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Photolysis of Iodoaromatic Compounds in Benzene[1]

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The photolysis of a series of iodoaromatic compounds in dilute benzene solutions, with a low-pressure cold-cathode mercury lamp, gives synthetically useful yields of products wherein iodine in the substrate is replaced by phenyl. Rearrangements were not observed. In accord with earlier considerations, a free-radical mechanism accounts for the results. The quantum yield, Φ_{I_2}, for conversion of 4-iodobiphenyl to *p*-terphenyl was 0.08 ± 0.01. The best yield of *p*-terphenyl was 91%, but about 8% biphenyl was also found. The latter does not form by photolytic reaction of iodine with benzene, or of benzene alone, and must arise by reduction of the 4-iodobiphenyl. As expected, the photochemical reduction of the latter occurs readily in dilute cyclohexane solution. The syntheses of 3,5-diphenyl-4-hydroxybenzaldehyde and 2,4,6-triphenylphenol, from the corresponding iodo compounds, suggest the potentials of the reaction for converting polyiodophenols to polyphenylphenols. 2-Iodophenol was also readily converted to 2-phenylphenol in 60% yield. Iodine release in many of the reactions was essentially quantitative, but there were some notable exceptions. A preliminary study of the relative initial rates of iodine release from various substrates, irradiated in benzene solution, showed that 2-, 3-, and 4-iodonitrobenzenes are decidedly slower than, *e.g.*, 2-iodophenol or iodobenzene. This appears to be related to the incomplete photolysis of 4-iodonitrobenzene in the preparative reactions and to the low yield of 4-nitrobiphenyl obtained. The question of the fate of the hydrogen atom released in the substitution of the benzene is discussed briefly. A description of the photolysis lamp used in the general reaction is included.

Classical synthetic applications for organic iodine compounds have long been known.[2] Nevertheless, the ease with which diverse types of organic iodine compounds can be prepared and the inherent reactivity of iodine atoms bound to carbon suggest that further unique synthetic applications of these substances may yet be anticipated. The present study, which extends our earlier communications,[3,4] suggests new directions for synthetic and mechanistic studies with iodoaromatic compounds.

Few of the earlier studies concern the photolysis of iodoaromatic compounds. Using photochemical techniques, Job and Emschwiller[5] investigated the strengths of carbon–iodine bonds; Olaerts and Jungers[6] and Iredale and co-workers[7] reported on the quantum yields for iodine release from iodoaromatic compounds under various conditions; Razuvaev and co-workers[8] studied the photolysis of iodo compounds, *e.g.*, iodobenzene, in presence of organometallic compounds, such as diphenylmercury; and Gragerov has been concerned with the mechanism of the photolysis of iodobenzene, by studying photolyses in deuterated benzenes.[9] In several papers, Szychlinski[10] has also investigated the photochemically induced hydrogen transfer reactions between haloarenes and methanol solvent, wherein the aromatic halogen compound is reductively dehalogenated (ArX → ArH). Suggestions for the homolytic scissions of the aryl to iodine bonds have been made in the publications noted above and further references to related studies are included.

Closely related to the present study are those of Bryce-Smith and co-workers, who investigated the photolysis of iodobenzene in isopropylbenzene[11] and of pure iodobenzene in the liquid state,[12] using a modified Hanovia S-500 mercury vapor ultraviolet lamp. Under the conditions used, these reactions led to complex mixtures and were not adaptable to synthetic procedures in spite of attempts to avoid the complications encountered. These workers also postulated that the photolysis of iodobenzene occurs *via* phenyl

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[1] This study was supported by Grants G-19732 from the National Science Foundation and A-703 from the National Institutes of Health, and, in part, by a supporting grant from the Upjohn Co. This assistance is gratefully acknowledged.

[2] *Cf., e.g.*, A. Roedig, in Houben-Weyl, "Methoden der Organischen Chemie," Vol. 5/4, 4th Ed., Georg Thieme Verlag, Stuttgart, 1960, pp. 517–776.

[3] W. Wolf and N. Kharasch, *J. Org. Chem.*, **26**, 283 (1961).

[4] N. Kharasch, W. Wolf, T. Erpelding, P. G. Naylor, and L. Tokes, *Chem. Ind.* (London), 1720 (1962).

[5] A. Job and G. Emschwiller, *Compt. rend.*, **179**, 52 (1924).

[6] E. Olaerts and J. C. Jungers, *Discussions Faraday Soc.*, **2**, 222 (1947).

[7] R. A. Durie, T. Iredale, and A. H. Kingsbury, *Nature*, **164**, 786 (1949).

[8] See, for example, G. Z. Razuvaev and M. A. Shubenko, *Zh. Obshch. Khim.*, **21**, 1974 (1951); *Chem. Abstr.*, **46**, 3411 (1952).

[9] I. P. Gragerov and M. Y. Turkina, *Zh. Obshch. Khim.*, **33**, 1894 (1963), and earlier papers; for English translation, see *J. Gen. Chem.*, **33**, 1843 (1963).

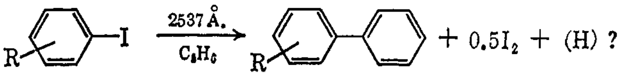
[10] J. Szychlinski and L. Litwin, *Roczniki Chem.*, **37**, 670 (1963).

[11] J. M. Blair, D. Bryce-Smith, and B. W. Pengilly, *J. Chem. Soc.*, 3174 (1959).

[12] J. M. Blair and D. Bryce-Smith, *ibid.*, 1788 (1960).

radicals and they compared the photochemically induced reactions of iodobenzene with analogous phenylation reactions involving the thermal decompositions of benzoyl peroxide.

In the present study we developed the photolysis of iodoaromatic compounds as a method of arylating benzene. The general reaction is shown in eq. 1.



(1)

While iodine is released in essentially quantitative amounts in several of the reactions, the fate of the hydrogen atom replaced by the phenyl group has not yet been established (see also below). The photolyses are carried out in dilute benzene solutions (*ca.* 0.01–0.05 *M*), using a low-pressure, cold-cathode mercury arc, housed in Vycor 7910 tubing, as described in the Experimental part. The selectivity and generality of reaction 1 are suggested by the examples of Table I. The conversions shown generally occurred cleanly, with little or no tar formation, although undesirable side reactions may occur, especially in cases such as photolysis of 2-iodotoluene or of 3,5-diiodo-4-hydroxybenzaldehyde. The quantum yield, Φ_{I_2}, for the photolysis of 4-iodobiphenyl in benzene was 0.08 ± 0.01. This substrate was selected as a typical example, with which we had considerable experience.

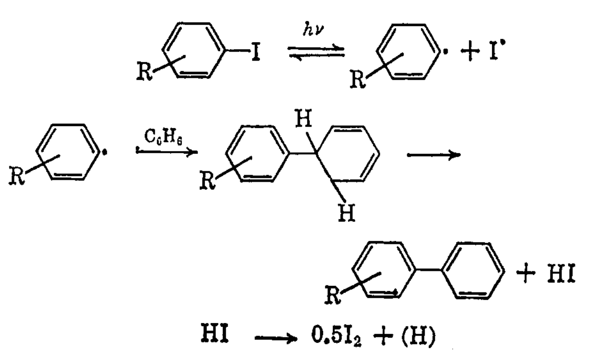
TABLE I

PHOTOLYSIS OF AROMATIC IODO COMPOUNDS IN BENZENE[a]

Substrate, *M*	% I_2 released[b]	Product isolated[c]	% yield
Iodobenzene, 0.03	98	Biphenyl	65
4-Iodobiphenyl, 0.02	100	*p*-Terphenyl	91[d]
Iodonaphthalene, 0.03	75	1-Phenylnaphthalene	50
2-Iodotoluene, 0.02	90[e]	2-Methylbiphenyl	13
3-Iodotoluene, 0.02	90[e]	3-Methylbiphenyl	50
4-Iodotoluene, 0.02	80[e]	4-Methylbiphenyl	75
2-Iodothiophene, 0.04	100	2-Thenylbenzene	70
2-Iodophenol, 0.01	100	2-Hydroxybiphenyl	60
4-Iodophenol, 0.05	100	4-Hydroxybiphenyl	60
3,5-Diiodo-4-hydroxybenzaldehyde, 0.02	100	3,5-Diphenyl-4-hydroxybenzaldehyde	25
2-Iodobenzoic acid, 0.02	100	2-Phenylbenzoic acid	73
4-Iodobenzoic acid, 0.03	100	4-Phenylbenzoic acid	80
4-Iodonitrobenzene,[a] 0.02	53	4-Nitrobiphenyl	..[f]
2-Iodoaniline, 0.01	60	2-Aminobiphenyl	20[g]
4-Iodoaniline, 0.02	75	4-Aminobiphenyl	38[g]
2,4,6-Triiodophenol, 0.015	100	2,4,6-Triphenylphenol[h]	75

[a] Photolyses were generally carried out for 24 hr. In the case of 4-iodonitrobenzene the photolysis period was 150 hr.; *cf.* also the Experimental part. [b] Measured at 5000 Å. in the Cary 14 spectrophotometer; estimated accuracy of the measurements, ±3%. [c] Identity of products was confirmed by melting point, mixture melting point, spectral analysis, and/or chromatographic means; *cf.* Experimental. [d] Biphenyl also found. Yields vary with oxygen content.[25] [e] Some interaction of the iodine with the substrates seemed to occur in these cases. These runs were made with the aid of L. Tokes. [f] The yield isolated was not determined in this case. [g] Isolated as the amine hydrochlorides. [h] Crude product, but of definite m.p. 140–141, raised to 147.5–149.5° by recrystallization from glacial acetic acid. Oxidation with $K_3Fe(CN)_6$ gave the 2,4,6-triphenylphenoxy radical in solution (*cf.* Experimental).

While studies of the mechanism of the reactions are still desirable, we agree with earlier workers[9,11] that the reaction proceeds *via* free radicals. A simplified formulation (eq. 2) may thus be kept in mind for visualizing the course of the reactions and for selecting further examples for study.



(2)

Since the appearance of our original communications,[3,4] other workers have also found this general technique of value. Plumb and Griffin[13] studied the photolysis of iodobenzene in the presence of phosphines to yield quaternary phosphonium compounds; Nickon and Aronoff[14] synthesized phenylated xylenols from iodophenol precursors; Badger and Whittles[15] photolyzed iodonaphthalene, in molten naphthalene, to obtain binaphthyls; Hutchinson, Hudson, and Doss[16] photolyzed iodobiphenyls in biphenyl, at 80°, in a study of the relative rate factors for the arylation of biphenyl; and Kupchan[17] has achieved the unique syntheses of pharmaceutically interesting phenanthrene derivatives by photolysis of appropriately substituted 2-iodostilbenes. Further work in this laboratory has been directed to finding new examples of the general reaction, involving other iodoaromatic compounds, as well as aliphatic derivatives as IC≡N, ICH_2COOH, ArC≡CI, ArC(O)I, etc.[18]; to studies of the isomer distribution ratios in phenylations of aromatic solvents[19]; and to hydrogen transfer reactions involving iodoarenes under photolytic conditions,[20] in the general conversion ArI → ArH.

The presence of iodine in the photolysate could retard the decomposition of the iodo compound, either by competitive absorption of radiation and/or by reversing the homolytic scission of the iodoaromatic compound as indicated in eq. 2. A quantitative study of such effects and of the stoichiometry of the reaction is now in progress.[21,22] Because of such possible effects of iodine, dilute solutions (0.01–0.05 *M*) were used in the synthetic procedures. Attempts to remove the released iodine by adding finely divided metals to the

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[13] J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, **27**, 4711 (1962); *cf.* also C. E. Griffin and K. R. Martin, *Chem. Commun.* (London), **1**, 154, (1965).

[14] A. Nickon and B. R. Aronoff, *J. Org. Chem.*, **27**, 3379 (1962).

[15] G. M. Badger and C. P. Whittles, *Australian J. Chem.*, **16**, 440 (1963).

[16] W. M. Hutchinson, P. S. Hudson, and R. C. Doss, *J. Am. Chem. Soc.*, **85**, 3358 (1963).

[17] S. M. Kupchan and H. C. Wormser, *Tetrahedron Letters*, **No. 6**, 359 (1965).

[18] N. Kharasch and L. Göthlich, *Angew. Chem.*, **74**, 651 (1962).

[19] N. Kharasch and P. G. Naylor, unpublished work.

[20] N. Kharasch and P. Friedman, Abstracts of Papers, Organic Chemistry Division, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 27S.

[21] The reversibility of the photochemical decomposition of 2-iodobiphenyl in benzene solution, under the conditions of the present study, has been demonstrated in a separate study in this laboratory (N. Kharasch and W. Wolf); using iodine-131 it was readily demonstrated that incorporation of the radioactive iodine into the iodoarene occurs rapidly on irradiation.

[22] For a discussion of the trapping of thermally generated phenyl radicals by iodine, *cf.* J. F. Garst and R. S. Cole, *Tetrahedron Letters*, **No. 11**, 679 (1963).

photolysis mixture were not promising (compare ref. 11). Rigorous removal of oxygen from the reaction mixtures was not made in the general procedures. The possible effects of residual oxygen are noted in a later section; for synthetic purposes oxygen may be desirable as a hydrogen scavenger.

The products shown in Table I contain the phenyl groups in the positions originally occupied by iodine in the substrates. It may thus be concluded that the reactions proceed without rearrangements and that the conversions of eq. 1 may be used to assign structures to new phenylated products on the basis of the known structures of iodo precursors. With the exception of 3,5-diphenyl-4-hydroxybenzaldehyde, whose structure was established unequivocally by analysis and infrared and n.m.r. spectra, the products of Table I are all known compounds and their identities were confirmed by superposition of properties with recorded values.

The photolysis of 4-iodonitrobenzene was incomplete even after 150 hr. of irradiation in the usual way. A preliminary investigation of the initial rates of iodine release, in benzene solution for the 2-, 3-, and 4-iodonitrobenzenes, compared with other substrates, showed that the release of iodine from the iodonitrobenzenes was slower and was not complete even on extended irradiation. While further studies are required to establish these differences more fully and to rationalize them on structural grounds, the behavior of the iodonitroaromatic compounds is markedly different from other cases and this must be taken into account in the synthetic work.

The yield of 2-methylbiphenyl, from photolysis of 2-iodotoluene in benzene, was also quite low (13%). Several side reactions, which were not investigated, appear to occur in this case. In contrast, the yields of the *meta* and *para* isomers were more attractive, 50 and 75%, respectively. A more complete study of the photolyses of the 2-iodotoluenes, and of other iodoalkylbenzenes, is thus indicated. 3,5-Diphenyl-4-hydroxybenzaldehyde could be obtained in a best yield of only 25.5%. In part, this appears ascribable to difficulties in isolating the product in pure form; however, by photolysis of the aldehyde itself, in benzene, losses were sustained which suggest that this aldehyde is not fully stable to the reaction conditions.

The question of whether iodine interacts with benzene under the photolytic conditions, leading to iodobenzene and hence to biphenyl, required examination in view of Ivanoff's report[23] that iodobenzene is formed in the photolysis of 1-iodopropane in benzene. While the conditions employed by Ivanoff were not stated explicitly, experiments, under our conditions, both in iodopropane–benzene photolysis and in the photolysis of dilute iodine solutions in benzene showed that only traces of iodobenzene and of biphenyl arise by this route in our work.

Besides the observations of earlier workers and those made in the present study, certain current extensions of the present work support a free-radical mechanism for the reactions of eq. 1: (1) Ingalls, Wolf, and Kharasch have obtained initial evidence for the formation of phenyl radical in the photolyses of iodobenzene in hydrocarbon melts, or in fluorocarbon melts, at 77°K.[24]; (2) a study of the isomer distribution ratios obtained for phenylations by photolysis of iodobenzene in substituted aromatic solvents is in excellent agreement with the isomer distribution ratios reported for similar phenylations involving thermally generated phenyl radicals from benzoyl peroxides[19]; and (3) the easy H transfer reaction demonstrated in the present study in the photolysis of 4-iodobiphenyl in cyclohexane, yielding 90% biphenyl, has been usefully extended[20] as a general method for the reductive deiodination of aromatic iodo compounds, using methanol, and the interpretations of the reactions are based on free-radical scissions of the carbon–iodine bonds in the iodoaromatic substances.

The fate of the hydrogen atom replaced in the substitution reactions (eq. 1) is also of interest. While this has not been elucidated as yet, certain observations made in this study are pertinent. In the case of photolysis of 4-iodobiphenyl, in benzene (Table I) there is formed, besides the high yield of *p*-terphenyl, biphenyl in yields of about 8%. A reasonable explanation for the formation of the biphenyl is that it results by means of a hydrogen transfer reaction from the intermediate xenylcyclohexadienyl radical (R = *p*-phenyl, eq. 2). Thus, the xenyl radical may compete with iodine or possibly with residual oxygen in the necessary removal of the H atom to form the *p*-terphenyl in this case.[25] The extent to which such reductive H transfers from the intermediate arylcyclohexadienyl radicals may occur with other substrates has not, however, been determined as yet. The possibility that hydrogen iodide is the active reducing agent must also be considered.

The above hydrogen transfer process can account for only a fraction of the displaced hydrogen. That some hydrogen may be present as hydrogen iodide after complete photolysis seems unlikely since iodine was found quantitatively in several cases. Some hydrogen may also unite with oxygen, and the possibility that dihydrobiphenyls and tetrahydroquaterphenyls may be present has also not been excluded. Such products were not found, although complete product balances must still be made.[26] The possibility that molecular hydrogen is formed in the photolyses was investigated in only one experiment, but no evolved hydrogen was found.

In conclusion, it may be noted that Cadogan[27] has reported an alternate synthesis of certain biphenyls by diazotizing aromatic amines in benzene solution with pentyl nitrite. This synthesis is attractive and should supplement, or in some cases supplant, the procedure used in the present study. Succeeding papers of this series will concern further synthetic and mechanistic aspects of the photolysis of iodo com-

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[23] N. Ivanoff, *Compt. rend.*, **239**, 806 (1954).

[24] R. B. Ingalls, W. Wolf, and N. Kharasch, Abstracts of Papers, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 6D.

[25] In current work, N. Kharasch and R. K. Sharma found that the extent of biphenyl formation in the photolysis of 4-iodobiphenyl, in experiments where oxygen removal is improved by freezing techniques, is measurably greater than the conversions (*ca.* 8%) where such precautions are not taken, *e.g.*, up to 30%, based on amount of 4-iodobiphenyl converted.

[26] In the photolysis of 4-iodobiphenyl in benzene, in presence of excess oxygen, 4-hydroxybiphenyl was found as one of the products; product balances for *p*-terphenyl and biphenyl, in usual photolyses in benzene, showed that only a few per cent of products are unaccounted for (N. Kharasch and R. K. Sharma, unpublished work).

[27] J. I. G. Cadogan, *J. Chem. Soc.*, 4257 (1962).

pounds. Of particular interest is the question of the energy-transfer process for photolyses of iodoaromatic compounds in benzene solution. Recent papers pertinent to this aspect include those of Morrison,[28] Wilkinson,[29] and others,[30] which suggest the importance of benzene as a sensitizer for photochemical reactions. In view of such suggestions and Wilkinson's study of the photolysis of 1-iodonaphthalene in benzene solution, similar considerations appear to apply in the present study. It is interesting to note that the value found for Φ_{I_2} by Wilkinson, at 3130 Å. for 1-iodonaphthalene, agrees with our value for 4-iodobiphenyl using the lamp of Figure 1. Further studies of the effects of iodine concentration on quantum yields and determinations of quantum yields in presence of other sensitizers are in progress.

Experimental

Light Sources.—The lamps used were modifications of the general low-pressure, cold-cathode type,[31] built to our specifications by Mr. Paul Dallons. A diagram of the typical lamp used for the synthetic work is shown in Figure 1. A short tube made of Vycor 7910 glass is surrounded by the reaction vessel; the cooling coil through the radiation tube is optional and is not critical to general operation. Tungsten electrodes allow current input to the mercury pool electrodes, which are conveniently cooled by water jackets. For alternating current operation, the arc was filled with argon at 1-mm. pressure, thus allowing the use of a conventional fluorescent tube ballast transformer. Under these conditions, with a tube of 15-mm. o.d. and a light path of about 12 cm., operating wattages of up to 200 w. could be obtained. The capacity of the reaction vessel was 150–175 ml. and connections could be made to vacuum pumps, gas inlets, etc., through the standard taper outlet. Several variations in design of these lamps were also made; an upright model, with large, well-cooled electrodes and a larger capacity vessel, was used for many of the earlier runs. While the performance of each lamp of a specific design varies somewhat, this was not found to be critical for preparative work with lamps in normal operating condition, judged for normal brightness visually. Thorough cleaning of the lamps, to remove film deposits on the illuminating surface is important from run to run. Rinsing with acetone, followed by rapid rinsing with *ca.* 10% aqueous hydrofluoric acid solutions, suffices generally; somewhat more concentrated hydrofluoric acid was used occasionally.

To determine the light output of the lamps, a nonjacketed lamp of the design of Figure 1 was inserted in a Cary ultraviolet spectrophotometer Model 14, as specified in the manufacturer's manual for mercury lamp calibrations, and the region from 2200–4500 Å. was scanned. The results are shown in Table II, from which is seen that in the higher energy region no radiation, particularly none at the 1849-Å. line, was detected. In silica-housed lamps, the latter wave length, which initiates formation of ozone, is transmitted, but it is completely filtered out by the Vycor envelopes of the lamp used in this study. These lamps may thus be used in the open laboratory, whereas quartz lamps must be used in a suitable hood. Protection against the ultraviolet glare was provided by a cardboard shield. Results for use of silica-housed lamps were not obtained in the present study.

TABLE II

RELATIVE EMISSION INTENSITIES OF A TYPICAL LAMP USED IN THIS STUDY

Wave length, Å.	Light emitted between 2200–4500 Å %	Light emitted between 2400–3400 Å %
2537	49	95
3125 + 3131	3	5
3651	12	..
4046	14	..
4358	22	..

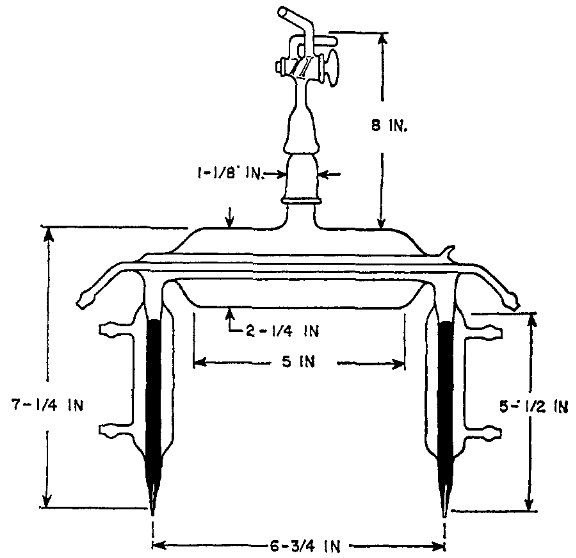

Figure 1.—Low-pressure, cold-cathode mercury arc, made of Vycor 7910 glass, with tungsten electrodes, used for irradiations in the study (about $^1/_5$ actual size); *cf.* text for details.

The total output of a typical lamp used in this work was determined by filling it with ethyl iodide, whose quantum yield (Φ_{I_2} = 0.13) had been determined accurately.[32] The iodine release, measured spectrophotometrically after 10- and 60-min. radiation, was 40.5 and 238 mg., respectively. From Φ_{I_2} = 0.13 = moles of I_2 released/moles of photons absorbed, the effective output (light emitted by lamp, which is capable of photolyzing iodo compounds) is 1.2×10^{18} photons/sec. or 7.2×10^{-3} einstein/hr. in the lamp tested.

Starting Materials.—The iodine compounds were purchased and purified as required, or synthesized by known procedures. The alumina for column chromatographic separations was Merck chromatographic grade, used directly as supplied.

Gas Chromatography.—These analyses were first made with a Perkin-Elmer 154 C unit, with thermal conductivity detector, using 0.25-in. columns with Apiezon-L and SE 30 coatings. In later work, an Aerograph 600 with a flame-ionization detector, was employed, using $^1/_8$-in. columns with similar coatings. Quantitative measurements were made with a Texas recorder (Servo-Riter Model) of 1-mv. scale, with a disk integrator, using calibration curves for the known components.

Relative Initial Rates of Iodine Release in Benzene.—These rates were measured by irradiating identical solutions (0.03 *M*) of the respective iodo compounds, in benzene, using silica cells which were symmetrically placed around a small central source of light of the same spectral characteristics as the larger lamps used. The cells were removed briefly at 9-min. intervals and the iodine release was measured in a Beckman D.U. spectrophotometer at 5000 Å. The curves were linear through 45-min. irradiation. The following relative rates for iodine release are based on the relative slopes: iodobenzene (1.0); 4-iodobiphenyl; 1-iodonaphthalene, 4-iodophenol, 4-iodotoluene (all 1.0); 2-iodonitrobenzene (0.31); 3-iodonitrobenzene (0.27); 4-iodonitrobenzene (0.24).

***p*-Terphenyl and Other Polyaryls.**—The preparation of *p*-terphenyl illustrates the general procedure. A solution of 1 g. of 4-iodobiphenyl in 200 ml. of pure, dry benzene was placed in the irradiation vessel, oxygen was purged at the water pump, and the solution was irradiated 20 hr. The temperature of the solution never exceeded 60°. The reaction solution was cooled to room temperature, transferred to a volumetric flask, and readjusted to 200 ml. by adding a few milliliters of pure benzene,

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[28] H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965).

[29] F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962).

[30] *Cf., e.g.,* references cited in *Ann. Rept. Progr. Chem*: (Chem. Soc. London), **60**, 89 (1963).

[31] L. J. Heidt and H. B. Boyles, *J. Am. Chem. Soc.*, **73**, 5728 (1951).

[32] (a) E. L. Cochran, W. H. Hamill, and R. R. Williams, Jr., *ibid.*, **76**, 2145 (1954); (b) D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **78**, 6228 (1956).

using the solvent first ro rinse the lamp reservoir. An aliquot of this solution was measured at 5000 Å., indicating a total of 456 mg. of iodine released; theoretical yield 454 mg. The walls of the reaction vessel were covered by a very thin film of a dark green product, insoluble in benzene and many other organic and inorganic solvents, and resistant to cleaning mixture (H_2SO_4–CrO_3). The nature of this film has not been determined, but its total weight is of the order of 20 mg. or less. The film was easily removed by rinsing with 5% hydrofluoric acid solution. The benzene solution, containing the free iodine and other products, was transferred to a separatory funnel; the iodine was removed with 5% sodium bisulfite solution, and the benzene layer was washed and dried over magnesium sulfate. The slightly colored benzene solution was then decolorized by passage through an alumina column, the solvent was distilled, and the residue was recrystallized, giving 750 mg., 91%, of *p*-terphenyl, m.p. 201–202°, raised to 205° by rechromatographing. The product did not depress the melting point of authentic *p*-terphenyl (m.p. 205°).

In several repetitions of this preparation, 80–90% yields were obtained. The formation of *ca.* 8% biphenyl was also noted.[25] Similar procedures as above also gave biphenyl (65%, from iodobenzene), 1-phenylnaphthalene (50%, from 1-iodonaphthalene), and 2-thenylbenzene (75%, from 2-iodothiophene). The infrared spectra of the products and the melting points agreed with authentic samples.

4-Methylbiphenyl.—*p*-Iodotoluene (1.03 g.) in 250 ml. of benzene was photolyzed 18 hr., giving 90% iodine release, measured spectroscopically at 5000 Å. The reaction mixture was washed twice with 5% sodium bisulfite solution, then well with water, dried over anhydrous sodium sulfate, and passed through a 1.5-cm. column containing 15 g. of alumina. Benzene was slowly distilled at atmospheric pressure, through a fractionating column, and the residue was fractionated from methanol, giving 0.18 g. (m.p. 47°) and 0.42 g. (m.p. 42–45°), lit.[33] m.p. 47–48°, total yield 74%.

3-Methylbiphenyl.—As above, 1.03 g. of 3-iodotoluene gave 0.45 g. of crude 3-methylbiphenyl, as an oil. The infrared spectrum and conversion with aqueous permanganate to 3-phenylbenzoic acid (0.31 g., 58%, m.p. 161°, lit.[34] m.p. 161°) confirmed the identity of the product. Two minor components were in the oil (*ca.* 5%, based on peak areas); the yield of product, corrected for the impurities, was 49%. A repeat run gave 50%.

2-Methylbiphenyl.—As above, irradiation of 2-iodotoluene also gave an oil, 0.12 g., whose identity as 2-methylbiphenyl was established by infrared analysis and retention time in gas chromatography. The product contained two small unidentified peaks, whose area was 15% of the total peak areas. The yield of 2-methylbiphenyl (judged on 85% purity) was 13%. Repetition of the reaction gave 18% of similar product.

2- and 4-Hydroxybiphenyls.—The preparation of 2-hydroxybiphenyl in 60% yield was previously recorded in detail.[3] A similar procedure with 4-iodophenol gave 60% 4-hydroxybiphenyl, identified by melting point and infrared analysis.

3,5-Diphenyl-4-hydroxybenzaldehyde.—3,5-Diiodo-4-hydroxybenzaldehyde (1.5 g.), m.p. 198–199°, was irradiated in 240 ml. of benzene for 22 hr. Complete solution of the substrate occurred only as the photolysis proceeded; 28% of the theoretical iodine release was found. The benzene solution was washed twice with 5% sodium bisulfite and three times with 25-ml. portions of water, then dried over anhydrous magnesium sulfate. The benzene was removed at room temperature with a Rotovac, leaving a black residue. The latter was dissolved in *ca.* 25 ml. of hot ethanol and charcoaled hot, and the mixture was filtered. Evaporation of the solvent left a yellow solid and dark green oil. The solid was separated, dissolved in concentrated aqueous ammonia and reprecipitated with concentrated hydrochloric acid (fraction 1). A yellow green residue, m.p. 100–152°, insoluble in concentrated ammonia, remained, but about half of it dissolved in 5% sodium hydroxide solution. Reprecipitation of the latter with concentrated hydrochloric acid gave fraction 2. The crude fractions were combined and recrystallized from hot 95% ethanol, to which just enough water was added to induce precipitation. Two crops of crystals were obtained (230 mg. of colorless needles, m.p. 166–168°, and 50 mg., m.p. 159–164°): total yield, 25.5%. The analytical sample, m.p. 168°, was obtained by recrystallization from hot aqueous ethanol, as above.

Anal. Calcd.: C, 83.21; H, 5.11. Found: C, 82.93; H, 4.97.

The product gave a positive test (crystalline product, m.p. 224–225°) on treatment with 2,4-dinitrophenylhydrazine reagent. The infrared spectrum (KBr pellet) showed expected absorptions for hydroxyl and carbonyl groups. The n.m.r. spectrum clearly showed the presence of four different kinds of hydrogen atoms in the expected ratios 1:2:10:1. The two nuclear hydrogens were not split, showing their identity in accord with the assigned structure.[35]

In the above preparations, treatment of 3,5-diphenyl-4-hydroxybenzaldehyde with concentrated ammonia appeared to cause decompositions. An attempt to purify the product by omitting the solubilization with ammonia, however, gave only 21% of product. In separate preparations, by essentially the same procedure as above, with ammonia solubilization, yields ranging from 20–30% were obtained.

2-Phenylbenzoic Acid.—2-Iodobenzoic acid (843 mg.) in 170 ml. benzene (0.02 *M*) was irradiated 24 hr. Iodine release in two separate runs was 100 and 94%, respectively. The photolysates were combined, solvent was evaporated, and the oily residue was dissolved in a minimum volume of 95% ethanol. The solution was decolorized by adding 5% aqueous sodium bisulfite and a few drops of hydrochloric acid. On standing and evaporation of the solvent, the crude product precipitated (980 mg., 73%, m.p. 97–104°). Repetition of the preparation gave 85% of the crude acid. The melting point was raised to 113–114°, with some difficulty, from aqueous methanol. The product was identical, melting point and mixture melting point, with that prepared by reaction of fluorenone with potassium hydroxide.

4-Phenylbenzoic Acid.—Irradiation of 1.5 g. of 4-iodobenzoic acid in 200 ml. of benzene (0.03 *M*) gave 100% of the calculated iodine release in 24 hr. Similar treatment, as above, gave 80% 4-phenylbenzoic acid, m.p. 216–218°,[34] whose identity was also confirmed by infrared and ultraviolet spectra.

4-Nitrobiphenyl.—4-Iodonitrobenzene (1 g.) in 170 ml. of benzene (0.024 *M*) was irradiated 150 hr. Iodine release was 53 and 51%, in two separate runs. Because of difficulties in the crystallization of the product, the per cent yield was not determined by isolation; however, 4-nitrobiphenyl, m.p. 113–114°, was isolated and characterized by the infrared spectrum. In the second run (51% iodine release), the 4-nitrobiphenyl content was determined by gas chromatography against a calibration curve for a sample of authentic 4-nitrobiphenyl, showing the presence of 43 ± *ca.* 5% of product. The retention times of the product in the mixture and of the known material were identical on a 6-ft. 1% S.E.-30 on 60–80 glass beads column. Gas chromatographic analysis similarly indicated 63 ± *ca.* 5% of unreacted 4-iodonitrobenzene.

2- and 4-Aminobiphenyl.—Irradiation of 0.4 g. of 2-iodoaniline in 170 ml. of benzene (0.01 *M*) for 24 hr. showed 60% iodine release. The mixture was filtered and the product precipitated as the amine hydrochloride by passing dry hydrogen chloride into the benzene filtrate. The salt was crystallized from methanol containing a little water and the 2-aminobiphenyl was released by adding 5% sodium hydroxide solution. The crude amine, 63 mg., 20% yield, melted at 53–55°. Similar photolysis, as above, of a 0.02 *M* solution of 4-iodoaniline in 170 ml. of benzene gave 75% iodine release. The yield of 4-aminobiphenyl, based on amine hydrochloride precipitated, was 38%.

2,4,6-Triphenylphenol.—Irradiation of 2.0 g. of 2,4,6-triiodophenol in 285 ml. of benzene (0.015 *M*) for 24 hr. released 1.65 g. (100%) of iodine, estimated spectroscopically and calculated for release of all three iodine atoms. The benzene solution was decolorized with 5% sodium bisulfite and dried over magnesium sulfate. Evaporation of the benzene left a yellow oil, which crystallized from glacial acetic acid, giving 1.6 g., 75%, of crude product, but of definite m.p. 140–141°. In methanol solution, this showed a maximum absorption at 2465 Å. and a minimum at 2278 Å. Oxidation of the phenol with potassium ferricyanide, as described by Dimroth and co-workers,[36] gave an orange-red color containing the 2,4,6-triphenylphenoxy radical,

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[33] F. K. Beilstein, "Handbuch der organischen Chemie," IVth Ed., V, H, p. 597.

[34] See ref. 33, IVth Ed., IX, p. 671.

[35] We are indebted to Dr. Lawrence Piette, of Varian Associates, Inc., for this spectrum and its interpretation. Confirmatory n.m.r. spectra on another sample were made by J. Gajewski.

[36] K. Dimroth, F. Falk, and K. Schlömer, *Ann.*, **624**, 51 (1959).

with absorption maxima, in benzene solution, at 5230, 2830, and 3450 Å., and at 5270 and 3750 Å. in carbon disulfide solution.

In another run, 1 g. of the triiodophenol in 170 ml. of benzene gave 99% of the calculated iodine release after 11 hr. of irradiation. Intermittent gas chromatographic analysis at 2, 3, 5, 7, and 9 hr. showed several major peaks, which diminished progressively with continued irradiation. None of the original triiodophenol was present after only 2 hr. of irradiation. The iodine in the photolysate was discharged with 5% sodium bisulfite solution, the benzene was evaporated, and the residue was recrystallized from glacial acetic acid, giving 76 mg. (19%) of colorless 2,4,6-triphenylphenol, m.p. 147–149.5°, lit.[30] m.p. 149–150°. A small amount of white solid, melting above 200°, was also noted.

Photolysis of 4-Iodobiphenyl in Cyclohexane.—Photolysis of 1 g. of 4-iodobiphenyl in 250 ml. of cyclohexane (reagent grade) gave rapid iodine release. After 24 hr., the reaction mixture was decolorized by treatment with aqueous sodium thiosulfate solution. The cyclohexane solution was filtered and dried over magnesium sulfate, and the reaction mixture was chromatographed on alumina, using hexane–benzene for elution, giving 494 mg. (90%) of biphenyl, m.p. 69°, not depressed on admixture with authentic biphenyl.

Photolysis of Pure Benzene and of a Dilute Solution of Iodine in Benzene. A.—Irradiation of reagent grade benzene with the lamp of Figure 1 causes formation of a yellow color.[37] When 150 ml. of pure benzene was photolyzed for 72 hr., the biphenyl was scarcely detectable with the flame-ionization detector of the Aerograph instrument. The gas chromatographic sample was prepared by evaporating the benzene from the reaction mixture at room temperature and diluting the "residue" with carbon disulfide. Using the 12 ft × $^1/_8$ in. column (0.2% Apiezon L on glass beads) as little as 1 mg. of biphenyl/l. can be detected. After 287 hr. of irradiation, only 640 γ (0.64 mg.) of biphenyl was found in the entire sample. This corresponds to only 5×10^{-4}% conversion. The reagent grade benzene, without irradiation, does not reveal any appreciable biphenyl in the chromatographic analysis.

B.—A solution containing 784 mg. of iodine in 200 ml. of reagent grade benzene was irradiated for 200 hr. No high-boiling products were detectable in the reaction mixture, using gas chromatography. Analysis, as above, showed only 20 mg. of biphenyl in the total mixture, representing only 0.01% conversion.

Photolysis of 1-Iodopropane in Benzene.—1-Iodopropane (3.14 g, 0.018 mole) in 200 ml. of benzene was irradiated 23 hr. Gas chromatography of the photolysate showed some starting material. A minute peak for iodobenzene and *ca.* 0.5% biphenyl were also noted. Iodine was also released in 68% yield. Some *n*-propylbenzene and isopropylbenzene were also observed.

Attempt to Detect Molecular Hydrogen.—4-Iodobiphenyl (5.6 g.) in 200 ml. of benzene (0.1 *M* solution) was photolyzed to 30% of the expected iodine release in an upright lamp which was connected with a gas-tight seal to a gas buret. The lamp was kept at 45 ± 0.5° in a constant-temperature bath. No gas evolution was detected; in fact, a slight decrease in volume was noted.[38]

Quantum Yield for Photolysis of 4-Iodobiphenyl in Benzene.—The quantum yield for release of iodine in the photolysis of 4-iodobiphenyl, 0.01 *M* in benzene, was found to be 0.08 and 0.09 in two separate runs. The value for Φ_{I_2} is based on the known value[30,32a] for photolysis of ethyl iodide. The latter was photolyzed for comparison under identical conditions; *cf.* also ref. 29.

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(37) *Cf.* H. J. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1964), who ascribed the color to formation of fulvene.

(38) Details of construction for the upright immersion-type lamp may be obtained from the authors.

The Reaction of Lead Tetraacetate with Aliphatic Alcohols[1]

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The oxidation of the primary alcohols 1-propanol through 1-hexanol, under various conditions, has been accomplished. The results indicate that lead tetraacetate effects the production of cyclic ethers even when the intramolecular functional groups are not spacially fixed. A discussion on the mechanism of oxidation is presented.

In 1959, Cainelli, *et al.*, introduced the reaction of lead tetraacetate with steroidal secondary alcohols to yield ethereal products.[2] Since that time the oxidative powers of lead tetraacetate have been extensively exploited and several recent papers have indicated the versatility of this reagent in organic synthesis.[3–6] This paper is of particular interest when taken in conjunction with that of Mihailovic, *et al.*, on the oxidation of the series, heptanol through nonanol.[1] Mihailovic has shown that oxidation produces primarily tetrahydrofuran ethers and that the process is nonstereospecific. The present work substantiates these results, using not only benzene as solvent, but also heptane, acetic acid, and chloroform. However, ether formation does not occur when pyridine is used as solvent. Further, photolysis and pyrolysis experiments, in the absence of solvent, suggest that a free-

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(1) Compare V. M. Micovic, R. I. Mamucic, D. Jeremic, and M. L. Mihailovic, *Tetrahedron*, **20**, 2279 (1964); C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1597 (1963); K. Heusler, *Tetrahedron Letters*, **No. 52**, 3975 (1964).

(2) G. Cainelli, M. L. Mihailovic, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **42**, 1124 (1959).

(3) K. Heusler and J. Kalvoda, *Angew. Chem., Intern. Ed. Engl.*, **3**, 525 (1964).

(4) E. Corey and J. Casanova, Jr., *J. Am. Chem. Soc.*, **85**, 165 (1963).

(5) E. Van Tamelen and S. Pappas, *ibid.*, **85**, 3297 (1963).

(6) C. Djerassi, "Steroid Reactions," Holden-Day, Inc., San Francisco, Calif., 1963, p. 327.