Speculations as to the nature of Giral's product,[1] have led to no fruitful conclusions unless he possessed a mixture whose rotation was determined incorrectly.[3]

Experimental

A vigorously stirred and boiling solution of 5 g. of pregnenolone benzoate (m. p. 192–193°, $[\alpha]^{20}D$ +47.4) in 75 cc. of glacial acetic acid was treated over a period of 1.5 hours with a mixture of 5 g. of lead tetraacetate and 75 cc. of glacial acetic acid. After cooling and diluting with water, the precipitate (5.2 g.) was collected and dried. Several crystallizations from methanol–chloroform afforded 1.25 g. (22%) of substantially pure Δ^5-pregnen-3β,21-diol-20-one 3-benzoate 21-acetate.

The combined mother liquors were refluxed for 45 minutes with 175 cc. of alcohol, 0.53 g. of semicarbazide hydrochloride and 0.75 g. of sodium acetate,[4] the solution cooled and the semicarbazone of pregnenolone benzoate was filtered; yield 1.53 g. (27%), m. p. 260–263°. The alcoholic solution was evaporated to dryness and the residue was recrystallized from methanol–chloroform to yield an additional 0.4 g. of the 3-benzoate-21-acetate together with 0.57 g. of the same product obtained on chromatographing the mother liquors on 80 g. of ethyl acetate washed alumina. The analytical sample crystallized from methanol–chloroform as colorless needles with m. p. 200–201° (Kofler), $[\alpha]^{20}D$ +48.95° (chloroform), identical in all respects with an authentic specimen prepared by benzoylation of Δ^5-pregnen-3β,21-diol-20-one 21-acetate.

Anal. Calcd. for $C_{30}H_{38}O_5$: C, 75.28; H, 8.00. Found: C, 74.96; H, 8.12.

Acknowledgment.—We wish to thank Syntex, S. A., for a generous gift of pregnenolone benzoate and 21-acetoxypregnenolone.

(3) An error in the rotation of Giral's product might explain his results, since some of the by-products in our lead tetraacetate oxidation showed relatively sharp melting points in the neighborhood of 170°, but exhibited $[\alpha]^{20}D$ of around +47°.

(4) Lead tetraacetate oxidations of various pregnenolone esters have demonstrated that unreacted ketone can be separated nearly quantitatively from the rest of the reaction mixture by treatment with a limited amount of semicarbazide. The corresponding 21-acetoxy derivatives do not form a semicarbazone. (Private communication from the research laboratories of Syntex, S. A.)

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CRUCES NO. 5
TACUBA, D. F.

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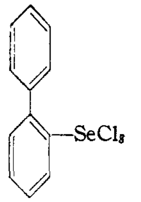
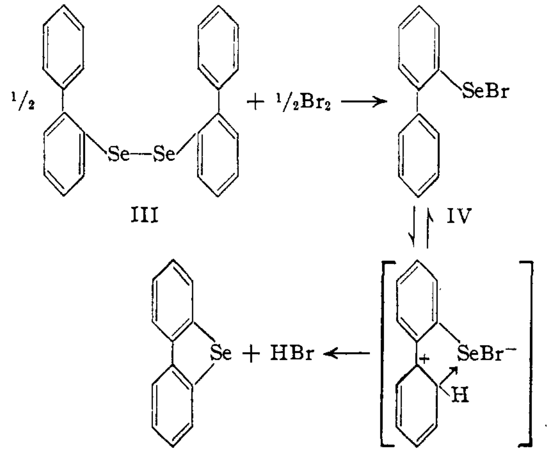
A New Synthesis of Dibenzoselenophene[1]

BY JAMES D. MCCULLOUGH, TOD W. CAMPBELL AND EDWIN S. GOULD

During work carried out in this Laboratory in attempts to resolve unsymmetric cyclic selenoxides, it became necessary to prepare a large quantity of dibenzoselenophene (I). The synthetic methods appearing in the literature[2,3,4] involve either low yields or a number of time-consuming steps. However, the method of Behagel and Hofmann, in which the compound was obtained by treatment of *o*-biphenylselenium trichloride (II) with potassium hydroxide in methanol, suggested that the corresponding tribromide, which presumably could be prepared more conveniently, might also yield dibenzoselenophene when treated with base. Although addition of bromine to a carbon tetrachloride solution of di-(*o*-biphenylyl) diselenide (III) yields a brick-red precipitate as stated by Behagel and Hofmann, the material rapidly loses hydrogen bromide and the result is apparently a mixture of dibenzoselenophene dibromide and bromodibenzoselenophene dibromide. This latter conclusion is based on our experimental equivalent weights[5] which range from 204 to 212 and from the fact that the solutions resulting from the titration are colorless rather than of the orange aryldiselenide color which normally results in the titration of an arylselenium tribromide. The theoretical equivalent weights are 157.4 for *o*-biphenylselenium tribromide, 195.5 for dibenzoselenophene dibromide and 235.5 for bromodibenzoselenophene dibromide. Although we were unable to isolate a compound whose properties and composition indicate it to be *o*-biphenylselenium tribromide, it was observed that dibenzoselenophene is formed in good yield when a solution containing equimolar amounts of di-(*o*-biphenylyl) diselenide (III) and bromine in carbon tetrachloride is kept at 70° for 48 hours. Indeed, by the correct choice of conditions, the yield of dibenzoselenophene becomes essentially quantitative. Since the diselenide (III) can be made in good yield by a two-step synthesis from *o*-aminobiphenyl, which is readily available, the new synthesis appears to be more direct than any other described up to this time.



II



I

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(1) Based on research performed under Task Order I of Contract N6-onr-275 between the Office of Naval Research and the University of California, Los Angeles.

(2) N. M. Cullinane, A. G. Rees and C. A. Plummer, *J. Chem. Soc.*, 151 (1939).

(3) C. Courtot and A. Monytamedi, *Compt. rend.*, 199, 531 (1934).

(4) O. Behagel and K. Hofmann, *Ber.*, 72B, 582 (1939).

(5) J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Ind. Eng. Chem., Anal. Ed.*, 18, 638 (1946).

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[6] 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).[4]—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 $C_{24}H_{18}Se_2$: Se, 34.0; equiv. wt., 77.4. Found: Se, 34.0; equiv. wt.,[5] 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[7] 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*-biphenylyl) 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 $C_{12}H_8Se$: 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.[8] 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 $C_{12}H_8SeO$: Se, 32.0; equiv. wt., 123.6. Found: Se, 32.1; equiv. wt. (iodometric), 123.7.

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(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).

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

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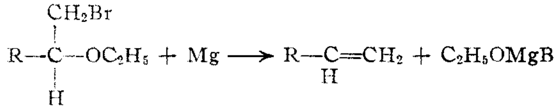
The Alpha Elimination in Grignard Preparations

BY L. S. MOODY

When β-chloroethoxytrimethylsilane reacts with magnesium in diethyl ether, the expected Grignard reagent is not obtained. Instead a gas, noncondensable 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[1] reported that β-chlorophenetole and magnesium gave ethylene and phenoxymagnesium bromide. Swallen and Boord[2] reported that β-bromo alkyl ethers underwent a similar elimination



$$R\text{—}\underset{\displaystyle H}{\overset{\displaystyle CH_2Br}{C}}\text{—}OC_2H_5 + Mg \longrightarrow R\text{—}\underset{\displaystyle H}{C}\text{=}CH_2 + C_2H_5OMgBr$$

Likewise, it has been shown[3] that from magnesium and ethylene dibromide, only ethylene and magnesium bromide are obtained as products.

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(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. Natl. University Peking*, **4**, 1–8 (1934); *C. A.*, **28**, 4376^4 (1934).

NEW PRODUCT DEVELOPMENT LABORATORY
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Furanization and Cleavage of 1,4-Diketones by Use of Polyphosphoric Acid

BY GENE NOWLIN[1]

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

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