

EXPERIMENTAL

Materials and methods

All the solvents used were purified and dried before use. Pet ether used had the boiling range 60° - 80° .

Diphenyl carbazone, G.R. E. Merck; dithizone, G.R. E. Merck and Oxine (8-hydroxy quinoline) A.R. B.D.H. were used. All the melting points were uncorrected. Known compounds were checked by mixed melting point determination with authentic samples.

Triphenyl tin dithizonate was prepared according to the method of Ghosh and Ghosh (15) by refluxing a mixture of triphenyl tin oxide (2.0g) and dithizone (1.43g) in chloroform (150 ml) for one hour. The deep coloured solution was filtered. The filtrate was concentrated, methanol was added in excess when after some time fine brick red crystals of triphenyl tin dithizonate (m.p. $144-45^{\circ}$) was obtained. On recrystallisation from chloroform-methanol mixture it afforded crystals of m.p. 146° [lit (15) m.p. $145-46^{\circ}$ C].

Diphenyl tin bis-dithizonate was prepared according to the method of Ghosh and Ghosh (15). A mixture of 0.88g of diphenyl tin dichloride and 1.28g of dithizone in 100 ml chloroform was heated on a water bath for 10 minutes. 7-8 drops of ammonia solution (17N) was added to neutralise the liberated hydrochloric acid and the precipitated ammonium chloride was filtered off. The filtrate was concentrated and methanol was added when 1.15g of

shining reddish crystals of diphenyl tin bis-dithizonate was obtained. This on recrystallisation from chloroform methanol mixture afforded crystals of m.p. $181-83^{\circ}$ [lit (15) m.p. $181-83^{\circ}\text{C}$].

Triphenyl tin N-phenyl benzohydroxamate was prepared by the method of Pradhan and Ghosh (16) by refluxing for four hours a mixture of 2.15g of bis-triphenyl tin oxide and 1.25g of N-phenyl benzohydroxamic acid (PBHA) in 50 ml benzene using a Dean-Stark Water Separator. The light yellow solution was filtered and evaporated to a pasty mass on a water bath which was crystallised from methanol. Yield was 2.50g and m.p. was 133°C [lit (16) m.p. 133°C].

Diphenyl tin bis-N-phenyl benzohydroxamate was prepared according to the method of Pradhan and Ghosh (16). This was crystallised from benzene and methanol. This was dried in vacuum and had a m.p. of 160° [lit (16) m.p. 160°].

Dimethyl tin bis-(N-phenyl-p-nitrobenzohydroxamate) was prepared according to the method of Chaudhuri (17) by refluxing a mixture of 1g of dimethyl tin oxide and 3g of N-phenyl p-nitro benzohydroxamic acid (nitro PBHA) in 150 ml benzene for two hours using a Dean and Stark Water Separator. The yellow coloured solution was filtered and concentrated to a pasty mass. Shining yellow crystals (3g) appeared after the addition of methanol. The compound on recrystallisation from methanol afforded crystals of m.p. 237°C [lit (17) m.p. 237°C].

N-phenyl-p-nitro benzohydroxamic acid was prepared by the reaction of p-nitrobenzoyl chloride with phenyl hydroxylamine (18). The compound was crystallised from rectified spirit and dried by heating in vacuum. M.P. was noted to be 159°C [lit (19) m.p. 159°C].

Triphenyl tin oxinate was prepared by reacting bis-triphenyl tin oxide with oxine. The compound had m.p. of 145°C [lit (20) m.p. $145-46^{\circ}\text{C}$].

Diphenyl tin dioxinate was prepared by reacting diphenyl tin dichloride and oxine. The liberated hydrogen chloride was neutralised by ammonia. M.P. was found to be $249-51^{\circ}\text{C}$ [lit (20) m.p. 251°C].

All the organotin diphenyl carbazonates, namely, triphenyl tin diphenyl carbazonate, diphenyl tin bis-diphenyl carbazonate, dimethyl tin bis-diphenyl carbazonate, dibutyltin bis-diphenyl carbazonate and dimethyl chlorotin diphenyl carbazonate have been described before.

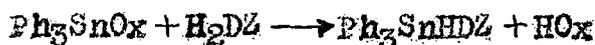
1. Reaction of Triphenyl tin oxinate with Dithizone

1.98g of triphenyl tin oxinate and 1.02g of dithizone were separately dissolved in 100 ml chloroform. These two solutions were mixed together and the mixture was refluxed for 2 hours on a water bath. The refluxed solution on cooling did not give any crystal but on concentration of the reaction mixture over a water

bath to one-fourth of the original volume and cooling, a fine deep brown coloured crystals of melting point $140-41^{\circ}\text{C}$ appeared. The yield was 2.20g. This compound on recrystallisation twice from chloroform-methanol mixture afforded crystals of m.p. $143-44^{\circ}\text{C}$. This compound showed no depression of melting point with an authentic sample of triphenyl tin dithizonate.

The mother liquor, after separation of triphenyl tin dithizonate, was further concentrated and kept for some time when fine shining yellowish crystals of m.p. $69-72^{\circ}\text{C}$ appeared. This was collected and on recrystallisation from chloroform-methanol mixture it afforded crystals of m.p. 75°C . This compound was confirmed as oxine as it showed no depression of melting point with an authentic sample of oxine. The yield was 0.50g.

On the basis of the products obtained we infer that the following reaction has taken place:



The conversion in this case was about 90% on the basis of isolation of triphenyl tin dithizonate (Ph_3SnHDZ).

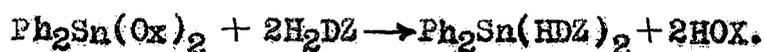
2. Reaction of Diphenyl tin dioxinate with Dithizone

0.56g of diphenyl tin dioxinate and 0.51g of dithizone were separately dissolved in 100 ml chloroform, in each case. Both these solutions were mixed when the colour of the mixture became yellowish-red. This mixture was then refluxed for one hour on a

water bath. The refluxed solution on cooling did not give any crystal. This was concentrated to one-fourth its original volume and kept for some time when a beautiful yellowish-black crystals of m.p. 72°C appeared and was collected. The yield was 0.27g. The compound on recrystallisation thrice from chloroform-methanol mixture afforded shining yellow crystals of m.p. 75°C and showed no depression of melting point with an authentic sample of oxine.

The mother liquor was further concentrated and kept in the refrigerator for two days when beautiful pink coloured crystals of melting point $177-79^{\circ}\text{C}$ were formed. This on further recrystallisation from chloroform methanol mixture afforded crystals of m.p. $181-82^{\circ}\text{C}$. This compound was identified as diphenyl tin bis-dithizonate since it showed no depression of melting point with an authentic sample of diphenyl tin bis-dithizonate. The yield was approximately 0.70g.

On the basis of the products obtained we infer that the following reaction has taken place.



The conversion was almost 89%.

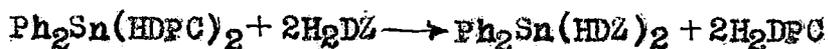
3. Reaction between diphenyl tin bis-diphenyl carbazonate and dithizone

0.75g of diphenyl tin bis-diphenyl carbazonate and 0.51g of dithizone were separately dissolved in chloroform and then mixed

together. The mixture after being refluxed on a water bath for about 2 hours did not give any crystal on cooling. It was then concentrated to one-fourth its original volume and cooled, but no crystals appeared. To it slight excess of methanol was added and the solution was kept for some time when beautiful red shiny crystals of m.p. 180-82°C appeared and was collected. This on recrystallisation twice from chloroform-methanol mixture afforded crystals of melting point 181-82°C. The yield was 0.74g. This compound was characterised as diphenyl tin bis-dithizonate since it gave no depression in melting point with an authentic sample of diphenyl tin bis-dithizonate.

After separating the shining red crystals, the mother liquor was concentrated almost to evaporation when after cooling this highly concentrated solution produced shining orange crystals of m.p. 153-158°C. The yield was 0.40g. This on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 155-57°C. This was diphenyl carbazone as was confirmed by mixed melting point checking with an authentic sample of diphenyl carbazone.

Thus, the following reaction has taken place here:



The percentage of conversion in this case was 94% .

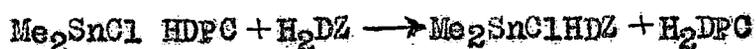
4. Reaction of dimethyl chlorotin diphenyl carbazonate with dithizone

0.42g of dimethyl chlorotin diphenyl carbazonate and 0.26g of dithizone were mixed and dissolved in 100 ml chloroform. The mixture was then refluxed on a water bath for about 3 hours. The refluxed solution on cooling did not give any crystal. It was then concentrated to one-fourth its original volume and cooled but no crystals appeared. To it slight excess of methanol was added and the mixture was kept for some time when fine shining reddish crystals of m.p. 180-81°C were formed and collected. This on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 183-84°C. This was found to be dimethyl chlorotin dithizonate since no depression of melting point of it with an authentic sample of dimethyl chlorotin dithizonate [lit (15a) m.p. 184°C] was noted. The yield was 0.40g.

After separating these crystals, the mother liquor was highly concentrated and allowed to stand for some time when beautiful shining orange crystals of m.p. 148-50°C appeared. This was collected. On recrystallisation from highly concentrated chloroform-methanol mixture it afforded orange coloured crystals of m.p. 154-55°C. The yield was 0.22g. This compound was confirmed as diphenyl carbazone by mixed melting point checking with an authentic sample.

A small amount of dimethyl chlorotin diphenyl carbazonate and dithizone could not be recovered.

Thus the following reaction has taken place in the above case:



In this reaction percent conversion = 91% [on the basis of dimethyl chlorotin diphenyl carbazonate] and percent recovery of diphenyl carbazone = 92%.

5. Reaction between diphenyl tin bis-(N-phenyl benzohydroxamate) and dithizone.

0.70g of diphenyl tin bis-(N-phenyl benzohydroxamate) and 0.50g of dithizone were mixed. To it added 100 ml benzene and refluxed for two hours on a water bath. The refluxed solution on cooling did not give any crystal. It was then concentrated and kept for some time when a gummy mass was found to be appeared. This gummy mass was extracted with methanol for several times when after some time a deep violet coloured crystal of m.p. 180-81°C was formed. This on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 180°C which showed no depression in melting point with an authentic sample of diphenyl tin bis-dithizonate. The yield was 0.65g.

After separating these crystals the mother liquor was further concentrated and cooled when again a gummy mass appeared. This was dissolved in carbon tetrachloride. Upon concentration and cooling the filtrate produced pale yellow crystals of m.p.

120-21°C. The yield was 0.38g. This on recrystallisation from carbon tetrachloride produced yellow crystals of m.p. 121-22°C. This was N-phenyl benzohydroxamic acid as it showed no depression in melting point with an authentic sample of N-phenyl benzohydroxamic acid.

So, in this reaction percent conversion = 83%

and percent recovery of N-phenyl benzohydroxamic acid = 89%.

Thus it is evident that the following reaction has taken place.



6. Reaction of triphenyl tin N-phenyl benzohydroxamate and dithizone:

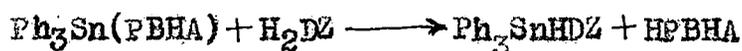
0.56g of triphenyl tin N-phenyl benzohydroxamate and 0.26g of dithizone were dissolved separately in carbon tetrachloride. These were then mixed and the mixture was refluxed on a water bath for about three hours. The refluxed solution on cooling gave no crystal. It was then concentrated and kept for sometime when snuff coloured crystals of m.p. 186-87°C were formed. The yield was 0.10g. Mixed melting point of this compound showed it as unreacted triphenyl tin N-phenyl benzohydroxamate.

After separating this product the mother liquor was further concentrated and allowed to stand for sometime when a violet coloured crystal (0.45g) of m.p. 146°C was formed and collected. This compound was confirmed as triphenyl tin dithizonate by mixed

melting point determination with an authentic sample.

This product was separated and the mother liquor was highly concentrated and kept for sometime when yellow crystals of m.p. 119-20°C. were formed and collected. On recrystallisation from carbon tetrachloride solution it afforded crystals of m.p. 122°C. This compound, N-phenyl benzo hydroxamic acid was separated and confirmed by noting no depression in melting point with an authentic sample of N-phenyl benzohydroxamic acid. The yield was 0.18g.

So, percent conversion on the basis of $\text{Ph}_3\text{SnPBHA} = 75\%$
Therefore, on the basis of the products obtained in the reaction, we infer that the following exchange reaction has taken place.

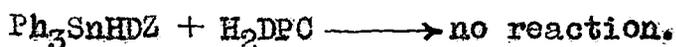


7. Reaction between triphenyl tin dithizonate and diphenyl carbazone:

0.61g of triphenyl tin dithizonate and 0.24g of diphenyl carbazone were separately dissolved in 100 ml chloroform. These were mixed and the mixture was refluxed on a water bath for two hours. The refluxed solution on cooling gave no crystal. It was then concentrated to one-sixth its original volume and kept for sometime when fine orange coloured crystals of m.p. 150°C were formed and collected. The yield was 0.22g. This on recrystallisation from chloroform methanol mixture afforded crystals of m.p. 155°C. This compound was found to be diphenyl carbazone.

After separating these orange coloured crystals the mother liquor was highly concentrated but did not give any crystal on cooling. To it a slight excess of methanol was added and kept for some time when fine reddish crystals of m.p. 140-41°C appeared. These were collected. The yield was 0.57g. On recrystallisation from chloroform-methanol mixture it afforded crystals of m.p. 145-46°C. This compound was triphenyl tin dithizonate.

Thus no reaction has taken place.

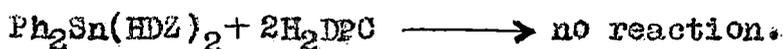


8. Reaction between diphenyl tin bis-dithizonate and diphenyl carbazone:

0.78 gms of diphenyl tin bis-dithizonate and 0.48 gms of diphenyl carbazone were weighed and dissolved separately in 100 ml chloroform. These were mixed together and the mixture was refluxed for four hours. On cooling it did not give any crystal. The refluxed solution was then concentrated to one-third its original volume and kept for some time when orange-coloured crystals of melting point 151-52°C separated out. This on recrystallisation from chloroform-methanol mixture afforded orange coloured crystals of melting point 155-56°C. The yield of this compound was 0.47 gms. It gave no depression in melting point with an authentic sample of diphenyl carbazone.

After the separation of the orange crystals the mother liquor was further concentrated to a small volume. The concentrated mother liquor on cooling did not give any crystal. To this concentrated mother liquor, excess methanol was added and this mixture was kept for some time when fine shiny red crystals appeared and was collected. Melting point of this crystal was found to be 180-81°C. This on further recrystallisation from chloroform-methanol mixture afforded crystals of melting point 181-82°C. The crystals gave no depression in melting point with an authentic sample of diphenyl tin bis-dithizonate. The yield was 0.78g.

On the basis of the observations it seems that no reaction has taken place in the above case.



9. Reaction between diphenyl tin bis-diphenyl carbazonate and oxine:

0.75g of diphenyl tin bis-diphenyl carbazonate and 0.29g of oxine were separately dissolved in chloroform and mixed together. The mixture was refluxed on a water bath for about two hours. The solution on cooling did not give any crystal. The reaction mixture was then concentrated to one-fourth its original volume which on cooling gave no crystal. To it a slight excess of methanol was added and the mixture was kept for one day when crystals appeared on recrystallisation twice from chloroform-methanol mixture it

afforded shining yellowish crystals of m.p. 250°C. These crystals were confirmed as diphenyl tin bis-oxinate by noting the mixed melting point. The yield was 0.52g.

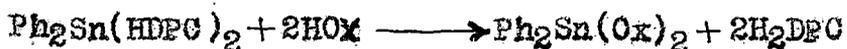
After separating the yellowish crystals the mother liquor was further concentrated but no crystals appeared on cooling. The mother liquor was then evaporated to dryness and the solid mass was dissolved in chloroform. This was kept for some time when beautiful shining orange crystals of m.p. 148-50°C appeared. The yield was 0.40g. This on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 154-55°C and was found to be diphenyl carbazone.

In the above reaction

percent conversion = 92.3%

and percent recovery of diphenyl carbazone = 84%.

So the following reaction has taken place.

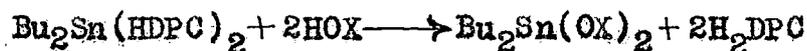


10. Reaction of dibutyl tin bis-diphenyl carbazonate with oxine:

0.62g of dibutyl tin bis-diphenyl carbazonate and 0.25g of oxine were mixed. To it added 100 ml chloroform and the mixture was refluxed for one hour on a water bath. The refluxed solution on cooling did not give any crystal. On concentration of the mixture over a water bath to one-fourth its original volume, no crystals

appeared. To it a slight excess of methanol was added and kept for sometime when beautiful shining yellowish-red crystals were formed and collected. These on further crystallisation from chloroform-methanol mixture afforded shining yellowish crystals of m.p. 150°C . This was dibutyl tin bis-oxinate as was confirmed by mixed melting point checking with an authentic sample $\left[\text{lit (20a) m.p. } 150-52^{\circ}\text{C} \right]$. The yield was 0.45g. After separating it the mother liquor was further concentrated to a small volume, when orange coloured crystals appeared. The yield was 0.42g. These crystals melted at 151°C . On recrystallisation from chloroform-methanol mixture it afforded crystals of m.p. $154-55^{\circ}\text{C}$. The crystals were confirmed as diphenyl carbazone by mixed melting point checking with an authentic sample of diphenyl carbazone.

So, the following reaction has taken place.



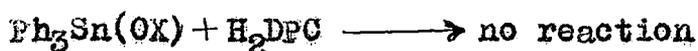
The conversion was practically quantitative in nature.

11. Reaction between triphenyl tin oxinate and diphenyl carbazone:

0.49g of triphenyl tin oxinate and 0.24g of diphenyl carbazone were separately dissolved in chloroform, mixed together and the mixture after being refluxed on a water bath for four hours did not give any crystal on cooling. The refluxed solution was then concentrated to one-fourth its original volume and kept for some time, but no crystals appeared. To this solution added a slight

excess of methanol. This solution, upon concentration, produced yellowish orange crystals. This was collected and recrystallised from chloroform-methanol mixture when beautiful shining yellowish crystals of m.p. 144°C was obtained. The yield was 0.47g. By mixed melting point checking the compound was confirmed as triphenyl tin oxinate.

After separating these yellow crystals the mother liquor was further concentrated and kept for some time when fine orange coloured crystals of m.p. $152-53^{\circ}\text{C}$ appeared. This was collected. The yield was 0.20g. On recrystallisation from highly concentrated chloroform/methanol mixture it afforded crystals of m.p. 155°C . This was confirmed as diphenyl carbazone by observing the mixed melting point. Thus, here, no reaction has taken place.



12. Reaction between dimethyl tin bis-(N-phenyl p-nitrobenzohydroxamate) and oxine:

0.33g of dimethyl tin bis-(N-phenyl p-nitrobenzohydroxamate) and 0.14g of oxine, i.e. 8-hydroxy quinoline were mixed. To it added 100 ml benzene and the mixture was refluxed for one hour on a water bath. The refluxed solution on cooling did not give any crystal. The solution was then concentrated to about one-fourth its original volume and the concentrated solution was kept for

sometime when fine pale yellow crystals of melting point 155-58°C appeared. This on recrystallisation from concentrated benzene solution afforded crystals of m.p. 159°C. This was confirmed as N-phenyl p-nitrobenzohydroxamic acid by mixed melting point checking with an authentic sample. The yield was 0.21g. After separating this product the mother liquor was evaporated to an oily liquid, this was then dissolved in methanol and the solution was kept for sometime when a fine yellow crystals of m.p. 230°C appeared. This was collected. On recrystallisation from methanol it gave crystals of melting point 231°C. This was dimethyl tin dioxinate as it showed no depression in melting point with an authentic sample [lit (20a) m.p. 231-33°C]. The yield was 0.20g.

Thus the following reaction has taken place here.



(LH = N-phenyl p-nitrobenzohydroxamic acid)

so, percent conversion in this case $\approx 84\%$.

13. Reaction between dimethyl tin bis-(N-phenyl p-nitro benzohydroxamate) and diphenyl carbazone:

0.33g of dimethyl tin bis-(N-phenyl p-nitro benzohydroxamate) and 0.24g of diphenyl carbazone were separately dissolved in benzene. The two solutions were mixed and the mixture was refluxed for one hour on a water bath. The refluxed solution on cooling gave orange-coloured crystals of m.p. 150-52°C. The yield was approximately 0.20g. This on recrystallisation from benzene-methanol mixture

afforded orange-coloured crystals of m.p. 155-56°C. This compound was diphenyl carbazone as it showed no depression in melting point with an authentic sample of diphenyl carbazone. After separating these crystals the mother liquor was concentrated to about one-fourth its original volume. This solution, on cooling, gave no crystal. To it slight excess of methanol was added and after some time this mixture produced a beautiful shining reddish crystals of melting point 192-93°C. The yield was 0.10g. After separating these crystals the mother liquor was concentrated to about one-fourth its original volume. On cooling, this solution gave beautiful shining reddish crystals of m.p. 131°C. This compound was found to be dimethyl tin bis-diphenyl carbazonate which showed no depression in melting point with an authentic sample. The yield was 0.05g. This product was separated and the mother liquor was concentrated almost to evaporation when yellow crystals of m.p. 236°C appeared. The yield was approximately 0.25g. This compound was unreacted dimethyl tin bis-(N-phenyl p-nitrobenzohydroxamate) as it showed no depression in melting point with an authentic sample.

On recrystallisation from chloroform-methanol mixture the crystals of m.p. 192-93°C gave two types of yellow crystals. One was obtained from moderately concentrated solution, the m.p. of which was 157°C. The yield was 0.05g. This was confirmed as N-phenyl p-nitrobenzohydroxamic acid by mixed melting point checking

with an authentic sample. The other yellow crystals (0.04g) was unreacted dimethyl tin bis-(N-phenyl p-nitro benzohydroxamate) as it showed no depression in melting point with an authentic sample. This product was obtained from highly concentrated solution.

The following reaction has taken place:



where LH = N-phenyl p-nitrobenzohydroxamic acid.

Percent of conversion in this case \approx 8%.

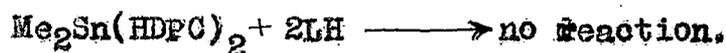
14. Reaction between dimethyl tin bis-diphenyl carbazonate and N-phenyl p-nitrobenzohydroxamic acid:

0.62g of dimethyl tin bis-diphenyl carbazonate and 0.51g of N-phenyl p-nitrobenzohydroxamic acid were mixed. To it added 50 ml chloroform and the mixture was refluxed for two hours. The refluxed solution on cooling did not give any crystal. The solution was then concentrated to one-third its original volume and a slight excess of methanol was added. The solution was kept for some time when beautiful shining reddish crystals of m.p. 130-32°C were formed. This product was collected and on recrystallisation from chloroform-methanol mixture it afforded shining reddish crystals of m.p. 130-31°C. The yield was 0.60g. This product was dimethyl tin bis-diphenyl carbazonate as it showed no depression in melting

point with an authentic sample.

After separating this product, the mother liquor was completely evaporated to a pasty mass on a water bath, which was dissolved in 20 ml benzene. This solution, upon concentration, gave pale yellow crystals of m.p. 155-57⁰C. The yield was approximately 0.5g. This on recrystallisation from benzene afforded crystals of m.p. 158-59⁰C. This was confirmed as N-phenyl p-nitro benzohydroxamic acid by mixed melting point checking.

From the observations of the products obtained we infer that no reaction has taken place in the above case.



where LH = N-phenyl p-nitro benzohydroxamic acid.