

651. Reactions of Alkyl Radicals. Part I. The Methylation of Benzene, Fluorobenzene, Chlorobenzene, and Bromobenzene with Methyl Radicals Formed by the Photolysis of Methylmercuric Iodide.

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Methyl radicals are formed in solution by photolysis of methylmercuric iodide with light of wavelength 3130 Å. Several aromatic solvents have thus been methylated in good yield, and the proportions of the isomeric products of monomethylation have been measured for fluoro-, chloro-, and bromo-benzene. The composition of the high-boiling residues also formed has been investigated; the results are consistent with a mechanism in which methyl radicals, formed by the direct photodissociation of methylmercuric iodide, add to the aromatic nuclei to give σ -complexes, some of which are dehydrogenated by methyl radicals, to give methane and products of methylation.

FORMATION of phenyl¹⁻⁴ and benzyl⁵ radicals by photolysis of organometallic compounds in solution has been reported. Since photolysis of methylmercuric iodide in the gas phase⁶ involves a bond dissociation energy $D(\text{CH}_3\text{-HgI})$ of 59 kcal. mole⁻¹,⁷ it should be possible to photolyse it in solution in Pyrex vessels, which transmit down to 3000 Å (\equiv 90 kcal. mole⁻¹) with the mercury 3130 Å line. The excessive energy of about 30 kcal. mole⁻¹ is not enough to excite electronically the methyl radicals formed, and must be located very largely in these radicals, distributed over the available degrees of freedom, because of momentum conservation.

Photolysis of Methylmercuric Iodide in Pure Solvents.—The yields from the photolysis of methylmercuric iodide in benzene are in Table 1. In two experiments (3 and 4), the

TABLE 1.
Photolysis of methylmercuric iodide in benzene.

Experiment	1	2	3	4
Benzene (ml.)	200	200	200	200
Methylmercuric iodide (mmole)	9.91	9.99	9.97	9.99
Period of photolysis (hr.)	4	4	4	4
Mercuric iodide (mmole)	4.82	4.92	4.82	4.84
Mercury (mmole)	4.72	4.87	5.04	5.01
Methylmercuric iodide accounted for by inorganic products (mmole)	9.54	9.59	9.56	9.85
Methane (mmole)	4.5	4.7	5.0	5.0
Ethane (mmole)	0.05	0.05	0.05	0.05
Toluene (mmole)	3.7	3.8	3.5	4.2
Xylenes (mmole)	0.1	0.1	0.1	0.1
Methylmercuric iodide accounted for by organic products (%)	84	88	86	95
Residue (g.)	0.25	0.03	0.04	0.06

TABLE 2.
Analysis of mixtures of isomeric xylenes.

Isomer (%)	<i>o</i> -	<i>m</i> -	<i>p</i> -
Synthetic mixture known (found)	60.6 (59.5)	30.0 (30.6)	9.5 (9.9)
Solution from expts. 1-4 (infrared method)	45	18	37
Solution from expts. 1-4 (gas chromatography)	35	—	—

solutions after photolysis were refluxed with *o*-chloranil to dehydrogenate any hydro-aromatic products.⁸ That (*a*) no evolution of hydrogen chloride was detected during this

¹ Razuvaev and Ol'dekop, *J. Gen. Chem. U.S.S.R.*, 1949, **19**, 711, 1485; 1951, **21**, 1225.

² Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.

³ Leighton and Mortensen, *J. Amer. Chem. Soc.*, 1936, **58**, 448.

⁴ Hey, Shingleton, and Williams, *J.*, 1963, 5612.

⁵ Hey, Shingleton, and Williams, *J.*, 1963, 1958.

⁶ Terenin and Prilezhaeva, *Acta Physicochim. U.R.S.S.*, 1934, **1**, 759.

⁷ Hartley, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1950, **46**, 1019; Charnley and Skinner, *J.*, 1951, 1921.

⁸ Hey, Perkins, and Williams, *J.*, 1963, 5604.

procedure and (b) the yield of toluene was unaffected by the treatment with *o*-chloranil, indicate that toluene was formed during the photolysis rather than by subsequent oxidation of hydroaromatic compounds. The relative proportion of isomeric xylenes formed in this reaction are in Table 2. The yields from the corresponding reactions in fluoro-, chloro-, and iodo-benzene are in Table 3, and the proportions of the isomeric products of monomethylation in Table 4.

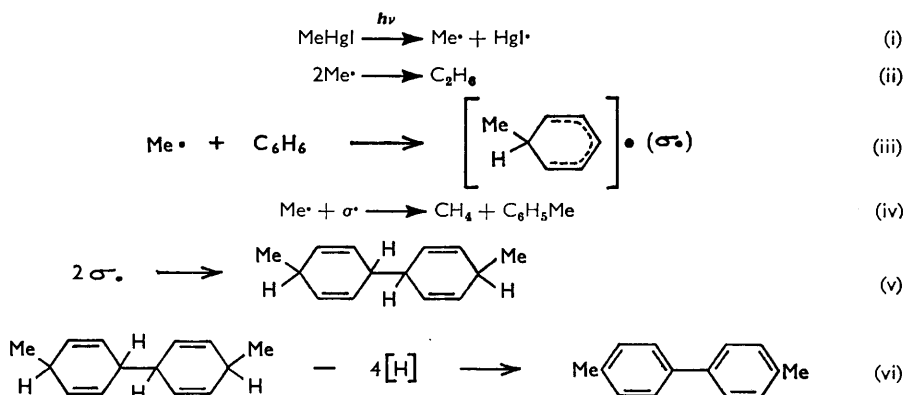
TABLE 3.
Photolysis of methylmercuric iodide in fluorobenzene, chlorobenzene, and bromobenzene.

Substrate (200 ml.)	Fluorobenzene		Chlorobenzene		Bromobenzene	
	5	6	7	8	9	10
Expt. No.	5	6	7	8	9	10
Methylmercuric iodide (mmole)	10.02	9.94	9.96	9.96	10.02	10.00
Period of photolysis (hr.)	3.5	4	2.5	2.5	2	2.5
Mercuric iodide (mmole)	4.98	4.90	4.90	4.52	5.60	5.49
Mercury (mmole)	4.94	4.92	—	4.95	4.35	4.38
Methylmercuric iodide accounted for by inorganic products (mmole)	9.92	9.82	—	9.47	9.97	9.87
Methane (mmole)	5.0	4.8	4.5	5.05	5.3	5.3
Ethane (mmole)	0.05	0.05	0.05	0.05	0.05	0.05
Halogenotoluenes (mmole)	2.36	2.54	2.69	2.45	3.43	3.42
Methylmercuric iodide accounted for by organic products (%)	75	75	73	76	88	88
Residue (g.)	0.21	0.25	0.22	0.21	0.470	0.435

TABLE 4.
Analysis of mixtures of isomeric methylation products.

Mixture	Components	Isomer (%)		
		<i>o</i> -	<i>m</i> -	<i>p</i> -
Synthetic (known)	Fluorotoluenes	58.9	30.6	10.5
" (found)	"	58.4	30.9	10.6
Expt. 5	"	57.1	37.5	5.4
Expt. 6	"	57.4	37.5	5.1
Synthetic 1 (known)	Chlorotoluenes	67.5	22.0	10.5
" 1 (found)	"	67.3	22.1	10.6
" 2 (known)	"	64.9	24.1	11.0
" 2 (found)	"	65.1	24.0	10.9
Expt. 7	"	61.8	28.6	9.6
Expt. 8	"	62.2	28.2	9.6
Synthetic (known)	Bromotoluenes	60.8	28.5	10.7
" (found)	"	61.1	28.4	10.5
Expt. 9	"	54.5	34.4	11.2
Expt. 10	"	56.1	32.8	11.2

The following mechanism is suggested for the reaction in benzene. Analogous schemes can be written for the other aromatic solvents.

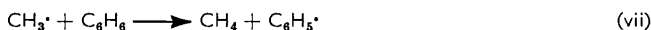


This mechanism shows that no more than half of the methyl radicals are available for nuclear methylation, so the yields of the simple methylation products in Tables 1 and 3 are excellent.

Reactions analogous to (v) and (vi) giving 2,2'- and 2,4'-dimethylbiphenyl can also be written. The methyl radical is probably at least partly responsible for the hydrogen-abstraction in reaction (vi), since the yields of methane usually exceed those of the mono-alkylation products.

Though reactions are known in which radicals abstract organic groups from diorgano-mercury derivatives,⁹ the possibility that radicals present in solution induce decomposition of methylmercuric iodide is not supported by the evidence. First, this basis leads to no scheme which allows for the formation of our observed products. Secondly, the intensity of light of wavelength 3000—4000 Å entering the reaction vessel was about 3×10^{-4} mole quanta min^{-1} , indicating a quantum yield of about 0.5 for the reaction in benzene. Chain reactions are probably unimportant, therefore except in the unlikely event that an initial photolysis, of low quantum yield, is followed by a short chain reaction. Neither this possibility, nor that of mercury photosensitisation, is considered in the following discussion.

The products of the reaction in benzene are consistent with the above mechanism, but not with alternatives in which methane is formed by abstraction of hydrogen from an aromatic nucleus, as in reaction (vii):



Although this reaction is thought to occur in the gas phase,¹⁰ there is considerable evidence that, in solution, methyl radicals add to the aromatic nucleus,¹¹ and our observation that the residue from the reaction of methylmercuric iodide with benzene contains the isomeric dimethylbiphenyls is difficult to account for other than by reactions (v) and (vi). Moreover, in the same reaction, there was no evidence for the formation of biphenyl. This precludes any significant occurrence of reaction (vii) under these conditions, since phenyl radicals so produced must react with the benzene to give biphenyl. The occurrence of about 20 components in the residues formed in reactions of methylmercuric iodide with monosubstituted benzenes is also consistent with this interpretation, since 21 such isomers can be formed by symmetrical and unsymmetrical coupling of the three isomeric σ -complexes. A reported isotope effect in the formation of methane in the reaction of methyl radicals (from acetyl peroxide) with tritiated benzene,¹² which was attributed to the occurrence of reaction (vii), may instead arise from the different rates of protium- and tritium-abstraction from the σ -complexes for nuclear methylation.

We think that small amounts of xylenes formed in the reaction of methylmercuric iodide with benzene probably arise largely by the combination of σ -complexes with methyl radicals to give dihydroxylenes, which are then oxidised, rather than by further methylation of toluene, for two reasons. Firstly, Buckley, Leavitt, and Szwarc's value of 1.7 being taken for the reactivity of toluene relative to benzene for the addition of methyl radicals,¹³ the amount of xylene expected to be formed by further methylation is only about 10% of the observed yield. Secondly, the xylenes so formed should be accompanied by bibenzyl, arising by hydrogen-abstraction from the side-chain of toluene, followed by combination of the resulting benzyl radicals, since the side-chain of toluene is 3 to 5 times more reactive than the nucleus.¹³ Little or no bibenzyl was, however, found among the products of this reaction.

⁹ Nesmeyanov, Borisov, Golubeva, and Kovredov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 1582; *Bull. Acad. Sci. U.S.S.R. (Chem. Sci.)*, 1961, 1477.

¹⁰ Trotman-Dickenson and Steacie, *J. Chem. Phys.*, 1951, 19, 329.

¹¹ Williams, "Homolytic Aromatic Substitution," Pergamon Press Ltd., London, 1960, Ch. 6.

¹² Antonovskii and Berezin, *Doklady Akad. Nauk S.S.S.R.*, 1960, 134, 860; *Proc. Acad. Sci. U.S.S.R. (Phys. Chem.)*, 1960, 134, 907.

¹³ Buckley, Leavitt, and Szwarc, *J. Amer. Chem. Soc.*, 1956, 78, 5557.

There are slight but appreciable discrepancies between the stoichiometry of the reaction in bromobenzene and that in the other solvents. Thus in bromobenzene (a) the apparent yield of mercuric iodide (estimated as Hg^{2+}) is distinctly higher than that of mercury, (b) the yield of methane is higher than that predicted by the proposed mechanism (0.5 mole per mole of methylmercuric iodide) and (c) if the residue is assumed to be formed only by combination of σ -complexes, and to be entirely dibromodimethylbiphenyls, the organic products, including the residue, account for $\sim 115\%$ of the available methyl radicals. All three observations are consistent with the postulate that a little bromobenzene was photolysed to phenyl radicals and bromine atoms. Iodobenzene is so photolysed,^{2,14} and it is reasonable to assume a similar process, to a smaller extent, with bromobenzene. Such a process would be expected to result in the oxidation of some mercury to mercuric bromide by the liberated bromine atoms, and in the phenylation of some bromobenzene to 2-, 3-, and 4-bromobiphenyls. These compounds were present in the residue, in addition to the expected isomeric dibromodimethylbiphenyls, and were formed in the same proportions as in the phenylation of bromobenzene with benzoyl peroxide. The increased yield of methane probably arises from hydrogen-abstraction by methyl radicals from the σ -complexes for phenylation, as well as from those for methylation. Moreover, the apparent increases in the yields of mercuric ion and methane, and the yield of phenylation products, are mutually quantitatively consistent.

The proportions in which the isomeric products of monoalkylation were formed are compared, in Table 5, with the corresponding results reported by Cowley, Norman, and Waters,¹⁵ who obtained methyl radicals from *t*-butyl peroxide. Yields of methylation products were not reported by Cowley, Norman, and Waters, but are likely to be very much lower than ours. Confirmation of these earlier results is therefore desirable. Except

TABLE 5.
Ratios of isomers formed by homolytic methylation.

Substrate	Radical source	Temp.	Isomer (%)		
			<i>o</i> -	<i>m</i> -	<i>p</i> -
Fluorobenzene	MeHgI	84°	57	37	5
Chlorobenzene	MeHgI	135	62	28	10
	(Bu ^t O) ₂	130	64	25	11
Bromobenzene	MeHgI	155	55	34	11
	(Bu ^t O) ₂	145	68	23	10

TABLE 6.
Photolysis of methylmercuric iodide in benzene-chlorobenzene.

	Expt.	11	12		Expt.	11	12
Methylmercuric iodide (mmole)...	10.08	9.94		Methylmercuric iodide accounted			
Benzene (ml.)	100	100		for by inorganic products (mmole)	9.64	9.88	
Chlorobenzene (ml.)	100	100		Methane (mmole)	4.71	4.68	
Period of photolysis (hr.)	3	3		Ethane (mmole)	0.05	0.05	
Mercuric iodide (mmole)	4.69	4.95		Toluene (mmole)	2.28	2.06	
Mercury (mmole)	4.95	4.93		Chlorotoluenes (mmole)	1.82	1.74	
				Methylmercuric iodide accounted			
				for by organic products (%)	88	86	
				Residue (g.) ..	0.277	0.271	

for the proportion of the *ortho*- and *meta*-isomers formed in the methylation of bromobenzene, the results agree well, suggesting that the free methyl radical in its ground state is the methylating agent in both reactions, and therefore confirming the conclusions reached above. Our results also confirm Cowley, Norman, and Waters's conclusion that the methyl radical is somewhat more nucleophilic than the phenyl.

Competitive Reactions.—Competitive reactions of methylmercuric iodide with mixtures

¹⁴ Blair and Bryce-Smith, *J.*, 1960, 1788.

¹⁵ Cowley, Norman, and Waters, *J.*, 1959, 1799.

of benzene and chlorobenzene (Table 6) indicate that the rate of methylation of chlorobenzene relative to benzene is about 0.9. This result is, however, somewhat uncertain, since only about 80% of the radicals which attack the aromatic nuclei can be accounted for by the combined yields of toluene and chlorotoluenes, the remainder being in the residue as dimethylbiaryls. If all the methyl radicals not accounted for are assumed to have first attacked chlorobenzene, a maximum value (~ 1.5) for the rate ratio can be calculated. Similarly, a minimum (~ 0.3) can be calculated by assuming that all the methyl radicals not accounted for had attacked benzene. These values may be compared with a figure of 4.2 ± 0.2 for the "methyl affinity" of chlorobenzene relative to benzene at 65° , reported by Heilman, Rembaum, and Szwarc.¹⁶ The discrepancy between these two results is too large to be attributable only to the different temperatures for the two sets of measurements. Heilman, Rembaum, and Szwarc's method was to measure the reduction in the yield of methane obtained in the decomposition of acetyl peroxide at low concentration in 2-methylheptane in the presence of an aromatic compound, compared with the yield obtained from the reaction in pure 2-methylheptane, and depends on the assumption that methane is formed only by hydrogen-abstraction from 2-methylheptane. Some support for this assumption, for reactions carried out under Heilman, Rembaum, and Szwarc's conditions comes from the work of Eliel, Rabindran, and Wilen,¹⁷ although they also showed that at higher stationary concentrations of methyl radicals, as in our experiments, the importance of reaction (iv) increases. In view of the discrepancy between our results, obtained from the yields of the products of methylation, and those of Heilman, Rembaum, and Szwarc, who isolated no product except methane, the validity of the above assumption in every case should, perhaps, be re-examined.

EXPERIMENTAL

Reagents.—Solvents and reference compounds were purified by standard methods, and their purity confirmed by gas chromatography and infrared spectroscopy.

Methylmercuric iodide was prepared by a modification^{18,19} of Frankland's method.²⁰ Mercury (20 g.), mercuric iodide (4 g.), and methyl iodide (40 ml.) were stirred under reflux, while being illuminated by a 150 watt tungsten-filament lamp, for 4 hr. Mercury (2 g.) was added, and the mixture boiled under reflux for 1 hr. to convert mercuric iodide into insoluble mercurous iodide. Filtration, and distillation of methyl iodide from the filtrate, gave a white product, which crystallised from methanol as methylmercuric iodide (23 g., m. p. $147\text{--}148.5^\circ$).

Methane and ethane were prepared from Grignard reagents with ether saturated with water. Methane was collected over saturated brine, and ethane by passage, with nitrogen, into a trap in liquid air. Nitrogen was then pumped out. The trap had a rubber serum-bottle cap, through which samples were withdrawn with a syringe.

2-Methylbiphenyl (b. p. $80\text{--}90^\circ/0.2$ mm.) was prepared by Cadogan's method.²¹ Gas chromatography revealed a slight, unidentified impurity. 3- and 4-Methylbiphenyl were gifts from Dr. M. J. Perkins.

2,2'-Dimethylbiphenyl (b. p. $75^\circ/0.2$ mm.) was prepared by the Ullmann reaction from 2-iodotoluene. 4-Iodotoluene similarly gave 4,4'-dimethylbiphenyl (m. p. 124°). Both products gave single peaks in gas chromatography. A similar reaction with a mixture of 2- and 4-iodotoluene gave a semi-solid showing three peaks. The retention times of the first and last of these were identical with those of 2,2'- and 4,4'-dimethylbiphenyl, respectively, and the other peak was attributed to the 2,4-isomer.

Purified specimens of 4-bromobiphenyl and potassium ferrioxalate were gifts from Professor D. H. Hey and Dr. J. N. Bradley, respectively. Tetrachloro-*o*-benzoquinone (*o*-chloranil) was prepared by Hey, Perkins, and Williams's method.⁸

Photolysis of Methylmercuric Iodide in Pure Solvents.—Boiling solutions of methylmercuric

¹⁶ Heilman, Rembaum, and Szwarc, *J.*, 1957, 1127.

¹⁷ Eliel, Rabindran, and Wilen, *J. Org. Chem.*, 1957, **22**, 859.

¹⁸ Maynard, *J. Amer. Chem. Soc.*, 1932, **54**, 2108.

¹⁹ Baldoni and Miyashiro, U.S.P. 2914451.

²⁰ Frankland, *J.*, 1854, **6**, 57.

²¹ Cadogan, *J.*, 1962, 4257.

iodide in the solvent, previously saturated with nitrogen, were irradiated under nitrogen with a Philips 300 w ultraviolet lamp (type 57265 F/28) until evolution of gas ceased, then for 1 hr. The gas was collected over saturated brine in a gas burette. After cooling, the apparatus was washed with ether, then 10% aqueous potassium iodide, and the washings added to the reaction mixture, together with solid potassium iodide to complete the conversion of the deposited mercurous iodide to mercuric iodide (in solution) and mercury, which, after separation, was dried *in vacuo*, and weighed. The aqueous layer, after separation, was made to 500 ml. with water, and 50 ml. aliquot portions were used to estimate mercury in solution as HgI_4^{2-} by Walton and Smith's method.²²

Most of the solvent was fractionally distilled from the dried organic layer, and analysed at intervals by gas chromatography. Distillation was stopped when 10–20 ml. of solution were left, or earlier if the monomethylation products began to codistil. The residue, which was an approximately 5% solution of the methylation products, was analysed by gas chromatography (Perkin-Elmer model 116) on a 2-metre column of didecyl phthalate–Celite 545, to give the yield of methylation products. Redistillation, *in vacuo* if necessary, then gave a volatile fraction, containing the products of mono-alkylation, and a residue. The volatile fractions were subjected to preparative-scale gas chromatography on didecyl phthalate–Celite 545. Several 2 ml. portions were so treated. The alkylation products were collected in cyclohexane, the solutions being subjected again to gas chromatography, if necessary, and analysed for the isomeric alkylation products by infrared spectrophotometry as described by Augood, Hey, and Williams.²³ The absorption maxima used for the analyses were: toluene, 726.2; *o*-, *m*-, and *p*-xylene, 739.7, 765.7, and 793.1; *o*-, *m*-, and *p*-fluorotoluene, 751.3, 774.6, and 816.3; *o*-, *m*-, and *p*-chlorotoluene, 745.1, 770.1, and 805.8; *o*-, *m*-, and *p*-bromotoluene, 743.5, 769.2, and 801.3 cm^{-1} , respectively. To check accuracy, synthetic mixtures were analysed in each case. It was also possible approximately to estimate *o*-xylene in the mixture of xylenes obtained from the reaction in benzene by gas chromatography.

The residues after distillation of the methylation products were subjected to gas chromatography in chloroform on a Pye "Argon" instrument with Apiezon "L" grease or polyethylene glycol adipate on Celite 545. The residue from the reaction in benzene was shown, by comparison of retention times with those of authentic specimens, to contain 2,2', 2,4', and 4,4'-dimethylbiphenyl, and possibly bibenzyl, but not biphenyl or 2-, 3-, or 4-methylbiphenyl. Several smaller peaks were not identified. The residues from the reactions in fluorobenzene and chlorobenzene gave 19 and 22 peaks, respectively, not further investigated. The chromatogram of the residue from the reaction in bromobenzene, which contained 25 peaks, was compared with that of 4-bromobiphenyl, and that of a mixture of 2-, 3-, and 4-bromobiphenyl prepared by refluxing a solution of benzoyl peroxide (1 g.) in bromobenzene (50 ml.) for 2 hr. The large peaks were thus assigned to 2-, 3-, and 4-bromobiphenyl as their retention times and relative heights in the two chromatograms were closely similar.

The gases evolved during photolysis were analysed using a 2-metre column, with silica gel, in the Perkin-Elmer instrument. Between 0.25 and 2 ml. samples were used, with hydrogen as carrier.

Actinometry.—Hatchard and Parker's method²⁴ (based on photolysis of potassium ferrioxalate) was used to determine the light intensity. Several determinations were in good agreement.

Photolysis of Methyl Iodide in Benzene.—Methyl iodide (0.71 g.), mercury (1.003 g.), and benzene (100 ml.) were irradiated as above. The solution soon became pink but after 9 hr. only 16 ml. of gas had been evolved, whereas the photolysis of an equivalent amount of methylmercuric iodide in benzene gave ~100 ml. of gas in 3 hr. (Expts. 1–4). Gas chromatography of the resulting solution after distillation as above showed the presence of a little toluene.

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²² Walton and Smith, *Analyt. Chem.*, 1956, **28**, 406.

²³ Augood, Hey, and Williams, *J.*, 1953, 44.

²⁴ Parker, *Proc. Roy. Soc.*, 1953, *A*, **220**, 104; Hatchard and Parker, *ibid.*, 1956, *A*, **235**, 518.