Role of Cobalt in the Decomposition of Grignard Reagents in the Presence of Cobaltous Halides

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Received May 16, 1960

Two reaction sequences have been proposed to explain the products formed in the reaction of a Grignard reagent, such as phenylmagnesium bromide, with an alkyl halide in the presence of a catalytic amount of cobaltous halide. Kharasch and Reinmuth,[1] on the basis of numerous investigations conducted by Kharasch and his co-workers, have proposed a cobaltous subhalide ($\cdot CoX$) as the active intermediate. Wilds and McCormack,[2] however, have proposed active cobalt metal as the intermediate, on the grounds that the reactivity of the mixture was reduced only slightly when the Grignard reagent and cobaltous halide were brought together several hours before the introduction of the alkyl halide. This argues strongly against the presence of an unstable intermediate such as a cobaltous subhalide.

Kharasch and Fields,[3] however, demonstrated that pyrophoric cobalt metal does not react with bromobenzene, although cobaltous bromide does catalyze the reaction of phenylmagnesium bromide and bromobenzene. More recently, Smith[4] has demonstrated that cobalt metal prepared by the reduction of cobaltous chloride with sodium-naphthalene complex does not react with ethyl bromide. Both of these observations were interpreted to be strong evidence against cobalt metal being the active intermediate.

In confirmation of Smith's results, we have found that cobalt metal produced *via* the sodium-naphthalene complex does not react with ethyl bromide. However, we have also observed that the addition of phenylmagnesium bromide (hereafter referred to as Grignard reagent) to this mixture produces an immediate evolution of ethane and ethylene. Also the ratio of ethylene to ethane closely agrees with that obtained by Smith[3] and Kharasch[5] for the same system in the absence of sodium-naphthalene.

In a second experiment, Grignard reagent was added to an equivalent amount of cobaltous chloride in tetrahydrofuran to produce dark brown, finely divided cobalt metal. Addition of ethyl bromide to this mixture did not produce any significant gas evolution. However, when a second addition of Grignard reagent was made, an immediate evolution of gas occurred. After evolution had ceased, the addition of more Grignard reagent caused more gas to be evolved. Analysis of several samples of the evolved gases showed them to contain ethane and ethylene in a fairly constant ratio.

We conclude, therefore, that cobalt metal is the active intermediate as proposed by Wilds and McCormack, but that both Grignard reagent and ethyl bromide must be present to effect reaction. The following reaction sequence is consistent with the data:

$$2\ C_6H_5MgBr + CoCl_2 \longrightarrow 2\ MgBrCl + (C_6H_5)_2Co \qquad (1)$$

$$(C_6H_5)_2Co \longrightarrow Co + 2\ C_6H_5\cdot \qquad (2)$$

$$C_6H_5MgBr + Co + C_2H_5Br \longrightarrow C_6H_5CoC_2H_5 + MgBr_2 \qquad (3)$$

$$C_6H_5CoC_2H_5 \longrightarrow Co + C_6H_5\cdot + C_2H_5\cdot \qquad (4)$$

$$2\ C_6H_5\cdot \longrightarrow C_6H_5\cdot C_6H_5 \qquad (5)$$

$$2\ C_2H_5\cdot \longrightarrow C_2H_4 + C_2H_6 \qquad (6)$$

$$C_6H_5\cdot + C_2H_5\cdot \longrightarrow C_6H_5C_2H_5 \qquad (7)$$

Ethane, ethylene, biphenyl, and ethylbenzene were identified as products of the reaction. However, the quantities recovered were not sufficient to account for the fate of all the radicals. The presence of larger amounts of ethylene than ethane indicates that some ethyl groups were consumed in reactions other than those producing ethylene, ethane, and ethylbenzene. Butanes were not a major product.

Reaction (3) is the essential reaction of the entire sequence and explains the necessity of having both the Grignard reagent and ethyl bromide present with the cobalt metal. A very similar reaction has been used for the synthesis of organolead compounds, as Gilman and Jones[6] have shown that lead metal will react with organolithium and Grignard reagents in the presence of an alkyl iodide or bromide to produce tetraalkyllead.

The reaction sequence proposed is also consistent with results reported by others for similar systems. This sequence can be used to explain the catalytic effect of other transition metal halides in similar systems. However, a more quantitative investigation of these systems is desirable in order to determine the fate of *all* the intermediates which are postulated.

EXPERIMENTAL

All reactions were conducted in a 300-ml., two necked flask equipped with a dropping funnel and a reflux condenser. The reflux condenser was connected to a gas buret filled with a saturated brine solution. Stirring was achieved with a magnetic stirrer. The gaseous products were analyzed using a Consolidated Engineering Corporation Type 21-102 mass spectrometer. All operations were conducted under nitrogen.

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[1] M. S. Kharasch and Otto Reinmuth, *Grignard Reactions of Non-Metallic Substances*, Prentice-Hall, Inc., New York, N. Y., 1954, p. 122.

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

[3] M. S. Kharasch and E. K. Fields, *J. Am. Chem. Soc.*, **63**, 2316 (1941).

[4] W. B. Smith, *J. Org. Chem.*, **24**, 703 (1959).

[5] M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, *J. Am. Chem. Soc.*, **65**, 495 (1953).

[6] H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **72**, 1760 (1950).

Reaction of ethyl bromide and phenyl Grignard reagent with active cobalt metal produced via sodium-naphthalene complex. A solution of sodium-naphthalene complex was prepared by treating 2.40 g. (0.104 mole) of finely dispersed sodium with 14.0 g. (0.109 mole) naphthalene in 150 ml. of tetrahydrofuran (dried by distillation from lithium aluminum hydride). To this solution was added 6.00 g. (0.0465 mole) of cobaltous chloride (dehydrated by the thionyl chloride method[7]) and the solution was stirred for 2 hr. after the initial vigorous reaction, during which brown-black solids were precipitated. The walls of the flask were rinsed with 40–50 ml. of fresh tetrahydrofuran to remove adhering cobaltous chloride and assure complete reduction to the metal. The resultant mixture was then treated with 7.85 g. (0.072 mole) of ethyl bromide and the formation of gaseous products was observed. A total of 27 cc. of gas (at S.T.P.) was evolved, probably from interaction of the excess sodium-naphthalene complex with ethyl bromide. To the same solution then was added 50 ml. of a tetrahydrofuran solution of phenyl Grignard reagent prepared from 1.30 g. (0.053 g.-atom) of magnesium metal and 7.85 g. (0.050 mole) of bromobenzene. An immediate evolution of gas occurred and the reaction mixture became warm. A total of 261 cc. of gas was evolved, 23% of the theoretical amount of available ethyl groups. This is somewhat lower than the 48% evolution observed by Smith,[4] but the difference can be attributed to the use of a larger volume of solvent in this case. Analysis of the gas indicated that it was primarily ethylene and ethane in a mole ratio of 1.3 to 1.[8] The reaction mixture was heated to the reflux temperature to evolve an additional 592 cc. of gas containing ethylene and ethane in a mole ratio of 1.3 to 1. No attempt was made to calculate total yield of gaseous products as no correction was made for gas displaced by vaporization of the tetrahydrofuran at reflux. The ethane to ethylene ratio is in good agreement with that reported by Kharasch, Lewis, and Reynolds[5] for the same reaction in the absence of sodium-naphthalene complex.

Stepwise reaction of phenyl Grignard reagent with cobaltous chloride and ethyl bromide followed by addition of more phenyl Grignard reagent. To 50 ml. of phenyl Grignard reagent (0.044 mole, prepared from bromobenzene and magnesium turnings in tetrahydrofuran) was added 2.82 g. (0.022 mole) of cobaltous chloride in a nitrogen box. Considerable heat was evolved and a dark brown precipitate was produced immediately. The reaction mixture was heated at reflux for 1 hr. To the cooled reaction mixture was added 10.22 g. (0.094 mole) of ethyl bromide. A total of 18 cc. (at S.T.P.) of gas was evolved upon addition of the ethyl bromide. After 30 min., a second 50-ml. aliquot of the Grignard reagent (0.044 mole) was added. Immediate evolution of gas occurred. A total of 615 cc. of gas was evolved at room temperature and an additional 260 cc. (corrected for vapor displacement) was collected when the solution was heated to reflux. After standing overnight, the solution was treated with another 48 ml. of Grignard reagent (0.042 mole). Again an immediate gas evolution occurred. A total of 500 cc. of gas was collected at room temperature and an additional 305 cc. of gas was evolved upon heating to reflux. The 875 cc. of gas (total) evolved upon the first addition is equivalent to 90% of theory. Mass spectographic analyses of the evolved gases at periodic intervals showed the mole ratios of ethylene to ethane to be between 1.2 and 1.4 to 1.

The reaction mixture was diluted with petroleum ether (b.p. 30–60°), extracted with dilute aqueous acid, and filtered. From the cold, concentrated filtrate was isolated 4.5 g. of biphenyl, (m.p. 69–69.5° uncorrected) equivalent to 45% of the phenyl groups charged originally as phenyl Grignard reagent. Mass spectrographic analysis of the residual liquor showed ethylbenzene to be present, but no quantitative analyses were made.

The experiment was repeated using 2.60 g. (0.020 mole) of cobaltous chloride, 0.041 mole of phenyl Grignard reagent, and a stoichiometric quantity of ethyl bromide (0.041 mole). No gas was evolved. A second addition of 0.041 mole of phenyl Grignard reagent caused the evolution of 658 cc. of gas (at S.T.P.), equivalent to 73% of the ethyl values charged as ethyl bromide. Mass spectrographic analysis showed the gases to contain primarily ethylene and ethane (mole ratio 1.3 to 1). Repeated extraction of the filtered reaction mixture with water produced a small volume of a dark water-immiscible liquid. Gas chromatographic analysis of this liquid gave two strong peaks with elution times identical to those obtained with standards of ethylbenzene and biphenyl. No quantitative determinations were made.

Acknowledgment. The author is indebted to Mr. J. B. Chidester for the mass spectrographic analyses and Dr. G. E. Nelson for the gas chromatographic analyses.

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(7) A. R. Pray, *Inorganic Syntheses*, **Vol. V**, McGraw-Hill Book Company, Inc., New York, N. Y., 1957, p. 154.

(8) The evolved gases always contained small amounts of butane and tetrahydrofuran. Higher hydrocarbons were not detected. In all experiments the molar concentrations of butane and tetrahydrofuran were each less than 1% of the total.

Addition of Hydrogen Bromide to the Nitrostyrenes[1]

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Received June 22, 1961

The addition of hydrogen bromide to styrene under ionic conditions gives α-phenethyl bromide, $C_6H_5CHBrCH_3$, to the exclusion of the β-isomer.[2] This result, similar to the ionic addition of hydrogen bromide to propylene to give isopropyl bromide,[3] has been explained somewhat vaguely in terms of electron-donation by the alkyl group attached to the ethylenic system[4]: $R—C{=}CH_2$. In the case of styrene, such an explanation would appear rather unattractive, however, since the inductive effect of the phenyl group is quite clearly electron withdrawing rather than electron donating. A more plausible explanation of the Markovnikov sense of addition of hydrogen bromide to olefins of the type $R—CH{=}CH_2$ is in terms of a product-determining intermediate or transition state of type $R—\overset{+}{CH}—CH_3$ which is favored over the alternate $R—CH_2—$

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(1) Presented in part before the Division of Organic Chemistry at the Buffalo, N. Y., Meeting of the American Chemical Society, March 1952.

(2) C. Walling, M. S. Kharasch, and F. R. Mayo, *J. Am. Chem. Soc.*, 61, 2693 (1939).

(3) F. R. Mayo and M. G. Savoy, *J. Am. Chem. Soc.*, 69, 1348 (1947). The reaction is not as clean-cut as is implied in some textbooks.

(4) *e.g.* R. Q. Brewster and W. E. McEwen, *Organic Chemistry*, 3rd ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1961, p. 73 for the case of the addition of hydrogen iodide to propylene.