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Photo-induced Reactions. III.[1),*1] The Synthesis of Biphenyls from Aromatic Bromo-Compounds

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Various bromobenzene derivatives were irradiated in benzene with a low-pressure mercury lamp. The corresponding biphenyl derivatives were formed as the main products. A mechanism for the reaction has been discussed.

In 1961, Wolf and Kharasch briefly reported that, when aromatic iodo-compounds were irradiated with ultraviolet light (2537 Å) in aromatic solvents, the corresponding biphenyl derivatives were obtained in synthetically useful yields.2) This reaction has since been applied to various iodo-compounds, including some aliphatic iodides. The primary reaction in the irradiation of iodo-compounds is now recognized to be a homolytic cleavage of the carbon-iodine bond.3-7) Such a homolytic cleavage also occurs in the photolysis of aromatic bromo-compounds.7-10) However, no synthetic applications have yet been undertaken.

We have carried out the photolysis of bromobenzene derivatives under conditions similar to those used by Wolf and Kharasch. When a 0.05 molar solution of bromobenzene in benzene was irradiated with a low-pressure mercury lamp (quartz) under bubbling nitrogen, biphenyl was obtained in a 40% yield, in addition to a non-volatile material which was assumed to be a mixture of polymers. Various bromobenzene derivatives were also photolyzed under the same conditions, and the products were either analyzed by vapor-phase chromatography or isolated. The results are summarized in Table I. In Experiments 1, 2, 5, 6, 7 and 10, the corresponding biphenyl derivatives were obtained in 30—40% yields, while *p*-bromoacetophenone (Exp. 9) gave 4-acetylbiphenyl in a lower yield. This is probably due to the presence of a carbonyl group which is photochemically reactive and which gives rise to side reactions.

The photolysis of *p*-bromoaniline (Exp. 8) and *m*- and *p*-bromonitrobenzene (Exps. 11 and 12) in benzene yielded no biphenyl derivative, but a large amount of the starting substance was recovered unchanged; also a small amount of a non-volatile material was formed.

The photolysis of *p*-bromophenol, *p*-bromoacetophenone and methyl *p*-bromobenzoate resulted in the reduction of the carbon-bromine bond, in addition to the formation of the corresponding biphenyls. Phenol, acetophenone, and methyl benzoate were respectively, detected in the reaction

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1) Part II: T. Matsuura, K. Omura and R. Nakashima, This Bulletin, **38**, 1358 (1965).

[*1] This work was presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

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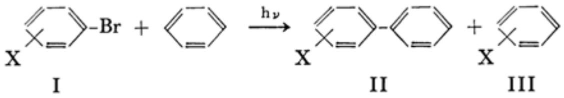
TABLE I. PHOTOLYSIS OF BROMOBENZENE DERIVATIVES IN BENZENE[a)]



Expt. No.	X in I	Irradiation period, hr.	Recovered I, %	Yield of II,[b)] %	Yield of III,[b)] %	Non-volatile products, g.
1	H	20	8	40	—	0.39
2[c)]	H	20	8	38	—	0.29
3[d)]	H	20	14	0.6	—	0.27
4[e)]	H	10.5	45	4.7	—	0.15
5	*p*-OH	22	39	31	10	0.44
6	*p*-OCH_3	40	9	37	—	0.39
7	*p*-CH_3	40	16	38	—	0.36
8	*p*-NH_2	40	57	—	—	0.16
9	*p*-$COCH_3$	20	5	23	8	0.98
10	*p*-$COOCH_3$	20	0	34	26	0.56
11	*p*-NO_2	24	73	—	—	0.08
12	*m*-NO_2	20	89	—	—	0.06

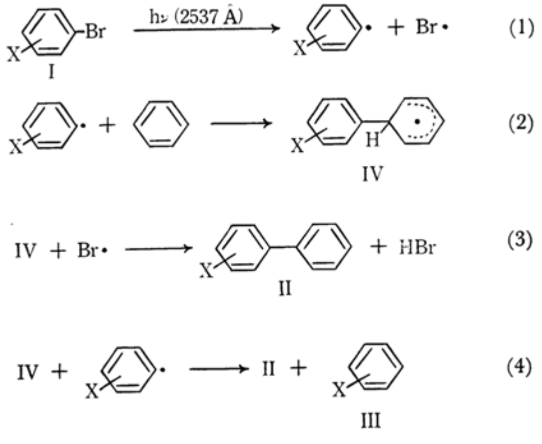
a) A solution of I (0.01 mol.) in benzene (200 ml.) was irradiated with a 40 W. low-pressure mercury lamp (quartz) under bubbling nitrogen, unless otherwise indicated.
b) Yields were based on the reacted I.
c) Irradiation was made with a 40 W. low-pressure mercury lamp (Vycor).
d) During irradiation oxygen was bubbled instead of nitrogen.
e) A solution of bromobenzene (0.02 mol.) in benzene (450 ml.) was irradiated with a 450 W. high-pressure mercury lamp with a pyrex jacket.

mixture. On the other hand, the corresponding reduction products could not be detected in the photolysis of bromobenzene, *p*-bromoanisole, or *p*-bromotoluene. In the case of bromobenzene the detection of benzene, which may be formed in the course of the reaction, is not possible. It is assumed that, in other cases, the corresponding reduction products might be formed in such small quantities that they could not be detected.

When the photolysis of bromobenzene in benzene was carried out with a low-pressure mercury lamp made of a Vycor tube in order to cut off short wavelength lights below about 220 mμ, biphenyl was obtained in a similar yield and the yield of the non-volatile products was slightly depressed. On the other hand, when the irradiation was made with a high-pressure mercury lamp using a pyrex filter which cut off lights below about 290 mμ, the reaction proceeded much more slowly and biphenyl was formed in only a small yield. The above results show that the reaction is initiated mainly by light near 2537 Å, which is known to be the most effective point of the light of a low-pressure mercury lamp.

A possible mechanism for the formation of biphenyls from bromobenzenes and benzene is shown by Eqs. 1—4.

The starting bromo-compound dissociates into a corresponding phenyl radical and a bromine atom by an ultraviolet light of 2537 Å (Eq. 1). The phenyl radical then attacks the solvent, benzene, to form a radical intermediate (IV) (Eq. 2). The last step of the reaction involves a hydrogen abstraction from the intermediate (IV) by either the bromine atom or the phenyl radical (Eqs. 3 and 4). Thus, a biphenyl derivative is formed simultaneously with the formation of a benzene derivative or hydrogen bromide respectively. This mechanism is supported by the findings that corresponding benzene derivatives were isolated in the photolysis of *p*-bromophenol (Exp. 5), *p*-bromoacetophenone (Exp. 9) and methyl *p*-bromobenzoate (Exp. 10), and that the liberation of hydrogen bromide was observed only when biphenyl derivatives were formed. In fact, hydrogen bromide was obtained in a 20% yield in the photolysis of bromobenzene in benzene.



Experimental

The melting points were determined in capillary tubes and were uncorrected. The infrared spectra were taken with a Nihon Bunko spectrophotometer, Model IR-S. The starting materials were commercially available, unless otherwise indicated, and their purities were checked by a melting point determination or by vapor-phase chromatography. The products were analyzed by vapor-phase chromatography under the following conditions: stationary phase, silicone DC 550 on celite; carrier gas, helium; gas pressure, 0.8 kg./cm^2.

The Photolysis of Bromobenzene.—Exp. 1.—A solution of 1.57 g. (0.01 mol.) of bromobenzene in 200 ml. of benzene was placed in a cylindrical vessel, into which a 40 W. low-pressure mercury lamp (quartz-made, unless otherwise indicated) was then inserted. During irradiation, a stream of nitrogen was bubbled through a sintered-glass disk jointed at the bottom of the vessel, which was cooled with tap water. The exhausted gas was then passed through ice-cooled water in order to trap the hydrogen bromide liberated from the reaction mixture. The aqueous solution was neutralized with 18.20 ml. of an aqueous 0.1 N sodium hydroxide solution. The yield of hydrogen bromide was calculated as 19.8% on the basis of the reacted bromobenzene. After being irradiated for 20 hr., the solvent was removed under reduced pressure and the residual liquid was distilled to yield 0.79 g. of a semi-solid, which boiled below 110°C/14 mmHg, and 0.39 g. of a non-volatile material. Vapor-phase chromatography of the semi-solid showed that it consisted of 0.13 g. (8.3%) of the starting material recovered, 0.57 g. (40%) of biphenyl, and 0.09 g. of an unknown product. The recrystallization of the semi-solid from methanol gave colorless crystals, m. p. 66—68°C, whose infrared spectrum was identical with that of an authentic sample of biphenyl.

Exp. 2.—Brombenzene was irradiated with a 40 W. low-pressure mercury lamp (Vycor), and the reaction mixture was treated in the way described in Exp. 1. The results are shown in Table I.

Exp. 3.—Bromobenzene was photolyzed as has been described in Exp. 1, except that the solution was bubbled with oxygen instead of nitrogen. The results are shown in Table I.

Exp. 4.—A solution of 3.14 g. (0.02 mol.) of bromobenzene in 450 ml. of benzene was irradiated for 10.5 hr. with a 450 W. high-pressure mercury lamp surrounded with a water-cooled pyrex jacket. The results are shown in Table I.

The Photolysis of *p*-Bromophenol (Exp. 5).—A solution of 1.73 g. of *p*-bromophenol in 200 ml. of benzene was photolyzed. The distillation of the products yielded three fractions; (i) 0.74 g. of a liquid, b. p. 40—78°C/28 mmHg, which was found by vapor-phase chromatography to consist of 0.68 g. of *p*-bromophenol and 0.06 g. of phenol; (ii) 0.33 g. of a solid, b. p. 90—110°C/16 mmHg, and (iii) 0.44 g. of a non-volatile material. The recrystallization of the fraction ii from benzene and cyclohexane gave 4-hydroxybiphenyl as crystals, m. p. 163—164°C. Lit. m. p. 163°C.[11]

The Photolysis of *p*-Bromoanisole (Exp. 6).—A solution of 1.88 g. of *p*-bromoanisole in 200 ml. of benzene was irradiated. The distillation of the products yielded three fractions: (i) 0.49 g. of a liquid, b. p. 30—70°C/6 mmHg, a preparative vapor phase chromatography of which, gave 0.16 g. of *p*-bromoanisole (ii) 0.64 g. of a solid, b. p. 72—105°C/6 mmHg, which showed only one peak in its vapor-phase chromatography and which was recrystallized from ethanol to give 4-methoxybiphenyl as colorless crystals, m. p. 86—87.5°C (lit. m. p. 89°C[12]), and (iii) 0.39 g. of a non-volatile material.

The Photolysis of *p*-Bromotoluene (Exp. 7).—A solution of 1.71 g. of *p*-bromotoluene in 200 ml. of benzene was irradiated. The distillation of the products yielded three fractions: (i) 0.32 g. of a liquid, b. p. 52—80°C/9 mmHg, which was found by vapor-phase chromatography to contain 0.27 g. of *p*-bromotoluene; (ii) 0.55 g. of a semi-solid, b. p. 82—102°C/9 mmHg, which was recrystallized from methanol to give 4-methylbiphenyl, m. p. 44—50°C (lit. m. p. 47.7°C[13]), and (iii) 0.36 g. of a non-volatile material.

The Photolysis of *p*-Bromoaniline (Exp. 8).—A solution of 1.73 g. of *p*-bromoaniline in 200 ml. of benzene was irradiated. During this irradiation brown materials were deposited on the surface of the lamp tube. The reaction mixture was then washed with an aqueous sodium hydroxide solution, dried over anhydrous sulfate, and evaporated. The distillation of the residual liquid yielded two fractions: (i) 0.99 g. of a solid, b. p. 90—106°C/15 mmHg, whose infrared spectrum was identical with that of *p*-bromoaniline, and (ii) 0.16 g. of a non-volatile material.

The Photolysis of *p*-Bromoacetophenone (Exp. 9).—A solution of 1.99 g. of *p*-bromoacetophenone in 200 ml. of benzene was irradiated. The distillation of the products yielded three fractions; (i) 0.24 g. of a semi-solid, which was found by vapor-phase chromatography to consist of 87 mg. of acetophenone and 105 mg. of *p*-bromoacetophenone; (ii) 0.44 g. of colorless crystals, which showed one peak in its vapor-phase chromatography and which were recrystallized from benzene and methanol to give 4-acetylbiphenyl as crystals, m. p. 119—121°C (lit. m. p. 120.5°C[14]), and (iii) 0.98 g. of a non-volatile material.

The Photolysis of Methyl *p*-Bromobenzoate (Exp. 10).—A solution of 1.50 g. (0.007 mol.) of the methyl ester[15] in 200 ml. of benzene was irradiated. The distillation of the products yielded three fractions: (i) 0.24 g. of a yellow liquid, whose infrared spectrum was identical with that of methyl benzoate; (ii) 0.52 g. of a solid, m. p. 98—114°C, which was recystallized from ethanol to give methyl *p*-phenylbenzoate as colorless crystals, m. p. 115—116°C (lit. m. p. 117.5°C[16]), and (iii) 0.56 g. of a non-volatile material.

The Photolysis of *p*-Bromonitrobenzene (Exp. 11).—A solution of 2.02 g. of *p*-bromonitrobenzene in 200 ml. of benzene was irradiated. The distillation of the products yielded two fractions: (i) 1.48 g. of crystals, b. p. below 66°C/ca. 1 mmHg and m. p. 117—123°C, which were recystallized from methanol to give

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[13] M. Gomberg and J. C. Pernert, *J. Am. Chem. Soc.*, **48**, 1372 (1926).

[14] H. C. Gull and E. E. Turner, *J. Chem. Soc.*, **1929**, 491.

[15] The ester was prepared by esterification of the parent acid with methanol and concentrated sulfuric acid, m. p. 77—79°C.

[16] W. Schlenk, *Ann.*, **368**, 295 (1909).

p-bromonitrobenzene as colorless crystals, m. p. 123—125°C, and (ii) 82 mg. of a non-volatile material.

The Photolysis of *m*-Bromonitrobenzene (Exp. 12).—A solution of 2.00 g. of *m*-bromonitrobenzene in 200 ml. of benzene was irradiated. The distillation of the products yielded two fractions: (i) 1.77 g. of colorless crystals, b. p. 87°C/7 mmHg and m. p. 52—56°C, whose infrared spectrum was identical with that of *m*-bromonitrobenzene, and (ii) 0.06 g. of a non-volatile material.