene in the form of long, glistening, maroon-coloured needles which are slightly

iridescent and do not melt below 300° . With sulphuric acid, it forms a deep violet blue liquid, and is but slightly attacked by nitric acid (sp. gr. 1.5) with gradual production of a deep violet-red solution.

Phloroglucinol-disazobenzene-azometanitrobenzene.—The formation of phloroglucinol-trisazobenzene from the corresponding disazobenzene-compound as shown above suggested the possibility of introducing two different azo-groups into phloroglucinol. The above compound is readily prepared by the addition of a diazometanitrobenzene sulphate to an alkaline solution of disazobenzene-phloroglucinol. By the cautious addition of boiling alcohol to a solution of this substance in hot nitrobenzene, it separates in a crystalline condition.

0.1085 gave 19.4 c.c. nitrogen at 22° and 760 mm. $N = 20.25$.

$C_6H_3O_3(C_6H_5N_2)_2(C_6H_4N_2 \cdot NO_2)$ requires $N = 20.28$ per cent.

As thus obtained, it forms a dull red, glistening mass of fine needles melting at 290° with decomposition, readily soluble in boiling nitrobenzene, almost insoluble in alcohol. With sulphuric acid, it yields a deep scarlet liquid.

Further work will, if possible, be carried out at a later date with the object of studying the reactive capacity of the various substituted diazobenzenes with this phenol. That this varies considerably is shown above and also from the work of previous investigators; thus, whereas phloroglucinol in sodium acetate solution combines with two molecules of diazobenzene, with orthodiazoisol, under similar conditions, a trisazo-derivative is formed; further, according to Stebbins (*J. Amer. Chem. Soc.*, 2, 240), and Weselsky and Benedikt (*Ber.* 12, 226), phloroglucinol-parazobenzenesulphonic acid, $C_6H_5O_3(C_6H_4N_2 \cdot SO_3H)$, and isomeric phloroglucinol-parazophenols, $C_6H_5O_3(C_6H_4N_2 \cdot OH)$, can readily be obtained.

CLOTHWORKERS' RESEARCH LABORATORY,
DYEING DEPARTMENT,
YORKSHIRE COLLEGE.