LXV.—*The Reduction of Triphenylhalogenomethanes.*

By JAMES CLIFFORD THOMAS, SYDNEY THOMAS BOWDEN, and WILLIAM JACOB JONES.

THE utility of certain heavy metals for the reduction of triphenyl-halogenomethanes has been demonstrated in the classical investig-ations of Gomberg (*Ber.*, 1900, **33**, 310) on the preparation of the free radical, triphenylmethyl, and in subsequent work (*Chem. Reviews*, 1924, **1**, 99) on various triarylmethyls. In the case of triphenylchloromethane in benzene solution it was shown that the halogen is quantitatively removed by zinc, and that the reduction is also effected by mercury and silver. Copper, in the form of

Naturkupfer-C, has been employed by Schlenk (*Annalen*, 1909, **372**, 17) for the same purpose, but in this instance the application of heat is usually necessary for the completion of the reaction. The investigation of the action of magnesium on triphenylchloromethane in ethereal solution by Schmidlin (*Ber.*, 1906, **39**, 4183) led to the elaboration of a method for the preparation of triphenylmethyl through the interaction of magnesium triphenylmethyl chloride with triphenylchloromethane (*Ber.*, 1908, **41**, 423).

More recently, Kraus and Kawamura (*J. Amer. Chem. Soc.*, 1923, **45**, 2756) have studied the action of sodium and potassium upon triphenylchloromethane in liquid ammonia, and have found that the primary reduction is followed by the combination of free radical with alkali metal to give the corresponding triphenylmethide. The colour which is produced when liquid ammonia solutions of triphenylmethyl are treated with metallic calcium led these authors to infer the existence of calcium triphenylmethide.

It was observed by Schlenk and Marcus (*Ber.*, 1914, **47**, 1678) that triphenylmethyl in ethereal solution on treatment with sodium is converted into *p*-benzhydryltetraphenylmethane. Sodium triphenylmethide, however, is obtained when an ethereal solution of triphenylchloromethane is treated with sodium amalgam. Grosse (*Ber.*, 1926, **59**, 2652) has shown that lithium, rubidium, and cæsium triphenylmethides may be obtained by agitating the aryl chloride in ethereal solution with the corresponding amalgam.

In view of the comparative ease with which triphenyl-chloro- and -bromo-methanes undergo reduction by the heavy metals, it is of interest to note that Blicke (*J. Amer. Chem. Soc.*, 1924, **46**, 1515) was not able to reduce triphenylfluoromethane by means of silver.

No systematic survey of the action of other metals on triphenyl-chloro- and -bromo-methanes has hitherto been undertaken, and we have accordingly carried out a preliminary investigation of the action of a series of representative elements.

The influence of the solvent upon the reaction between triphenyl-halogenomethanes and metals is very marked, and is to be referred primarily to two factors. The first is largely a physical influence, and in view of the heterogeneity of the reaction system, it follows that in those cases where an " active " metallic surface is maintained, as a result of the solution or disintegration of the metallic halide formed on the surface of the metal, an increase will be evident in the rate and extent of reduction. The second is the purely chemical influence, in which the constitutional effect of the solvent is evident in modifying the molecular state of the aryl halide in solution, and in further determining the character of the interfacial phenomena which obtain at the metal–solution interface. These factors are

brought into special prominence in the present investigation by a comparison of the behaviour of acetone and of benzene with that of *n*-hexane. Reduction of triphenylchloromethane in *n*-hexane is effected by only few metals; even with mercury and silver, reaction proceeds much more slowly than in benzene.

Cadmium, thallium, lead, tin, arsenic, antimony, bismuth, selenium, tellurium, and iron were found to react with triphenyl-chloro- and -bromo-methanes in benzene, toluene, and ethereal solution. The rate of reaction differs considerably in the various cases, the most reactive metal being iron and the least reactive lead. The reduction of triphenylchloromethane by cadmium takes place considerably more slowly than by zinc. Triphenylchloromethane in benzene, toluene, bromobenzene, hexane, or ether is not attacked by cobalt or nickel, and only to a slight extent by manganese and chromium.

In several cases the direct reduction is followed by secondary reactions, which may involve (a) combination of metallic halide with unchanged aryl halide, (b) interaction of the liberated free radical with the metallic halide, (c) combination of the free radical with unchanged element, and (d) interaction of the metallic halide with the solvent. Triphenylbromomethane is rapidly reduced by zinc and tin, the initial reaction being followed by the combination of the metallic bromide with unchanged aryl bromide to give highly coloured addition compounds. The addition of finely divided iron to a benzene solution of triphenylchloromethane immediately produces a yellow coloration, which rapidly increases in intensity until the final colour is greenish-yellow. This solution does not contain free triphenylmethyl, and no triphenylmethyl peroxide is obtained by the prolonged action of oxygen. The evidence would seem to indicate the existence in solution of a stable triphenyl-methyl–ferrous chloride complex.

Aluminium, as pure powder, appears to have no action on benzene solutions of triphenylchloromethane at the ordinary temperature, but reaction occurs fairly rapidly with the turnings of the commercial metal. In this reaction, the primary reduction is followed by the formation of an addition compound with aluminium chloride. When, however, the reaction is carried out in acetone, interaction occurs between the aluminium chloride and the solvent, and in some cases the solution sets to a gel in the course of a few days.

The behaviour of cobalt, manganese, and chromium towards triphenylchloromethane in acetone is remarkable, inasmuch as rapid and complete reduction to triphenylmethyl takes place. This reactivity is in direct contrast to the behaviour of these metals towards solutions of the substance in benzene, toluene, bromobenzene,

ether, and hexane. In this connexion, it may be mentioned that tritolylchloromethane in acetone solution has been shown by Norris (*Amer. Chem. J.*, 1907, **38**, 627) to conduct the electric current. In like manner, we find that triphenylchloromethane exhibits a marked conductivity in this solvent, but that in the fused state it is not a conductor.

In several cases anomalous results were obtained with acetone solutions of triphenyl-chloro- and -bromo-methanes, and we have ascertained that this is due to a reaction other than that between metal and the aryl halide. Even at the ordinary temperature, triphenylbromomethane interacts slowly with the enolic form of acetone, the solution assuming a dark brownish colour in the course of a few days. This reaction will be the subject of a further communication.

Both calcium and nickel are entirely non-reactive towards the triphenylhalogenomethanes in all the solvents examined (except possibly acetone), and magnesium is also extremely lethargic except with ethereal solutions. In the latter case, magnesium triphenyl-methyl chloride is formed on prolonged agitation at the ordinary temperature and in the absence of external catalyst.

EXPERIMENTAL.

In order to avoid the complicating influences of atmospheric oxidation, all the experiments were conducted in the entire absence of air. In general, therefore, the reactions were carried out at the ordinary temperature in sealed tubes. Excess of the element was placed in a suitably constricted tube, and after all the air had been displaced by pure dry carbon dioxide, the tube was almost completely filled with a standard solution of the triphenylhalogenomethane. A small amount of the pure solvent was added in order to remove the film of solution from the constriction, and the tube was then sealed under carbon dioxide. The tubes, together with standard comparison tubes containing silver or mercury, were placed in a shaking machine, and their contents agitated in the dark for specified periods and then examined. Triphenylmethyl was recognised by its characteristic colour, and by its conversion into triphenylmethyl peroxide under the influence of oxygen or into diphenylbisdiphenylene-ethane on irradiation.

In many cases it was necessary to conduct the experiments on a larger scale, and for this purpose the triphenyl-chloro- or -bromo-methane solution and the finely powdered element were placed in a flask, which could be charged with carbon dioxide. After the contents had been agitated for the stipulated period, the solution was drawn under carbon dioxide through a suitable filter into a

partly evacuated vessel, where its nature was examined.   The following experiment is representative of the methods employed.

Triphenylchloromethane (5 g.) in acetone (50 c.c.) was agitated under carbon dioxide with excess of metallic cobalt for 3 hours. The resulting greenish-blue solution was filtered in an atmosphere of carbon dioxide, and the filtrate divided into two parts.   Air was passed through the first portion, whereupon the solution assumed a blue colour with simultaneous precipitation of finely crystalline triphenylmethyl peroxide, m. p. 183°;   yield 60%.   The second portion of the filtrate was exposed in a sealed tube to direct sunlight. Photochemical decomposition proceeded more rapidly than with the ordinary yellow solutions of triphenylmethyl in benzene (Bowden and Jones, J., 1928, 1150); the solution became blue, and diphenyl-bisdiphenylene-ethane, m. p. (in a vacuum) 248—250°, was precipitated.   The presence of cobaltous chloride in the above solutions was demonstrated by the usual tests.

Interaction of Triphenylbromomethane with Acetone.—Pure recrystallised triphenylbromomethane (10 g.) was dissolved in dry, acid-free acetone (245 c.c.) in a flask which was then sealed and kept in the dark at the ordinary temperature.   The freshly prepared solution was colourless, but after standing for 3 or 4 days, it was brownish-yellow, which changed to a deep dark brown after 12 weeks. At the end of this period the solution was divided into two portions, solution A (205 c.c.) and solution B (40 c.c.), which were examined in the following manner.

Solution A.   This portion was subjected to careful fractionation through a long Vigreux column, the receiving flask being cooled in a freezing mixture in order to ensure the retention of low-boiling products.   Examination of the first portions of the distillate showed the absence of hydrogen bromide and of β-bromopropylene, b. p. 48°.   After removal of the bulk of acetone, the residual liquid (40 c.c.) was placed in a tightly-stoppered flask and cooled in ice. After some hours, impure triphenylcarbinol (1·2 g.) was deposited. The filtrate was agitated under nitrogen with excess of metallic silver for several hours, after which the solution was filtered in an atmosphere of nitrogen.   Dry air was passed through the filtrate in order to effect the complete oxidation of triphenylmethyl formed by the reduction of unchanged triphenylbromomethane.   In this manner, crude triphenylmethyl peroxide (0·22 g.), m. p. 175—178°, was obtained.

Solution B.   This solution was agitated under nitrogen with excess of silver for several hours, filtered in a stream of nitrogen, and the clear filtrate oxidised by means of a current of air.   The precipitated peroxide (0·18 g.) was practically white; m. p. 182—183°.

Preliminary experiments showed that the yield of peroxide obtainable from freshly prepared solutions of triphenylbromomethane was 65%. On this basis, the above results show that 79.2% of the triphenylbromomethane interacted with acetone at the ordinary temperature.

Addition Compounds of Triphenylbromomethane.—The following addition compounds of triphenylbromomethane with metallic bromides were prepared during the course of the investigation.

With aluminium bromide. Anhydrous aluminium bromide, dissolved in carbon disulphide, was added to a slight excess of triphenylbromomethane in benzene solution. The dark red oil, which separated immediately, was washed rapidly with benzene, and finally with carbon disulphide. After being preserved for some hours in a vacuum, it crystallised in cubes, m. p. 120—123° [Found : C, 37.9; H, 2.6; Br, 53.5; Al, 4.4. $(C_6H_5)_3CBr,AlBr_3$ requires C, 38.6; H, 2.5; Br, 54.2; Al, 4.6%].

With zinc bromide. This *compound* was precipitated by mixing benzene solutions of triphenylbromomethane and zinc bromide. The dark red oil could not be induced to crystallise [Found : C, 41.0; H, 3.1; Br, 42.9; Zn, 11.6. $(C_6H_5)_3CBr,ZnBr_2$ requires C, 41.6; H, 2.8; Br, 43.7; Zn, 11.9%].

With stannic bromide. This *compound*, prepared as in the preceding case, was obtained in the crystalline condition, m. p. 171°, after treatment with hexane [Found : C, 29.1; H, 2.1; Br, 52.3; Sn, 15.1. $(C_6H_5)_3CBr,SnBr_4$ requires C, 29.9; H, 2.0; Br, 52.5; Sn, 15.6%].

THE TATEM LABORATORIES, UNIVERSITY COLLEGE,
        CARDIFF.