Evaporation of the solvent at reduced pressure left a colorless liquid residue which was distilled through a 10-in. Vigreux column.

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The Question of Active Cobalt in the Decomposition of Grignard Reagents in the Presence of Cobaltous Halides

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Kharasch, Lewis, and Reynolds[1] have proposed the following reaction scheme to account for the products formed when phenylmagnesium bromide is allowed to react with an alkyl halide in the presence of a cobaltous halide.

$$C_6H_5MgBr + CoX_2 \longrightarrow C_6H_5CoX + MgBrX$$

$$2C_6H_5CoX \longrightarrow C_6H_5C_6H_5 + 2\cdot CoX$$

$$RX + \cdot CoX \longrightarrow R\cdot + CoX_2$$

Wilds and McCormack[2] have pointed out several weaknesses of the above scheme, such as the fact that organocobalt compounds of this type have not been prepared before, nor is there any evidence for the existence of the cobalt subhalide radical. Furthermore, they found that the reactivity of the mixture was only somewhat diminished if the Grignard reagent and the cobaltous halide were brought together several hours before the introduction of the alkyl halide; a fact which argues against the presence of a thermally unstable intermediate. As an alternative path they have proposed finely divided, active cobalt as the reactive intermediate.

$$2RMgX + CoX_2 \longrightarrow 2MgX_2 + CoR_2$$

$$CoR_2 \longrightarrow Co + 2R\cdot$$

$$Co + 2R'X \longrightarrow CoX_2 + 2R'\cdot$$

Walling[3] has stated a preference for this latter proposal and has cited as additional evidence the work of Chu and Friel[4] who found that the sodium-naphthalene radical ion in tetrahydrofuran solution instantly reduced cobaltous chloride to metallic cobalt in a highly reactive colloidal form which reacted with air and reduced cupric chloride to the cuprous state.

In order to test the hypothesis of active cobalt as the reactive intermediate in the reactions of Grignard reagents with alkyl halides in the presence of cobaltous halides, a tetrahydrofuran solution of active cobalt was prepared by the method of Chu and Friel. Treatment of this solution with ethyl bromide failed to produce any gaseous reaction products. A further test of this hypothesis was conducted by adding a suspension of cobaltous chloride and ethyl bromide in tetrahydrofuran to a solution of the sodium-naphthalene radical ion. Again no gaseous products were produded.

In order to rule out the possibility that the solvent or the naphthalene was entering into the above reactions a solution of phenylmagnesium bromide in tetrahydrofuran was prepared. A portion of naphthalene was also added to this solution. Addition of ethyl bromide and cobaltous bromide in tetrahydrofuran now produced an immediate evolution of gas which amounted to 48% of the theoretical amount. Analysis of this gas showed that it was 28% ethane and 72% ethylene. These findings are in good agreement with the observations of Kharasch, Lewis, and Reynolds[1] who reported a similar yield for the reaction of phenylmagnesium bromide, ethyl bromide, and cobaltous chloride in ethyl ether.

While the above results do not allow one to draw any further conclusions regarding the mechanism proposed by Kharasch *et al.*, it seems reasonable that the postulation of reactive colloidal cobalt may now be abandoned. It is not likely that the state of the cobalt produced by the Grignard reagent is sufficiently different from that produced by the reaction with the sodium-naphthalene radical ion to account for the complete inactivity toward ethyl bromide in the latter case.

EXPERIMENTAL

All reactions were carried out in a 500 ml., two necked flask equipped with a dropping funnel and a condenser. The apparatus was flushed with nitrogen before each reaction. Stirring was provided by a magnetic stirrer. All gases were collected over a saturated brine solution. Gas analysis was carried out by chromatography over a charcoal filled column at 32° with helium as the eluting gas.

Reaction of ethyl bromide with active cobalt. A solution of the sodium-naphthalene radical ion was prepared by reacting 2.4 g. of finely dispersed sodium with 14 g. of naphthalene in 150 ml. of anhydrous tetrahydrofuran. To the dark green solution was added a mixture of 6.5 g. of anhydrous cobaltous chloride and 7.85 g. of ethyl bromide in 100 ml. of tetrahydrofuran. The reaction immediately turned to dark black, and heat was evolved. However, no gas was given off.

In another experiment the cobaltous chloride was added to the solution of the radical ion before the addition of the ethyl bromide in the tetrahydrofuran. Again the solution turned dark black, and no gas was evolved.

Reaction of phenylmagnesium bromide, ethyl bromide, and cobaltous bromide. A solution of phenylmagnesium bromide in tetrahydrofuran was prepared from 7.85 g. (0.05 mole) of bromobenzene, 1.30 g. of magnesium, and 50 ml. of tetrahydrofuran. The mixture was heated for 0.5 hr. after the initial vigorous reaction had subsided. The mixture was

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(1) M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, *J. Am. Chem. Soc.*, **65**, 495 (1943).

(2) A. L. Wilds and W. B. McCormack, *J. Org. Chem.*, 14, 45 (1949).

(3) Cheves Walling, *Free Radicals in Solution*, John Wiley and Sons, New York, 1957, p. 589.

(4) T. L. Chu and J. V. Friel, *J. Am. Chem. Soc.*, **77**, 5838 (1957).

cooled to room temperature, and 5 g. of naphthalene was added. To this stirred mixture was slowly added a solution of 1.0 g. of cobaltous chloride and 5.45 g. (0.05 mole) of ethyl bromide in 40 ml. of tetrahydrofuran. Gas was evolved continuously throughout the addition (535 ml. at S.T.P., 48% of the theoretical yield). Analysis of this gas indicated that it was 28% ethane and 72% ethylene.

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Crystalline Complexes of the Phosphoryl Group with Polyphenols[1]

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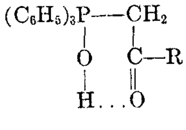
The "quasi-phosphonium" compounds,[3] for instance $[R_3P(OR')X]$, constitute an interesting variation of the phosphonium structure, $[R_4PX]$, in which one or more R groups are replaced by OR groups. This structural change might conceivably alter significantly the bonding characteristics of the phosphorus atom. A substance of composition $[R_3PO, HX]$ could be formulated as a hydrogen-bonded complex, $[R_3PO...HX]$, a phosphonium hydroxide, $[R_3P(OH)]^+X^-$, or as a structure with pentacovalent phosphorus, $[R_3P(OH)X]$. Halmann and Pinchas[4] have discussed recently the structure of triphenylphosphine oxide hydrate, which they formulate as $[(Ph_3PO)_2, H_2O]$. It was concluded that the hydrate is a molecular complex between the phosphine oxide and the water molecule, and that it does not have the dihydroxy structure, $[Ph_3P(OH)_2]$.

We have recently shown[5] that the "acylphosphinemethylene hydrates" which had been previously formulated[6] with pentacovalent phosphorus, such as in I[6a] or II,[6b] are actually *ylides* of type III. These ylides have a strong tendency to retain water.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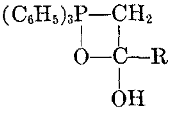
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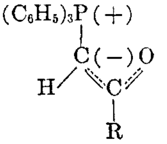
III

In another investigation,[7] it was shown that the crystalline, sharp-melting adducts formed from triphenylphosphine oxide and tetrachlorohydroquinone do not have the quasi-phosphonium structure $[(C_6H_5)_3P(OAr)(OH)]$. These adducts are formed: (a) when the oxide and the polyphenol are fused together in a 2:1 molar ratio or (b) when an alcoholic solution containing the oxide and the polyphenol is evaporated to dryness or is diluted with water. The adducts were formulated as hydrogen-bonded complexes, such as IV. Related compounds[8] are probably of the same type.

We have now extended these observations to include other polyphenols, as shown in Table I. Furthermore, it was found that certain *phosphate esters* also form crystalline, sharp-melting complexes with tetrachlorohydroquinone. The infrared spectra of these complexes, the ease with which they are formed and the ease with which they are split into their components by cold, dilute alkali, are consistent with the hydrogen-bonded formulations VIII, IX, X, and XI. The substances listed in Table 1 were obtained by addition of water to an alcoholic solution containing the phosphoryl derivative and the polyphenol in the proper molar ratio. The melting point of the original precipitate does not change significantly by recrystallization. It should be noted that the solubility of the polyphenol itself in a nonpolar solvent like benzene is quite small; the adducts, however, are appreciably soluble in benzene. The adducts derived from phosphate esters are quite soluble even in cyclohexane.

TABLE I

CRYSTALLINE COMPLEXES OF THE PHOSPHORYL GROUP ($\geqslant$PO) WITH POLYPHENOLS[a]

Formula	Molar Ratio[b]	M.P.,[c] °C.	Analyses[d]			
			Calcd.		Found	
			C	H	C	H
IV	2:1	180–182	62.7	4.0	62.3	4.3[e,]
V	2:1	164–165	68.6	4.7	68.5	4.9[f,]
VI	2:1	144–146	75.7	5.5	75.9	5.9[f]
VII	1:1	120–121	54.8	3.3	54.9	3.4[f]
VIII	2:1	106–108	29.2	2.0	29.3	2.2[h]
IX	2:1	74–75	33.9	3.0	33.6	3.3[i]
X	1:1	193–194	27.0	2.0	27.4	2.2[j]
XI	1:1	140–141	31.3	2.9	31.8	3.1[h]

[a] A methanol solution containing the components in the molar ratio indicated, was diluted with water. The crystalline precipitate was dried and its m.p. determined; the m.p. did not change significantly upon repeated recrystallizations. For the preparation of the phosphoryl components see ref. 12. [b] Phosphoryl derivative: polyphenol. [c] Corrected capillary – m.p. [d] Micro-Tech Laboratories, Skokie, Ill. [e] Calcd.: P, 7.7; Cl, 17.6. Found: P, 7.6; Cl, 17.5. [f] Recrystallized from benzene–petroleum ether. [g] Calcd.: P, 8.4; Cl, 9.4. Found: P, 8.5; Cl, 9.5. [h] Recrystallized from cyclohexane. [i] Recrystallized from hexane. [j] Recrystallized from benzene.

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(3) G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1950, Chapter II.

(4) M. Halmann and S. Pinchas, *J. Chem. Soc.*, 3264 (1958).

(5) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

(6) (a) G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954); (b) A. Michaelis and E. Kohler, *Ber.*, **32**, 1566 (1899).

(7) F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956).

(8) W. Lommel and H. Munzel, U. S. Patent **1,844,015** (1932); *Chem. Abstr.*, **26**, 1941 (1932).