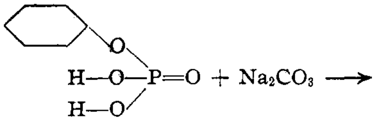
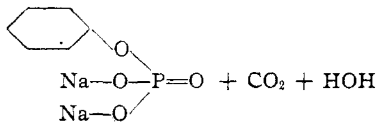
tends to hold any phenol in solution and to prevent hydrolysis of the salt. The product, when taken up in water and reprecipitated again with a mixture of alcohol and ether, showed in a water solution only a faint trace of phenol. The yield of the disodium phenyl phosphate after thorough drying in a vacuum desiccator was 700 g. (68.2%).





Summary

Disodium phenyl phosphate, which showed in a water solution only a faint trace of phenol, was obtained in good yields starting with phenol and phosphorus oxychloride.

MANHATTAN, KANSAS RECEIVED DECEMBER 31, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS]

Mercuration of Diphenyl Ether and Some of its Derivatives

BY W. D. SCHROEDER AND R. Q. BREWSTER

In continuation of the study of iodinated derivatives of diphenyl ether which is being conducted in this Laboratory,[1] it seemed that these iodine compounds might be obtained by mercuration of diphenyl ether, or some of its derivatives, and subsequent replacement of the mercuri group by iodine. It was particularly desirable to obtain compounds in which the mercury atom was joined to the nucleus at the position ortho to the oxygen since its replacement by iodine would then lead to the formation of 2-iodo derivatives which are not readily obtainable by direct iodination. This end, however, was not attained. In all cases 4-mercuri compounds were produced which upon heating with iodine chloride in acetic acid solution gave 4-iodo substituents. Nevertheless the mercury compounds themselves seem to warrant a brief description since they are easily prepared and in some instances heating of the mercurated diphenyl ethers with aryl halides leads to the precipitation of mercuric halides and the formation of a carbon–carbon bonding which is rather unusual for organic mercurials.

Experimental Part

Mercuration of Diphenyl Ether.—Mercuration with mercuric acetate in glacial acetic acid solution was found to give the best results. In order to obtain as large a proportion as possible of the monoacetoxymercuri diphenyl ether an excess of the diphenyl ether was necessary. One mole (216 g.) of mercuric oxide was dissolved in 800 cc. of glacial acetic acid and the solution made nearly anhydrous by the addition of 100 g. of acetic anhydride. Two moles (340 g.) of diphenyl ether was added, the solution was heated on the steam-bath until a test portion was free from ionic mercury (two and one-half to three hours) and poured into 2 liters of water. The pasty precipitate consisted of unchanged diphenyl ether, 4-acetoxymercuri diphenyl ether (I) and 4,4′-diacetoxymercuri diphenyl ether (III). The water solution was poured off and the precipitate washed several times with cold ligroin (b. p. 90–100°) to remove most of the unmercurated diphenyl ether. Separation of I from III was best accomplished by extraction with hot ligroin in which the former is moderately soluble and the latter practically insoluble. Ten such extractions with 1.5 liters of boiling ligroin each time gave 200 g. of 4-acetoxymercuri diphenyl ether (I), m. p. 150°, and recrystallization of the residue from 95% ethyl alcohol gave 175 g. of 4,4′-diacetoxymercuri diphenyl ether (III), m. p. 195–200°.

The mercuration proceeds slowly at room temperature and after about 3 weeks' standing the solution is free from ionic mercury. The proportion of I and III is about the same as when the reaction is conducted on the steam-bath.

Each of these substances in acetic acid solution reacts with inorganic reagents in the normal manner. Warm mineral acid converts I to diphenyl ether, sodium chloride solution gives 4-chloromercuri diphenyl ether (II), bromine produces 4-bromodiphenyl ether and iodine chloride (but not iodine) gives 4-iododiphenyl ether. Likewise the 4,4′-diacetoxymercuri diphenyl ether (III) with the above reagents yields, respectively, diphenyl ether, 4,4′-dichloromercuri diphenyl ether (IV), 4,4′-dibromodiphenyl ether and 4,4′-diiododiphenyl ether all of which were identical with known samples.

Mercuration of Diphenyl Ether Derivatives.—Molar proportions of 4-bromodiphenyl ether (or 4-iododiphenyl ether) and mercuric acetate combine in the foregoing manner to produce 4-bromo-4′-acetoxymercuri diphenyl ether (V) and the corresponding iodo derivative (VII). 4-Hydroxydiphenyl ether upon mercuration gave a mixture of poly-mercurated products which were inseparable. Analysis of the mixture showed 62% of mercury which corresponds approximately to the triacetoxymercurihydroxydiphenyl ether. Likewise no individual mer-

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[1] Brewster and Strain, THIS JOURNAL, 56, 117 (1934).

TABLE I

MERCURATED DIPHENYL ETHER DERIVATIVES

No.	Compound	M. p., °C.	% Hg	
			Calcd.	Found
I	$C_6H_5OC_6H_4HgOAc$(4)	150	46.73	46.86
II	$C_6H_5OC_6H_4HgCl$(4)	192	49.50	49.31
III	$O(C_6H_4HgOAc)_2$(4-4′)	195–200	58.38	58.44
IV	$O(C_6H_4HgCl)_2$(4-4′)	>250	62.60	62.76
V	4-Br-C_6H_4O-C_6H_4HgOAc(4′)	152–155	39.49	39.26
VI	4-Br-$C_6H_4OC_6H_4HgCl$(4′)	190	41.40	41.18
VII	4-I-$C_6H_4OC_6H_4HgOAc$(4′)	174	36.11	35.98
VIII	4-I-C_6H_4O-C_6H_4HgCl(4′)	250–260	37.75	37.57
IX	(4)C_6H_5OO-$OC_6H_4OC_6H_4HgOAc$(4′)	165	36.51	36.32
X	$(C_6H_5OC_6H_4)_2Hg$(4)	135–137	37.16	37.17

curated product could be prepared from 4-methoxydiphenyl ether. The benzoyl derivative of 4-hydroxydiphenyl ether, however, underwent mercuration normally producing the 4′-acetoxymercuri compound (IX). In each of the above cases where a pure mercurated product could be isolated the mercuri group was readily replaced by iodine upon treatment with iodine monochloride in acetic acid solution. Table I shows the melting points and analyses of these mercury derivatives.

4-Mercuri bis-Diphenyl Ether $(C_6H_5OC_6H_4)_2Hg$(X).—4-Bromodiphenyl ether (50 g.), 15 cc. of ethyl acetate, 400 cc. of dry toluene and 150 g. of 3% sodium amalgam were heated in an oil-bath at 120° for twelve hours. The toluene solution was then filtered and concentrated. Upon cooling white flakes of 4-mercuri-bis-diphenyl ether (X) separated; yield 12 g. After recrystallization from ligroin the product melted at 135–137°. Boiling acetic acid converts X to 4-acetoxymercuri diphenyl ether (I) and iodine chloride gives 4-iododiphenyl ether.

Formation of Carbon–Carbon Bondings. Reaction of 4-Chloromercuri Diphenyl Ether (II) with Halides.

Benzyl Chloride.—4-Chloromercuri diphenyl ether (41 g. —0.10 mole) and 15 g. (2.3 g. excess of 0.1 mole) of benzyl chloride were heated at 100° for six to eight hours.[2] At the end of this time water was added and the slight excess of benzyl chloride removed by distillation in steam. The residual oil was separated from the water solution of mercuric chloride and dried over calcium chloride. Fractionation of this oil at reduced pressure gave 9 g. of 4-benzyl-diphenyl ether (XI), b. p. 193–196 (4 mm.) and 8 g. of 4,4′-dibenzyl diphenyl ether (XII), b. p. 260–270 (4 mm.). Addition of alkali to the solution of mercuric chloride precipitated 21 g. of mercuric oxide which accounted for all of the mercury.

Anal. of XI. Calcd. for $C_{19}H_{16}O$: C, 87.6; H, 6.16. Found: C, 87.2; H, 6.27.

Anal. of XII. Calcd. for $C_{26}H_{22}O$: C, 89.13; H, 6.28. Found: C, 89.50; H, 6.20.

The formation of the 4,4′-dibenzyl diphenyl ether could be explained on the assumption that mercuric chloride was liberated from the reaction of benzyl chloride and chloromercuridiphenyl ether and this mercuric chloride then formed a chloromercuri derivative at the 4′-position which was replaced by another mole of benzyl chloride. In such a case the previous isolation of 4-chloromercuri-diphenyl ether should not be necessary. In order to test this idea 51 g. (0.3 mole) of diphenyl ether, 38 g. (0.3 mole) of benzyl chloride and 2.7 g. (0.01 mole) of mercuric chloride were heated in an oil-bath at 140–150° for four to five hours. Copious evolution of hydrogen chloride occurred. Distillation of the reaction product with steam removed 2 cc. of benzyl chloride and fractionation of the residual oil at 4 mm. pressure gave 15 g. (0.088 mole) of unchanged diphenyl ether; 27 g. (0.105 mole) of 4-benzyl diphenyl ether, 21 g. (0.06 mole) of 4,4′-dibenzyl diphenyl ether and a few grams of tarry non-distillable material. Hence this reaction is of the Friedel and Crafts type. The mercuric chloride reacts repeatedly and may be used in much smaller quantities than is customary when aluminum chloride is the catalyst.[3]

4-Bromo-4′-chloromercuri diphenyl ether (VI) when heated with benzyl chloride at 150° for four hours gives 4-bromo-4′-benzyl-diphenyl ether (XIII), b. p. 250–260° (5 mm.).

Anal. Calcd. for $C_{19}H_{15}OBr$: Br, 23.60. Found: Br, 23.41. The same product (XIII) was obtained in 15 g. yield by six hours of heating at 150° of 24.9 g. (0.1 mole) of 4-bromodiphenyl ether and 12.6 g. (0.1 mole) of benzyl chloride with 2.7 g. (0.01 mole) of mercuric chloride as catalyst.

Benzoyl Chloride.—Equimolar proportions of II and benzoyl chloride when heated in an oil-bath at 150° for one hour gave a 70% yield of 4-benzoyl-diphenyl ether (4-phenoxybenzophenone) (XIV) which was purified by two crystallizations from ligroin; m. p. 66°. *Anal.* Calcd. for $C_{19}H_{14}O_2$: C, 83.15; H, 5.11. Found: C, 82.67; H, 5.35. Compound XIV also was prepared by heating a mixture of 34 g. of diphenyl ether, 28 g. of benzoyl chloride and 2.7 g. of mercuric chloride at 150–160° for one hour. Evolution of hydrogen chloride was rapid and the yield of purified product amounted to 15 g. No dibenzoyl derivative was obtained by either method.

***t*-Amyl Chloride.**—Four hours of heating of 34 g. (0.2 mole) of diphenyl ether, 22 g. (0.01 mole) of *t*-amyl chloride and 2.7 g. (0.01 mole) of mercuric chloride at 150° resulted in the evolution of hydrogen chloride and

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(2) At 150° the reaction is complete in two hours.

(3) Although phenol combines with benzyl chloride in the absence of a catalyst, this is not true of diphenyl ether. Anhydrous cadmium chloride and anhydrous zinc chloride are more efficient catalysts than mercuric chloride and the use of these salts for syntheses in the diphenyl ether series is being investigated.

the production of 15 g. of 4-*t*-amyl diphenyl ether, b. p. 190–200 (23 mm.).

Anal. Calcd. for $C_{17}H_{20}O$: C, 85.00; H, 8.33. Found: C, 84.42, 84.67; H, 8.15, 8.23.

Summary

The mercuration of diphenyl ether has been described and a number of the mercurated products have been isolated and analyzed. These substances give the normal reactions of organic mercury compounds except that they react with certain halides giving carbon–carbon syntheses. This reaction has been observed with only a few organic mercurials.

LAWRENCE, KANSAS RECEIVED NOVEMBER 15, 1937

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Reflection and Absorption of Visible Radiation in the System Potassium Chloride–Cupric Chloride

BY GEO. GLOCKLER AND R. E. DIETMEIER[1]

The blue color of cupric salts is due to a region of transmission at about 4900 Å., located between two large absorption bands, one situated in the ultraviolet and another one in the infrared. All blue or green colored copper compounds are hydrated whereas anhydrous copper compounds are colorless or reddish-brown to red. The latter must transmit or reflect red light and should therefore show a reflection or transmission maximum in this region. The system KCl–CuCl$_2$ was studied in powder form by measuring the reflection coefficient with a Keuffel and Esser color analyzer. The two anhydrous salts were melted together and the percentage of reflected light was determined as a function of wave length, using a magnesium carbonate block as a standard. Since during the process of melting some cupric chloride is decomposed, certain of the mixtures were also prepared in the wet way and dehydrated at 132° (asterisk in Table I). No difference in behavior was found. It is seen that all samples containing a sufficient amount of cupric chloride show a maximum of reflection at 6390 ± 20 Å. as does anhydrous cupric chloride (6404 ± 8 Å.). This maximum of reflection is interpreted to correspond to a maximum of transmission or to a minimum of absorption of radiation, since the light from the analyzer passes through the crystal powder before it is finally reflected from the heterogeneous crystalline mass. The minimum of absorption at 6400 Å. is produced by the approach of two large absorption bands as in the case of the hydrated copper salts.

TABLE I

Mole fraction KCl	Absorption max., Å.	Reflection max., Å.
0.0	..	6404 ± 8[a]
.1	..	6460
	..	6380
.2	5300	6380
	5500	6420
.3	5350	6400
	5350	6400
.4	5350	6360
	5300	6400
.5	5600	6430
	5400	6360
	5450*	6380*
	5340*	6380*
	5350*	6370*
0.6	5350	6400
	5350	6360
.67	5500	6400
	5450	6360
	5350*	6360*
	5350*	6400*
.7	5350	6400
	5450	6410
.8	5350	6400
	5300	6360
.9	5400	6400
	5400	6380
1.0	..	..
	..	..
Av.	5387 ± 63	6390 ± 20

[a] Pure anhydrous CuCl$_2$ (13 measurements).

* Prepared in wet way and dehydrated at 132°.

More interesting and important is the absorption maximum (reflection minimum) discovered at 5387 ± 63 Å. (Table I and Fig. 1). This absorption region has been subtracted from the large band which reaches into the ultraviolet by drawing in the line AB (Fig. 1). Above the point A and below B, the same difference of ordinate exists between the actual reflection curve and the dotted line. Hence the curve C starts and ends in a horizontal line. The maximum is clearly shown in all the experiments where the mole fraction of potassium chloride is greater than twenty per cent.

Since the absorption at 5387 Å. is not observed in anhydrous cupric chloride, but is found in mixture of this salt with potassium chloride, the agency responsible for the light absorption must be a complex between the two substances. It is

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(1) Based on a thesis presented to the faculty of the Graduate School of the University of Minnesota by R. E. Dietmeier in partial fulfilment of the requirements for the degree of Master of Science, 1937.