481. *Preparation of Organo-cobalt Compounds.*

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Organo-cobalt bromides and iodides have been prepared by the interaction of Grignard compounds of the 1-naphthyl and 2-naphthyl series with cobalt halides in ethereal solution. The compounds are tetraco-ordinated. Some physical and chemical properties of the compounds are described.

Attempts have been made to prepare organo-cobalt compounds by thermal decomposition of cobalt toluene-*p*-sulphinate, thermal decomposition of phenyldiazonium cobaltinitrite (Hodgson and Marsden, *J.*, 1944, 22) in acetone, thermal and catalysed decomposition of the black cobalt chloride adducts of diazonium chlorides, the boiling of diphenyliodonium iodide with finely divided cobalt powder in propanol (Makarova and Nesmeyanov, *Izv. Akad. Nauk S.S.S.R.*, Chem. Class, 1945, 617), the boiling of aromatic compounds with cobalt acetate and aliphatic alcohols in a Dean–Stark apparatus, the boiling of phenyl bromide with pyrophoric cobalt powder in anisole or pyridine, direct cobaltation of furfuraldehyde with cobalt acetate in the presence of mercuric acetate, and heating di-1-naphthylmercury with cobalt halides. All these attempts failed, although in some cases traces of benzene-soluble organic materials with varying cobalt contents were obtained (Ingles, Ph.D. Thesis, University of Tasmania).

When anhydrous cobalt bromide or cobalt iodide in ethereal solution was added to RMgX (R = 1-naphthyl or 2-naphthyl; X = Br or I) dark green precipitates were obtained. The extraction of such precipitates with cold benzene gave green or blue-green solutions which deteriorated on storage and deposited black, blue, or green solids of varying composition. Addition of light petroleum or dioxan in excess to the benzene solutions afforded organic cobalt compounds of the types $RCoX_3$, R_2CoX_2, $RCoX_3,R_2CoX_2$, and, in one instance, R_3CoI. Magnesium (up to 11%) was found in the products obtained by using this technique. When the Grignard compounds were added to the cobalt halide solutions, the organo-cobalt compounds were obtained free from magnesium. The compounds could be purified by reprecipitation from ethereal solution. The compounds were shown to be organometallic by decomposition with water or dilute acids which afforded mainly dinaphthyls (Gilman and Lichtenwalter, *J. Amer. Chem. Soc.*, 1939, **61**, 957; Kharasch and Fields, *ibid.*, 1941, **63**, 2316; Kharasch and Tawney, *ibid.*, p. 2308; Kharasch and Lambert, *ibid.*, p. 2315) in addition to cobalt hydroxide and cobalt salts. Most of the isolated dinaphthyls were impure, which indicates that hydrolytic and thermal decomposition may occur simultaneously; further work will be necessary to clarify this matter.

RMgBr and cobalt iodide or RMgI and cobalt bromide gave the organo-cobalt iodides. Similar observations have been made on the reaction of platinum chloride with methylmagnesium iodide (Pope and Peachey, *J.*, 1909, **95**, 571) and of phenylmagnesium bromide with chromium chloride (Hein, *Naturwiss.*, 1940, **28**, 93). The residue left after extraction of the crude reaction products of the Grignard compounds and cobalt halides with cold benzene did not contain metallic cobalt. The benzene extracts are not identical with the organo-cobalt compounds which have been finally isolated, since the latter are practically insoluble in benzene. Light petroleum precipitates compounds of the types $RCoI_3$ and $R_3Co_2Br_5$. The latter may be written tentatively as $RCoBr_3,R_2CoBr_2$. Dioxan precipitates R_2CoX_2; these compounds are obtained in poorer yields than the foregoing since they are not quite insoluble in dioxan, which slowly decomposes all organo-cobalt compounds hitherto investigated. Through decomposition in dioxan the organo-cobalt compounds tend towards an empirical formula of the type R_3CoX, but no compound of this type could be isolated in sufficient purity.

The organo-cobalt compounds are unstable; the iodides are more unstable than the bromides, and the R_2CoX_2 compounds more than the others. The compounds decompose on heating without definite melting points. Approximate temperatures of decomposition have been noted. Sublimation in a vacuum leads to decomposition with the liberation of free halogen. All the compounds are insoluble in benzene or light petroleum, slightly soluble in chloroform, soluble in ether, and slightly soluble in dioxan with decomposition. Molecular weights could not be determined by the usual methods but special techniques are being evolved for this purpose and it is proposed to report on this later. In view of the tetramerism of alkylplatinum halides (Rundle and Sturtevant, *J. Amer. Chem. Soc.*, 1947, **68**, 1561) it is possible that polymerism will be demonstrated also for the organo-cobalt compounds. Magnetochemical measurements could not be carried out owing to lack of suitable equipment (offers of assistance have been recieved from other Institutes but the difficulties of storing and mailing the unstable compounds have not yet been overcome). All the bromides are blue, the $RCoI_3$ compounds yellow-green, and the R_2CoI_2 compounds reddish-brown.

Silver nitrate quantitatively removes halogen. Attempts to prepare halogen-free organo-cobalt compounds, possibly involving cobalt chains, by reaction of our products with sodium or powdered potassium (Gilman and Lichtenwalter, *J. Amer. Chem. Soc.*, 1938, **60**, 3085) were unsuccessful.

Grignard compounds prepared from methyl iodide, ethyl iodide, propyl iodide, *iso*propyl iodide, and phenyl bromide were brought into reaction with cobalt halides and worked up as indicated before. The products had approximately the correct cobalt : halogen ratios required by the types noted in the naphthyl series. The absolute values were low, but the discrepancy could be explained by assuming molecular association between the organo-cobalt compounds and integral (1 or 2) numbers of benzene molecules. Substitution of 1-chloronaphthalene for benzene in an experiment with ethylmagnesium iodide and cobalt iodide has afforded a compound of the empirical formula $EtCoI_3,C_{10}H_7Cl$. The organo-cobalt compounds of the naphthyl series do not contain benzene, since reprecipitation from ether does not significantly alter the analytical figures. The organo-cobalt compounds of the phenyl and aliphatic series were impure. They require further study.

The yields varied considerably from experiment to experiment. Maximum yields will be quoted in the experimental section. The yields appear to decrease in the order : 1-naphthyl, 2-naphthyl, phenyl, aliphatic series; iodides, bromides; $RCoI_3$, $R_3Co_2Br_5$, R_2CoX_2.

Analogous experiments with iron and nickel halides were unsuccessful. The final products contained magnesium but no iron or nickel.

EXPERIMENTAL.

Naphthyl-cobalt Compounds.

Naphthyl halides (20 g.) were converted into the Grignard compounds with the calculated amounts of magnesium in ether (100 c.c.). The clarified Grignard solution was added to a solution of anhydrous cobalt halide (1—5% excess) in ether (300 c.c.) at room temperature, and the mixture heated under reflux for 15 minutes. The dark green precipitate was freed from ether by decantation and suction in vacuum. Benzene (100 c.c.) was added, with exclusion of air. After storage overnight, the coloured benzene solution was filtered and made up to a known volume, and 10-c.c. portions were used for further experiments. Yields are calculated on this basis. In some experiments which afforded unstable compounds in very small and variable yields no yields are quoted. In all such cases the yields are estimated as $<1\%$ unless indicated otherwise.

1-*Naphthylmagnesium iodide and cobalt iodide.* Addition of light petroleum (b. p. 40—60°, 50 c.c.) precipitated yellow-green crystals, decomp. 150—160° (Found : Co, 10·1; I, 68·0. $C_{10}H_7I_3Co$ requires Co, 10·3; I, 67·5%); yield 2·68 g., 60%. Decomposition with water gave 1 : 1′-dinaphthyl, m. p. 158° (m. p. of picrate 143°), and cobaltous hydroxide and iodide in the ratio 1 : 5. Addition of dioxan (50 c.c.) to the benzene extract gave a reddish-brown *dinaphthylcobalt di-iodide*, decomp. 150° (Found: Co, 10·8; I, 44·5. $C_{20}H_{14}I_2Co$ requires Co, 10·3; I, 44·8%). This was decomposed by water to give a mixture of hydrocarbons (m. p. of picrate 112°), and cobaltous hydroxide and iodide in the ratio 63 : 37. 1-*Naphthylcobalt tri-iodide* slowly dissolved in dioxan with a red colour. The iodine content of the residue gradually decreased to 24·2% (*tri*-1-*naphthylcobalt iodide*, $C_{30}H_{21}ICo$, requires Co, 22·4%.)

1-*Naphthylmagnesium iodide and cobalt bromide.* The same products were obtained as above but the yield of $RCoI_3$ was only 2%.

1-*Naphthylmagnesium bromide and cobalt iodide.* The same products were obtained but the yield of $RCoI_3$ was 25%, and R_2CoI_2 was isolated in a yield of 1·23 g. (55%).

1-*Naphthylmagnesium bromide and cobalt bromide.* Light petroleum precipitated blue crystals, decomp. 120° (Found: Co, 13·3; Br, 45·0. *Tri*-1-*naphthyldicobalt pentabromide* requires Co, 13·2; Br, 45·0%). Water decomposed this to impure hydrocarbons (m. p. of picrate 115°) and cobaltous hydroxide and bromide; yield 0·06 g., 2%. Dioxan precipitated a blue *compound*, decomp. 120° (Found: Co, 12·8; Br, 33·7. $C_{20}H_{14}Br_2Co$ requires Co, 12·4; Br, 33·8%).

2-*Naphthylmagnesium iodide and cobalt iodide.* Light petroleum precipitated yellowish-green crystals of *naphthylcobalt tri-iodide*, decomp. 160° (Found: Co, 10·8; I, 67·2. $C_{10}H_7I_3Co$ requires Co, 10·3; I, 67·5%). Decomposition by water gave impure aromatic material, m. p. 145° (m. p. of picrate 155°). Dioxan precipitated reddish-brown *di*-2-*naphthylcobalt di-iodide*, decomp. 90° (Found: Co, 10·8; I, 44·5. $C_{20}H_{14}I_2Co$ requires Co, 10·3; I, 44·8%). M. p. of picrate of decomposition products in aqueous filtrate, 150°.

2-*Naphthylmagnesium iodide and cobalt bromide.* The same results were obtained as in the preceding experiment.

2-*Naphthylmagnesium bromide and cobalt iodide.* The same results were obtained as in the preceding experiments but the yield of $RCoI_3$ was 47%.

2-*Naphthylmagnesium bromide and cobalt bromide.* Light petroleum precipitated blue crystals, decomp. 150—160° (Found: Co, 13·0; Br, 46·0. $C_{30}H_{21}Br_5Co_2$ requires Co, 13·2; Br, 45·0%); yield, 0·28 g., 9%. M. p. of the picrate of the decomposition products in water, 142°. Dioxan precipitated blue crystals of the *dibromide*, decomp. 65° (Found: Co, 12·8; Br, 33·7. $C_{20}H_{14}Br_2Co$ requires Co, 12·4; Br, 33·8%). M. p. of picrate of decomposition products in water, 153°.

Other Cobalt Compounds.

Experiments using the same technique and on the same scale were applied to phenyl bromide and aliphatic iodides.

Phenylmagnesium bromide and cobalt bromide. Light petroleum gave a blue solid (Found: Co, 14·4; Br, 51·8. $PhCoBr_3,C_6H_6$ requires Co, 13·0; Br, 52·8%). Dioxan gave another blue solid (Found: Co, 12·0; Br, 36·5. Ph_2CoBr_2,C_6H_6 requires Co, 13·1; Br, 35·5%). The yields did not exceed 4%. The *compounds* were impure and were not further investigated.

Methylmagnesium iodide and cobalt iodide. Dioxan precipitated a brown oil which was decomposed by water to cobalt hydroxide with evolution of gas. Light petroleum precipitated yellowish-green crystals (Found: Co, 9·9; I, 60·5. $MeCoI_3,2C_6H_6$ requires Co, 9·7; I, 62·3%). Water decomposed them to cobalt hydroxide with evolution of gas.

Ethylmagnesium iodide and cobalt iodide. Dioxan precipitated a brown oil. Light petroleum precipitated a yellow-green solid (Found: Co, 10·5; I, 61·7. $EtCoI_3,2C_6H_6$ requires Co, 9·5; I, 60·9%). 1-Chloronaphthalene being used instead of benzene, light petroleum precipitated yellowish-green crystals (Found: Co, 10·2; I, 60·2. $C_2H_5I_3Co,C_{10}H_7Cl$ requires Co, 9·3; I, 60·3%). The *compound* contained 1-chloronaphthalene, which separated on decomposition in water (m. p. of picrate, 136°). Cobalt hydroxide and gas were also formed.

n-*Propylmagnesium iodide and cobalt iodide.* Dioxan gave a brown oil. Light petroleum precipitated a yellowish-green solid (Found: Co, 9·4; I, 66·3. $C_3H_7I_3Co,C_6H_6$ requires Co, 10·2; I, 67·9%).

iso*Propylmagnesium iodide and cobalt iodide.* Dioxan gave an oil. Light petroleum precipitated a yellowish-green solid (Found: Co, 9·2; I, 67·3. $C_3H_7I_3Co,C_6H_6$ requires Co, 10·2; I, 67·9%).

The yields of the aliphatic organo-cobalt compounds varied between 4 and 8%. Decomposition in water occurred qualitatively in the same manner with all of them. Owing to combination with solvent, the decomposition points were not significant. Decomposition occurred around 130° in each case, but solvent must have been lost at lower temperatures.

Analysis.—The sample was decomposed with concentrated hydrochloric acid, and the dissolved cobalt determined by precipitation with 1-nitroso-2-naphthol. Alternatively, the sample was ignited and weighed as Co_3O_4. Halogen was determined by the Volhard method. N-Silver nitrate solution rapidly removes the halogen of organo-cobalt compounds on gentle heating. After experiments with mixed halides, the silver halide precipitate was tested to check the homogeneous nature of the halogen; mixed silver halides were never observed.

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