NOTES.

The Structure of Quinizarin. By ALBERT GREEN.

Two alternative schemes were advanced (J., 1926, 1430) for the reaction between quinizarin and thionyl chloride, the second of which suggested the replacement of a carbonyl oxygen atom by two atoms of chlorine. This is now shown to be improbable, for diacetylquinizarin (4 g.), m. p. 207—208°, after boiling with an excess of thionyl chloride for 2 hours, crystallised in the polymorphic form (3·8 g.), which was free from chlorine and melted, either alone or mixed with an authentic specimen, at 200°.

Although this lack of reactivity on the part of a derivative, in which the probably mobile hydrogens of the hydroxyl groups are replaced, would appear to invalidate the second mechanism suggested for the formation of 10-chloro-1-hydroxy-4 : 9-anthraquinone from quinizarin, it should not be held to dispose of it entirely, since there are many examples of carbonyl groups in free hydroxyanthraquinones showing properties different from those they display in simple derivatives. The *meso*-carbonyl groups influence, and are influenced by, substituents in the α-positions of anthraquinones : *e.g.*, whilst anthraquinone itself yields an oxime only with difficulty, 1-chloroanthraquinone easily gives the oxime; 1-hydroxyanthraquinone cannot be oximated, yet its ethers yield monoximes (Freund and Achenbach, *Ber.*, 1910, **43**, 3251).

Whilst it is clear, therefore, that any deduction from an experimental result obtained with an alkylated or acylated hydroxyanthraquinone should be applied to the hydroxy-compound itself with caution, nevertheless the work described above strengthens the first suggestion (*loc. cit.*), that quinizarin assumes a reactive *ortho*-quinonoid state (1 : 10-dihydroxy-4 : 9-anthraquinone) when it reacts with thionyl chloride to yield 10-chloro-1-hydroxy-4 : 9-anthraquinone. Furthermore, in this reaction only one of the hydroxyl groups is affected, and this affords experimental support

for the suggestion of Perkin (J., 1899, **75**, 433) that, although the two hydroxyls of quinizarin, under suitable conditions, may assume a double quinonoid change, in the case of the second hydroxyl group this change is not readily achieved and is of an unstable nature.

The materials used in this work were purchased from a grant made by the Research Fund Committee of the Chemical Society, whom the author wishes to thank.—THE EDWARD DAVIES LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. [*Received, June 28th*, 1927.]

Solubility of Cupric Sulphide in Alkali Sulphides in Presence of Sulpharsenates. By CHRISTINA DAVIES and ALEXANDER DONALD MONRO.

ALTHOUGH the slight solubility of cupric sulphide in yellow ammonium sulphide is well known, the enhanced solubility in presence of metals of the arsenic group has been little studied. Wohler (*Annalen*, 1840, **34**, 236) and Storch (*Ber.*, 1883, **16**, 2015) have shown that the sulpho-salts of these acids promote the solubility of cupric sulphide, but as no quantitative data were available a further study of the Cu–As system was made.

Solutions of various quantities of arsenic trioxide in hydrochloric acid were diluted and to each was added a solution containing 0·200 g. of copper. The mixture was completely precipitated as sulphide, which was filtered off, washed, and warmed with 50 c.c. of yellow ammonium sulphide [78·47 g. of sulphur and 73·26 g. of ammonia per litre, *i.e.*, approximately $(NH_4)_2S_2$]. The resulting mixture was filtered, and the filtrate treated with hydrochloric acid to precipitate copper and arsenic sulphides. After another filtration the precipitate was treated with warm dilute nitric acid to separate the copper, which, after evaporation with sulphuric acid, was precipitated and weighed as thiocyanate. The following results were obtained :

As present (mg.) ...	0	83·3	113·6	253·2	254·5	265·2	349·7	613·5
Cu dissolved (mg.)..	7·8	29·5	34·5	52·0	52·2	53·0	61·0	80·4

The amount of copper dissolved rises steadily with increasing amounts of arsenic until it becomes ten times its original value. This agrees with our observation that it is possible for small amounts of copper in copper–arsenic mixtures to be entirely missed in a qualitative analysis, unless the arsenic group is examined for copper.

A second series was tried in which colourless ammonium sulphide was substituted for yellow ammonium sulphide. No copper was found in the arsenic filtrate. Pure sodium sulphide gave irregular results. With 0·1600 g. of arsenic, 0·0373 g. of copper appeared

in the filtrates, but although two other results gave appreciable dissolved copper, other experiments gave negative results. Qualitative experiments showed that copper sulphide dissolved appreciably in presence of arsenic sulphide, giving unstable solutions from which cupric sulphide was reprecipitated on warming.

A solution of sodium polysulphide (16 g. of sulphur and 120 g. of $Na_2S,9H_2O$ per litre, *i.e.*, Na_2S_2) gave stable solutions containing arsenic and copper. The influence of arsenic was not so great as in the first series of experiments, but was by no means negligible. The results were as follows :

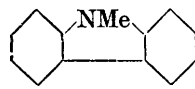
Cu taken, 0·200 g.; 50 c.c. of Na_2S_2 solution.

As (mg.)	0	149·2	237·7	365·5	480·0	620·2
Cu diss. (mg.).....	41·8	48·5	50·7	51·8	52·0	53·0

—UNIVERSITY OF GLASGOW. [*Received, June 25th*, 1927.]

9-*Methylcarbazole*-3-*arsinic Acid and its Reduction Products.* By HAROLD BURTON and CHARLES STANLEY GIBSON.

3-AMINO-9-METHYLCARBAZOLE was prepared from 9-methylcarbazole (Burton and Gibson, J., 1924, **125**, 2501) by nitration in acetic acid solution and reduction of the 3-nitro-9-methylcarbazole by means of tin and hydrochloric acid (Lindemann, *Ber.*, 1924, **57**, 555; Morgan and Read, J., 1922, **121**, 2715). It was characterised by its m. p., 173—174°, and by its acetyl derivative, m. p. 208—209° (Found : C, 75·65; H, 5·65. Calc. : C, 75·6; H, 5·9%). Lindemann (*loc. cit.*) gives m. p.'s 174° and 210°, respectively. On diazotisation in hydrochloric acid solution at the ordinary temperature (compare Morgan and Read, *loc. cit.*) and addition of an alkaline solution of β-naphthol, the deep red *9-methylcarbazole-3-azo-β-naphthol* separated. This compound was obtained from its solution in acetic acid in small, deep red needles, m. p. 212° (decomp.) (Found : C, 78·5; H, 5·2; N, 12·1. $C_{23}H_{17}ON_3$ requires C, 78·6; H, 4·9; N, 12·0%).

9-*Methylcarbazole*-3-*arsinic Acid*,  —A suspension of 3-amino-9-methylcarbazole (19·6 g.) in a mixture of water (250 c.c.) and concentrated hydrochloric acid (25 c.c.) was cooled below 10° and diazotised with sodium nitrite solution. The diazo-solution was then cooled to 0° and neutralised with cold sodium hydroxide solution. The neutralised solution was added gradually with stirring at room temperature to a solution of sodium arsenite (arsenious oxide, 15 g.; sodium carbonate, 24 g.; water, 105 c.c.), to which 10 c.c. of a 10% solution of copper sulphate

previously treated with ammonia had been added. After the addition was complete, the mixture was stirred for 1 hour, boiled, and filtered from tarry matter. The filtrate on acidification deposited the crude acid (10·5 g.); this crystallised from glacial acetic acid in clusters of small, colourless needles, which did not melt below 300° (Found: As, 24·3. $C_{13}H_{12}O_3NAs$ requires As, 24·6%).

9-*Methylcarbazole*-3-*arsenious Chloride*.—A boiling solution of 9-methylcarbazole-3-arsinic acid (5 g.) in alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.) containing a trace of iodine was saturated with sulphur dioxide for 10 minutes. On cooling, the crude *chloroarsine* separated as a gummy mass which gradually solidified. It was purified by dissolving it in benzene, adding light petroleum to the hot solution until all the colouring matter was precipitated, and then filtering and cooling it; the chloroarsine separated in small, colourless prisms, m. p. 121—122° (Found: As, 22·6. $C_{13}H_{10}NCl_2As$ requires As, 23·0%).

9-*Methylcarbazole*-3-*arsenious Oxide*.—A solution of the chloroarsine in acetone was treated with ammonia, and the mixture well shaken. The precipitate was filtered off, washed with water until free from chloride, and dried. The *oxide* is insoluble in the ordinary organic solvents. It has m. p. 182—185° (decomp.) (Found: As, 27·3. $C_{13}H_{10}ONAs$ requires As, 27·7%).—Guy's Hospital Medical School (University of London), S.E.1. [*Received, July 26th*, 1927.]

Derivatives of o-*Aminophenylarsinic Acid*. By Harold Burton and Charles Stanley Gibson.

During the course of investigations which have been carried out on heterocyclic arsenic compounds, a number of simple arsinic compounds have been prepared which might be useful to other investigators.

o-*Ethylaminophenylarsinic Acid*, $NHEt{\cdot}C_6H_4{\cdot}AsO(OH)_2$.—Ethyl sulphate (17 g.) was added to a constantly stirred solution of *o*-aminophenylarsinic acid (21·7 g.) in sodium hydroxide solution (45 c.c., 10%), heated on the water-bath, and the clear solution heated for 10 minutes after the initial reaction had finished. The red oil which separated on cooling solidified and was recrystallised from water, forming colourless needles, m. p. 128—129° (yield, 6 g.) (Found: As, 30·7. $C_8H_{12}O_3NAs$ requires As, 30·6%). The *nitroso*-derivative was prepared by adding a solution of sodium nitrite (2·5 g.) to a solution of the acid (2 g.) in dilute hydrochloric acid. The crystalline product (1·7 g.), which gave Liebermann's nitrosoamine-reaction, was recrystallised from water and obtained in colourless needles, m. p. 160° (decomp.) (Found: As, 27·0.

$C_8H_{11}O_4N_2As$ requires As, 27·35%). The *acetyl* derivative (m. p. 187—188°), prepared in the usual way, was readily soluble in water and in the common organic solvents; its *silver* salt was analysed and the acid shown to be dibasic (Found: Ag, 43·0. $C_{10}H_{12}O_4NAsAg_2$ requires Ag, 43·1%).

3-*Nitro*-6-*diethylaminophenylarsinic Acid*,

$$NEt_2 \cdot C_6H_3(NO_2) \cdot AsO(OH)_2.$$

—For the preparation of this acid we required 4-*nitro*-2-*aminodiethylaniline*. This was prepared by the ammonium sulphide reduction of 2 : 4-dinitrodiethylaniline, and the product isolated as the crystalline *hydrochloride*, yellow prisms, m. p. 205—206°. The *benzylidene* derivative formed yellow needles, m. p. 97—98°, from alcohol (Found: C, 68·4; H, 6·6. $C_{17}H_{19}O_2N_3$ requires C, 68·7; H, 6·4%). The base itself was obtained as a red, viscous oil. The hydrochloride was suspended in water, diazotised, and reduced with sodium stannite, giving *p*-nitrodiethylaniline, m. p. 75°.

A mixture of 4-nitro-2-aminodiethylaniline hydrochloride (24·5 g.), water (150 c.c.), and concentrated hydrochloric acid (25 c.c.) was diazotised at 0° with a sodium nitrite solution (7 g.; 20 c.c.). This diazo-solution was added to a stirred solution consisting of sodium arsenite (arsenious oxide, 15 g.; crystalline sodium carbonate, 65 g.; water, 105 c.c.; 5*N*-sodium hydroxide, 40 c.c.) and 10 c.c. of a 10% solution of copper sulphate which had been treated with an excess of ammonia. The mixture was stirred until frothing had subsided and then warmed until all effervescence had ceased. After cooling, it was stirred with decolorising charcoal, filtered, and the filtrate acidified with hydrochloric acid (Congo-red). The acid (5·5 g.) was filtered off and crystallised from a large volume of water, from which it separated in glistening, yellow needles, m. p. 195—196° (decomp.) (Found: As, 23·5. $C_{10}H_{15}O_5N_2As$ requires As, 23·6%).

3-*Nitro*-6-*diethylaminophenylarsenious Chloride*,

$$NEt_2 \cdot C_6H_3(NO_2) \cdot AsCl_2.$$

—3-Nitro-6-diethylaminophenylarsinic acid (3·2 g.), in alcohol (20 c.c.) and concentrated hydrochloric acid (10 c.c.) containing a trace of iodine, was saturated with sulphur dioxide for 30 minutes. On cooling, a yellow, crystalline product separated (3·0 g.); this crystallised from benzene in deep yellow prisms, m. p. 143—144° (Found: As, 22·1; Cl, 20·8. $C_{10}H_{13}O_2N_2Cl_2As$ requires As, 22·1; Cl, 20·9%).

When *o*-ethylaminophenylarsinic acid or its acetyl derivative was reduced under similar conditions, arsenic was eliminated from the molecule.—GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON), S.E.1. [*Received, July 26th*, 1927.]