

Some Liquid Phase Photobrominations of Biphenyl

GARETH H. WILLIAMS, M. IQBAL BHANGER* AND ROGER BOLTON

**Chemistry Department, University of Baluchistan, Quetta, Pakistan.*

Department of Chemistry, Bedford College University of London London NW 1 England.

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Summary: Liquid phase photobromination of biphenyl (50-60°C) yields *o*-, *m*-, and *p*-bromobiphenyls, accompanying small amount of side-products, possibly adducts. The isomer distributions were measured by gas liquid chromatography. Unlike many heterolytic reactions, substitution at the meta-position takes place quite significantly. Tentative explanation for these findings are being communicated. Relative rates and partial rate factors for photobromination of biphenyl and bromobenzene were also derived. Results are discussed on the basis of the reactivity of biphenyl against the attacking bromine radicals. The validity of the competitive methods is also taken into consideration.

Electrophilic halogenation reactions of benzene derivatives have been extensively studied¹. These reactions occur rapidly in biphenyl than in benzen the major products being the para-substituted, although a little proportion of ortho-substituted products have also been formed. The electron withdrawing effect (-I) of the phenyl substituent is considered to have a deactivating influence on the meta-position.²

Reactions involving free radical halogenation of biphenyl are less investigated. They are different from electrophilic reactions in the sense that both the nuclear addition and the nuclear substitution products are formed. Kooyman and his coworkers^{3,4} have reported some gas phase and liquid phase chlorination reactions of biphenyls which resulted in the formation of monochlorobiphenyl and phenylhexachlorocyclohexane, respectively. There is, however, no work reported on the photochemical bromination of biphenyl. The present work is an extension of the photobromination of benzene derivatives⁵. Reaction between biphenyl and bromine in carbon tetra-chloride solution was performed, at 50-60°C, using U.V light as free radical initiator. Monobromobiphenyl and small quantities of dibromobiphenyls (ca. 3%) were formed along with some unidentified products, possibly adducts. In separate competition reactions approximate relative rates of bromination and partial rate factors of biphenyl were determined. The results suggested the following order of reactivity to bromine atom:

biphenyl > benzene > bromobenzene

Discussion

Orientation in the substitution of hydrogen by bromine: Table 1 shows the distribution ratios of monobromobiphenyl isomers, similar ratios from ionic bromination of biphenyl are also mentioned here, for comparison.

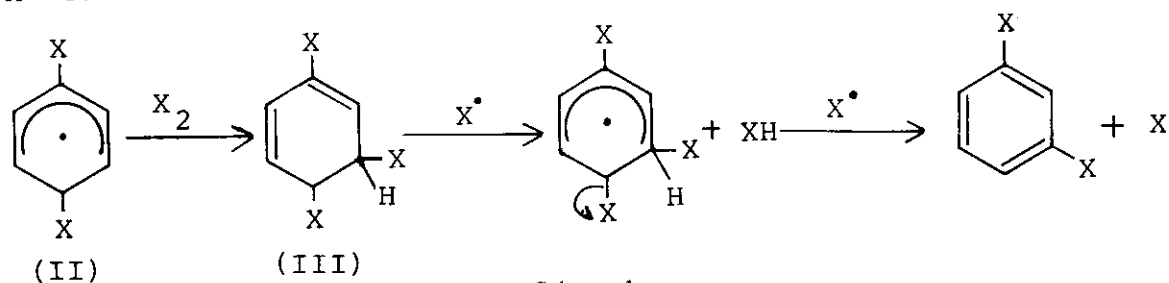
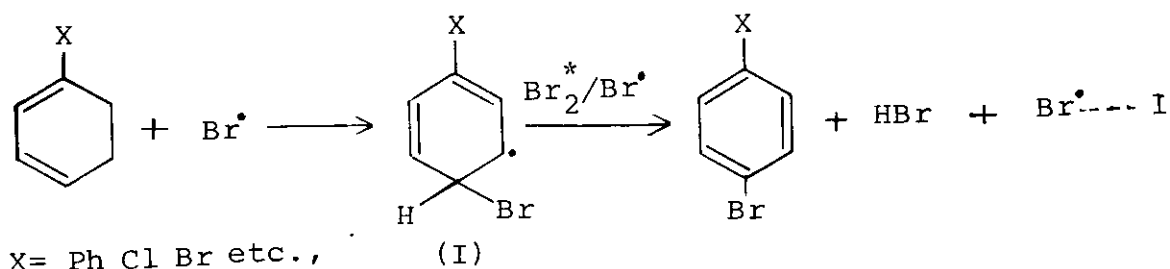
The above results reveal that significant amount of meta-isomer is formed in the photobromination. This position, as may be seen in Table 1, is usually deactivated in the heterolytic reactions. This effect was also pointed out by Kooyman⁸ in the gas phase halogenation of benzene derivatives where a greater proportion of meta-isomers were reported to be formed. Gouverneur and Soumillion⁹ also found significant amount of meta-bromochlorobenzene (> 60%) in the liquid phase photobromination of chlorobenzene. In such nuclear substitution reactions, there appears a parallelism between the results for gas phase and the liquid phase halogenation.

The origin of bromobiphenyls, here, requires, some discussion. The reaction conditions are conducive to free-radical mechanism, therefore, reactivity considerations, here, are similar to those usually applied in the ionic reactions. An addition-elimination mechanism may be proposed: The intermediate radical (I) loses hydrogen to another species, possibly bromine. This has obvious analogies to the heterolytic mechanism, and may favoured over the process in which bromine atoms bring about the aromatisation of the δ -complex under conditions where very low standing concentration of these atoms

*Present address: National Centre of Excellence in Analytical Chemistry, University of Sind, Jamshoro, Pakistan.

Table 1.

Process	Monobromobiphenyl %			Ref.
	o-	m-	p-	
Photobromination of biphenyl in carbontetrachloride solution	24	27	49	This work.
Bromination of biphenyl in 50% aqueous acetic acid.			~ 95	6
Acid catalysed bromination of biphenyl in 50% dioxane using hypobromous acid.	56.8	1.5	41.7	7



Scheme 1

occur. However, the second process in reaction (1) is endothermic by ca. 25 K. cal mole⁻¹, and so would be likely only when one or the other of the reagent molecules possessed this degree of excitation energy. As this is less than the energy needed to rupture the bond in the bromine molecule (46 K. cal mole⁻¹), the incidence of aromatisation in reaction (1) is thermodynamically likely, but only with bromine molecule possessing some degree of extra activation energy. This is represented in reaction (1) as Br₂^{*}.

Kooyman and coworkers⁸ suggested a one-step bimolecular mechanism involving an intermediate ion pair, ArHX₂⁻, to account for the nuclear substitution reactions in gas phase. Benson and coworkers¹⁰

proposed a free radical mechanism for such systems, involving cyclohexadienyl radical (II) and substituted cyclohexadiene (III) as intermediates. This is outlined in Scheme 1.

In the photobromination of biphenyl, the olefinic system like (II) so produced, would be relatively reactive to further addition leading to dihydrodibromoarene analogous to (III), rather than elimination. The relative extent to which bromine atom is found attached in bromobiphenyls, to the original site of attack, is determined by the relative rates of the two competing decompositions. The proposed mechanisms by Kooyman⁸ and Benson¹⁰, although for gas phase nuclear substitution, focus attention

upon similar aspects of molecular energetics, hence, they may be regarded as equivalent. The possibility of Benson's interpretation, which is substantiated by detailed kinetic analysis, means that the observed orientation of attack upon an arene may neither reflect nor simply parallel the relative extent to which bromine attack took place, for the formation of bromobiphenyl relies not only on this factor but also upon the various possible modes of decomposition of the dihydrodibromoarene (III). Substitution may not necessarily be preceded by addition; but when addition occurs, this may be reflected by the course of reaction.

Partial rate factors. The relative rates of photobromination of biphenyl and the partial rate factors were determined. The values are given in Table 2.

Table 2

Relative rate $\frac{\text{PhPh}}{\text{PhH}}$	Partial rate factors		
	F_{o-}	F_{m-}	F_{p-}
8.17	3.88	2.33	17.31

The limitations of these figures and the validity of the partial rate factors derived under these conditions are also discussed; it is unlikely that they may allow a simple interpretation. The relative rate of photobromination of bromobenzene with respect to biphenyl, and the partial rate factors were also determined. They were then converted into the relative rate with respect to benzene by making the following conversions.¹¹

$$\frac{\text{PhX}}{\text{PhH}} K = \frac{\text{PhX}}{\text{PhY}} K \cdot \frac{\text{PhX}}{\text{PhH}} K$$

where PhX and PhY represent the substituted benzenes. The results are given in Table 3.

Table 3

Relative rate $\frac{\text{PhBr}}{\text{PhH}} K$	Partial rate factors		
	F_{o-}	F_{m-}	F_{p-}
0.058	0.33	0.061	0.157

This shows a decrease in the rate of bromination of bromobenzene which is apparently deactivated by the bromo-substituent. Similarly, all the three nuclear positions are considerably less reactive, compared to biphenyl towards attack by bromine radical.

The validity of the partial rate factors for biphenyl is somewhat complicated owing to the fact that the exact mechanism, by which the isomeric monobromobiphenyls were formed, is not clearly established. The relative yields of say, *p*-bromobiphenyl and bromobenzene in a competition experiment with biphenyl - benzene may be linked, in principle, with the rate of attack by bromine upon a para-position in biphenyl compared to that upon a single position in benzene. But, there are number of assumptions involved in such an assertion. Apart from the reservation that the molecularity of the substitution process is same in each case, and that the step linking product formation with this substitution step are the same or proceed to the same extent whether competition occurs or not. There is, however, a certain possibility that there may be a variety of routes to any of the substitution product, and these may contribute to different extent in the presence of a competing process.

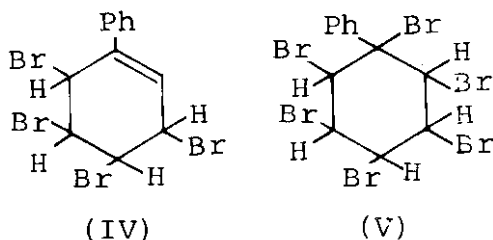
A comparison of the derived relative rates of reactions of biphenyl experimentally determined in the present work, with those derived under different conditions also present some interesting features. As shown in Table 4, the derived relative rate of photobromination is significantly higher than the corresponding relative rate for phenylation. This shows that the substrate biphenyl is more reactive towards bromine radical than towards phenyl radical which

Table 4

Process	$\frac{\text{PhPh}}{\text{PhH}} K$	Reference
Photobromination of biphenyl in carbon tetrachloride solution.	8.17	This work
Bromination of biphenyl in 50% aqueous acetic acid.	3.94×10^3	6
Homolytic phenylation of biphenyl with benzoyl peroxide.	2.94	12

is regarded as neutral or slightly nucleophilic in character¹². This is also consistent with the electrophilic behavior of bromine atoms. The relative rate of photobromination derived in the present work, is very much low from that reported for heterolytic bromination. This is because in the former case the reaction is of free radical in nature.

The above calculations determining the reactivity of bromine - biphenyl system, although an approximate evaluation, provide information on the liquid phase photochemical reactions of biphenyl. The formation of some side products, possibly adducts, tends to complicate the results. Of the total bromine consumed, in the photobromination of biphenyl in carbon tetrachloride solution, some bromine (ca. 25%) could not be accounted for. Therefore, it is assumed that some polybromo adducts eg. (IV) or (V) are formed. Any of these adducts could not be isolated and characterized, though the presence of these adducts could not be isolated and characterized, though the presence of some kind of adduct/s in the reaction product was inferred through chemical methods (see experimental).



Experimental

Photobromination of biphenyl in carbon tetrachloride solution at ca. 50-60°C. A mixture of bromine (16g, 0.1 mole) and biphenyl (77g, 0.5 mole) was dissolved in redistilled, dry carbon tetrachloride (500 ml). The mixture was irradiated with u.v. light for twelve hours. A 1L Hanovia low-pressure mercury arc lamp (pyrex glass) emitting u.v. light at 354 nm was used for this purpose. Free bromine (60×10^{-3} mole) and hydrogen bromide formed (30×10^{-3} mole) were estimated by titration methods¹³. The carbon tetrachloride solution was washed with water then sodium metabisulphite and finally with water again. After drying with anhydrous magnesium sulphate, excess of the solvent was evaporated by fractional distillation. Gas chromatography of the reaction product showed the presence of isomeric monobromobiphenyls (29×10^{-3} mole) together with minor quantities of a component which

has the same retention time as that for pure sample of 4,4'-dibromobiphenyl.

Attempt was made to identify the presence of an addition product e.g. tetrabromo-tetrahydrobiphenyl (IV) or hexabromo-hexahydrobiphenyl (V) in reaction product. Part of the carbon tetrachloride layer was removed from the mixture soon after the experiment was stopped. This was washed with 10% sodium metabisulphite, 20% sodium carbonate solutions and then with water, to remove the free bromine and hydrogen bromide. After drying the solvent was evaporated under reduced pressure. The residue was washed with petroleum ether (60-80°C) and divided into three portions.

The first portion was boiled in toluene for two hours. No benzyl bromide could be seen in the gas chromatograph. The same toluene solution was again refluxed with added benzoyl peroxide (0.24 g, 1 m. mole). Benzyl bromide was found to be present; this indicated the presence of some unidentified source of bromine radicals in this reaction. This was assumed to be some polybromo adduct.

The second portion was treated with alcoholic silver nitrate solution. Precipitates of silver bromide were formed which were soluble in ammonia and insoluble in nitric acid.

The third portion was hydrolysed with methanolic potassium hydroxide solution. This is analogous to the method reported earlier¹² for the hydrolysis of hexabromocyclohexane^{14,15}. Gas chromatography revealed the absence of any isomer of tribromobiphenyl which could result through the dehydrobromination of hexa bromo-adduct of biphenyl.

Photobromination of biphenyl in benzene and also in bromobenzene. The competitive reactions. To a solution of biphenyl (154 g, 1 mole) in redistilled, dry benzene (500 ml, 5.5 mole) was added bromine (16 g, 0.1 mole) and the contents were irradiated with U.V. light for twelve hours, at 50-60°C. The amount of hydrogen bromide formed and the bromine consumed were measured by the usual methods¹³. Gas chromatography showed the presence of bromobenzene (14×10^{-3} mole), dibromobenzene (7.0×10^{-3} mole) and isomeric monobromobiphenyls (27×10^{-3} mole). From these data the relative rate and the partial rate factors for biphenyl were approximately calculated. A solution of biphenyl (115.5g, 0.75 mole), bromobenzene

(437 ml, 4.12 mole) and bromine (16g, 0.1 mole) was subjected to the same treatment as above. Isomeric dibromobenzenes (3.8×10^{-3} mole) and monobromobiphenyls (40×10^{-3} mole) were formed. From this data the approximate relative rate of bromination and the partial rate factors were derived.

Materials

Authentic samples of pure isomeric dibromobenzenes, monobromobiphenyls and 4,4-dibromobiphenyl were obtained from Aldrich Chemicals. They were used without any further purification. Commercially available benzene, carbon tetrachloride, bromobenzene, bromine and biphenyl obtained from BDH Chemicals were used. All the reaction products were analysed on a Pye 104 gas chromatograph using 1% FFAP and 2% PEGA columns.

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