LXXVIII.—*Some Mixed Phosphonium Derivatives.*

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During several years past we have been occupied in attempts to prepare optically active phosphonium compounds containing no asymmetric atom other than one of quinquevalent phosphorus. Although these attempts have hitherto proved unsuccessful, a number of results of interest have been arrived at which it seems desirable to record.

Preparation of Phosphenyl Chloride.

The method of preparing phosphenyl chloride devised by Michaelis (*Annalen*, 1876, **181**, 283), which consists in slowly distilling a mixture of equal volumes of benzene and phosphorus trichloride through a red-hot porcelain tube, is a satisfactory one. An essential improvement on the original method consists, however, in keeping a slow stream of carbon dioxide continually passing through the apparatus; the yield of pure phosphenyl chloride is then considerably greater than that obtained by Michaelis, and one litre of the mixture affords about 140 grams of the pure product per nine hours. The fractional distillation of the product is conveniently carried out in a stream of carbon dioxide, and the phosphenyl chloride preserved in glass-stoppered bottles filled with carbon dioxide.

Mercury Dibenzyl, $Hg(CH_2{\cdot}C_6H_5)_2$.

Magnesium powder (12 grams) and benzyl chloride (87 grams) are caused to react in ether solution under the conditions described by Kipping (Trans., 1907, **91**, 720); finely powdered mercuric chloride (52 grams) is then added in small portions with constant agitation. The mixture is finally heated on the water-bath for two hours, and, after cooling, treated successively with water and dilute hydrochloric acid. The mercury dibenzyl is extracted with benzene, the benzene extract evaporated, and the residue crystallised from boiling benzene after washing with ether:

0·4024 gave, by the Carius method, 0·2452 HgS. Hg = 52·51.

$C_{14}H_{14}Hg$ requires Hg = 52·34 per cent.

Mercury dibenzyl crystallises from benzene in thin, lustrous, doubly-refracting plates, melting at 104°. It is readily soluble in carbon disulphide or chloroform, moderately so in benzene or ethyl acetate, and very sparingly so in cold alcohol. It is practically insoluble in ether or light petroleum; it is insoluble in water, and is not decomposed on boiling with that solvent. The substance possesses a characteristic, sweet odour, which becomes nauseating when large quantities of the material are dealt with.

A similar method to the above was used by Pfeiffer and Truskier (*Ber.*, 1904, **37**, 1125) for the preparation of mercury diphenyl, and it was anticipated that by heating mercury dibenzyl with phosphenyl chloride it would be possible to prepare phenylbenzylchlorophosphine in accordance with a well-known reaction stated by Michaelis. This reaction does not proceed, however, in this case, because mercury dibenzyl decomposes into mercury and dibenzyl at about 170°, whilst reactions of the type referred to do not set in until a much higher temperature has been attained. Similarly, it was not found possible to isolate the secondary chlorophosphine from the product of reaction of phosphenyl chloride with magnesium benzyl chloride; even on treating phosphenyl chloride with magnesium methyl iodide the only product which could be isolated in any quantity was an oil which when treated with methyl iodide gave phenyltrimethylphosphonium iodide. The latter was identified by analysis, and crystallises from alcohol in long, colourless prisms, melting at 226—227°, instead of at 205°, as stated by Michaelis (*loc. cit.*, p. 363).

p-*Tolylmercuric Bromide.*

In view of the failure to cause interaction between phosphenyl chloride and mercury dibenzyl, it was decided to introduce the *p*-tolyl group into the phosphorus compound by the aid of a mercury compound; on treating magnesium *p*-tolyl bromide with mercuric chloride, the previously unknown *p*-tolylmercuric bromide was obtained.

p-Bromotoluene (120 grams) was slowly added to magnesium dust (12 grams) suspended in ether, reaction being allowed to proceed with but little rise of temperature; mercuric chloride (52 grams) was then added in portions, and the solution heated on the water-bath for four to six hours. After distillation of the ether, dilute hydrochloric acid was added, the solid product collected, and freed from di-*p*-tolyl and *p*-bromotoluene by extraction with alcohol and chloroform. The residue was obtained in thin scales of a pearl-grey lustre, melting at 228°, by crystallisation from boiling benzene:

0·5610 gave 0·2751 AgBr. Br = 20·87.

C_7H_7HgBr requires Br = 21·54 per cent.

The p-*tolylmercuric bromide* thus obtained (48 grams) represents a 70 per cent. yield; it is sparingly soluble in the ordinary solvents when hot, and practically insoluble in the cold.

Phenyl-p-*tolylchlorophosphine.*

On heating phosphenyl chloride (78 grams) with *p*-tolylmercuric bromide (60 grams) for two to three hours at 270° in a flask provided with a reflux condenser, through which a stream of dry carbon dioxide passes, vigorous reaction occurs; on cooling, the product is extracted with benzene, and the benzene solution fractionally distilled after filtering. Phosphenyl chloride (24 grams) is recovered, and a 63·5 per cent. yield of phenyl-*p*-tolylchlorophosphine (30 grams), boiling at 230—240°/100 mm., was obtained; the latter product was further identified with the compound obtained by Michaelis by conversion into phenyl-*p*-tolylphosphinic acid, and by comparison with the substance prepared as described by this author (*Annalen*, 1896, **293**, 263).

It is obvious that the reaction between mercury di-*p*-tolyl and phosphenyl chloride proceeds in accordance with the following equation:

$$2(C_6H_5)PCl_2 + (C_6H_4Me)_2Hg = 2C_6H_4Me(C_6H_5)PCl + HgCl_2,$$

and not in accordance with that given by Michaelis.

Phenyl-p-*tolylmethylallylphosphonium Iodide,*
$C_6H_5(C_6H_4Me)(C_3H_5)(CH_3)PI$.

Phenyl-*p*-tolylmethylphosphine (22 grams), prepared by the action of phenyl-*p*-tolylchlorophosphine on zinc methyl as described by Michaelis, was treated with allyl iodide (20 grams) in dry ether solution; after remaining for a short time in a freezing mixture, a crystalline deposit was formed, and this, when action was at an end, was crystallised from alcohol containing a little water, and finally from a mixture of alcohol and ether. The substance forms colourless, glistening needles, which begin to decompose at 170° and melt at 175—177°; it is soluble in water or alcohol, less so in acetone, and insoluble in ether, benzene, or light petroleum:

0·2108, titrated with $AgNO_3$ and NH_4CNS, indicated 0·0698 I. I = 33·14.

$C_{17}H_{20}IP$ requires I = 33·22 per cent.

On treating this iodide with equivalent quantities of the silver salts of *d*-camphor-β-sulphonic acid, *d*-α-bromocamphor-π-sulphonic acid, and *d*-α-bromocamphor-β-sulphonic acid respectively in aqueous solution and evaporating the filtrate, viscid residues were obtained, which could not be caused to crystallise.

The iodide is decomposed with effervescence by treating with silver hydroxide in presence of water, and the corresponding phosphonium hydroxide could not be obtained.

Phenyl-p-*tolylbenzylmethylphosphonium Bromide*, $C_6H_5(C_6H_4Me)(C_6H_5\cdot CH_2)(CH_3)PBr$.

This substance crystallised rapidly from a mixture of equivalent quantities of phenyl-*p*-tolylmethylphosphine and benzyl bromide cooled in a freezing mixture, and was purified by recrystallisation from a mixture of acetone and ether. It forms thin, colourless plates, melting at 211—212°, is easily soluble in acetone, and insoluble in ether or benzene:

0·1972, with $AgNO_3$ and NH_4CNS, showed 0·0408 Br. Br = 20·67.

$C_{21}H_{22}BrP$ requires Br = 20·70 per cent.

dl-*Phenyl*-p-*tolylbenzylmethylphosphonium* d-*α-Bromocamphor-π-sulphonate*, $C_6H_5(C_6H_4Me)(C_6H_5\cdot CH_2)(CH_3)P\cdot O\cdot SO_2\cdot C_{10}H_{14}OBr$.

On treating the phosphonium bromide with the corresponding amount of the silver salt of the optically active acid in hot alcoholic solution, filtering and evaporating the filtrate, a gum remains which crystallises on being kept in a desiccator. The salt is purified by several crystallisations from boiling benzene, and then forms colourless needles, which on rapid heating sinter at 122° and melt at 129—131°:

0·5752 lost 0·0174 at 105° in three hours. $H_2O = 3·02$.

0·1070 * gave 0·2364 CO_2 and 0·0626 H_2O. C = 60·25; H = 6·49.

$C_{31}H_{36}O_4BrSP,1H_2O$ requires $H_2O = 2·84$ per cent.

$C_{31}H_{36}O_4BrSP$ requires C = 60·49; H = 5·90 per cent.

On subjecting the salt to systematic fractional crystallisation from a mixture of ethyl acetate and acetone, it was resolved into three fractions, which exhibited the specific rotatory powers for mercury green light of [α] +53·9°, +53·4°, and +53·9° respectively in 1 per cent. aqueous solutions. It is thus indicated that the phosphonium base is not resolved into optically active components by crystallisation with the optically active acid employed.

The rotation constants of the salt were determined in aqueous solution, using a carefully purified sample; 0·2658 gram in 30 c.c., examined in a 4-dcm. tube at 15°, gave the following values:

	$Mercury_{green}$.	$Mercury_{yellow}$.	$Sodium_{yellow}$.
α............	+ 1·91°	+ 1·625°	+ 1·555°
[α]	53·9	45·85	43·74
[M].........	331	282	269

The rotatory dispersions are for $Hg_{green}/Na_{yellow} = 1·232$ and for $Hg_{yellow}/Na_{yellow} = 1·048$.

For purposes of comparison, careful determinations were made of the rotation constants of ammonium *d*-α-bromocamphor-π-sulphonate in an aqueous solution of equivalent concentration; 0·1464 gram of

* Anhydrous.

the ammonium salt, made up to 30 c.c. and examined in a 4-dcm. tube at 15°, gave the following values:

	Mercury$_{green}$.	Mercury$_{yellow}$.	Sodium$_{yellow}$.
α …………	+ 2·03°	+ 1·715°	+ 1·64°
[α] ………	104·0	87·9	84·0
[M] ………	341	288	276

The rotatory dispersions are for $Hg_{green}/Na_{yellow} = 1·238$ and for $Hg_{yellow}/Na_{yellow} - 1·046$.

The several fractions of the salt were treated in aqueous solution with potassium iodide, and the crystalline iodide which was precipitated was found to be optically inactive in methyl-alcoholic solution. It is thus proved that the asymmetric phosphonium compound has not been resolved into optically active components by crystallisation of its *d*-α-bromocamphor-π-sulphonate.

dl-*Phenyl*-p-*tolylbenzylmethylphosphonium* d-*Camphor-β-sulphonate.*

The above salt was prepared in a similar manner to the preceding one, and crystallises readily from ethyl acetate containing a little alcohol in colourless needles melting at 134—137°. It is readily soluble in alcohol or acetone, but sparingly so in ethyl acetate:

0·1101 gave 0·2792 CO_2 and 0·0732 H_2O. C = 69·15; H = 7·39.
$C_{31}H_{37}O_4SP$ requires C = 69·33; H = 6·95 per cent.

After careful fractional crystallisation from ethyl acetate and alcohol, the several fractions proved to have the same specific rotatory power, and the following determinations establish the constants for the salt; 0·3175 gram, made up to 30 c.c. with water, gave the following values in a 4-dcm. tube at 15°:

	Mercury$_{green}$.	Mercury$_{yellow}$.	Sodium$_{yellow}$.
α ………………	+ 0·52°	+ 0·42°	+ 0·39°
[α] ……………	12·3	9·9	9·2
[M] ……………	66	53	49

The rotatory dispersions are for $Hg_{green}/Na_{yellow} = 1·333$ and for $Hg_{yellow}/Na_{yellow} = 1·075$.

The following determinations of the rotation constants of ammonium *d*-camphor-β-sulphonate in aqueous solution of equivalent concentration serve for comparison; 0·1494 gram was made up to 30 c.c. with water and examined in a 4-dcm. tube at 15°:

	Mercury$_{green}$.	Mercury$_{yellow}$.	Sodium$_{yellow}$.
α ………………	+ 0·53°	+ 0·43°	+ 0·40°
[α] ……………	26·6	21·6	20·1
[M] ……………	66	54	50

The rotatory dispersions are for $Hg_{green}/Na_{yellow} = 1·325$ and for $Hg_{yellow}/Na_{yellow} = 1·075$.

On addition of potassium iodide to the aqueous solutions of the several fractions, the corresponding phosphonium iodide is precipitated, and each sample thus obtained proved optically inactive in methyl-alcoholic solution. It is thus indicated that the resolution of the asymmetric phosphonium salt into optically active components has not been effected.

Phenyl-p-*tolylbenzylmethylphosphonium Iodide*, $C_6H_5(C_6H_4Me)(C_6H_5\cdot CH_2)(CH_3)PI$.

This substance is obtained by the addition of potassium iodide to the aqueous solution of any of its above soluble salts; on crystallisation from alcohol it is obtained in colourless, glistening plates, melting at 215—216·5°. It dissolves readily in methyl alcohol, less so in hot alcohol, and is practically insoluble in ether, benzene, or light petroleum:

0·3538, with $AgNO_3$ and NH_4CNS, indicated 0·1030 I. I = 29·11.
$C_{21}H_{22}IP$ requires I = 29·38 per cent.

Phenyl-p-*tolylbenzylmethylphosphonium Platinichloride*, $[C_6H_5(C_6H_4Me)(C_6H_5\cdot CH_2)(CH_3)P]_2PtCl_6$.

This salt is precipitated as a yellow, crystalline powder on addition of chloroplatinic acid to the aqueous solution of either of its above soluble salts; it is practically insoluble in all the ordinary solvents, and melts at 214—215°:

0·1131 gave 0·2040 CO_2 and 0·0491 H_2O. C = 49·14; H = 4·82.
$(C_{21}H_{22}P)_2PtCl_6$ requires C = 49·52; H = 4·35 per cent.

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