

A possible mechanism for this reaction, in which the formation of dibenzoselenophene proceeds through the intermediate, *o*-biphenylselenenyl bromide, (IV), is shown below. The presence of the selenenyl bromide is indicated by the dark violet color of the solution, a color typical of compounds of this type. This color disappears as the reaction progresses. When very pure diselenide is used, the completion of the reaction is indicated by almost complete disappearance of the monobromide and by cessation of hydrogen bromide evolution.

#### Experimental

***o*-Selenocyanobiphenyl.**—Eighty-six grams of technical grade *o*-aminobiphenyl was dissolved in 75 cc. of warm concentrated sulfuric acid. This solution was added to 2.5 liters of ice-water in a large enamelware pail, mechanical stirring was initiated and 36 g. of solid sodium nitrite was added in small portions, keeping the temperature below 7°. Solid sodium acetate was added to the diazonium solution until the solution no longer turned congo red paper blue. A solution of 0.5 mole of sodium selenocyanate<sup>6</sup> was slowly added to the buffered solution while thorough stirring was maintained. The mixture was allowed to decompose for an hour, after which the brown oil produced was extracted with 1500 ml. of benzene. The benzene extractions were dried with anhydrous sodium sulfate and the benzene stripped off. Distillation at 157–160° (1.1 mm.), using a short-path distilling flask with a built in spray-trap, yielded 95 g. (71%) of an orange oil, the crude selenocyanate.

**Di-(*o*-biphenyl) Diselenide (III).**<sup>4</sup>—To a solution of 60 g. of potassium hydroxide in 240 g. of methanol was added 86 g. of *o*-selenocyanobiphenyl. The mixture was swirled vigorously, allowed to stand for 30 minutes, then added to a separatory funnel containing 2 liters of saturated aqueous boric acid and one liter of benzene. After vigorous shaking, the aqueous layer was discarded and the benzene layer washed twice with 1500-ml. portions of distilled water. The benzene solution was then dried with anhydrous magnesium sulfate, the solvent removed by evaporation on a steam-bath and the residue was recrystallized twice from 250-ml. portions of acetone. The diselenide forms large, canary-yellow crystals, m. p. 100–101°. The yield was 62 g. (80%).

*Anal.* Calcd. for C<sub>24</sub>H<sub>18</sub>Se<sub>2</sub>: Se, 34.0; equiv. wt., 77.4. Found: Se, 34.0; equiv. wt.,<sup>5</sup> 76.8.

Behagel and Hofmann report a m. p. of 77–78°. The identity of our compound was substantiated both by analysis and by oxidation to *o*-biphenylseleninic acid<sup>7</sup> which was shown to be non-identical to both the meta and para isomers. The latter two compounds are described in another communication.

**Dibenzoselenophene.**—To a solution of 62 g. of twice recrystallized di-(*o*-biphenyl) diselenide in 250 ml. of redistilled carbon tetrachloride was added 23 g. of bromine. The solution was allowed to stand on a sand-bath at 78–80° for 36 hours, at the end of which time the intense color had almost completely disappeared, the evolution of hydrogen bromide gas had ceased and the total volume of solution had been reduced to about 170 ml. The solution was decolorized once, the carbon tetrachloride removed by evaporation on a steam-bath, and the almost colorless residue purified either by recrystallization from a mixture of 25 ml. of carbon tetrachloride and 400 ml. of methanol or by vacuum distillation (136–139° at 1.5–2.0 mm.). The yield was 60 g. (97%). When less pure diselenide was used, the reaction was severely retarded, for the reaction mixture did not fade, even after standing on the sand-bath for 48 hours. In such cases, the reaction was accelerated by evaporating off the solvent and keeping the dark-colored residue at 120–130° until evolution of hydrogen bromide

has ceased. Subsequent vacuum distillation produced a water-white product, m. p. 73°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>8</sub>Se: Se, 34.2. Found: Se, 34.1.

**Dibenzoselenophene Oxide.**—To 4 g. of dibenzoselenophene was added dropwise a 40% solution of peracetic acid in glacial acetic acid.<sup>8</sup> The solution immediately became hot, and the solid disappeared. The mixture was then allowed to cool to room temperature and 5 ml. of concentrated ammonium hydroxide was added, precipitating the selenoxide as a white solid. The oxide was recrystallized from 100 ml. of water and dried for one hour in an Abderhalden pistol at 90° over phosphoric anhydride. The product melted at 229–230° (dec.). The yield was 1.9 g. (48%).

*Anal.* Calcd. for C<sub>12</sub>H<sub>8</sub>SeO: Se, 32.0; equiv. wt., 123.6. Found: Se, 32.1; equiv. wt. (iodometric), 123.7.

(8) Obtained from the Buffalo Electrochemical Co., Buffalo, N. Y.

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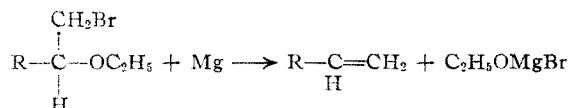
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### The Alpha Elimination in Grignard Preparations

By L. S. MOODY

When  $\beta$ -chloroethoxytrimethylsilane reacts with magnesium in diethyl ether, the expected Grignard reagent is not obtained. Instead a gas, non-condensable at Dry Ice-toluene temperature, is steadily evolved during the course of the reaction. The gas will readily decolorize bromine dissolved in glacial acetic acid and is presumed to be ethylene. A heavy precipitate of the magnesium salt of trimethylsilanol is formed during the reaction. No products from the expected Grignard reagent have been found.

The elimination of the trimethylsiloxy group from the molecule is analogous to known eliminations. Thus Grignard<sup>1</sup> reported that  $\beta$ -chlorophenetole and magnesium gave ethylene and phenoxymagnesium bromide. Swallen and Boord<sup>2</sup> reported that  $\beta$ -bromo alkyl ethers underwent a similar elimination



Likewise, it has been shown<sup>3</sup> that from magnesium and ethylene dibromide, only ethylene and magnesium bromide are obtained as products.

(1) Grignard, *Compt. rend.*, **138**, 1048 (1904).

(2) L. C. Swallen and C. E. Boord, *THIS JOURNAL*, **52**, 651 (1930).

(3) Chao-Lun Tseng and Fu-Min. *Fam. Science Quart. Nat. University Peking*, **4**, 1–8 (1934); *C. A.*, **28**, 4376<sup>a</sup> (1934).

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### Furanization and Cleavage of 1,4-Diketones by Use of Polyphosphoric Acid

By GENE NOWLIN<sup>1</sup>

The present paper reports the effectiveness of polyphosphoric acid, originally used for cyclodehy-

(1) du Pont Postdoctoral Fellow 1949–1950. Research and Development, Phillips Petroleum Company, Bartlesville, Oklahoma.

(6) T. W. Campbell and J. D. McCullough, *THIS JOURNAL*, **67**, 1965 (1945).

(7) J. D. McCullough and E. S. Gould, *ibid.*, **71**, 674 (1949).