The solid residue from the distillation was refluxed with two 25-ml. portions of diethyl ether, and the cloudy solution was filtered. There was obtained 2.7 g. of a mixture of products. Metallic tin was physically separated from the white powder which was identified as tetraphenyltin by the fact that admixture with an authentic sample of tetraphenyltin did not depress the melting point.

The ether was evaporated, and the crude product was recrystallized from ethanol. There was obtained 22.5 g. (68.4%) of triphenyltin chloride, m.p. 104–105°, melting point undepressed on admixture with an authentic sample of triphenyltin chloride.

Reaction of triphenyltin hydride with benzylamine. Triphenyltin hydride[4] (60.0 g., 0.1708 mole) was placed in a dry 250-ml. flask fitted with a Claisen head, truebore-stirrer, and condenser. Freshly distilled benzylamine (9.15 g., 0.0854 mole), b.p. 77.5–78° (19 mm.), was added in one portion, and the system was evacuated. The mixture was stirred at room temperature under 1 atm. of nitrogen for 24 hr.

During the course of the reaction the system was evacuated often to remove the ammonia vapors, but was always returned to the original 1 atm. of nitrogen. After 11 hr., the first indications of solid materials became evident. At the end of 24 hr. the reaction mixture had become a thick white paste. The ammonia vapors were taken off *in vacuo*, and the mixture was heated to 80° ± 5° until there was no further evidence of ammonia being evolved. This required about 2.5 hr. The temperature was reduced to 65°, and the mixture was distilled under slight vacuum. The infrared spectrum of the distillate was superimposable upon that of an authentic sample of toluene.

The gray-black residue was refluxed with seven 150-ml. portions of diethyl ether and filtered. Evaporation of the ether gave 1.5 g. of a yellow powder, m.p. 140–150°. Repeated recrystallization from benzene yielded a white powder, m.p. 223–225°, melting point undepressed on admixture with an authentic sample of tetraphenyltin.

The granular residue from the ether extractions was recrystallized from benzene. There was obtained 45.3 g. (75.8%) of hexaphenylditin, m.p. 237–238°, melting point undepressed on admixture with an authentic sample of hexaphenylditin.

Reaction of triphenyltin hydride with dl-α-methylbenzylamine. Run No. 1. Triphenyltin hydride[4] (15.0 g., 0.0427 mole) was added to a dry 100-ml. flask fitted with a true bore-stirrer and condenser. *dl*-α-Methylbenzylamine (2.6 g., 0.0214 mole) was added in one portion, and the mixture was heated to 80° ± 5° under a running stream of nitrogen with stirring.

After 8 hr. the thick paste was dissolved in benzene, and the solution was allowed to remain in the refrigerator overnight. The solution was evaporated to one fourth its original volume and refrigerated again. The yellow granular material which crystallized was recrystallized twice from benzene. There was obtained 5.0 g. (34%) of hexaphenylditin, m.p. 229–230°, melting point undepressed on admixture with an authentic sample of hexaphenylditin.

Run No. 2. Triphenyltin hydride[4] (60.0 g., 0.1708 mole) was placed in a dry 250-ml. flask equipped with a Claisen head, truebore-stirrer, and condenser. *dl*-α-Methylbenzylamine (10.34 g., 0.0854 mole) was added in one portion, and the system was evacuated. The mixture was stirred at room temperature under 1 atm. of nitrogen for 24 hr.

During the course of the reaction the system was evacuated often to remove the ammonia vapors. The system was always returned to the original 1 atm. of nitrogen. After 24 hr. the pasty white mixture was heated to 80° ± 5° until there was no further evidence of ammonia being evolved. This required about 2.5 hr. The mixture was vacuum distilled (pot temperature to 85°). The colorless distillate, b.p. 71–75° (*ca.* 20 mm.), weighed 5.0 g. The infrared spectrum of the distillate was superimposable upon that of *dl*-α-methylbenzylamine. Careful redistillation of the distillate failed to yield any ethylbenzene.

The residue was refluxed with seven 150-ml. portions of diethyl ether. Evaporation of the ether gave 1.3 g. of a light tan powdery solid. Repeated recrystallization from benzene yielded a white powder, m.p. 223–225°, melting point undepressed on admixture with an authentic sample of tetraphenyltin.

The granular residue from the ether extractions was recrystallized from benzene. There was obtained 31.5 g. (52.7%) of hexaphenylditin, m.p. 234–236°, melting point undepressed on admixture with an authentic sample of hexaphenylditin.

Further processing of the mother liquor yielded 6.5 g. of a fluffy white solid, m.p. 295–300°. Repeated recrystallization from benzene-ethanol gave 2.0 g. of a white solid, m.p. 304–307°. This material was not identified. The infrared spectrum was essentially identical to those of tetraphenyltin and hexaphenylditin.

DEPARTMENT OF CHEMISTRY
ST. JOHN'S UNIVERSITY
JAMAICA 32, N. Y.

Attempted Polymerization of 2-Substituted Tetrahydrofurans

C. L. HAMERMESH AND V. E. HAURY

Received May 15, 1961

Although the polymerization of tetrahydrofuran by Lewis-type acids is well known, very little has been published on the ring opening and polymerization of tetrahydrofurans substituted at the 2-position.

We have found that 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran do not polymerize under conditions which readily polymerize tetrahydrofuran (Table I).

In all runs with the substituted compounds, no diol was obtained on workup but instead almost 100% recovery of starting material was realized.

Polymerization of a mixture of equal weights of tetrahydrofuran and 2-methyltetrahydrofuran yielded only the homopolymer of the former. 98% of the latter compound was recovered unchanged. The catalyst employed in this experiment was antimony pentachloride (10% total weight of both compounds).

The polymerizability of tetrahydrofuran to the polytetramethyleneglycol and the inability to obtain the branched chain polyglycol from the 2- or 2,5- derivatives is more likely a question of the steric conditions associated with the attack of a ring-opened structure on a second molecule rather than the ability to form the coordinate compound of the ring and metal. Thus, it was observed that for all compounds, heat was generated when catalyst was added to the reaction medium regardless of the substitution on the furan ring. Table II describes the change in temperature of the reaction

TABLE I

POLYMERIZATION OF TETRAHYDROFURAN AND SUBSTITUTED TETRAHYDROFURAN

Monomer	Catalyst	Mole, %	Reaction Time, Hr.	Reaction Temp.	Monomer Recovered
Tetrahydrofuran	$SbCl_5$	1.2	24	12–20	8
2-Methyltetrahydrofuran	$SbCl_5$	2.8	168	12–20	100
2,5-Dimethyltetrahydrofuran	$SbCl_5$	3.3	24	12–20	96
Tetrahydrofuran	BF_3-etherate	20	24	12–20	76
2-Methyltetrahydrofuran	BF_3-etherate	27	168	12–20	100
2,5-Dimethyltetrahydrofuran	BF_3-etherate	32	192	12–20	100

TABLE II

TEMPERATURE RISE WHEN BF_3-ETHERATE[a] WAS ADDED TO TETRAHYDROFURANS

	Temperature Rise
Tetrahydrofuran	16
2-Methyltetrahydrofuran	14
2,5-Dimethyltetrahydrofuran	11

[a] 10 g. of boron trifluoride etherate to 20 g. of compound.

medium upon addition of a boron trifluoride catalyst.

RESEARCH DEPARTMENT
ROCKETDYNE DIVISION
NORTH AMERICAN AVIATION
CANOGA PARK, CALIF.

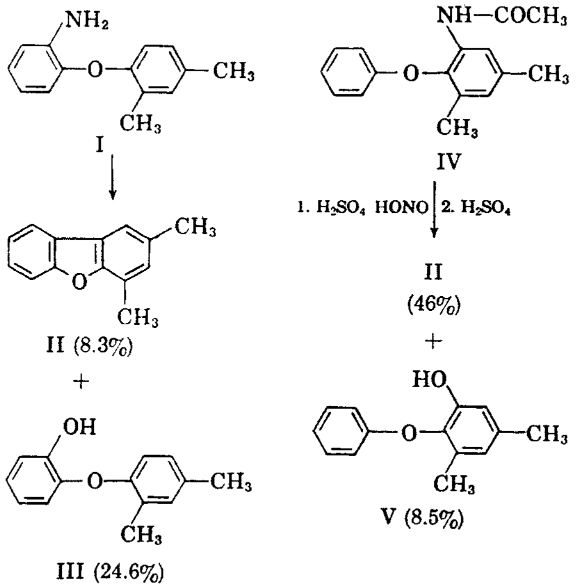
2,4-Dimethyldibenzofuran

WILLIAM E. PARHAM AND ROGER W. STRASSBURG[1]

Received May 17, 1961

Previous studies[2] have led to the conclusion that the synthesis of 4-substituted dibenzofurans from *o*-aminodiphenyl ethers, by diazotization and subsequent intramolecular coupling of the resulting diazonium salt, must be effected on diphenyl ethers that have the amino group in the same ring as the group which will ultimately occupy the 4-position in the resulting dibenzofuran. While there appears to be no apparent theoretical justification, there is considerable experimental data to support this concept.[3] Thus far success has attended every synthesis in which these conditions were fulfilled, and every attempt in which these conditions were not met has ended in failure. We have reexamined this procedure as applied to the synthesis of 2,4-dimethyldibenzofuran (II), and the synthesis of II, several nitro derivatives of II, and a variety of new diphenyl ethers, constitutes the subject of this report.

Reaction of the diazonium salt derived from 2 aminophenyl 2,4-xylyl ether (I) with hot dilute sulfuric acid (1:1) afforded a mixture, from which 2,4-dimethyldibenzofuran (II, 8.3%) and 2-hydroxyphenyl 2,4-xylyl ether (III, 24.6%) were isolated. Treatment of the isomeric 6-amino-2,4-xylyl phenyl ether, (derived from IV), in a similar manner, afforded 2,4-dimethyldibenzofuran (II, 46%) and 6-hydroxy-2,4-xylyl phenyl ether (V, 8.5%). These results definitely establish that ring closure to a dibenzofuran from a diphenyl ether possessing an *ortho* amino group in either ring is possible, despite the fact that the resulting product contains a substituent in the 4-position. There was, however, a marked difference in the proportion of products formed in the two cases, and the results generally support previous experience relative to yield.



Oxidation experiments were conducted in an effort to produce dibenzofuran-2,4-dicarboxylic acid. Potassium dichromate was used in 1:1 sulfuric acid, but only a trace of white acidic solid was obtained. Potassium permanganate was used as the oxidizing agent in three attempts in which the solvents were dilute sodium hydroxide, acetone, and water. Again, only traces of acidic materials were isolated.

---

[1] From the Ph.D. Thesis of Roger W. Strassburg, the University of Minnesota, 1950.

[2] H. Gilman, M. W. Van Ess, and D. M. Hayes, *J. Am. Chem. Soc.*, 61, 643 (1939).

[3] *Heterocyclic Compounds*, Vol. 2, R. C. Elderfield, ed., Wiley, New York, 1951, p. 125.