241. *The Preparation of Triethyl-, Tri*ïso*butyl-, and Triphenyl-thallium.*

By Stanley F. Birch.

The following work was carried out in 1932 during a search for petrol-soluble organic thallium derivatives required to test Egerton and Gates's suggestion (*J. Inst. Pet. Tech.*, 1927, **13**, 247) that thallium, like lead, should possess marked knock-suppressing properties in an internal-combustion engine. The compounds obtained were petrol-soluble, but their anti-knock properties were only about one-tenth of that of lead tetraethyl.

Groll (*J. Amer. Chem. Soc.*, 1930, **52**, 3000) first obtained triethylthallium by the action of ethyl-lithium (Schlenk and Holtz, *Ber.*, 1917, **50**, 262) on diethylthallium chloride suspended in light petroleum; he subsequently obtained it, in very poor yield, by the action of ethyl chloride on thallium–sodium alloy.

The simpler methods of preparation described below are based upon Gilman's method for obtaining lithium alkyls and aryls (*J. Amer. Chem. Soc.*, 1932, **54**, 1957). No special apparatus is necessary, but it is essential to work in an inert atmosphere. Preliminary experiments using phenyl-lithium, prepared in ethereal solution from bromobenzene and lithium, showed that reaction with diphenylthallium bromide suspended in the same solvent readily occurred, with the formation of a compound having the properties of the expected *triphenylthallium*. The triethyl and the *triïsobutyl* compound were similarly prepared. A greatly simplified form of Schlenk and Holtz's apparatus was devised for the purpose; it was only used to prepare the thallium compounds in quantities of a few grams at a time, but with little modification, it could be used for the preparation of much larger quantities.

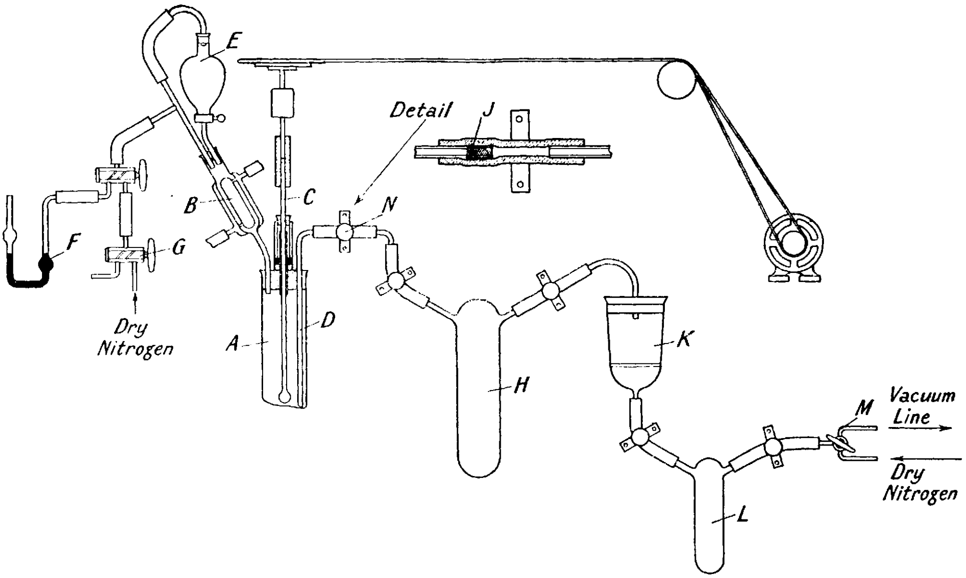
The required compounds could also be prepared, but less satisfactorily, in one operation by the action of the lithium compound upon thallous chloride suspended in a suitable solvent. The quantity of metallic thallium formed by reduction indicates that the reaction probably takes place through the mono-alkyl- or -aryl-thallium : $3LiR + 3TlCl = (3TlR + 3LiCl) = TlR_3 + 2Tl + 3LiCl$. This is in agreement with the work of Menzies and Cope (J., 1932, 2864), which appeared shortly after the present work was discontinued. These authors proved the formation of triethylthallium when ethylmagnesium bromide and thallous chloride react in ether, but did not isolate it. Their method of demonstrating its presence, *viz.*, treatment with aqueous acetic acid followed by precipitation of the bromide with potassium bromide solution, had been devised independently, but glacial acetic acid was used; this is essential when dealing with triphenylthallium, for otherwise the very insoluble oxide is formed; there is no need to convert diphenylthallium acetate into the iodide, as it can be separated and weighed as such.

The reaction of lithium alkyls with dialkylthallium halides should give a useful method for the preparation of mixed thallium alkyls. An attempt to prepare diethyl*iso*butyl-thallium by the action of *iso*butyl-lithium upon diethylthallium bromide was being made when the investigation was abandoned; fractionation of the product gave small quantities of yellow liquids lighter in colour than the triethyl derivatives and apparently less stable, but no analyses were obtained.

Experimental.

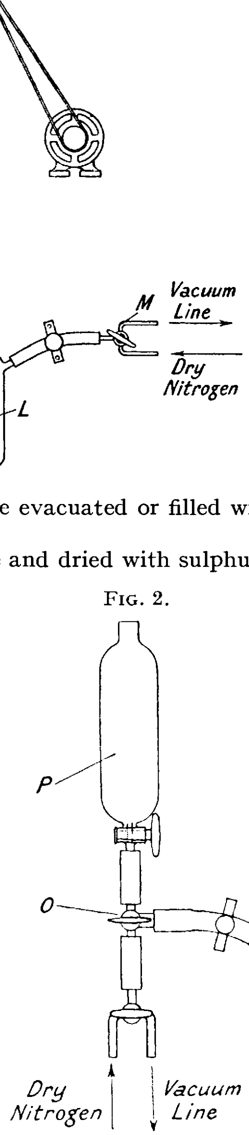
The apparatus employed is shown in Fig. 1. The short wide Pyrex tube (*A*), about 11 cm. long and 3·8 cm. in diameter, was fitted with a small double-surface condenser (*B*), a mercury-sealed stirrer (*C*), and a tube (*D*), which reached into a depression blown in the bottom of *A* so that the latter could be drained through *D* as completely as possible. Attached to the top of *B* was a small tap-funnel (*E*), so arranged that it could be closed with a mercury seal (*F*) or a stream of nitrogen passed through the apparatus by means of the tap (*G*). The tube *D* was attached by means of heavy-walled rubber tubing to the main reaction vessel (*H*), a filter of copper gauze (*J*) being fitted over the end of *D* and held in place by the rubber tube. This coarse filter served to hold back any unattacked lithium. The vessel *H* consisted of a tube, 15·5 cm. × 3·8 cm., sealed at both ends, with side arms of wide bore, 8—9 mm. in internal diameter, placed at an angle of approximately 120°, which facilitated filling and emptying, similar to those used by Schlenk (*loc. cit.*). *H* was attached to a sintered Jena-glass filter (*K*), the coarseness of which was varied as required, and this in turn was attached to a second smaller reaction vessel (*L*), 12 × 2·5 cm. Pressure tubing with a screw clip was used for each connexion, thus allowing the arrangement of the apparatus to be altered at will or any part to be vigorously shaken. A number of vessels similar to *L* were stored ready for use in a desiccator. By means of the three-way stop-cock (*M*) attached to *L*, *H*, *K*, and *L* could be evacuated or filled with nitrogen.

FIG. 1.



The nitrogen was stored in an aspirator over alkaline pyrogallate and dried with sulphuric acid and phosphoric oxide.

FIG. 2.



Procedure.—In carrying out an experiment, the procedure was as follows: The reaction vessels *A*, *H*, and *L*, together with the tube *D*, the funnel *K*, and the corresponding rubber connexions, were dried in the oven, placed in position while still warm, and a current of dry nitrogen passed through the apparatus for an hour. *A* was then removed, the required amount of lithium, previously cut under light petroleum into very small pieces, placed in it, and the light petroleum replaced by decantation with dry ether or benzene. *A* was then replaced, the required amount of bromide diluted with some of the solvent placed in *H*, and the apparatus again swept out with nitrogen.

The reaction was started by adding a little of the bromide from the funnel *E* and warming gently, and the addition was continued at such a rate as to maintain a steady reaction. When reaction became slow, the contents of *A* were kept gently boiling for about ½ hour, and were then allowed to cool. Slight reduction of the pressure in *H* and opening of the screw clip *N* allowed the contents of *A*, consisting of lithium alkyl or aryl, solvent, lithium bromide, and unchanged lithium, to be drawn over into *H*, which had been previously cooled in ice. Any unchanged lithium escaping from *A* was caught on the gauze *J*; *A* was then washed out with fresh solvent added from the tap-funnel *E*, and the washings drawn over into *H*. At this stage the clip *N* was closed and the tube *B* replaced, as in Fig. 2, by a three-way stop-cock (*O*) and small tap funnel (*P*). The vigorous reaction in *H* ceased as soon as the contents had been thoroughly mixed, and these were then tipped into the funnel *K* and filtered into *L*, the pressure in which had been slightly reduced. Trouble was sometimes experienced at this stage by the clogging of the sintered glass through evaporation of solvent and crystallisation of dissolved salts; for this reason it was advisable to use plenty of solvent and not to reduce the pressure in *L* more than necessary. Owing to the solubility of lithium bromide, when ether was used it was necessary to remove it by gentle warming under reduced pressure, either before filtration while still in *H* or afterwards while in *L*. The residue was then extracted with benzene (in the preparation of triphenylthallium) or pentane (preparation of thallium alkyls), filtered, and the solvent removed from the filtrate. By varying the arrangement of the apparatus it was possible to crystallise triphenylthallium from benzene–light petroleum, filter off the crystals, and dry them in nitrogen. The thallium alkyls were transferred to a small Claisen flask in a current of nitrogen and distilled under reduced pressure.

Triphenylthallium.—A rough estimation of the yield of triphenyl-lithium from bromobenzene and lithium in ether was made by decomposing the reaction products with water and titrating the lithium hydroxide with standard acid using phenolphthalein as indicator; it showed that, under the following conditions, the yield was *ca.* 60%.

Lithium (0·4 g.) in small pieces was suspended in ether (30 c.c.), and bromobenzene (4·5 g.) in ether (10 c.c.) slowly added. The reaction started readily on slight warming and was complete in an hour; after being gently refluxed for a further ½ hour, the contents were slowly transferred to a reaction vessel (cooled in ice) containing diphenylthallium bromide (11 g.) suspended in ether (20 c.c.), and vigorously shaken. Although diphenylthallium bromide is insoluble in all the usual organic solvents, it reacted and disappeared as fast as the triphenyl-lithium was added. At the same time the whole became brownish-black, and heat sufficient to boil the ether was developed. After a short time, during which the ice was removed, the slight excess of diphenylthallium bromide was filtered off. Two layers were then obtained, being presumably solutions of thallium bromide and of triphenylthallium in ether; on warming they became completely miscible. After removal of the ether under slightly reduced pressure, the *triphenylthallium* was extracted from the residue of lithium bromide and unchanged diphenylthallium bromide by means of warm benzene, from which it crystallised on addition of light petroleum (b. p. 60—80°) in short, stout, white needles, m. p. 188—189°, decomp. 215—216°. It was filtered off and dried in a current of dry nitrogen; yield 5 g. (Found: Tl, 46·27. $C_{18}H_{15}Tl$ requires Tl, 46·71%).

Triphenylthallium is readily soluble in benzene, but insoluble in light petroleum. It rapidly oxidises in solution, but is unaffected on short exposure to dry air when free from solvent. When heated, it decomposes suddenly to give metallic thallium and a vapour possessing an odour of diphenyl.

On allowing the benzene–light petroleum mother-liquor to evaporate in air, 1·3 g. of a pale biscuit-coloured solid separated. This was very insoluble in the usual solvents but separated from pyridine in small white needles, m. p. above 300°; it was identified as diphenylthallium oxide (Goddard and Goddard, J., 1922, **121**, 486).

Diphenylthallium Acetate.—Triphenylthallium (2·5 g.) was added to glacial acetic acid (10 c.c.) diluted with benzene (5 c.c.); heat was developed, but further warming was necessary before solution was complete. On removal of the solvent and excess of acetic acid under reduced pressure, diphenylthallium acetate was left as a white solid; it was washed with light petroleum (b. p. 60—80°); yield 2·4 g. Recrystallised from cellosolve (ethylene glycol monoethyl ether), it formed fine colourless needles, m. p. 265° (cf. Goddard and Goddard, *loc. cit.*).

Triethylthallium.—(a) *Ethyl-lithium.* A rough estimation of the yield of ethyl-lithium was made as follows: Lithium (0·8 g.) was suspended in benzene (15 c.c.), and ethyl bromide (5·5 g.) diluted with benzene (5 c.c.) slowly added. When the bromide had been added and the reaction had become slow, the whole was gently warmed for ½ hour and then cooled. The contents were transferred to another vessel, the residual lithium washed several times with ether, and the ethyl-lithium in the solution and washings decomposed with water. The lithium hydroxide formed was titrated with standardised acid, and showed a yield of 28% based upon the lithium taken.

(b) *Triethylthallium.* (First method.) Lithium (2·4 g.), cut in very small pieces, was suspended in benzene (40 c.c.), and ethyl bromide (16·5 g.) diluted with benzene (10 c.c.) slowly added. The reaction was complete in 3 hours, and the products were gently warmed for a further ½ hour, then cooled and slowly transferred to a reaction tube (cooled in ice-water) containing diethylthallium bromide (20 g.) suspended in benzene (25 c.c.). An immediate reaction took place, the whole became warm, and a grey precipitate of metallic thallium was formed.

After a short time the benzene was removed under reduced pressure,* and the residue thoroughly extracted with dry ether. On filtering the ethereal extract, a yellow solution was obtained which gave a deep yellow liquid on removal of the solvent. On distillation the liquid distilled almost entirely at 50—51°/1·5 mm.† without signs of decomposition to give a deep yellow heavy oil which fumed in moist air and possessed a rather nauseating sweet odour resembling that of the lead tetra-alkyls. The yield (crude) was 66%. Triethylthallium burns with a green flame and decomposes suddenly into thallium and free hydrocarbon, presumably butane, when heated in a tube.

On adding glacial acetic acid (2—3 c.c.) to light petroleum (250 c.c.) containing triethylthallium (2·85 g.), an immediate white precipitate was formed which afterwards dissolved. The diethylthallium acetate (2·9 g.) left on removal of solvent crystallised from methyl alcohol in fine colourless needles, m. p. 232° (cf. Goddard, J., 1922, **121**, 36).

(Second method.) Diethylthallium bromide (7·2 g.) was suspended in pentane (20 c.c.), and lithium (0·6 g.) added in very small pieces. Ethyl bromide (4 c.c.) diluted with pentane (10 c.c.) was then slowly added. The reaction, as shown by darkening of the bromide, commenced almost immediately and was over in about an hour. After being stirred for a further ½ hour, the whole was filtered and the residue washed with pentane. The triethylthallium was not isolated but converted into diethylthallium acetate by adding acetic acid until the yellow colour disappeared. The crude acetate, left on removal of the solvent and freed from traces of acetic acid by means of caustic potash in a desiccator, weighed 5·5 g. (80%).

Diethylthallium cyanide, which is precipitated from an aqueous solution of the acetate by means of potassium cyanide, crystallises from water in colourless micaceous plates which darken at 240° but do not melt when heated in a sealed tube above 310° (Found : Tl, 70·89. $C_5H_{10}NTl$ requires Tl, 70·85%).

Ethyl-lithium and thallous chloride. Ethyl-lithium, prepared from lithium (0·6 g.) suspended in pentane (20 c.c.) and ethyl bromide (5 g.) diluted with the same solvent (10 c.c.), was slowly added to thallous chloride (20 g.) suspended in pentane (30 c.c.) and cooled in ice-water. An immediate blackening occurred and some heat was developed. After the addition was complete, the reaction tube was vigorously shaken and the contents filtered. The residue was washed several times with pentane, and the filtrate and washings treated with acetic acid followed by water. The diethylthallium iodide, precipitated from the aqueous layer by means of potassium iodide, after being washed with water, and dried, weighed 3·1 g., corresponding with 1·6 g. of thallium. The recovered thallous chloride, when treated with dilute nitric acid to remove the metallic thallium, washed with water, and dried, weighed 14 g., showing that 6·0 g. of thallous chloride had taken part in the production of 3·1 g. of diethylthallium iodide; *i.e.*, $Tl(C_2H_5)_3$: Tl = 1 : 2·2, in good agreement with the equation on p. 1132.

*Tri*iso*butylthallium.*—(a) iso*Butyl-lithium.* A rough estimation of the yield of *iso*butyl-lithium was made as in the case of ethyl-lithium, except that the solvent employed was ether. Approximately 50% of the lithium taken was converted into *iso*butyl-lithium.

(b) *Tri*iso*butylthallium.* Lithium (1·2 g.) in small pieces was suspended in dry ether (20 c.c.), and *iso*butyl bromide (11 g.) in ether (10 c.c.) slowly added. The reaction started almost immediately and was complete in 1½ hours, after which the whole was boiled under reflux for a further ½ hour. It was then cooled and slowly transferred to a reaction tube (cooled in ice) containing di*iso*butylthallium bromide (16 g.) and ether (30 c.c.). The bromide rapidly disappeared, and the solution became dark owing to separation of metallic thallium. When all the lithium alkyl had been added, together with the ethereal washings from the unchanged lithium, the solvent was removed by evaporation and replaced by pentane. On filtration and removal of the solvent, a pale yellow liquid containing a little white solid (di*iso*butylthallium bromide ?) was left. The liquid distilled at 74—76°/1·6 mm. (slight decomp.) to give a pale

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* As considerable bumping frequently occurred during removal of solvents in this way, a second empty reaction tube was placed between that containing the liquid being evaporated and the vacuum line.

† The considerable discrepancies frequently to be found in the b. p.'s of compounds at pressures below about 5 mm. can no doubt be traced to variations in the form of apparatus used for distillation. The flow of vapours round sharp bends in the flask and side-arm, through constrictions such as taps in Perkin triangles and narrow-bore condensers, the practice of using leaks to prevent bumping and of connecting the gauge and the apparatus by means of a length of small-bore rubber tubing, all tend to indicate a lower pressure on the gauge than actually exists at the thermometer (cf. Hickman, *J. Franklin Inst.*, 1932, **213**, 124).

lemon-yellow liquid which tended to decompose and deposit metallic thallium on exposure to light; yield 10·9 g., 73%. It was analysed by breaking a bulb containing a small weighed amount under water; the heavy oil, which remained at the bottom, slowly decomposed, evolving a gas which burnt with a luminous flame tinged with green, presumably *iso*butane contaminated with traces of *tri*iso*butylthallium*. The oil eventually disappeared, aided by addition of a little alcohol, and the di*iso*butylthallium hydroxide formed was determined by adding an excess of 0·969 × $N/2$-sulphuric acid and titrating back with $N/10$-sodium carbonate solution (methyl-orange) (2·1646 g. required 11·9 c.c. of acid. $C_{12}H_{27}Tl$ requires 11·9 c.c. Found: Tl, 54·04. $C_{12}H_{27}Tl$ requires Tl, 54·41%).

*Di*iso*butylthallium acetate* was obtained in theoretical yield when tri*iso*butylthallium and acetic acid were allowed to react in pentane solution. It crystallised from absolute alcohol in long, fine, colourless needles, m. p. 215° (decomp.) (Found: Tl, 54·63. $C_{10}H_{21}O_2Tl$ requires Tl, 54·13%).

*Attempt to prepare Diethyl*iso*butylthallium*.—A rough estimation of the yield of *iso*butyllithium, using pentane instead of ether as the solvent, indicated that the yield is approximately 60%.

Lithium (3·2 g.) in small pieces in pentane (50 c.c.) was treated with *iso*butyl bromide (30 g.) diluted with the same solvent (50 c.c.). The reaction took much longer in starting, and 4 hours had elapsed before it became very slow. The reaction mixture was refluxed gently for another hour and then, after being cooled in ice-water, was slowly added to a similarly cooled suspension of diethylthallium bromide (18 g.), which had been very finely ground and passed through a 100-mesh sieve, in pentane (30 c.c.). So much solvent was present that hardly any heating effect was noticeable, but blackening of the bromide at once occurred, followed by precipitation of metallic thallium. After filtration, the solvent was removed under reduced pressure and a pale yellow heavy oil remained. This oil was less stable than either the triëthyl or the tri*iso*butyl compound and decomposed on standing, particularly in light. On distillation, much thallium was formed but it was impossible to get any true indication of the pressure. In an improved apparatus, the b. p. was 50—65°/3·2 mm. Most of the distillate was treated with acetic acid in pentane solution, but the acetates formed, which appeared to be a mixture of the diethyl- and the di*iso*butyl-thallium salt, could not be fractionally crystallised.

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THE RESEARCH DEPARTMENT, ANGLO-PERSIAN OIL CO., LTD.,
SUNBURY-ON-THAMES.

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