SYNTHESIS OF 2,3,7,8-TETRAMETHYLDIBENZOFURAN

I. V. Mazere, I. A. Meirovits,
V. A. Ozolinya, and O. Ya. Neiland

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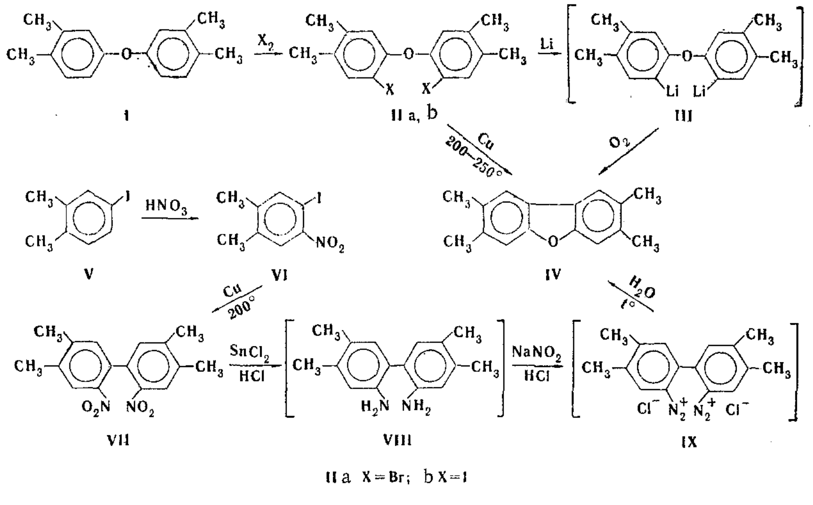
3,4,3',4'-Tetramethyldiphenyl ether readily forms 2,2'-dihalo derivatives on bromination and iodination. Heating 2,2'-diiodo-4,5,4',5'-tetramethyldiphenyl ether with copper powder or oxidation of 2,2'-dilithio-4,5,4',5'-tetramethyldiphenyl ether gives 2,3,7,8-tetramethyldibenzofuran, the structure of which was proved by alternative synthesis from 2,2'-dinitro- and 2,2'-diamino-4,5,4',5'-tetramethyldiphenyls.

We have synthesized 2,3,7,8-tetramethyldibenzofuran (IV) in order to obtain dibenzofuran-2,3,7,8-tetracarboxylic acid.

The starting compound for the synthesis of IV is 3,4,3',4'-tetramethyldiphenyl ether (I) [1-4], which gives good yields of colorless crystalline substances – 2,2'-dibromo- (IIa) and 2,2'-diiodo-4,5,4',5'-tetramethyldiphenyl ether (IIb) – on bromination and iodination in glacial acetic acid. A dilithio derivative (III) is formed on treatment of an ether solution of IIa with lithium metal under argon. The reaction of an ether solution of III with oxygen for 4-5 h leads to closing of the ring to give 2,3,7,8-tetramethyldibenzofuran (IV) in low yield (10%). The yield of IV increases to 17% in the presence of anhydrous cobalt chloride.

It is known that diaryls (Ullmann reaction) [5-7] are obtained by the action of copper powder on aromatic halo derivatives at elevated temperatures. In view of the low yield in the cyclization of the dilithio derivative (III), we checked the possibility of cyclization via the Ullmann reaction. We were able to show that the cyclization of IIb proceeds successfully, and IV is obtained in high yield (55%). The cyclization of IIa does not occur even on heating to 300°C.

The structure of IV was proved by alternative synthesis from 4-iodo-o-xylene (V), which was obtained by direct iodination of o-xylene [8] and separation of the iodination products (3-iodo- and 4-iodo-o-xylenes) by freezing out [9]. Compound V was then nitrated with a nitrating mixture to give 4-iodo-5-nitro-o-xylene (VI) along with other nitration products. The location of the nitro group in the VI molecule was



IIa X=Br; b X=I

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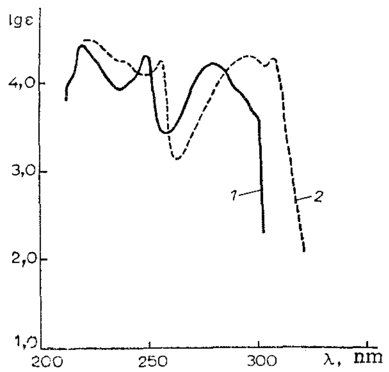

Fig. 1. Absorption spectra (in 96% ethanol): 1) dibenzofuran; 2) 2,3,7,8-tetramethyldibenzofuran.

confirmed by the IR spectrum (at 650-900 cm^{-1}), which was identical to the spectrum of the compounds obtained from 5-nitro-4-xylidine [10] via the Sandmeyer method.

By heating VI with copper powder, we obtained 2,2'-dinitro-4,5,4',5'-tetramethyldiphenyl (VII) in good yield; VII was reduced with stannous chloride. The diamine (VIII) was diazotized, and the bisdiazonium salt was decomposed with water. The product isolated was identical to the compound synthesized as a result of cyclization of IIb or III.

The UV spectrum of 2,3,7,8-tetramethyldibenzofuran is characterized by the presence of two absorption maxima at 220-260 and 290-310 nm. In comparison with unsubstituted dibenzofuran [11] (see Fig. 1), IV has a bathochromic shift, which is due to the effect of the alkyl group.

EXPERIMENTAL*

2,2'-Dibromo-4,5,4',5'-tetramethyldiphenyl Ether (IIa). A 22.6-g (0.1 mole) sample of 3,4,3',4'-tetramethyldiphenyl ether was dissolved in 150 ml of glacial acetic acid, and a solution of 38.4 g (0.24 mole) of bromine in 50 ml of glacial acetic acid was added gradually. The mixture was stirred while maintaining the temperature at 15-20°. After several hours, the mixture was poured into water, and the colorless crystalline precipitate was removed by filtration and washed with sodium hydroxide solution (10%) and water. Two crystallizations from ethanol gave 27.3 g (71%) of IIa with mp 145-147°. Found,%: Br 41.8. $C_{16}H_{16}Br_2O$. Calculated,%: Br 41.6.

2,2'-Diiodo-4,5,4',5'-tetramethyldiphenyl Ether (IIb). A solution of 8.0 g (0.045 mole) of periodic acid in 30 ml of water was added in the course of 1 h to a refluxing solution of 22.6 g (0.1 mole) of 3,4,3',4'-tetramethyldiphenyl ether and 22.0 g (0.087 mole) of iodine in 300 ml of glacial acetic acid. The solution was cooled and poured into water, and the colorless crystalline precipitate was removed by filtration and washed with 10% sodium hydroxide solution and water to give 38.7 g (81%) of IIb with mp 190-193° (from dimethylformamide). Found,%: I 52.8. $C_{16}H_{16}I_2O$. Calculated,%: I 53.1.

4-Iodo-5-nitro-o-xylene (VI). A. A mixture of 57 g of concentrated H_2SO_4 and 38.5 g of nitric acid (sp. gr. 1.42) was added dropwise in the course of 1-1.5 h, while maintaining the temperature at 20-25°, to 58 g of 4-iodo-o-xylene with vigorous stirring. The product was poured over ice, washed with water and alkali solution, dried, and vacuum distilled to give 25.6 g of an oily substance with bp 175-180° (12 mm); the product began to crystallize on standing. Two crystallizations from hexane–chloroform (10 : 1) gave 9.5 g (13.6%) of VI with mp 69-70°. Found,%: I 45.6; N 5.0. $C_8H_8INO_2$. Calculated,%: I 45.8; N 5.1.

B. A 3.6-g sample of 4-amino-5-nitro-o-xylene [10] was dissolved in 50 ml of concentrated H_2SO_4, and the solution was stirred and cooled to 0-5° and treated with 1.7 g of sodium nitrite in small portions. Stirring was continued for 30 min, after which the reaction mixture was poured over ice. The aqueous mixture was filtered, and the solution was added to a cooled (to 0°) solution of 5.2 g of potassium iodide in water. The precipitate was removed by filtration after 12 h to give 3.8 g (57%) of VI with mp 69-70° (from ethanol). The IR spectra of the compounds obtained by both methods were identical at 650-900 cm^{-1}: 662 (34), 726 (34), 752 (40), 816 (66); 884 (48), 897 (29).

2,2'-Dinitro-4,5,4',5'-tetramethyldiphenyl (VII). A mixture of 13.85 g of 4-iodo-5-nitro-o-xylene and 10 g of copper powder was heated at 150-160° for 1 h, after which the temperature was slowly raised to 190-200° in the course of 30 min. The mixture was cooled, treated with chloroform, and filtered. The filtrate was evaporated to give 6.32 g (84.2%) of VII with mp 237-239° (from dioxane). Found,%: C 64.0; H 5.4; N 9.6. $C_{16}H_{16}N_2O_4$. Calculated,%: C 64.0; H 5.4; N 9.3.

2,3,7,8-Tetramethyldibenzofuran (IV). Method 1. A. A 2.1-g (0.3 g-atom) sample of finely cut up purified lithium was added to 30 ml of absolute ether, and the flask was heated on a water bath until the

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*B. Malere participated in this part of the research.

ether began to reflux. A solution of 19.2 g (0.05 mole) of 2,2'-dibromo-4,5,4',5'-tetramethyldiphenyl ether in 500 ml of absolute ether was added in small portions through a dropping funnel. The reaction was carried out under argon. After all of the solution had been added, heating was continued for 2-3 h. In order to monitor the reaction, a sample was removed every hour and titrated with 0.1 N hydrochloric acid. At the end of the reaction, the solution contained 90-95% of the dilithio compound (III). The unchanged lithium was separated, and oxygen was bubbled through the solution for 4-5 h, after which the solution was poured into water. The ether layer was separated and dried, and the solvent was removed by distillation to give 1.15 g (10%) of IV with mp 185-186° (from ethanol). Found,%: C 85.3; H 7.6. $C_{16}H_{16}O$. Calculated,%: C 85.7; H 7.2.

B. A solution of 0.5 g of anhydrous cobalt chloride in absolute ether was added to an ether solution of III, and the mixture was stirred and heated on a water bath for 2-3 h. It was then worked up as in method A to give 1.96 g (17%) of product.

Method 2. A 10-g sample of copper powder was added to 9.56 g of 2,2'-diiodo-4,5,4',5'-tetramethyldiphenyl ether (IIb), and the mixture was heated at 200-220° for 1 h. The temperature was slowly raised to 250° in the course of 30 min, and the reaction product was removed by distillation at 180-200° (10 mm) to give 2.49 g (55.5%) of IV with mp 185-186° (from dimethylformamide).

Method 3. A solution of 3.5 g of stannous chloride in 7 ml of concentrated HCl was added to a suspension of 0.6 g of 2,2'-dinitro-4,5,4',5'-tetramethyldiphenyl (VII) in 10 ml of ethanol. The mixture was refluxed for 15 min, during which VII dissolved completely. The mixture was cooled, made alkaline with 10% sodium hydroxide solution, and extracted with ether. The solvent was evaporated, and 10 ml of 17% hydrochloric acid was added to the residue. The resulting solution was cooled to 0°, and a solution of 0.3 g of sodium nitrite in 2 ml of water was added in small portions. The following day, the mixture was refluxed on a water bath for 10 min, cooled, and filtered. The precipitate was washed with acetone to give 0.17 g (19%) of IV with mp 186-187° (from dimethylformamide).

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