results from the fact that both the benzoyl and phenylsulfonyl groups have their maximal absorptions at about this position[13] and in this particular structure the two chromophores show little interaction. The spectrum of the corresponding hydrazone is more complex since in addition to the maximum at 245 mμ there is also apparent an inflection point at about 270 mμ. The corresponding azine has an extremely strong absorption peak at 247 mμ (ε 45,500) which is almost equivalent to a double hydrazone peak, but there is also present a second peak at 295 mμ. The breadth and intensity of this secondary peak, suggests the presence of a masked absorption band at about 320 mμ which could be attributed to the typical benzalazine absorption.

While the spectrum of 2-thienyl phenyl ketone has two well-defined maxima at 263 and 295 mμ,[14] there are found in the spectrum of the corresponding hydrazone two similar bands, but they overlap to a great extent. The absorption curve of the corresponding azine is of great interest since it presents two distinct bands at 277 and 353 mμ. The first of these bands resembles closely the 277 mμ band of the azine of benzophenone and the 265 mμ band of the azine of 2-thienyl methyl ketone.[3] The second band, however, differs in position from the benzalazine band in benzophenone azine (*ca.* 310 mμ) and also the 335 mμ band of the azine of 2-thienyl methyl ketone.[3] The large difference in the maxima of these two thiophene ketazines suggests that the chromophoric system in the azine of 2-thienyl phenyl ketone contains one thiophene and one benzene ring each.

Acknowledgment.—We wish to acknowledge the aid of the Research Corporation in defraying a part of the cost of this project.

PITTSBURGH 19, PENNA. RECEIVED JUNE 18, 1951

[13] The absorption spectra of various sulfones have been recently studied by Fehnel and Carmack (THIS JOURNAL, **71**, 231 (1949); **72**, 1292 (1950)); and Koch (*J. Chem. Soc.*, 408 (1949)).

[14] H. H. Szmant and A. J. Basso, THIS JOURNAL, **73**, 4251 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Action of Aluminum Bromide on Benzyl Phenyl Ether

BY D. STANLEY TARBELL AND JOHN C. PETROPOULOS

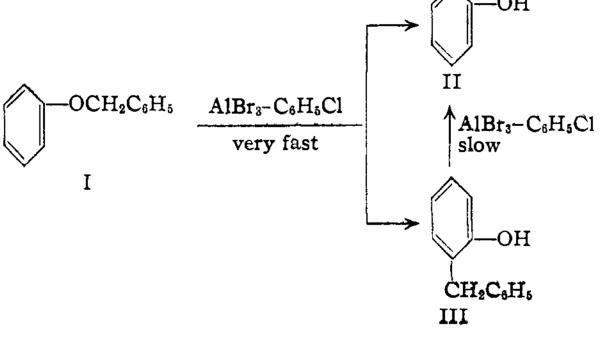
Benzyl phenyl ether has been found to be converted very rapidly by aluminum bromide in chlorobenzene solution to a mixture of about 40% phenol, 55% *o*-benzylphenol and dichlorodiphenylmethane. The ratio of the phenolic products is the same at −40° as at 25°, and is unaffected by the use of benzene or nitrobenzene as solvent. The *o*-benzylphenol produced in the initial rapid reaction is converted to phenol at a slower measurable rate, the first order rate constant of which is identical with the rate constant obtained from pure *o*-benzylphenol under the same conditions. *p*-Benzylphenol has been shown not to be an intermediate in the rapid formation of phenol from benzyl phenyl ether. The *o*-benzylphenol is believed to be formed from the ether by an intramolecular process, and the contrast between the action of the aluminum bromide on benzyl phenyl ether and the corresponding sulfide (previously studied) is discussed. The dichlorodiphenylmethane, formed in chlorobenzene from aluminum bromide and benzyl phenyl ether or benzyl bromide, is shown to be a mixture of roughly equivalent amounts of 3,3′- and 3,4′-dichlorodiphenylmethane.

We have studied the reaction between benzyl phenyl ether (BPE) and aluminum bromide, in order to compare the action of this strong Lewis acid on the oxygen ether with its action on the sulfur analog, benzyl phenyl sulfide.[1]

In the initial experiments, the rate of formation of phenol from BPE by aluminum bromide in chlorobenzene solution was followed; the phenol was extracted from a mixture of chlorobenzene–ethyl ether with 20% alkali, after quenching the reaction, and was determined by the bromate method.[2] By this procedure, there was observed an extremely rapid formation of about 40% of phenol, followed by slower measurable increase in the amount of phenol, until phenol formation was virtually complete. This unusual behavior was eventually traced to the fact that there was an initial very rapid reaction to form about 40% phenol (II) and about 55% of *o*-benzylphenol (III); the latter was not extracted by alkali under the conditions mentioned above, and hence had not been determined. By a slight change in the procedure, it was possible to determine both phenol and *o*-benzylphenol in the same solution.

It was shown that the slow production of phenol was due to conversion of *o*-benzylphenol to phenol, with transfer of the benzyl group to the solvent. The scheme shown below was established by isolation experiments, in which BPE and aluminum bromide in chlorobenzene were mixed under conditions comparable to those used in the rate runs; the reaction was quenched within a few seconds, phenol (II) and *o*-benzylphenol (III) were isolated, and were identified by comparison of crystalline derivatives of authentic samples.

The possibility that the initial rapid formation of phenol occurred through *p*-benzylphenol as intermediate was ruled out by showing that, al-



[1] (a) Harnish and Tarbell, THIS JOURNAL, **70**, 4123 (1948); (b) Wilson and Tarbell, *ibid.*, **72**, 5200 (1950).

[2] Redman, Weith and Brock, *Ind. Eng. Chem.*, **5**, 389 (1913); Day and Taggart, *ibid.*, **20**, 545 (1928).

though the latter formed phenol under the conditions of the experiment, the reaction was too slow to account for the results; no *p*-benzylphenol could be obtained in the isolation runs, and it could have been present only in traces, if at all.

The ratio of phenol to *o*-benzylphenol (*i.e.*, II/III) produced in the initial rapid reaction was not affected appreciably by a change in temperature from 25 to −40°, and by changing the solvent from chlorobenzene to nitrobenzene. Even at −40°, the rapid reaction was complete in less than five seconds. In nitrobenzene, the slow reaction (conversion of *o*-benzylphenol to phenol) did not occur. The data are given in Table I; the isolation of dichlorodiphenylmethane derivatives, which are discussed in detail below, is also indicated in the table.

TABLE I

ACTION OF ALUMINUM BROMIDE ON BENZYL PHENYL ETHER (BPE)[a]

(BPE) mole/l.	($AlBr_3$) mole/l.	Time, sec.	Temp., °C.	Phenol (II), %	*o*-Benzylphenol (III) %
0.0257	0.11	<5	−40	41.7[b]	55.3[b]
.0257	.11	<5	25	42.0[b]	54.5[b]
.10	.25	<5	25	28.8[c]	39[c,d]
.10	.25	5.5 hr.	25	62.5[c,e]	...
.099	.20	15	25	46.7[b]	...
.099	.20	4 hr.	25	96.8[b]	...
.0251[f]	.11[f]	<5	25	43.3[b]	54.2[b]
.0243[g]	.11[g]	<5	25	48.3[b]	54.3[b]
.0121[h]	.11	<5	25	45.0[b]	51.3[b]

[a] Solvent chlorobenzene unless specified. [b] Figures determined by titration. [c] Figures determined by isolation. [d] 44% of 4,4′-dichlorodiphenylmethane isolated in this run. [e] 87% of mixed dichlorodiphenylmethanes isolated in this run. [f] Using nitrobenzene as solvent. [g] Using benzene as solvent. [h] Phenol (0.0215 m./l.) was present in this run. No *p*-benzylphenol was isolated.

A change in the ratio $[AlBr_3]/[BPE] = r$ did not change the initial amounts of phenol and *o*-benzylphenol formed, as long as $r > 1$; for $r < 1$, however, the initial percentages of both phenol and *o*-benzylphenol were decreased, the latter more so than the former; for example, when $r = 0.25$ after 15 sec. the per cent. of phenol was 19.3 compared to 18.9 of *o*-benzylphenol. Allowing the reaction to continue for 60 min. increased the per cent. of phenol to 45.7 and *o*-benzylphenol to 31.0.

These results implied that the structure C_6H_5-$OAlBr_2$, the product of reaction of aluminum bromide and phenol, must be effective in converting BPE to phenol and *o*-benzylphenol. This was proved by runs in which a premixed solution of equimolar amounts of aluminum bromide and phenol was added to BPE, and produced after 15 sec. about 67% of phenol and 32% of *o*-benzylphenol; after 20 hours the percentages of products remained virtually the same. Similarly, a premixed solution of equimolar quantities of aluminum chloride and phenol, when added to BPE, produced, after 10 min., about 40% of phenol and 51% of *o*-benzylphenol. This was the only method by which aluminum chloride, in view of its insolubility, could be compared with aluminum bromide.

The slow conversion of *o*-benzylphenol to phenol was found to be more rapid in chlorobenzene than in benzene, apparently being favored by a solvent of higher dielectric constant; the reaction did not occur in nitrobenzene solution, however, presumably because the solvent could not be alkylated by the benzyl group. The rate in chlorobenzene was not much affected by increasing r (the $[AlBr_3]/[BPE]$ratio) from 4.4 to 8.9, but when r was less than 2, the rate was extremely slow.

The rate of the conversion was measured on two different systems. A pure solution of *o*-benzylphenol (III) in chlorobenzene was treated with aluminum bromide ($[AlBr_3]/[III] = 3$), and the rate of appearance of phenol was found to depend on the first power of [III], the constant being 1.6×10^{-3}. The rate of production of phenol in a solution of BPE of similar concentration and aluminum bromide ($r = 3$) in chlorobenzene was found likewise to depend on the first power of the *o*-benzylphenol concentration known to be present in this solution from rapid rearrangement of the BPE. The first order constant for phenol formation was 1.7×10^{-3}, calculated by correcting the phenol concentration for the 40% formed in the initial rapid reaction. The agreement of the two first order constants for phenol formation is strong support for the reaction scheme outlined above. The first order dependence of phenol formation was supported by the observation that the half-time of complete conversion to phenol was unaffected by halving the BPE concentration in the reaction mixture.

The fate of the benzyl group from the BPE was established as follows. From a mixture of BPE and aluminum bromide in chlorobenzene which was quenched within a few seconds, 4,4′-dichlorodiphenylmethane was isolated in 44% yield, and was identified by oxidation with selenium dioxide to 4,4′-dichlorobenzophenone, and by comparison with an authentic sample of this ketone.[3] If the original BPE reaction mixture was allowed to react longer before quenching, a mixed dichlorodiphenylmethane was formed. This was converted by selenium dioxide to a substance melting at 91°, having the composition of a dichlorobenzophenone not identical with any of the dichlorobenzophenones, all of which, except the 2,3-isomer, are known.

The 91° material was shown to be a eutectic, consisting of a 60–40 mixture of 3,4′- and 3,3′-dichlorobenzophenone, by conversion to the mixed oximes and Beckmann rearrangement of these. Hydrolysis of the resulting mixed anilides yielded 3-chlorobenzoic acid as the principal acid, with a small amount of impure 4-chlorobenzoic acid. A melting point–composition curve was made for mixtures of synthetic 3,3′- and 3,4′-dichlorobenzophenone,[4] and it was found that an artificial mixture of the above composition had the properties of the eutectic obtained from the oxidation, and gave no depression on mixed m.p. Furthermore, the artificial eutectic and the one from the oxidation gave identical infrared spectra over the whole 3–14 μ range.

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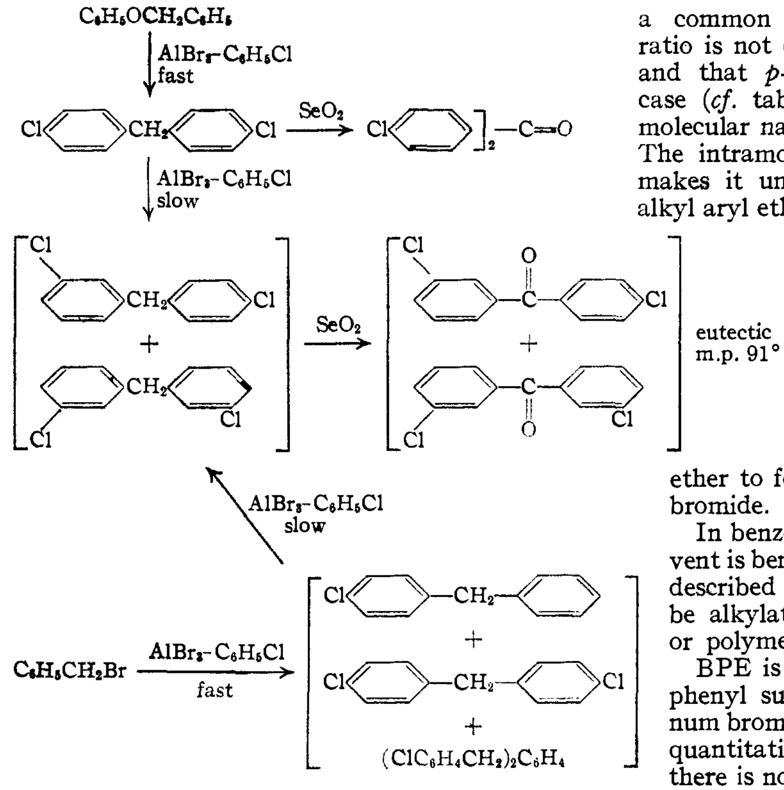
(3) Dittrich, *Ann.*, **264**, 174 (1891).

(4) Haller, Bartlett, Drake and Newman, *et al.*, THIS JOURNAL, **67**, 1591 (1945). We are indebted to Professor M. S. Newman for samples of some dichlorobenzophenones.



It was found that the action of benzyl bromide and aluminum bromide on chlorobenzene formed the same mixture of 3,3'- and 3,4'-dichlorodiphenylmethane, when the reaction was quenched after ten minutes or four hours. The reaction mixture, when quenched at once, yielded about 17% of 4,4'-dichlorodiphenylmethane, 32% of 4-chlorodiphenylmethane and a smaller amount of a bis-(chlorobenzyl)-benzene. These compounds were identified by oxidation to the corresponding ketones, although the structure of the bis-(chlorobenzoyl)-benzene was not established. The formation of the dichlorodiphenylmethanes must involve either chlorine transfer or exchange of an aryl group in the diphenylmethane; both of these reactions would be catalyzed by aluminum bromide.

Discussion

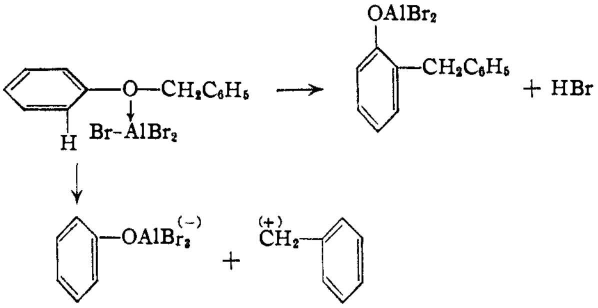
The rapid initial formation of *o*-benzylphenol from BPE is considered to be an intramolecular rearrangement; previous studies on the rearrangement of BPE by heat[5] or by treatment with zinc chloride[6] at 100–200° led to a poor yield of *o*- and *p*-benzylphenols, and some of the 2,4-dibenzyl derivative. Furthermore, Friedel–Crafts alkylation of phenol with aluminum chloride and benzyl halides usually gives much of the *p*-isomer and some disubstitution product,[7] in contrast to the present case.

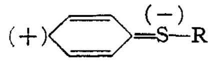
The constant ratio of phenol–*o*-benzylphenol found over a wide range of temperature and solvents indicates that both products may result from a common intermediate.[8] The fact that this ratio is not changed by addition of excess phenol and that *p*-benzylphenol is not formed in this case (*cf.* table) is further support for the intramolecular nature of the *o*-benzylphenol formation. The intramolecular nature of the rearrangement makes it unique for acid-catalyzed cleavages of alkyl aryl ethers[9]; whether this behavior is limited to aluminum bromide, because of its very strong electrophilic character and solubility, will have to be decided by further experiment.

The fast reaction must be regarded as proceeding through a transition state which can give both an intramolecular shift of the benzyl group, and a cleavage of the ether to form a benzyl carbonium ion or benzyl bromide.

In benzene or chlorobenzene solution, the solvent is benzylated, with the subsequent changes described above; in nitrobenzene, which cannot be alkylated, the benzyl group must dimerize or polymerize.

BPE is thus markedly different from benzyl phenyl sulfide[1a] in its behavior toward aluminum bromide. The sulfide is split to thiophenol quantitatively at a measurable rate at 25°, and there is no evidence for the formation of any *o*-benzylthiophenol. The results in the two cases emphasize two striking differences between oxygen and sulfur compounds. The first is the greater rate of splitting of an ether compared to a sulfide by acidic reagents.[10] The second is the fact that the hydroxyl or alkoxyl group is far more effective in promoting electrophilic substitution in the aromatic nucleus than are the corresponding sulfur-containing groups. This is probably due to the fact that the sulfur compounds have an electron-withdrawing effect due to contributions from structures such as IV, in which the sulfur has expanded its valence shell.[11]





IV

Other evidence for this deactivating effect of sulfur is the more positive sigma value for $-SCH_3$

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[5] Behaghel and Freiensehner, *Ber.*, **67** 1368 (1934).

[6] Short, *J. Chem. Soc.*, 528 (1928); Short and Stewart, *ibid.*, 553 (1929).

[7] Summary in Thomas, "Anhydrous Aluminum Chloride," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 178–185.

[8] A similar situation is observed in the benzidine rearrangement, in which the ratio of benzidine to diphenyline is unaffected by a considerable change in temperature and acidity (Carlin, Nelb and Odioso, THIS JOURNAL, **73**, 1002 (1951)).

[9] For other examples of intramolecular alkylation by alkyl aryl ethers, see, in addition to ref. 6, Smith, THIS JOURNAL, **55**, 849, 3718 (1933); *ibid.*, **56**, 717 (1934).

[10] *Cf.* Harnish and Tarbell, *Chem. Revs.*, **49**, 1 (1951).

[11] *Cf.* Matsen, THIS JOURNAL, **72**, 5246 (1950).

compared to $-OCH_3$,[12] the slower thermal rearrangement of allyl aryl sulfides compared to the ethers,[13] the coupling of diazonium compounds with thiophenols to form diazo sulfides, ArS—N=N—Ar[14]; instead of diazothiophenols, and the condensation of thiophenols with tertiary alcohols, in the presence of acid, to yield sulfides[15] instead of nuclear alkylation products.

Experimental[16]

Benzyl phenyl ether (BPE) was prepared from benzyl chloride and phenol by the usual method, and recrystallized from ethanol; it melted at 38–38.5°. The reported m.p. is 39°.[6]

Chlorobenzene[17] was purified by washing with concentrated sulfuric acid followed by drying over potassium carbonate and then fractional distillation.

Aluminum bromide[18] was purified by distillation and kept in a tightly stoppered flask.

Reactions of Benzyl Phenyl Ether or Monobenzylphenols with Aluminum Bromide in Chlorobenzene.—Stock solutions of the ether or substituted phenols and of aluminum bromide were prepared and brought to the desired temperature. Then, by means of a glass pump previously described,[19] aliquots of each stock solution were transferred into glass stoppered flasks. At the specified times, the reactions were stopped by hydrolyzing with 5 cc. of water. Peroxide-free ether (30 cc.) was added and the contents were extracted twice with 10-cc. portions of 20% aqueous sodium hydroxide which only removed phenol. The aqueous alkaline solutions were neutralized with 30% sulfuric acid using phenolphthalein as the indicator. Standard potassium bromate-bromide solution, in which the concentration of potassium bromate and potassium bromide was 0.0330 and 0.63 *m*, respectively, was added. This was followed by the addition of 10 cc. of 30% sulfuric acid to liberate bromine which, when allowed to react for five minutes, converted the phenol into tribromophenol. The excess bromine was converted into iodine with 5 cc. of 40% potassium iodide and the iodine was titrated with standard thiosulfate solution (0.1 *N*) using starch as the indicator.

Aqueous sodium hydroxide (20%) would not extract from an ether solution the monobenzylphenols used in these experiments. Use of this property was made in determining the amount of monobenzylphenol present, as well as phenol, at any time during the reaction. After the phenol was removed by the method described, the ether was removed by evaporation and 30 cc. of purified heptane was added to facilitate separation of layers. The heptane layer was then extracted twice with 10-cc. portions of Claisen alkali. From this stage on the same analytical method was used as in the determination of phenol. Blanks were run demonstrating this method to be satisfactory for analysis of phenol and monobenzylphenols.

The experiments at −40° were quenched with 5 cc. of peroxide free ethyl ether and blanks showed this reagent was satisfactory for stopping the reaction.

In every experiment where the reactants or conditions were varied, the products of reaction, after bromination, were collected and identified by comparison in m.p. and mixed m.p. with authentic samples of tribromophenol and 2-benzyl-4,6-dibromophenol.

The Reaction between BPE and Aluminum Bromide in Chlorobenzene (A) Initial Products.—To a solution of BPE (16.3 g.) in chlorobenzene (685 cc.) was added a solution of 59.4 g. of aluminum bromide in 200 cc. of chlorobenzene. Immediately after mixing the two solutions, 300 cc. of water was added to quench the reaction. Heptane (1 l.) was added to facilitate the removal of the water layer; the organic layer was extracted twice with 400-cc. portions of 20% aqueous sodium hydroxide and dried. Removal of the heptane and chlorobenzene by distillation gave a reddish oily residue which yielded by fractional distillation 9.3 g. (44%) of a colorless liquid, b.p. 145–160° (2 mm.), $n^{25}\mathrm{D}$ 1.5930. This was shown to be **4,4′-dichlorodiphenylmethane** by oxidation with 4.6 g. of selenium dioxide for 45 min. at 200–210°.[20] The product (700 mg.) after crystallization from methanol, melted at 146.5–147°, and gave no depression when mixed with an authentic sample of 4,4′-dichlorobenzophenone.[8] The starting material recovered from oxidation (4.4 g.) was oxidized to the same ketone by chromic acid.

The combined aqueous alkali extracts were washed four times with 200-cc. portions of ether and dried. Evaporation of the ether gave 6.3 g. (39%) of a yellow oil which became colorless on fractional distillation, b.p. 145–160° (10–12 mm.), $n^{25}\mathrm{D}$ 1.5977. This was shown to be *o*-benzylphenol (III) by preparation of the phenylurethan, m.p. 120.5–121°, and the dibromo compound, m.p. 92–92.5°, and by mixed m.p.'s of these with the derivatives of an authentic sample of *o*-benzylphenol.[21]

The remaining aqueous alkaline layer was acidified with hydrochloric acid, extracted four times with 200-cc. portions of ether and dried. After the ether was removed, 3.15 g. of a residue was obtained which gave 2.5 g. (28.8%) of phenol by distillation, b.p. 181°. The remaining residue was found to contain some *o*-benzylphenol, identified as the dibromo and phenylurethan derivatives.

B. **Final Products.**—To a solution of BPE (16.3 g.) in chlorobenzene (685 cc.) was added a solution of 59.4 g. of aluminum bromide in 200 cc. of chlorobenzene. After 5.5 hours at room temperature, the contents were hydrolyzed with 300 cc. of water; hexane (500 cc.) was added to facilitate the removal of the water layer. The organic layer was extracted five times with Claisen alkali (100 cc. per extraction); the combined extractions were acidified with hydrochloric acid and extracted with ether. The combined ether extracts were dried, and after the solvent was removed, reddish crystals were obtained which distilled at 70° (10 mm.) to give 5.9 g. (62.5%) of phenol. The phenol was identified as the tribromo derivative which gave no melting point depression with an authentic sample.

The hexane–chlorobenzene layer was dried, and after the solvent was removed, a reddish oily residue was obtained and distilled, to give 18.06 g. of colorless oil, b.p. of pure liquid 131° (1–2 mm.), $n^{26}\mathrm{D}$ 1.5932, corresponding to 87% yield of mixed dichlorodiphenylmethanes. Elementary analysis showed chlorine and no bromine to be present.

Anal. Calcd. for $C_{13}H_{10}Cl_2$: C, 65.84; H, 4.25. Found: C, 65.90; H, 4.62.

The compound (2 g.) was oxidized to the mixed dichlorobenzophenones by heating with selenium dioxide at 210–230° for 45 min. After cooling, the solid mass was dissolved in ether and filtered to remove the selenium. Evaporation of the ether yielded a solid which was chromatographed on an activated alumina column. Elution with benzene removed a solid, m.p. 107–111°, from the column and four recrystallizations from hexane raised the m.p. to 121–122°. Enough sample was not available for additional recrystallization to obtain a constant m.p., however, the mixed m.p. with 3,3′-dichlorobenzophenone (m.p. 123–123.5°) gave no depression. Elution of the column with benzene–chloroform (50/50) removed the main product, which, on repeated recrystallizations from hexane, melted at 89.5–91°.

Anal. Calcd. for $C_{13}H_8OCl_2$: C, 62.18; H, 3.21. Found: C, 61.92; H, 3.02.

This material was shown to be a mixture of 3,3′- and 3,4′-dichlorobenzophenone by the following procedure.

The oxime of the mixture was prepared, and melted, after five recrystallizations from heptane, at 123–133°.

Anal. Calcd. for $C_{13}H_9Cl_2NO$: C, 58.63; H, 3.41. Found: C, 58.71; H, 3.48.

The oxime (450 mg.) was refluxed in 10 cc. of dry pyridine

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(12) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

(13) Hurd and Greengard, THIS JOURNAL, **52**, 3356 (1930); McCall and Tarbell, unpublished.

(14) Hantzsch and Freese, *Ber.*, **28**, 3237 (1895).

(15) Finzi and Bellavita, *Gazz. chim. ital.*, **62**, 699 (1932).

(16) Analyses by Miss Claire King; all melting points are corrected.

(17) Generously supplied by the Dow Chemical Company.

(18) Obtained from Westvaco Chlorine Products Corporation through the kindness of Mr. F. von Bergen.

(19) Harnish and Tarbell, *Anal. Chem.*, **21**, 968 (1949).

(20) Postowsky and Lugowkin, *Ber.*, **68**, 852 (1935).

(21) Prepared by the Claisen alkylation (Claisen, Kremers, Roth and Tietze, *Ann.*, **442**, 237 (1925); Huston, *et al.*, THIS JOURNAL, **55**, 2148 (1933)). Claisen reports the phenylurethan to melt at 117.5–118°, and Huston reports 90–91° as the m.p. for the dibromo compound.

containing 1.0 g. of benzenesulfonyl chloride for 15 min., and let stand 75 min. at room temperature. The mixture was poured into 62 cc. of 6 *N* sulfuric acid, and the mixture was extracted with ether; the extracts were dried, and the solvent was removed. A viscous residue was obtained and recrystallized twice from heptane to yield 150 mg. (33%) of amide, m.p. 95–101°.

The amide (150 mg.) was refluxed with 20 cc. of 10% sodium hydroxide for one hour, and the cooled solution was extracted with ether to remove the amine. Acidification of the alkaline solution precipitated a white solid which was collected, and, when recrystallized from an alcohol–water mixture, melted at 158°. The mixed m.p. with an authentic sample of *m*-chlorobenzoic acid gave no depression.

Ether extraction of the acid solution followed by evaporation of the ether gave a solid acid whose m.p., after two recrystallizations from an alcohol–water mixture, remained constant at 145–146°. Analysis showed this substance to be a monochlorobenzoic acid. The mixed m.p. with *o*-chlorobenzoic acid gave a depression while the mixed m.p. with either the *m*-isomer, the *p*-isomer or a mixture of the meta and para isomers gave no depression.

3,3′-Dichlorobenzophenone[4] was obtained by a Grignard reaction between *m*-bromochlorobenzene and *m*-chlorobenzonitrile in 75% yield; m.p. 123–123.5°.

3,4′-Dichlorobenzophenone was obtained by a Grignard reaction between *p*-bromochlorobenzene and *m*-chlorobenzonitrile in 70% yield, m.p. 112.5–113.5°.

Melting Point Diagram of 3,4′- and 3,3′-Dichlorobenzophenone.—Standard solutions of each of the above isomers were prepared by dissolving 100 mg. of solid in pentane and diluting the solutions to 50 cc. with pentane. Aliquots of each solution were mixed, evaporated to dryness and the melting points, listed below, were determined.

3,4′-Isomer, %	3,3′-Isomer, %	M.p., °C.
100	0	112.5-113.5
80	20	101-106
65	35	86.5-90
60	40	89-90
55	45	87-90
50	50	90.5-99
40	60	93-104
20	80	111-117
0	100	123-123.5

A mixture of 1.2 g. of the 3,4′-isomer and 0.8 g. of the 3,3′-isomer was recrystallized from 30 cc. of methanol to give 1.68 g. of solid, m.p. 90.5–91.5°.

The dichlorobenzophenone obtained by oxidation of the mixed dichlorodiphenylmethane was recrystallized from methanol and had a m.p. of 89.5–91°. The mixed m.p. with the above sample was 90.5–91.5°. Both samples gave identical infrared absorption curves, thus establishing the identity of the mixed dichlorobenzophenones.

The Reaction between Benzyl Bromide, Chlorobenzene and Aluminum Bromide. A. The Initial Products.—A solution of 25 g. of benzyl bromide in 100 g. of chlorobenzene was mixed at 25° with a solution of 3.9 g. of aluminum bromide in 65 g. of chlorobenzene. The reaction mixture was hydrolyzed immediately after mixing. The product was distilled and the following fractions were taken: (1) 8.7 g.; b.p. 153–156° (13 mm.), n^{25}_{D} 1.5858 (32%); (2) 5.8 g.; b.p. 175–195° (13 mm.), n^{25}_{D} 1.5920 (17%); (3) 4.8 g.; b.p. 230–245° (3 mm.), n^{25}_{D} 1.6123 (29%).

Fraction 1 (2.0 g.) was dissolved in 10 cc. of glacial acetic acid and 2.0 g. of chromic acid was added slowly. After one hour, the green solution was poured into 100 cc. of water. A solid which precipitated was collected by filtration, leaving a considerable portion of oil in the filtrate. After recrystallization of the solid from hexane, crystals were obtained which melted at 118–130°. The solid then was chromatographed on alumina; elution with benzene removed a fraction which, when recrystallized from hexane, melted at 145–146°. A mixed m.p. with an authentic sample of 4,4′-dichlorobenzophenone gave no depression.

In a second oxidation on fraction 1, the aqueous solution was allowed to remain overnight in a refrigerator. An oily mass of crystals were obtained by filtration of the aqueous solution. In this experiment no oil was observed in the filtrate. Recrystallization from hexane gave crystals which melted at 84–94°. Concentration of the mother liquor gave crystals which melted at 71–72°; recrystallization from pentane raised the melting point to 73–74°. The mixed melting point with an authentic sample of 4-chlorobenzophenone (m.p. 75.5°)[22] melted at 74–75.5°. Thus fraction 1 consisted mainly of 4-chlorodiphenylmethane with some 4,4′-dichlorodiphenylmethane.

Oxidation of fraction 2 employing the method described above gave crystals which, when recrystallized from hexane, melted at 145–146°. The mixed m.p. with an authentic sample of 4,4′-dichlorobenzophenone gave no depression.

Oxidation of fraction 3 with chromic acid gave a viscous oil which dissolved in hot methanol. Cooling yielded crystals, which, when recrystallized from a hexane–benzene mixture, melted at 197–198°.

Anal. Calcd. for $C_{20}H_{12}O_2Cl_2$: C, 67.62; H, 3.41; Cl, 19.97. Found: C, 67.88; H, 3.45; Cl, 19.64.

Fraction 3 is undoubtedly some isomer of a dichlorodibenzylbenzene. The yields given in the parenthesis are based on the identity of each fraction.

B. The Final Products.—The quantities of reactants were those given above. The reaction mixture was hydrolyzed at the end of four hours.[23] Distillation of the product gave 24.8 g. (72%) of a colorless liquid, b.p. 175–183° (15 mm.), n^{25}_{D} 1.5922.

Oxidation with chromic acid (as described above) gave crystals which, when recrystallized from hexane, melted at 89–90°. The mixed m.p. with the synthetic mixture of 3,4′- and 3,3′-dichlorobenzophenone gave no depression.

***p*-Benzylphenol** was prepared by Clemmensen reduction of *p*-hydroxybenzophenone,[24] and melted at 84°; the reported value is 84°.[25] Blank determinations showed that this phenol could be determined by the procedure used for *o*-benzylphenol. A rate run with aluminum bromide in chlorobenzene showed that phenol was formed, somewhat more rapidly than from *o*-benzylphenol; the first-order rate "constants" fell during the course of the reaction.

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[22] The reported m.p. is 75.5–76° (Kollarits and Merz, *Ber.*, **6**, 547 (1878)).

[23] The same products were isolated after ten minutes of reaction.

[24] Martin, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 164.

[25] Paterno, *Ber.*, **5**, 288 (1872).