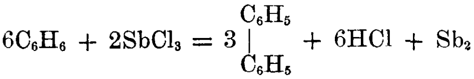
VI.—*A new method for preparing the Hydrocarbons, "Diphenyl" and "Iso-dinaphthyl," and on the action, at a high temperature, of Metallic Chlorides upon certain Hydrocarbons.*

By WATSON SMITH, F.C.S.

Benzene and Antimony Trichloride.

THE mixed vapours of benzene and antimony trichloride were passed through a red-hot tube, when the following equation was realised:—



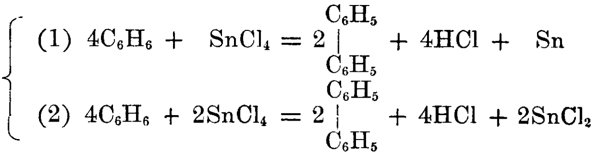
$$6C_6H_6 + 2SbCl_3 = 3\begin{array}{c}C_6H_5\\|\\C_6H_5\end{array} + 6HCl + Sb_2$$

The distillation was repeated several times. It was found that though the yield was greatly increased by this method above that obtained with benzene alone, yet that it was not as large as could be desired. The diphenyl was separated from the mixture of diphenyl, metallic antimony, and excess of antimony chloride by treatment with hydrochloric acid, and finally distilling with water, in the vapour of which the hydrocarbon is carried over. The experiment was now repeated with *tetrachloride of tin.*

Benzene and Tin Tetrachloride.

On passing the mixed vapours of these bodies through a red-hot tube filled with pumice-stone fragments, hydrochloric acid gas was copiously evolved, and the following equations were realised, both metallic tin and stannous chloride being reduced and found in the receiver :—

The mixed result is what is obtained



$$\left\{\begin{array}{l} (1)\ 4C_6H_6 + SnCl_4 = 2\begin{array}{c}C_6H_5\\ |\\ C_6H_5\end{array} + 4HCl + Sn \\ (2)\ 4C_6H_6 + 2SnCl_4 = 2\begin{array}{c}C_6H_5\\ |\\ C_6H_5\end{array} + 4HCl + 2SnCl_2 \end{array}\right.$$

By this method diphenyl is formed in large quantity, being found in the receiver in solid cakes, consisting of a mixture of diphenyl with some stannous chloride. It is undoubtedly the simplest and quickest method for procuring diphenyl in quantity.

Toluene and Antimony Trichloride.

Large volumes of hydrochloric acid evolved and much metallic antimony reduced. However, a tarry, oily mass was obtained, which yielded on distillation no stilbene, but at 270° a red oil smelling like burnt cheese; at from 280°—300° another oil, with a still ranker and more disagreeable odour, and at 350° or thereabouts a thick gummy oil, which crystallised, forming a striated mass of crystals. I am experimenting further in this direction.

Naphthalene and Antimony Trichloride through a red-hot Tube.

Considerable quantities of hydrochloric acid were evolved, metallic antimony reduced, and a largely increased yield of iso-dinaphthyl obtained. This is shown as follows :—

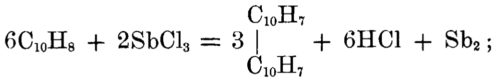
	Per cent.
Naphthalene alone used : After eight distillations through red-hot tube, crude substance obtained	= 17·23
Naphthalene and Antimony Trichloride : After three distillations through red-hot tube, crude substance obtained....................................	= 48·5
(After distilling to purify. Yellow crystalline substance partially purified	= 31·4)

In purifying the crude substance by triturating and washing with petroleum-spirit, a yellow substance is dissolved communicating a red tint to the spirit; from this solution crystals in wart-like masses gradually separate. This substance I shall now endeavour to isolate.

Naphthalene and Tin Tetrachloride.

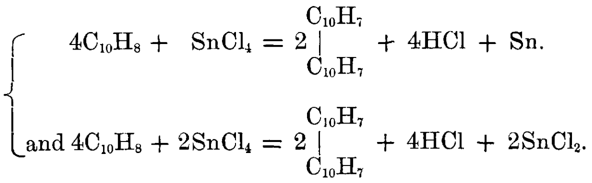
The results of this experiment were hydrochloric acid gas, together with a considerable separation of carbon, metallic tin, and stannous chloride, and the formation of chlorinated substitution-products of naphthalene, and of a considerable amount of iso-dinaphthyl. It was found, however, that, owing to the frequent stopping up of the tube with reduced carbon, and continual danger of explosions, the method with antimony trichloride is much to be preferred, as it is quite easy of performance and presents neither of the above disadvantages.

In the above reactions it would appear that, in the *first case*, the following equation is realised:—



$$6C_{10}H_8 + 2SbCl_3 = 3\begin{array}{l}C_{10}H_7\\ |\\ C_{10}H_7\end{array} + 6HCl + Sb_2;$$

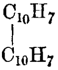
in the second—



$$\left\{\begin{array}{l}4C_{10}H_8 + SnCl_4 = 2\begin{array}{l}C_{10}H_7\\ |\\ C_{10}H_7\end{array} + 4HCl + Sn.\\ \text{and } 4C_{10}H_8 + 2SnCl_4 = 2\begin{array}{l}C_{10}H_7\\ |\\ C_{10}H_7\end{array} + 4HCl + 2SnCl_2.\end{array}\right.$$

Of course these equations represent only approximately what actually and totally takes place, other bodies being formed in small quantity.

The melting point and boiling point of the substance obtained in both the reactions named agreed with those of iso-dinaphthyl. A combustion was also made and gave the following results:—

	Found.	Calculated for  $\begin{array}{c}C_{10}H_7\\ \vert \\ C_{10}H_7\end{array}$
Carbon..........	93·97	94·48
Hydrogen	5·50	5·52
	99·47	100·00

Melting Point = 186° *to* 187°.

This I find is also the melting point of iso-dinaphthyl, prepared from naphthaline alone, and the number I formerly gave (204°) is erroneous, having been obtained by too rough a method. The corrected melting point is therefore 187°. I have also discovered a new solvent for iso-dinaphthyl, viz., glacial acetic acid, from which the hydrocarbon separates on cooling in most beautiful and perfect rhomboïdal plates, exhibiting a delicate blue fluorescence.

I cannot forget to thank Prof. Merz, of Zürich University, for his kind assistance in this investigation.