

brium  $\text{HOBr} + \text{H}^+ \rightleftharpoons (\text{H}_2\text{OBr})^+$ , in which the completeness of electron octets is preserved.

Since free hypobromous acid is best prepared by distilling a mixture of bromine-water and silver sulphate, it logically followed that an active brominating agent should be obtained by treating acidified bromine-water with a salt of silver, lead or other cation capable of removing bromide anions from solution. Our tests have shown that this is indeed the case. Benzene can be brominated in high yield (at least 80 per cent calculated on  $\text{Br}_2$ ) by stirring with bromine in a large volume of cold 2*N* nitric acid and then dropping in slowly an equivalent of silver nitrate solution. Lead nitrate acts similarly but less efficiently on account of the greater solubility of lead bromide; but with this latter mixture toluene is very easily brominated in the nucleus.

Since acetic acid appears to be inert to the bromine cation  $\text{Br}^+$ , this novel reaction is capable of wide extension to substances which are only sparingly soluble in water. From preliminary experiments, the speed of bromination appears to be dependent upon the strength of the mineral acid employed.

We propose to study more extensively both the scope and the kinetics of this reaction.

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<sup>1</sup> Hinshelwood, C. N., *J. Chem. Soc.*, 696 (1947).

<sup>2</sup> Weiss, J., *Chemical Society, Ann. Reports*, 44, 79 (1947).

### Organo-Cobalt Compounds

WE have attempted to prepare organo-cobalt compounds by various methods, including thermal decomposition of cobalt *p*-toluenesulphinate, thermal and copper catalysed decomposition of addition compounds of cobalt chloride and diazonium chlorides and of phenyldiazonium cobaltinitrite<sup>1</sup>, and refluxing diphenyliodonium iodide with finely divided cobalt powder in *n*-propanol<sup>2</sup>. All these experiments were unsuccessful, although in some cases traces of benzene-soluble organic materials with varying cobalt contents were obtained.

Organo-cobalt compounds were obtained by the following technique.  $\text{RMgX}$  ( $R = 1$ -naphthyl or 2-naphthyl,  $X = \text{Br}$  or  $\text{I}$ ) in ether was added to ethereal solutions of cobalt bromide or cobalt iodide at room temperature. The dark precipitate was extracted with benzene at room temperature. The green benzene solution was treated with five volumes of low-boiling petrol ether. The precipitates were filtered, analysed and found to correspond to the formulæ  $\text{RCoI}_3$  and  $\text{R}_2\text{CoBr}_5$ . Precipitation from benzene solution with dioxane yielded compounds of the formulæ  $\text{R}_2\text{CoI}_3$  and  $\text{R}_2\text{CoBr}_2$ . Compounds of the type  $\text{R}_2\text{CoX}_2$  were somewhat less pure than the products obtained by precipitation with petrol ether.

It was found that dioxane slowly decomposes all organo-cobalt compounds prepared by us. The organo-metallic nature of the products was established by their decomposition in water, which afforded the expected dinaphthyls<sup>3</sup> in addition to cobalt hydroxide, cobalt iodide and varying amounts of free iodine. The residue which was left behind after the extraction with benzene did not contain cobalt metal.

With the exception of  $1\text{-RCoI}_3$ , which gave fairly pure 1,1'-dinaphthyl, the dinaphthyl preparations from the aqueous decomposition of the organo-cobalt compounds were impure owing to contamination with naphthalene and possibly polynaphthyls.

Naphthylmagnesium bromides and cobalt iodide gave  $\text{RCoI}_3$ , and the same products were obtained from reactions between naphthylmagnesium iodides and cobalt bromide. The iodine derivatives were obtained in better yields than the corresponding bromine derivatives. The average yields were better in the 1-naphthyl series (60 per cent for  $\text{RCoI}_3$  and 20 per cent for  $\text{R}_2\text{Co}_2\text{Br}_5$ ) than in the 2-naphthyl series (47 per cent for  $\text{RCoI}_3$  and 9 per cent for  $\text{R}_2\text{Co}_2\text{Br}_5$ ). The yields of the compounds  $\text{R}_2\text{CoX}_2$  were considerably lower, particularly for the compounds  $\text{R}_2\text{CoBr}_2$ , which are appreciably soluble in dioxane. Both  $\text{RCoI}_3$  compounds are green and decompose around 160°. Both  $\text{R}_2\text{CoI}_2$  compounds are reddish-brown; the 1-compound decomposes at about 150–160° and the 2-compound at about 90°. The bromine compounds are blue. The approximate temperatures of decomposition are: 1- $\text{R}_2\text{Co}_2\text{Br}_5$ , 120°; 2- $\text{R}_2\text{Co}_2\text{Br}_5$ , 150°; 1- $\text{R}_2\text{CoBr}_2$ , 120°; and 2- $\text{R}_2\text{CoBr}_2$ , 65°.

The bromine derivatives are less soluble in chloroform or in ether than the corresponding iodine compounds. The solubility in benzene of all the compounds examined is very slight. This indicates that the original benzene extract does not contain the organo-cobalt compounds in the forms in which they have been identified. Lack of equipment has prevented us from carrying out magnetic measurements; but offers have been received from other institutes to supply these vital data. Unfortunately, the preparations are unstable and difficulties arising out of this fact have not been overcome.

Attempts have been made to prepare similar organo-cobalt compounds with methyl, ethyl, propyl, isopropyl and phenyl radicals by similar techniques. Compounds of the type  $\text{RCoI}_3 \cdot 2\text{C}_6\text{H}_6$  were obtained with the aliphatic radicals, and an equimolecular addition compound of  $\text{EtCoI}_3$  and 1-chloronaphthalene was also obtained. Phenylmagnesium bromide and cobalt bromide afforded  $\text{PhCoBr}_3 \cdot \text{C}_6\text{H}_6$  and  $\text{Ph}_2\text{CoBr}_2 \cdot \text{C}_6\text{H}_6$ . These experiments, however, will require further confirmation.

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<sup>1</sup> Hodgson and Marsden, *J. Chem. Soc.*, 22 (1944).

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### Water-Insoluble Complexes of Simple Aryl Sulphonates and Gelatin

THE combination of organic anions such as alkyl sulphates, acid dyes, and commercial detergents with proteins has been the subject of considerable published work<sup>1-7</sup>. When alkyl sulphates (not less than ten carbon atoms in the paraffin chain), such detergents as 'Teepol' (secondary alkyl sulphate) or alkyl-aryl sulphonates combine with gelatin, complexes may