[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Triphenylindium[1]

BY HENRY GILMAN AND R. G. JONES

Less work has been reported on organometallic compounds of indium than with the related gallium and thallium types. Of the several organoindium compounds prepared,[2] there is no report on their reactivity with organic functional groups like carbonyl. The present study is concerned primarily with a comparison of the relative reactivity of triphenylindium with triphenylgallium and triphenylthallium.

Mercury.—Triphenylindium was prepared in essential accordance with the procedure of Schumb and Crane[2c] from diphenylmercury and indium.

$$3(C_6H_5)_2Hg + 2In \longrightarrow 2(C_6H_5)_3In + 3Hg$$

However, an excess of metallic indium appears to be unnecessary for we have shown that mercury is without effect on a boiling benzene solution of triphenylindium. Under corresponding conditions triphenylthallium reacts with mercury to give diphenylmercury and thallium amalgam.[3a]

We have observed that triphenylindium melts at 208° and not at 291° as reported. If air and moisture be not rigorously excluded[4] incidental to the determination of the melting point, the oxidation and hydrolysis products significantly raise the melting point, as is also the case with triphenylthallium.

Oxygen.—Oxidation of triphenylindium in benzene gave a higher yield of phenol than was obtained with the related triphenylaluminum[5] and triphenylthallium.[3a] In addition to phenol, there was also obtained a 20% yield of biphenyl. A similar coupling reaction was noted by Dennis and co-workers[2b] in their low temperature oxidation of trimethylindium.

$$4(CH_3)_3In + O_2 \longrightarrow 2[(CH_3)_2In]_2O + 2C_2H_6$$

Coupling incidental to the oxidation of some arylmetallic compounds is not unusual, and has been noted particularly with organolithium compounds.[6] However, one might perhaps have expected significant quantities of alcohol by the oxidation of an alkylindium compound inasmuch as with moderately reactive RM compounds like the Grignard reagents alcohols are formed from alkylmetallic types to a greater extent than phenols from the arylmetallic types.

Carbon Dioxide.—Although carbon dioxide was used as the "inert" atmosphere in the earlier studies[2c] with triphenylindium, we have observed that carbon dioxide reacts slowly with triphenylindium to give benzoic acid. Historically, it is interesting to note that although carbon dioxide has long been used as the inert atmosphere for manipulating organozinc compounds, reaction does take place slowly with carbon dioxide.[5]

An 18% yield of benzoic acid was obtained by passing carbon dioxide through a refluxed xylene solution of triphenylindium. Inasmuch as no biphenyl was isolated it is highly improbable that the benzoic acid was formed from phenylindium subsequent to the following pyrolysis[7] which is known to take place with triphenylthallium (see following paper).

$$(C_6H_5)_3In \longrightarrow C_6H_5C_6H_5 + C_6H_5In \xrightarrow[{[HOH]}]{[CO_2]} C_6H_5CO_2H$$

Benzaldehyde.—Normal and abnormal reactions were observed with benzaldehyde. The expected benzohydrol was isolated from reactions of benzaldehyde with triphenylindium, with diphenylindium iodide and phenylindium diiodide. Reactions with the R_2InX and $RInX_2$ types are of peculiar interest because related "mixed" compounds of thallium (like diphenylthallium halides) are relatively inert. There is a possibility that the "mixed" indium types may have reacted in the form of the simple triphenylindium in accordance

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[1] Paper XXXII in the series of "Relative Reactivities of Organometallic Compounds." The preceding paper, XXXI, is in THIS JOURNAL, **62**, 1514 (1940).

[2] (a) Goddard, in Friend, "Textbook of Inorganic Chemistry," Charles Griffin and Co., London, 1928, Vol. XI, Part I, p. 235; (b) Dennis, Work, Rochow and Chamot, THIS JOURNAL, **56**, 1047 (1934); (c) Schumb and Crane, *ibid.*, **60**, 306 (1938); see also, Spencer and Wallace, *J. Chem. Soc.*, **93**, 1827 (1908); Thiel and Kölsch, *Z. anorg. allgem. Chem.*, **66**, 320 (1910); and Groll, U. S. Patents 1,938,179 and 1,938,180 (Dec. 5, 1933).

[3] (a) Gilman and Jones, THIS JOURNAL, **61**, 1513 (1939). Unpublished studies show a similar reversal in reaction with mercury and phenyl derivatives of cadmium and lead. (b) Gilman and Jones, *ibid.*, **62**, 980 (1940).

[4] Professor Schumb has informed us that an inert atmosphere was not used in Mr. Crane's melting point determinations. His analytical samples, however, were manipulated in a dry, oxygen-free atmosphere.

[5] Gilman and Marple, *Rec. trav. chim.*, **55**, 133 (1936).

[6] Gilman, Cheney and Willis, THIS JOURNAL, **61**, 951 (1939); Pacevitz and Gilman, *ibid.*, **61**, 1603 (1939); Müller and Töpel, *Ber.*, **72**, 273 (1939).

[7] This is also consistent with the facts that indium, unlike thallium has only one stable valence state, and triphenylindium is more stable thermally than triphenylthallium.

with the equilibria[8]: $RInI_2 \rightleftarrows R_2InI + InI_3$ and $R_2InI \rightleftarrows R_3In + InI_3$.

The somewhat anomalous reaction was observed when a 3:1 mole ratio of benzaldehyde and triphenylindium was refluxed in benzene. Under these conditions, benzophenone but not benzohydrol was isolated. This is analogous to the formation of ketones from reactions between Grignard reagents and *excess* benzaldehyde.[9]

In comparable rate studies using a definite excess of RM compound, the times required for completion of reaction with benzaldehyde were: triphenylgallium, eleven to fourteen hours; triphenylindium, six to nine hours, and triphenylthallium forty to fifty hours.

Benzalacetophenone.—Triphenylindium underwent a 1,4-addition to benzalacetophenone to give an excellent yield of β,β-diphenylpropiophenone. This was the exclusive product, as was the case with triphenylgallium.[3b] With triphenylthallium both β,β-diphenylpropiophenone and β-phenyl-α-benzoyl-α-benzohydrylbutyrophenone were formed,[3a] and these products are characteristic of 1,4-addition.[10]

Although organoindium compounds are more reactive than the corresponding gallium and thallium compounds, they are to be classed with the moderately reactive RM types, and no 1,2-addition was to have been expected with the conjugated system in benzalacetophenone. It now appears quite general[11] 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.

Benzoyl Chloride.—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; and with R_3Tl compounds only one R group enters into reaction under corresponding conditions. With benzoyl chloride as the reactant, all three R groups are involved with triphenylindium, as is also the case with triphenylgallium. In agreement with these observations is the high yield of benzophenone from benzoyl chloride and diphenylindium iodide.

In the Entemann–Johnson[12] series of relative reactivities of functional groups, benzoyl chloride and benzophenone are of approximately equal reactivity toward phenylmagnesium bromide. However, we have observed that with triphenylindium, benzoyl chloride is more reactive than benzophenone. This supports the recent generalization[13] that the order of reactivity of benzoyl halides and benzophenone with RM compounds that are less reactive than Grignard reagents is unlike the order established with phenylmagnesium bromide.

Benzophenone.—Triphenylindium reacted normally with benzophenone to give triphenylcarbinol, whereas under the same conditions triphenylgallium did not react. Only when an excess of triphenylgallium was used did it react with benzophenone and the product obtained was triphenylmethane. The reducing action with triphenylgallium appears to be associated with the generally more pronounced tendency of less reactive RM compounds to effect reduction.

Color Test.—The results obtained with the color test[14] are apparently anomalous. Although the other reactions mentioned establish quite definitely that triphenylindium is more reactive than triphenylthallium, the color test is obtained more promptly with triphenylthallium. This discrepancy appears not to be wholly associated with the formation of coördinate compounds, for a higher concentration of triphenylindium did not give an appreciably prompter test. However, coördination compounds (with the Michler ketone used in the color test) are very probably responsible for the absence of a color test with triphenylgallium, unless this RM compound is used in excess. Although a correlation has been indicated[14b] between the tendency of organometallic compounds to form coördinate compounds and the relative reactivities of organometallic compounds, the results with triphenylindium appear at this time to be anomalous. A relatively stable coördinate compound was probably not formed in the reaction between triphenylindium and benzo-

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(8) Equilibria of this type are quite common with RMX compounds, and the current elegant studies by Calingaert and Beatty, THIS JOURNAL, **61**, 2748 (1939), on organolead halides are pertinent. Unpublished studies by R. G. Jones indicate the following equilibria with organomercurials and halides of all the alkali metals: $R_2Hg + NaCl \rightleftarrows RHgCl + RNa$.

(9) Marshall, *J. Chem. Soc.*, **105**, 527 (1914); **107**, 509 (1915); Meisenheimer, *Ann.*, **446**, 76 (1925).

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

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

(12) Entemann and Johnson, THIS JOURNAL, **55**, 2900 (1933).

(13) Gilman and Nelson, *ibid.*, **61**, 743 (1939); see, also, refs. 3a and 3b.

(14) (a) Gilman and Schulze, *ibid.*, **47**, 2002 (1925); (b) Gilman and Jones, *ibid.*, **62**, 1243 (1940).

phenone, even though an excess of the ketone was used. Reaction with triphenylgallium (which has a marked tendency to form coördination compounds) only took place when an excess of this RM compound was used with benzophenone.

The varying effects of coördination compounds in the color test indicate that the test is of doubtful value in measuring relative reactivities of RM compounds by the time required for a direct color test. However, the color test can be used indirectly for this and other related rate studies inasmuch as the test is most effective when, paradoxically, it is *negative:* that is, when the RM compound is used up.

Relative Reactivities of Triphenylgallium, Triphenylindium and Triphenylthallium.—Before reactions of organometallic compounds of gallium, indium and thallium with organic functional groups were examined, the broad postulate was made[15] that the order of decreasing reactivity would be: R_3Ga, R_3In, R_3Tl. On the basis of the present results with triphenylindium together with the strictly comparable results reported on triphenylgallium and triphenylthallium,[3a,b] it is clear that although R_3Ga and R_3In are more reactive than R_3Tl, the R_3In type is slightly more reactive than the R_3Ga type.

In an attempt to correlate the experimental findings with some fundamental properties of the metals, we are suggesting that the relative reactivities of many RM compounds parallel and may be directly related to the ionization potentials of the corresponding metallic atoms. In a given group or sub-group, the lower the ionization potential of the metal the more reactive will be its simple[16] organometallic compounds. The ionization potentials[17] in volts of the metals under consideration are: In, 5.76; Ga, 5.97; Tl, 6.07.

In another comparable study[18a] involving a chemical comparison of the relative reactivities of organoalkali compounds, the following order of increasing reactivities was noted: RLi, RNa, RK, RRb, RCs. The ionization potentials[17] of the respective metals are: 5.36, 5.12, 4.32, 4.16, 3.87. Incidentally, the small difference in the ionization potentials of potassium and rubidium is paralleled by a small difference in chemical reactivity of the corresponding RM compounds. In the study of organoalkali compounds attention was directed to some limitations in correlating chemical reactivities of the RM compounds with conductivities of the RM compounds or with the electromotive series of the metals. A striking discrepancy in the e. m. f. series comparison is lithium which has the highest electrode potential with respect to its ion in water solution, and yet forms the least reactive RM compound in the alkali metal group. It is clear that the ionization potentials of the corresponding gaseous metallic atoms follow exactly the present order of chemical reactivities of the RM compounds of the gallium sub-group and lithium group. A detailed consideration of this correlation will be discussed elsewhere, but it may be stated at this time that although there appear to be some exceptions,[18b] relative reactivities of RM compounds toward organic functional groups like carbonyl parallel ionization potentials of the corresponding gaseous metallic atoms.

Experimental Part

Preparation of Triphenylindium.—In a typical experiment, 3.0 g. (0.0262 g. atom) of indium,[19] cut in small pieces, was sealed in a Schlenk tube with 10.0 g. (0.0282 mole) of diphenylmercury in an atmosphere of dry nitrogen. The tube and contents were heated at 130° for at least forty-eight hours; after opening, the white crystalline product was dissolved in 25 cc. of hot chloroform. Subsequent to filtration the hot solution was allowed to cool, and the mass of long needles which separated was collected on a sintered glass plate and washed with dry petroleum ether (b. p. 65–68°). The yields ranged from 65 to 81%. Operations were carried out in an atmosphere of pure, dry nitrogen.[20] Numerous observations showed the melting point to be 208°.

Anal.[21] Calcd. for $(C_6H_5)_3In$: In, 33.20. Found: In, 33.46.

Color Test.[14]—A 0.02 *M* benzene solution of triphenylindium with an equal volume of benzene saturated with

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[15] Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938, p. 435; Gilman and Nelson, *Rec.t rav. chim.*, **55**, 518 (1936).

[16] Where only R groups and no salt-forming or acid radicals are attached to the metal.

[17] Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, N. Y., 1938, p. 14.

[18] (a) Gilman and Young, *J. Org. Chem.*, **1**, 315 (1936). (b) An interesting case is with the RM compounds of zinc, cadmium and mercury. Most of the reactions indicate the following order of decreasing reactivity: R_2Zn, R_2Cd, R_2Hg. However, there are occasional reactions which warrant placing them in this decreasing order of reactivity: R_2Cd, R_2Zn, R_2Hg. The latter order is supported by the ionization potentials: Cd, 8.96; Zn, 9.36; Hg, 10.38. Incidentally, absorption spectra studies indicate that the carbon–metal bond in diethylcadmium is more easily broken than in diethylzinc [Thompson and Linnett, *Proc. Roy. Soc.* (London), **A156**, 108 (1936)].

[19] The indium metal was 96.75% pure. The authors are very grateful to Mr. Burkey for the indium.

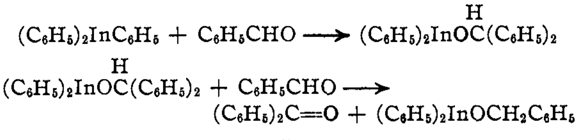
[20] For a description of the apparatus and general technique, see Schlenk and Thal, *Ber.*, **46**, 2840 (1913). It is quite probable that the conventional three-necked flask could be used if the preparation were carried out in a high-boiling solvent like that used in the case of diphenylindium chloride.[2a]

[21] The analytical procedure was that of Schumb and Crane.[2c]

Michler ketone gave a positive color test only after heating the solution for thirty minutes at 80°. Higher concentrations of triphenylindium were also tried, but in no case was the color test positive when the solution was heated for less than thirty minutes prior to hydrolysis and the addition of the acetic acid–iodine reagent.

Benzaldehyde.—A solution of 1.24 g. (0.0035 mole) of triphenylindium and 0.42 g. (0.0040 mole) of benzaldehyde in 20 cc. of benzene was refluxed for five hours. This reaction as well as all others described in this report was carried out in a nitrogen atmosphere. Subsequent to hydrolysis by 20 cc. of 0.3 *N* hydrochloric acid, there was isolated 0.6 g. or 82% of benzohydrol. All solid reaction products were identified by the method of mixed melting points.

When a solution of 0.0040 mole of triphenylindium and 0.0123 mole of benzaldehyde in 40 cc. of benzene was refluxed for fifteen hours, no benzohydrol was obtained subsequent to hydrolysis. However, treatment of the reaction product with hydroxylamine yielded 0.16 g. or 20% of benzophenone oxime. The formation of benzophenone is probably associated with the initial reaction of one of the phenyl groups in triphenylindium in essential accordance with the following reactions.



$$(C_6H_5)_2InC_6H_5 + C_6H_5CHO \longrightarrow (C_6H_5)_2InO\overset{H}{C}(C_6H_5)_2$$

$$(C_6H_5)_2InO\overset{H}{C}(C_6H_5)_2 + C_6H_5CHO \longrightarrow (C_6H_5)_2C{=}O + (C_6H_5)_2InOCH_2C_6H_5$$

A solution of diphenylindium iodide was prepared by adding 1.40 g. (0.0055 mole) of iodine in benzene to 1.90 g. (0.0055 mole) of triphenylindium in 30 cc. of benzene. To this solution was added 0.63 g. (0.0060 mole) of benzaldehyde, and the mixture was refluxed for ten hours. The yield of benzohydrol (on the basis of benzaldehyde) was 66%.

To a benzene solution of phenylindium diiodide (prepared from 0.0040 mole of triphenylindium and 0.0080 mole of iodine) was added 0.0040 mole of benzaldehyde. After refluxing the mixture for fourteen hours, there was obtained a 19% yield of crude benzohydrol (m. p. 64° after recrystallization from petroleum ether (b. p. 60–68°)).

The rate studies with a deficiency of benzaldehyde (see introductory part) were those used in the previously reported comparison of triphenylgallium and triphenylthallium.[3b]

Benzoyl Chloride.—A solution of 0.55 g. (0.0016 mole) of triphenylindium and 0.665 g. (0.0048 mole) of benzoyl chloride in 10 cc. of benzene was refluxed for one hour and then allowed to stand at room temperature for twenty-four hours. After destroying the unreacted benzoyl chloride with alcoholic sodium hydroxide, the benzene solution was washed and evaporated. The yield of benzophenone was 0.35 g. or 40%, based on benzoyl chloride and three phenyl groups reacting.

Inasmuch as there was a possibility that some of the benzophenone might have formed by a modified Friedel–Crafts reaction between the solvent benzene, benzoyl chloride and some indium chloride (formed by interaction of triphenylindium and benzoyl chloride), the experiment was repeated using 25 cc. of petroleum ether (b. p. 65–68°) as the medium. From a mixture of 1.23 g. (0.0035 mole) of triphenylindium and 1.51 g. (0.0107 mole) of benzoyl chloride, refluxed for three and one-half hours, there was obtained 0.59 g. or 31% of benzophenone on the basis of three phenyl groups reacting.

To a solution of diphenylindium iodide (prepared by adding 0.0059 mole of iodine to 2.05 g. (0.0059 mole) of triphenylindium in 40 cc. of chloroform) was added 1.70 g. (0.0121 mole) of benzoyl chloride. After refluxing for ten hours, the mixture was hydrolyzed, the solvent removed, and the product treated with hydroxylamine. The yield of benzophenone oxime was 70%.

Oxidation.—Oxygen was admitted to a rapidly stirred solution of 1.34 g. (0.0039 mole) of triphenylindium in 25 cc. of benzene. The solution soon assumed a dark brown color, and there was an initial heat evolution. Oxygen was passed slowly through the stirred mixture for forty-eight hours. The benzene solution was extracted with 5% sodium hydroxide, and acidification of this extract followed by addition of bromine water yielded 0.65 g. or 17% of tribromophenol on the basis of all three phenyl groups reacting.

From the non-aqueous layer there was obtained a 20% yield of biphenyl, calculated on the basis of the following reaction

$$2(C_6H_5)_3In + 1/2O_2 \longrightarrow [(C_6H_5)_2In]_2O + C_6H_5{\cdot}C_6H_5$$

The oxidation experiment was checked.

Benzalacetophenone.—After refluxing a solution of 1.12 g. (0.00324 mole) of triphenylindium and 0.675 g. (0.00324 mole) of benzalacetophenone in 20 cc. of benzene for seven hours, hydrolysis was effected by ammonium chloride solution. The yield of pure β,β-diphenylpropiophenone was 92%.

Carbonation.—A solution of 1.65 g. (0.00475 mole) of triphenylindium in 25 cc. of xylene was refluxed for twenty-four hours in an atmosphere of dry carbon dioxide. The yield of benzoic acid was 0.10 g. or 18% on the basis of one phenyl group reacting. No products other than benzoic acid were isolated.

Benzophenone.—A solution of 0.0046 mole of triphenylindium and 0.0138 mole of benzophenone in 20 cc. of xylene was refluxed for twenty-four hours. The oily product remaining after hydrolysis and removal of the solvent was subjected to prolonged steam distillation. The non-volatile residue yielded 0.70 g. of triphenylcarbinol, or a 58% yield on the basis of one phenyl group reacting.

After refluxing triphenylindium and benzophenone in *benzene* for fourteen hours, no triphenylcarbinol was isolated and 93% of the original benzophenone was recovered as the oxime.

Miscellany.—There was no evidence of reaction when 0.002 mole of triphenylindium in 10 cc. of benzene was refluxed for twelve hours in the presence of 10 g. of mercury. Subsequent to hydrolysis, neither the aqueous nor the benzene layer gave any test for mercury compounds. When 0.0043 mole of diphenylindium iodide, prepared from iodine and triphenylindium, was refluxed in benzene in the presence of metallic mercury for thirty hours, a very small quantity (0.05 g.) of crystalline product was obtained subsequent to hydrolysis. This substance was sparingly soluble in benzene, insoluble in water, did not melt at 240° and gave qualitative tests for mercury and iodine. It was probably phenylmercuric iodide and may have resulted from the action of metallic mercury on the iodobenzene which was present.

There was no evidence of reaction when ethyl benzoate and triphenylindium were refluxed in xylene solution for twenty-four hours. Of the ethyl benzoate used, 99% was recovered as benzoic acid.

Triphenylindium did not react with benzonitrile when a xylene solution of the two compounds was refluxed for twenty-four hours.

Acknowledgment.—The authors are grateful to Margaret M. Burkey for assistance.

Summary

An examination has been made of a series of reactions of triphenylindium. The order of decreasing activity of the triphenyl derivatives of gallium, indium and thallium is: R_3In, R_3Ga, R_3Tl. Attention is directed to correlations of ionization potentials of metals with the relative reactivities of corresponding organometallic compounds toward functional groups like carbonyl.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Phenylthallium[1]

BY HENRY GILMAN AND R. G. JONES

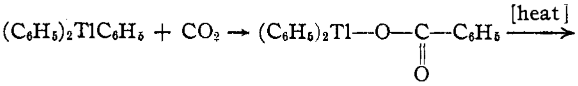
This paper presents, among other things, evidence for the transitory formation and the reactions of a new type of organometallic "radical" or compound, phenylthallium.

High Temperature Carbonation of Triphenylthallium.—As mentioned in the preceding paper,[2a] triphenylthallium is less reactive than triphenylgallium and triphenylindium. The passage of carbon dioxide through a benzene solution of triphenylthallium for a long period gave no benzoic acid.[2b] However, when carbon dioxide was added to a refluxing xylene solution of triphenylthallium there resulted a 70% yield of benzoic acid and a 73% yield of biphenyl. This suggests the following reactions:

$$(C_6H_5)_3Tl \xrightarrow{[heat]} C_6H_5Tl + C_6H_5{\cdot}C_6H_5 \qquad [I]$$

$$C_6H_5Tl + CO_2 \xrightarrow{[HOH]} C_6H_5CO_2H \qquad [II]$$

An alternative sequence of reactions makes unnecessary the postulate of the intermediate phenylthallium, and involves carbonation of one of the phenyl–thallium bonds in triphenylthallium



$$(C_6H_5)_2TlC_6H_5 + CO_2 \rightarrow (C_6H_5)_2Tl{-}O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}C_6H_5 \xrightarrow{[heat]}$$

$$C_6H_5{\cdot}C_6H_5 + C_6H_5COOTl \qquad [III]$$

$$C_6H_5COOTl \xrightarrow{[HOH]} C_6H_5CO_2H \qquad [IV]$$

Although reaction [III] has some plausibility because of the known distinctly higher reactivity of one of the phenyl groups in triphenylthallium, it was shown experimentally to be invalid. An authentic sample of the diphenylthallium benzoate postulated in reaction [III] was refluxed in xylene in an atmosphere of carbon dioxide, but no benzoic acid or biphenyl was formed, and the diphenylthallium benzoate was recovered practically quantitatively.

As supplementary support for reaction [I], pyrolysis of triphenylthallium in xylene gave metallic thallium and biphenyl. Indirect evidence is presented later for the thermal conversion of phenylthallium to thallium and biphenyl.

Reactions with Benzophenone and Benzonitrile.—There was no reaction between triphenylthallium and benzophenone in benzene.[2b] However, at the more elevated temperature provided by boiling xylene, reaction took place and triphenylcarbinol and biphenyl were formed. These products are consistent with the pyrolysis of triphenylthallium to biphenyl and phenylthallium, and the reaction of the latter *in situ* with benzophenone: $C_6H_5Tl + (C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_3COH$. Under corresponding conditions, triphenylthallium and benzonitrile gave thallium, the trimer of benzonitrile, benzophenone and biphenyl: $C_6H_5Tl + C_6H_5CN \longrightarrow (C_6H_5)_2C{=}O$.

Ethyl Benzoate.—In the Entemann–Johnson[3] series of relative reactivities of functional groups with phenylmagnesium bromide, ethyl benzoate is more reactive than benzonitrile. However, we have observed that under conditions where triphenylthallium reacted with benzonitrile, there

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[1] This is paper XXXIII in the series "Relative Reactivities of Organometallic Compounds." The preceding paper is in THIS JOURNAL, **62**, 2353 (1940).

[2] (a) Gilman and Jones, *ibid.*, **62**, 2353 (1940); (b) Gilman and Jones, *ibid.*, **61**, 1513 (1939).

[3] Entemann and Johnson, *ibid.*, **55**, 2900 (1933).