not appear to conflict with his theory, and if the theory is correct then it would appear that in the oxidation of monohydric phenols, the latter must first combine or form a complex with the cuprous copper before it is oxidized to the o-dihydric condition. It also follows that the lengthening of the initial lag period by oxidizing agents, in the oxidation of monohydric phenols, might be attributed to the oxidation of the cuprous copper instead of the o-dihydric phenol as suggested in the earlier part of this paper. The oxidation of the cuprous copper would tend to prevent the formation of the cuprous complex necessary for the oxidation of the monohydric phenol.

Summary

1.   It has been shown that o-benzoquinone does not oxidize spontaneously phenol or p-cresol to their respective o-dihydric phenols.

2.   Tyrosinase cannot catalyze the insertion of a hydroxyl group in p-cresol by hydrogen peroxide.

3.   Tyrosinase cannot catalyze the oxidation of p-cresol by homoquinone.

4.   The length of the initial lag in, the rate of aerobic oxidation of p-cresol by tyrosinase was found to be: (a) shortened by reducing agents such as potassium ferrocyanide, alanine, hydroquinone and hydrogen peroxide, all of which reduce o-quinones; (b) prolonged by oxidizing agents capable of oxidizing homocatechol to homoquinone, such as potassium ferricyanide, a suspension of manganese dioxide and laccase; (c) prolonged by the addition of sodium benzenesulfinate; (d) shortened as the solution becomes more alkaline.

5.   A mechanism has been offered concerning some of the reactions involved in the aerobic oxidation of monohydric phenols when catalyzed by tyrosinase.

Relative Reactivities of Organometallic Compounds. XXVII. Triphenylthallium

By Henry Gilman and R. G. Jones

Introduction

The few simple organothallium compounds now known were made available in recent years,[1] and there is no report of their reaction with an organic functional group like carbonyl. On the basis of other evidence, the prediction was made that one of the R groups in R_3Tl compounds might be more reactive than the R group in a symmetrical R_2Hg compound.[2] This finds support in experiments reported at this time. For example, triphenylthallium reacts after the manner of moderately reactive organometallic compounds with compounds like benzaldehyde, phenyl isocyanate and benzoyl chloride. The essential absence of reaction, under corresponding conditions, with ethyl benzoate and benzonitrile suggests that the Entemann–Johnson series[3] of relative reactivities of some functional groups applies not only to phenylmagnesium bromide but also to triphenylthallium. However, there may not be a rigorous correlation. In the series established with phenylmagnesium bromide, benzophenone and benzoyl chloride are of approximately equal reactivity, but we observed with triphenylthallium a prompt reaction with benzoyl chloride and practically no reaction with benzophenone. Recent studies[4a] have shown that the order of reactivity of benzoyl halides with RM compounds that are less reactive than Grignard reagents is unlike the order established with phenylmagnesium bromide.

In reactions of Group III organometallic compounds with organic functional groups, the three R groups of R_3Al compounds participate; but only two of the R groups in R_3B compounds are involved under corresponding conditions, one of the products in the latter case being a monosubstituted boric acid,[4b] $RB(OH)_2$. With triphenylthallium, only one R group enters into reaction, and an invariable product is a diphenylthallium salt. We have now shown that triphenylaluminum[4c] and tri-p-tolylaluminum react much more readily with benzaldehyde than does triphenylthallium.

(1) (a) Groll, This Journal, **52**, 2998 (1930); (b) Menzies and Cope, J. Chem. Soc., 2862 (1932); (c) Birch, ibid., 1132 (1934).

(2) See p. 437 of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N.Y, 1938.

(3) Entemann and Johnson, This Journal, **55**, 2900 (1933).

(4) (a) Gilman and Nelson, ibid., **61**, 743 (1939); (b) Gilman and Marple, Rec. trav. chim., **55**, 76 (1936); (c) **55**, 133 (1936).

Benzalacetophenone.—Studies on the extension of the Entemann–Johnson series[5] have shown that benzalacetophenone is close to benzaldehyde and acetophenone in reactivity. It was not surprising, therefore, to obtain satisfactory yields of β,β-diphenylpropiophenone and β-phenyl-γ-benzoyl-γ-benzohydrylbutyrophenone from the reaction between benzalacetophenone and triphenylthallium. Those reaction products are characteristic of 1,4-additions,[6] and 1,4-addition was to be expected with an RM compound somewhat less reactive than the Grignard reagent. It was shown recently[7] that extremely reactive RM compounds add exclusively 1,2 to benzalacetophenone; that moderately reactive RM compounds add exclusively 1,4; and that RM compounds of intermediate reactivity, like phenyllithium, add both 1,2 and 1,4.

Oxygen.—A benzene solution of triphenylthallium was oxidized by gaseous oxygen to give phenol. The oxidation proceeded very slowly and was incomplete at the end of forty-eight hours. Unfortunately, the low yields of phenol in this slow reaction do not permit a decisive explanation of the low yields of phenols from oxidation of ether solutions of arylmagnesium halides. The low yields of phenols from arylmagnesium halides may be due to secondary reactions of the RMgX compound with the oxidation products of ethyl ether.[8] Triphenylthallium appeared to be a satisfactory compound to test that explanation, for it is not only a moderately reactive RM compound[9] but it is also soluble in benzene.

Mercury.—Metallic mercury and triphenylthallium react to give diphenylmercury. Likewise, diphenylthallium bromide reacts with mercury to give an excellent yield of diphenylmercury, and the other product is thallous bromide. These metallic-replacement reactions, which are probably equilibria, are noteworthy because of the ready formation of a *less* reactive RM′ compound (diphenylmercury) from an RM compound and a metal.

Experimental Part

Triphenylthallium was prepared in accordance with the directions of Birch[1c] by the addition of 0.045 mole of

(5) By H. D. Gooch.

(6) Kohler and Peterson. THIS JOURNAL, **55**, 1073 (1933).

(7) Studies by R. H. Kirby; see p. 89 of paper by Gilman and Bailie, *J. Org. Chem.*, **2**, 84 (1937).

(8) Gilman and Wood, THIS JOURNAL, **48**, 806 (1926).

(9) A more reactive compound like phenyllithium gives on oxidation in a non-ether medium, phenol, *p*-phenylphenol and significant quantities of biphenyl.

phenyllithium in ether to a slight excess of diphenylthallium bromide suspended in ice-cold ether. The apparatus was simplified by the use of conventional three-necked flasks and rubber connections; and the yields (averaging about 70%) were appreciably higher than those reported.[1c] All operations were carried out in a nitrogen atmosphere. When the reaction was complete, the ether was removed by distillation from a water-bath. The crystalline residue was extracted with hot benzene and, after filtration, the triphenylthallium was precipitated as a mass of fine needles by the addition of an equal volume of petroleum ether (b. p. 65–68°). After decanting the cold mother liquor, the crystals were washed two or three times with petroleum ether and then dried in the flask. The melting point under nitrogen was 169–170°.

Anal.[10] Calcd. for $(C_6H_5)_3Tl$: Tl, 46.95. Found: Tl, 47.16.

Color Test.—Optimal conditions for the color test[11] were to heat a sample of the RM compound with one cc. of a saturated solution of Michler's ketone in benzene for five to seven minutes at 70–80°, prior to hydrolysis. A less intense positive test was obtained after heating for one minute at 65°. The production of a positive color test was always accompanied by the appearance of a white precipitate, probably a diphenylthallium salt formed as a consequence of the hydrolysis and acid treatment which concludes the color test reactions.

Triphenylgallium (m. p., 166°) gives no color test, possibly because of complex formation with the dimethylamino groups in Michler's ketone. It does, however, react smoothly with benzaldehyde to give a 70% yield of benzohydrol.

Benzaldehyde.—A negative color test was obtained after refluxing 1.05 g. (0.01 mole) of benzaldehyde and 2.0 g. (0.0046 mole) of triphenylthallium in 25 cc. of benzene for two hours. The yield of benzohydrol was 76%. The other product isolated, subsequent to hydrolysis by hydrochloric acid, was diphenylthallium chloride.

Anal. Calcd. for $(C_6H_5)_2TlCl$: Tl, 51.92. Found: Tl, 51.71.

All operations were carried out in an atmosphere of nitrogen, and concordant results of the experiments described in this paper were obtained on check runs.

Phenyl Isocyanate.—A 40% yield of benzanilide was obtained after refluxing 0.0053 mole of triphenylthallium and 0.0056 mole of phenyl isocyanate in benzene for seven hours.

Benzoyl Chloride.—The addition of 0.006 mole of benzoyl chloride to a benzene solution of 0.0050 mole of triphenylthallium gave an immediate precipitate. After refluxing for two hours, the precipitate was filtered (*without* hydrolyzing) and shown by analysis to be diphenylthallium chloride (yield, 97%). The benzene filtrate, after shaking with 10% sodium hydroxide solution to remove unreacted benzoyl chloride, yielded 89% of pure benzophenone.

(10) Analyses were carried out in essential accordance with the procedure of Goddard and Goddard, *J. Chem. Soc.*, **121**, 488 (1922). After decomposition by a mixture of nitric and sulfuric acids, the thallium was precipitated and weighed as the chromate.

(11) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

Benzalacetophenone.—A solution of 0.0053 mole of triphenylthallium and 0.005 mole of benzalacetophenone in 20 cc. of benzene was refluxed for four hours, and then allowed to stand at room temperature for twenty-four hours. After hydrolysis by aqueous ammonium chloride solution, the benzene layer was separated, dried and then distilled to remove the benzene. The resulting yellow oil was dissolved in 95% ethanol, and on cooling there was deposited a 30% yield of β-phenyl-γ-benzoyl-γ-benzohydrylbutyrophenone (mixed m. p.). The alcoholic mother liquor was diluted with an equal volume of petroleum ether (b. p. 60–68°), and the resulting solution was concentrated to 15 cc. The crystals which deposited on standing for several days were recrystallized from petroleum ether to give a 41% yield of β,β-diphenylpropiophenone (mixed m. p.).

Mercury.—A solution of 1.91 g. (0.0044 mole) of triphenylthallium in 25 cc. of benzene was refluxed with 20 g. of pure mercury. The solution soon assumed a dark brown color. Refluxing was continued for three and one-half hours, and after standing for an additional twenty-four hours at room temperature, 20 cc. of 0.1 N sodium hydroxide solution was added, and the benzene was removed by distillation. From the residue was isolated a 45% yield of diphenylmercury. The thallium amalgam on exposure to the air assumed a black coating of thallous oxide.[12]

Diphenylthallium bromide[13] (1.1 g. or 0.0025 mole) in 10 cc. of dry pyridine was refluxed with 20 g. of mercury. Shortly after applying heat the diphenylthallium bromide dissolved, and soon thereafter a white precipitate appeared. Refluxing was continued for eight hours. The yield of diphenylmercury was 90%. The pyridine-insoluble product was shown to be thallous bromide (85% yield). The mercury recovered probably contained no metallic thallium, for long exposure to moist air revealed no thallous hydroxide.[14]

Oxidation.—After bubbling dry oxygen through a solution of 1.12 g. of triphenylthallium in 25 cc. of benzene for forty-eight hours there was a positive color test. The yield of phenol (isolated as tribromophenol) was 11%. There was also an odor of biphenyl. Undoubtedly because of the slow oxidation, no chemiluminescence was observed in a dark room when oxygen was bubbled through an ether solution of triphenylthallium.

Triphenylthallium is apparently stable at room temperature. A specimen kept in a rubber-stoppered container in a desiccator for several weeks showed no decomposition. Also, exposure of the dry compound to the air for a short time appeared to cause no deterioration.

Triphenylthallium has an odor remindful of tetraphenyllead.

Reactivity Relative to R_3Al Compounds.—To a 0.20 molar benzene solution prepared by dissolving 3.73 g. of triphenylthallium in 43 cc. of benzene was added 1 g. of purified benzaldehyde so that the mole ratio of triphenylthallium to benzaldehyde was 1:1.1. The mixture was stirred at 25 ± 1°, and a negative color test was obtained in the average time of eighty-one hours (±5 hours). When a 0.20 molar solution of triphenylthallium in benzene was treated with sufficient benzaldehyde to form a ratio of 1:3.3, a negative color test was obtained in twenty-seven hours (±1 hour).

Under corresponding conditions a 0.20 molar solution of tri-p-tolylaluminum in xylene was treated with sufficient benzaldehyde so that the mole ratio of tri-p-tolylaluminum to benzaldehyde was 1:3.3. A negative color test was obtained in the average time of 0.58 hour (±0.04 hour).[15]

Miscellany.—From an experiment with benzophenone and triphenylthallium in benzene, there was formed a very small quantity of brown oil which so far has yielded no identifiable product. The yield of recovered benzophenone was 80%.

Gaseous carbon dioxide was bubbled through a solution of triphenylthallium in benzene for thirty-one hours at room temperature. No benzoic acid was isolated, and only a trace of a brown unidentified oil was obtained.

A positive color test was obtained after refluxing a benzene solution of triphenylthallium and an equimolecular quantity of ethyl benzoate for twenty-six hours. No crystalline compound has yet been isolated from the minute quantity of oily reaction product.

Carbonation of triphenylthallium in boiling xylene gives a 70% yield of benzoic acid and a 73% yield of biphenyl. From this and other reactions to be reported later, it appears that triphenylthallium is converted to the highly reactive phenylthallium and biphenyl.

Summary

Triphenylthallium undergoes some of the typical reactions with organic functional groups shown by moderately reactive organometallic compounds. It is less reactive than related R_3Al compounds. Only one R group participates in reactions, the other product being a diphenylthallium salt. Mercury reacts with both triphenylthallium and diphenylthallium bromide to give diphenylmercury.

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(12) Richards and Daniels, THIS JOURNAL, **41**, 1732 (1919).

(13) Prepared in accordance with the directions of Goddard and Goddard, *J. Chem. Soc.*, **121**, 256 (1922).

(14) The higher yield from the mixed compound finds its counterpart in reactions of other RMX and R₂M compounds with mercury. Also mixed RM compounds like R₃PbX and R₂PbX₂ are more readily reduced catalytically than simple compounds like R₄Pb.

(15) As predicted,[2] triphenylindium is more reactive than triphenylthallium. Also, unpublished studies show that the three R groups in R₃In compounds participate in reactions, and that both diphenylindium iodide and phenylindium diiodide react with a compound like benzaldehyde to give benzohydrol.