Triphenylgallium[1]

By Henry Gilman and R. G. Jones

Trimethylgallium and triethylgallium have been examined in recent years,[2] but nothing is known of their behavior with a simple organic functional group like carbonyl. For purposes of comparison with other phenyl-metallic compounds, we have prepared triphenylgallium in adequate quantities from the expensive metal to permit examination of sufficient reactions to warrant broad correlations with related organometallic compounds. Triphenylgallium (m. p. 166°) is conveniently prepared in satisfactory yields (82%) by interaction of diphenylmercury with gallium.

The expected reaction with benzaldehyde was observed: namely, formation of benzohydrol. Inasmuch as H. D. Gooch[3] has shown that, in general, benzalacetophenone has a reactivity close to that of benzaldehyde and acetophenone, reaction was expected with the conjugated system in benzalacetophenone. 1,4-Addition did take place, and an 85% yield of β,β-diphenylpropiophenone resulted. There was no evidence of 1,2-addition, and this finding is in accordance with the generalization[4] that only extremely reactive RM compounds add 1,2; that moderately reactive RM compounds add 1,4; and that RM compounds of intermediate reactivity, like phenyllithium, add both 1,2 and 1,4.

Series of Relative Reactivities of Functional Groups.

—On the basis of the series of relative reactivities of functional groups prepared by Entemann and Johnson[5] from their studies with phenylmagnesium bromide, benzonitrile is quite low in reactivity. Accordingly, it was not surprising to find that benzonitrile did not react with triphenylgallium under the selected conditions. Inasmuch as groups like the azo and anil linkages are of lesser activity than the nitrile group, reactions were not attempted with compounds like azobenzene and benzophenone-anil.

Again,[3] an inconsistency was observed with benzoyl chloride and benzophenone. Both of these compounds are of approximately equal reactivity with phenylmagnesium bromide. However, with triphenylgallium only benzoyl chloride and not benzophenone reacted under customary conditions. These results together with others[3,6] reported recently demonstrate rather conclusively that the order of reactivity of benzophenone and benzoyl halides with RM compounds that are less reactive than Grignard reagents is unlike the order established with phenylmagnesium bromide. Under unusual conditions, a liberal excess of triphenylgallium and extensive refluxing in xylene, reaction did take place with benzophenone, but the product isolated in 35% yield was triphenylmethane. Benzyl chloride and triphenylgallium gave undoubtedly diphenylmethane, for the oil resulting yielded benzophenone on oxidation.

Color Test.—The most surprising result was the absence of a color test[7] under usual conditions inasmuch as a color test has always been noted with those organometallic compounds sufficiently reactive to add to the carbonyl group in benzaldehyde and to the conjugated system in benzalacetophenone. Undoubtedly, the absence of a color test under customary conditions is associated in part with the pronounced tendency of gallium compounds to form coördinate linkages. For example, Dennis and Patnode[2a] have shown that the simple triethylgallium reacts violently with water, the etherate vigorously, and the ammine only very slowly. It is quite probable that the dimethylamino groups in the Michler ketone used in the color test may have tied up some of the triphenylgallium in the form of the less reactive ammine. Also, the carbonyl group in Michler ketone and in benzophenone may have participated in the formation of coördinate complexes. In any event, a color test was obtained by heating with an excess of triphenylgallium in benzene for about fifteen minutes. It is significant that the color tests were much weaker than those observed with triphenylthallium,[3] which is less prone to form coördinate linkages.

(1) Paper XXIX in the series of "Relative Reactivities of Organometallic Compounds." The preceding paper, XXVIII, is THIS JOURNAL, 62, 344 (1940).

(2) (a) Dennis and Patnode, THIS JOURNAL, 54, 182 (1932). (b) Renwanz, Ber., 65B, 1308 (1932). (c) Kraus and Toonder, Proc. Natl. Acad. Sci. U. S., 19, 292, 298 (1933) [C. A., 27, 2646 (1933)]; THIS JOURNAL, 55, 3547 (1933).

(3) Gilman and Jones, ibid., 61, 1513 (1939).

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

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

(6) Gilman and Nelson, ibid., 61, 743 (1939).

(7) Gilman and Schulze, ibid., 47, 2002 (1925).

Relative Reactivities of Triphenylgallium and Triphenylthallium.—In preceding studies on the relative reactivities of organometallic compounds, the color test has been found most convenient. The necessity of using an excess of triphenylgallium for a color test precluded its use in a comparison with triphenylthallium. However, the relative reactivities of these two R_3M compounds was established by an indirect procedure involving benzaldehyde, which reacts with each of them. Under parallel conditions, a solution of known concentration of benzaldehyde was added separately to each of the R_3M compounds, and the periodic removal of samples on which tests were made for benzaldehyde showed that triphenylgallium is more reactive than triphenylthallium. The rate studies were carried out at room temperature to avoid the thermal conversion noted earlier[3] of triphenylthallium to the highly reactive phenylthallium.

The 79% yield of benzophenone based on interaction of one mole of triphenylgallium with three moles of benzoyl chloride shows that with some reactants all three phenyl groups are available. With triphenylthallium, only one R group enters into reaction and an invariable product is a diphenylthallium salt.

Experimental Part

Preparation of Triphenylgallium.—A mixture of 1 g. (0.0143 g. atom) of gallium metal and 5.45 g. (0.0153 mole) of diphenylmercury was heated in a Schlenk tube which had been thoroughly flushed out with nitrogen. Heating was effected at 130° in an oven, and after fifty hours the molten diphenylmercury had given place to a white crystalline mass. The tube was opened under nitrogen and 10 cc. of dry chloroform was added. After warming the chloroform to dissolve all of the solid, the solution was filtered and then subjected to distillation (under nitrogen) until crystals began to appear in the hot solution, about 4 cc. of which remained. The mass of shiny needle-like crystals which separated on cooling were filtered off on a sintered glass plate, and washed with petroleum ether (b. p. 65–68°). The product was redissolved in 3 cc. of hot chloroform, and the crystals which separated on cooling were again filtered, washed with petroleum ether, and dried under nitrogen. The triphenylgallium (1.85 g.) melted at 166°; the clear colorless melt quickly solidified on cooling and remelted at the same temperature.

Anal.[8] Calcd. for $C_{18}H_{15}Ga$: Ga, 23.18. Found: Ga, 23.27 and 23.38.

Better yields of triphenylgallium were obtained when the theoretically required quantities of gallium and di-

(8) The analytical procedure was that used by Dennis and Bridgman, THIS JOURNAL, **40**, 1546 (1918).

phenylmercury were used. Thus, from 1.92 g. (0.0275 g. atom) of gallium and 14.5 g. (0.0405 mole) of diphenylmercury, heated at 130° for seventy-five hours, 6.68 g. or an 82% yield was obtained of triphenylgallium which melted at 165–166° without recrystallization.

On short exposure, dry air appeared to have little effect on triphenylgallium. However, in the presence of any moisture the compound quickly decomposed, and one of the products was benzene. Complete solution of triphenylgallium in warm dilute sulfuric acid, incidental to analysis, required about twenty-four hours.

Benzaldehyde.—A solution of 0.83 g. (0.00277 mole) of triphenylgallium and 0.294 g. (0.00277 mole) of benzaldehyde in 20 cc. of benzene was refluxed for ten hours. After hydrolysis with 25 cc. of 2 N hydrochloric acid, the benzene layer was separated and washed with 40% sodium bisulfite solution. Removal of the benzene by distillation left an oil which crystallized on cooling to give a 70% yield of benzohydrol, melting at 65-66° after two crystallizations from petroleum ether (b. p. 60–68°). Identification was completed, as was done by all solids described in this paper, by the method of mixed melting points with an authentic specimen.

Benzalacetophenone.—A solution of 1.1 g. (0.00365 mole) of triphenylgallium and 0.76 g. (0.00365 mole) of benzalacetophenone in 20 cc. of benzene was refluxed for eight and one-half hours. Subsequent to hydrolysis by hydrochloric acid and then working up by customary procedures there was obtained 0.88 g. or an 85% yield of β,β-diphenylpropiophenone.

Benzoyl Chloride.—A solution of 1.44 g. (0.00478 mole) of triphenylgallium and 2.01 g. (0.0143 mole) of benzoyl chloride in 25 cc. of benzene was refluxed (under nitrogen, as usual) for eleven hours. The yield of benzophenone was 2.05 g. or 79%.

In another experiment, a mixture of 1.06 g. (0.0035 mole) of triphenylgallium suspended in 25 cc. of petroleum ether (b. p. 65–68°) containing 1.47 g. (0.0105 mole) of benzoyl chloride was heated for nine hours. The ketone was isolated in this case as benzophenone oxime, the yield of which was 1.4 g. or 68.4%.

It is interesting to note that generally satisfactory yields of ketones are obtainable from organometallic compounds of group III metals in their reactions with acid halides and acid anhydrides. This applies in a noteworthy extent to the organoaluminum halides. In most of these reactions of ketone formation, the acid anhydrides are superior to acid halides, both with RM compounds in group III and RM compounds like those of cadmium in group II.

Benzophenone.—After refluxing for twenty-four hours a solution of 1.00 g. (0.0033 mole) of triphenylgallium and 1.82 g. (0.01 mole) of benzophenone in 20 cc. of xylene, 94.5% of the benzophenone was recovered as the oxime, and no triphenylcarbinol was isolated. The experiment was repeated with xylene as the solvent, and also with benzene as the solvent. In the latter case, 95.5% of the benzophenone was recovered as the oxime.

An additional experiment was carried out with an excess of triphenylgallium. A solution of 1.51 g. (0.0050 mole) of triphenylgallium and 0.3 g. (0.00167 mole) of benzophenone in 15 cc. of xylene was refluxed for twenty-

four hours. A small quantity of white amorphous precipitate formed. After cooling, the reaction mixture was shaken with 25 cc. of dilute hydrochloric acid and 25 cc. of benzene. The aqueous layer was separated and the benzene–xylene layer was washed with dilute hydrochloric acid and then with water. The residue from the organic extract was subjected to steam distillation subsequent to removal of the solvents. The steam distillate yielded an oil which partially solidified on standing, and when crystallized from a mixture of 1 cc. of 95% ethanol and 1 cc. of petroleum ether (b. p. 60–68°) gave a 35% yield of triphenylmethane.[9]

Benzyl Chloride.—To a suspension of 1.36 g. (0.0045 mole) of triphenylgallium in 25 cc. unsaturate-free petroleum ether (b. p. 65–68°) contained in a conventional three-necked flask provided with a mechanical stirrer, was added slowly a solution of 1.71 g. (0.0135 mole) of benzyl chloride in 25 cc. of petroleum ether. There was no evidence of reaction until about one-third of the benzyl chloride solution had been added, when suddenly a large quantity of red, tarry precipitate appeared accompanied by some heat of reaction. Subsequent to hydrolysis, the oily residue remaining after removal of the organic solvents was oxidized by potassium dichromate and sulfuric acid to give 0.1 g. or a 9% yield of benzophenone, isolated and characterized as the oxime.

Color Test.—In preliminary tests, about 0.05 g. of solid triphenylgallium was added to about 1 cc. portions of benzene containing Michler ketone. Both saturated and 1% Michler ketone solutions were used. In every case the test was negative, even when the mixtures were heated at 70° out of contact with air or moisture for as long as two and one-half hours prior to hydrolysis.

A mixture of 0.57 g. (0.0019 mole) of solid triphenylgallium and 0.1 g. (0.00038 mole) of solid Michler ketone was placed in a flask containing nitrogen. Next 12.5 cc. of dry benzene was added, the time noted, and 1-cc. samples were removed periodically and tested by hydrolyzing and adding the acetic acid–iodine solution.[7] The test was negative after four hours at room temperature. The mixture was then heated on the water-bath at 65–75°, and after one hour a 1-cc. sample gave a good color test.

The experiment was repeated using 0.43 g. (0.00143 mole) of triphenylgallium, 0.13 g. (0.00048 mole) of Michler ketone and 16 cc. of benzene. The solution was heated immediately on the water-bath at 70°. A faint positive test was obtained in fifteen minutes; a better test in thirty minutes; and a good test in one hour. In all cases, the colors given in triphenylgallium tests were weaker than the color of a positive test for triphenylthallium.

Relative Reactivities of Triphenylgallium and Triphenylthallium.—In parallel experiments, a solution was prepared by mixing quickly benzaldehyde and R_3M compound in benzene, so that the initial concentration of benzaldehyde was 0.16 molar and that of R_3M was 0.20 molar. The solution was stirred constantly at room temperature, and at regular intervals 1-cc. samples were withdrawn and tested for benzaldehyde.[10] The end-point of the reaction was taken when three samples (removed within a period of ten minutes) no longer gave positive tests for benzaldehyde. The times in two experiments with triphenylgallium were eleven and fourteen hours; and the times in corresponding experiments with triphenylthallium were forty and fifty hours.

Summary

Triphenylgallium (m. p. 166°), prepared from gallium and diphenylmercury, reacts normally with benzaldehyde, benzalacetophenone and benzoyl chloride. Because of the probable formation of coördinate compounds with Michler ketone and benzophenone, there is no color test and no reaction with benzophenone under customary conditions. Extended heating with an excess of triphenylgallium gives a color test with Michler ketone, and benzophenone reacts to give triphenylmethane. Rate studies with benzaldehyde show triphenylgallium to be more reactive than triphenylthallium.

(9) Schorigin, *Ber.*, **41**, 2723 (1908), obtained triphenylmethane from a reaction between phenylsodium and carbon dioxide.

(10) Barlet and Vandier, *Ann. chim. anal. chim. appl.*, **1**, 325 (1896), [*Chem. Zentr.*, **68**, II, 226 (1897)].