no unreacted fulvene could be isolated. Other attempts to isolate the starting fulvene also were unsuccessful.

Acknowledgment. The research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 18(600)-648. The hexachlorocyclopentadiene was a gift of the Shell Chemical Company. The analyses were performed by Galbraith Laboratories.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF COLORADO
BOULDER, COLO.

Preparation of *o*-Phenylenebis(dichloroarsine) and *o*-Phenylenebis(dimethylarsine)

KENNETH C. EBERLY AND GEORGE E. P. SMITH, JR.

Received April 18, 1957

Kalb[1] failed to convert *o*-benzenediarsonic acid by the action of concentrated hydrochloric acid and sulfur dioxide into *o*-phenylenebis(dichloroarsine), obtaining 1,3-dichloro-1,3-dihydrobenzofurarsan instead. This observation was also made by Hamilton and Ludeman.[2] Chatt and Mann[3] converted 1,3-dichloro-1,3-dihydrobenzofurarsan into *o*-phenylenebis(dichloroarsine) by the action of thionyl chloride. However, Goldsworthy and associates[4] converted *p*-benzenediarsonic acid into *p*-phenylenebis(dichloroarsine) in a single step by the action of alcoholic hydrogen chloride and sulfur dioxide. In our hands, by means of the modified procedures as detailed below, *o*-phenylenebis(dichloroarsine) has been prepared in 65% yield in a single step from *o*-benzenediarsonic acid, and *o*-phenylenebis(dimethylarsine) in 88% yield from the bis(dichloroarsine). The yields obtained are significantly higher by the simplified procedures than those previously reported.

EXPERIMENTAL

o-Benzenediarsonic acid. o-Benzenediarsonic acid was prepared by treating diazotized arsanilic acid with sodium arsenite solution according to the method of Kalb.[1] The yield of air-dried acid containing one molecule of water of crystallization (did not melt at 360°) was 56.2%.

o-Phenylenebis(dichloroarsine). A solution of 178.4 g. (0.5187 mole) of the above *o*-benzenediarsonic acid in 3000 ml. of concentrated hydrochloric acid (37.25%) containing 2.0 g. of potassium iodide was treated with a brisk stream of sulfur dioxide until precipitation ceased (35 min.). The orange-colored solid was removed by filtration and pressed as dry as possible on a sintered glass filter (435.8 g.). The moist, oily solid was treated with 400 ml. of carbon disulfide whereby some material dissolved, and two liquid layers were obtained. The aqueous layer was separated and discarded. Evaporation of the remaining carbon disulfide solution on a water bath and subsequent cooling yielded crystals. Recrystallization from carbon disulfide yielded colorless crystals of pure *o*-phenylenebis(dichloroarsine) (123.45 g. or 64.7%) melting at 96°.

Anal. Calcd. for $C_6H_4As_2Cl_4$: C, 19.59; H, 1.10; Cl, 38.57. Found: C, 19.44; H, 1.15; Cl, 38.61.

o-Phenylenebis(dimethylarsine). o-Phenylenebis(dimethylarsine) was prepared by a modification of the method of Chatt and Mann.[3] A Grignard solution was prepared in a 3-l. flask from 48.15 g. (1.98 atoms) of magnesium turnings, 281.05 g. (1.98 moles) of dry methyl iodide, and 500 ml. of sodium-dried ether. With rapid stirring and ice cooling in an argon atmosphere, a solution of 121.4 g. (0.330 mole) of *o*-phenylenebis(dichloroarsine) in 570 ml. of dry ether was added (1 hr.). After stirring at room temperature for another hour, a solution of 413.0 g. of ammonium chloride in 1150 ml. water was added with ice-cooling (40 min.). The organic layer was separated, then the inorganic layer was extracted with 300 ml. of ether and rejected. After drying the combined organic solutions with sodium sulfate under argon, the ether was removed by fractional distillation. The residual liquid was fractionated at reduced pressure, bleeding in argon, collecting the fraction boiling at 153–158° at 20 mm. The yield was 82.75 g. (87.6%) of pale yellow liquid, *o*-phenylenebis(dimethylarsine), having the following physical properties: f.p., −12° (sharp); and n_D^{20}, 1.6204. The substance is rapidly oxidized by air, and must be stored under argon.

Chatt and Mann[3] obtained a yield of 26%, and mentioned only the b.p. of the product (156° at 20 mm.).

CHEMICAL AND PHYSICAL LABORATORIES
FIRESTONE TIRE AND RUBBER COMPANY
AKRON 17, OHIO

---

(1) L. Kalb, *Ann.*, **423**, 39 (1921).

(2) C. Hamilton and C. Ludeman, *J. Am. Chem. Soc.*, **52**, 3284 (1930).

(3) J. Chatt and F. Mann, *J. Chem. Soc.*, 610 (1939).

(4) L. Goldsworthy, W. Hook, J. John, S. Plant, J. Rushton, and L. Smith, *J. Chem. Soc.*, 2208 (1948).

Cyclization of an Unsaturated Benzyl Ether to a Hydrofuran

E. M. FRY

Received April 18, 1957

The work reported in this communication is the outgrowth of another problem and owes its genesis to the failure of the amino ketone I[1] to react with the methyl Grignard reagent. That this inertness probably is not due to steric factors was made evident by the normal reaction of II with this reagent. Some ketone was always recovered from the reaction mixture however. On refluxing with acetic anhydride–pyridine the tertiary alcohol from II lost the elements of water to give the dihydro compound III, the structural assignment being based on the following consideration: The ultraviolet absorption had too small an extinction coefficient for ring conjugated absorption, eliminating the possibility of a double bond shift. From the results of previous work on the relative stabilities of the *endo- vs.* the *exo-* double bond the *exo-* methylene structure can tenta-

---

(1) E. L. May and J. G. Murphy, *J. Org. Chem.*, **20**, 257 (1955).