CLV.—*The Preparation of Diphenyl Ethers.*

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IT has been shown by Groves, Turner, and Sharp (J., 1929, 512) that the use of copper-bronze in the preparation of 2-nitrodiphenyl ethers is unnecessary, since it does not increase the yield, and hampers manipulation. The following experiments have been done in order to try to determine the most favourable conditions for the preparation of such ethers, and if possible to eliminate the necessity of extensive purification, owing to the presence of much unchanged material. The effects of different proportions of halogenonitro-compound, phenol, and potassium hydroxide were studied, also the variation of time and temperature, and the use of copper, and the elimination of water, in the operations.

The method used in the condensations was as follows: the water was added to the potassium hydroxide, which was then fused. The phenol was added to the potassium hydroxide, and the two were heated until all the solid had dissolved. The halogenonitro-compound was then added, and the mixture was heated in a metal-bath, in a flask fitted with a short air-condenser. The mixture was then diluted with water, alkali was added, and the oil was extracted with carbon tetrachloride, washed with water, dried over sodium sulphate, and distilled in a vacuum, the purity of the product being determined by its constant boiling point.

Series A.—Variation of the proportion of phenol and potassium hydroxide.

	I.	II.	III.	IV.
o-Chloronitrobenzene ...	1 mol.	1 mol.	1 mol.	1 mol.
Phenol	1 mol.	1·5 mols.	1·75 mols.	3 mols.
Potassium hydroxide ...	1 mol.	1·25 mols.	1·33 mols.	2 mols.
Water	0·1 mol.	0·1 mol.	0·1 mol.	0·1 mol.
Yield, %	68	70	72·4	60·5

The condensation was effected at 160—180°, for 2 hours.

The most favourable conditions are those given in experiment III.

Series B.—Variation of the time of condensation.

Experiment I. The conditions used in experiment III of series A were repeated, the time of the experiment being varied. When the mixture was heated for ½ hour only, the reaction was incomplete, since the yield of 2-nitrodiphenyl ether was only 57%.

Experiment II. When the condensation was prolonged for 4 hours, the yield was 73%, showing that no improvement had been obtained.

Series C.—Variation of the temperature of condensation.

Experiment I. The conditions used in Experiment III, series A were repeated in the following experiments: When the mixture was heated at 200—210° for 1 hour, a yield of 95·5% of ether was obtained.

Experiment II. The same experiment was repeated, the condensation being allowed to occur for only ½ hour; an 84% yield was obtained, showing that the reaction was less complete.

Experiment III. A further experiment was done by heating the mixture at 240° for 1 hour, but the yield was only 90%, showing that no improvement had occurred.

The condensation was effected under the conditions of experiment III, series A, but with omission of the water (0·1 mol.); the yield was only 63%.

When experiment III, series A, was repeated in the presence of copper-bronze, the yield obtained was 72%, showing that no benefit is derived from its use, even when the more favourable proportions of phenol and potassium hydroxide are taken.

Series D (a).—In order to determine whether the conditions described in the previous experiments were generally applicable to diphenyl ethers, a series of experiments was performed with different phenols, *o*-chloronitrobenzene being the halogenonitro-compound. A control set of experiments was performed; equimolecular proportions of halogenonitro-compound, phenol, and potassium

hydroxide were used, the condensation being effected at 200—210° for 1 hour. The amount of water used was 0·1 mol.

Phenol ...	*o*-Chlorophenol	*p*-Chlorophenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
Yield of ether, %	80	66	72	70	73

Series D (b).—The series was repeated under the conditions of experiment I, series C.

Phenol ...	*o*-Chlorophenol	*p*-Chlorophenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
Yield of ether, %	91	86	85	87	87

Comparison of the two series shows that the yields are increased between 10—20% by using the increased proportions of phenol and potassium hydroxide.

The fifth experiment in series D (b) was repeated, 95 g. of *o*-chloronitrobenzene, 114 g. of *p*-cresol, and 45 g. of potassium hydroxide being used. At the end of the reaction, the condensation mixture was shaken with very dilute alkali solution until cold; a crystalline meal then separated. After being dried in the air, this weighed 129 g. (94% yield). As a result of the improved conditions worked out, it is possible to prepare ethers similar to the above, without extraction with a solvent, and subsequent vacuum distillation.

Series E.—The comparison of yields obtained by using different halogenonitro-compounds was also made.

Experiment I. 2 : 5-Dichloronitrobenzene was condensed with phenol, under the conditions described in the series of experiments D (a), and the yield of ether obtained was 74%. When the experiment was repeated under the conditions of experiments D (b), the yield was increased to 85%.

Experiment II. According to Fox and Turner (this vol., p. 1115), when 2 : 5-dibromonitrobenzene is condensed with phenol at 160—180° for 6 hours, 1 mol. of halogenonitro-compound, 1 mol. of phenol, 1 mol. of potassium hydroxide, and 0·1 mol. of water being used, the yield of 4-bromo-2-nitrodiphenyl ether is 48% of the theoretical. When the condensation was effected under the conditions of experiments D (b), the yield was increased to 85%.

It appears, therefore, that the best conditions for the preparation of substituted diphenyl ethers consist in having increased proportions of phenol and potassium hydroxide, and in working at a temperature not below 200°.

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