Summary

1. The initial rate of dissolution of nickel sulfide is dependent upon the concentration of hydrogen sulfide in the system.
2. Nascent hydrogen increases the rate of dissolution.
3. Hydrogen sulfide is more strongly adsorbed on nickel sulfide than on other sulfides investigated, and this adsorption increases with acid concentration.
4. Analysis shows the nickel sulfide to have the composition NiS_x, where x is equal to or greater than one and increases with increase in the hydrogen sulfide concentration in the system.

MOSCOW, IDAHO RECEIVED DECEMBER 28, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Racemization in the Preparation of the Grignard Reagent

BY C. W. PORTER

In the hope of synthesizing an optically active compound with one atom of hydrogen and one of deuterium attached to the asymmetric carbon atom, the Grignard reaction was applied to two optically active alkyl bromides and one active alkylaryl bromide.

Methyl-*n*-hexylcarbinol was resolved into active components by the method of Kenyon[1] and from these the corresponding bromides were obtained by treatment with phosphorus tribromide. No attempt was made to secure optically pure compounds. The bromides obtained had rotations of +22.7 and −20.4° when read in 10-cm. tubes with a sodium arc as the source of light. No racemization occurred under the influence of phosphorus tribromide and good yields of the alkyl bromides were obtained.

In a typical experiment the Grignard reagent was made by mixing 40 g. of active octyl bromide, 120 g. of dry ether, 8 g. of magnesium and a crystal of iodine. The mixture was protected from air and moisture by an atmosphere of dry nitrogen until the reaction, which proceeds spontaneously, was completed. The ether solution of $C_8H_{17}MgBr$ displayed slight optical activity, but this was due to unchanged octyl bromide. When a portion of the Grignard reagent was condensed with acetone and the resulting carbinol was purified by vacuum distillation, the condensation product was found to be optically inactive. An aliquot part of the ether solution of the Grignard reagent was decomposed by water and when the unchanged octyl bromide in this sample was recovered, it was found to be adequate to account for the activity observed in the ether solution of the Grignard reagent.

A series of similar experiments in which optically active methylphenylbromomethanes were substituted for active octyl bromides gave rise to racemic Grignard reagents in the same way.

Conclusion

It is evident that complete racemization occurs when an optically active halide reacts with magnesium in the formation of a Grignard reagent.

BERKELEY, CALIFORNIA RECEIVED APRIL 23, 1935

---

[1] Jos. Kenyon, *J. Chem. Soc.*, **121**, 2540 (1922).