206. *Decomposition Reactions of the Aromatic Diazo-compounds. Part V. Reactions of Benzenediazonium Chloride with Sulphur, Selenium, and Tellurium.*

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Benzenediazonium chloride under acetone reacts with tellurium in the cold with formation of diphenyltellurium dichloride. It reacts, after warming, with both sulphur and selenium, giving diphenyl sulphide and diphenyl selenide respectively, but does not appear to react with red phosphorus, boron or silicon.

The occurrence of reaction with the elements of Group VI confirms the hypothesis that free neutral phenyl radicals are produced during the decomposition of the benzenediazonium chloride.

THE elements selenium and tellurium have already proved to be exceedingly useful for detecting free alkyl radicals. It was therefore of interest to find whether they would also react with decomposing benzenediazonium chloride under acetone, for there is good reason to believe that in this mixture the free phenyl radical has a transient existence (Parts II and IV; J., 1937, 2007; this vol., p. 843).

As anticipated, tellurium reacted in the cold with benzenediazonium chloride under acetone containing chalk, and diphenyltellurium dichloride was easily isolated. Tellurium thus behaves as a metal, resembling antimony and mercury in its brisk reaction with the diazonium chloride.

In contrast, selenium did not react with the cold diazonium salt, but when the mixture was warmed until a gentle decomposition set in, some reaction occurred, for a little diphenyl selenide was proved to be formed. With sulphur again there was no reaction in the cold, but, after warming, a considerable amount of diphenyl sulphide and probably also of diphenyl disulphide was formed.

These observations confirm the hypothesis that the diazonium chlorides decompose under acetone by the non-ionic mechanism $(PhN_2)^+Cl^- \longrightarrow Ph{\cdot}N{:}NCl \longrightarrow Ph{\cdot} + N_2 + {\cdot}Cl$ giving transient free neutral aryl radicals which are identical in chemical behaviour with the neutral alkyl radicals which have been studied in the gaseous phase.

Since antimony reacts energetically with diazonium chlorides under acetone, it was of interest to see whether phosphorus would react also. For the sake of safety in manipulation red phosphorus was used, but there was no sign of its reaction with benzenediazonium chloride either in the cold or after heating. With amorphous boron, amorphous silicon, and charcoal also there was no reaction. Immediate reaction with solid metals (Part II) but not with solid non-metals thus seems to be a characteristic feature of the non-ionic decomposition of benzenediazonium chloride. This absence of reaction may be due to the fact that non-metals possess crystal structures built up by covalent linkages, which consequently have not electrons available for union with free radicals. Elementary sulphur, and possibly selenium too, might react as solutes in the warm acetone.

A search for further syntheses of organo-metallic compounds by the use of diazonium salts is in progress.

EXPERIMENTAL.

Reaction with Tellurium.—15 G. of powdered tellurium were added to 20 g. of benzenediazonium chloride and 20 g. of chalk in 300 c.c. of acetone. The reaction was controlled by cooling in ice and was completed by refluxing for 1 hour. After cooling, the solution was filtered, and the filtrate evaporated on the water-bath. The residue, which smelt strongly of chloroacetone, was extracted with light petroleum (b. p. 40—60°); the extract on cooling deposited colourless crystals of diphenyltellurium dichloride (1 g.), m. p. 159° (Found: Te, 36·2; Cl, 20·0. Calc.: Te, 36·2; Cl, 20·1%). By using the double salt of benzenediazonium chloride and zinc chloride (from 20 g. of aniline) a better yield was obtained (3 g.).

Reaction with Sulphur.—20 G. of sulphur powder, 20 g. of chalk, 20 g. of benzenediazonium chloride and 200 c.c. of acetone were mixed. No action occurred until the mixture was heated to above 50°. Reaction was completed by refluxing; the liquid was then filtered, and the filtrate evaporated on the water-bath. The residue, containing much chloroacetone, was treated with an excess of sodium hydroxide solution and distilled in steam. The crude diphenyl sulphide thus separated was distilled under reduced pressure (5 g., b. p. 144—150°/15 mm.) and identified by oxidation with chromic acid in acetic acid, diphenylsulphone (3 g.), m. p. and mixed m. p. 128°, being obtained. The alkaline residue from the steam distillation was acidified and again steam distilled. The benzenethiol obtained was identified by oxidation to diphenyl disulphide (1 g.), m. p. and mixed m. p. 61°. Since the original reaction product did not smell of benzenethiol, it is probable that diphenyl disulphide was a primary reaction product and that this was reduced to the thiol by the hydroxyacetone formed by the action of the alkali on the chloroacetone.

Reaction with Selenium.—30 G. of black selenium powder, 40 g. of chalk, 40 g. of benzenediazonium chloride, and 300 c.c. of acetone were mixed. Again reaction occurred only on heating, and was completed by refluxing for 2 hours. After filtration and removal of the acetone, the residue was made strongly alkaline and distilled in steam; about 1 c.c. of a yellow oil was then obtained. The residue, after being made acid and subjected to steam distillation, gave no volatile product. The yellow oil proved to be diphenyl selenide, for, after extraction with carbon tetrachloride and drying, it was treated with bromine in the same solvent; orange-yellow needles of diphenylselenium dibromide were obtained (*ca.* 0·2 g.), m. p. 148—150° (decomp.) (Found: Se, 20·2. Calc.: Se, 20·1%). Krafft and Lyons (*Ber.*, 1894, **27**, 1765) give the decomposition temperature as about 148°; Behaghel and Siebert (*Ber.*, 1932, **65**, 815) give m. p. 144°.

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