

Photochemical Reactions of Methyl Iodide with Aromatic Compounds¹

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The photolysis of methyl iodide in an excess of aromatic compounds (ArH) gave the ring-methylated aromatics in rather high yields (40–70%) but no side-chain-methylated compounds. The observed orientation was abnormal, i.e., $o/2 \approx m/2 \approx p$, compared with that in ordinary Me radical substitutions ($o/2 > p > m/2$), especially with alkylbenzenes, where 2 is the statistical factor. The effect of wavelength on the yield of iodine was also observed, i.e., a higher yield of I₂ at 254 nm and a lower yield of I₂ and a higher yield of HI and ArI at >290 nm. Both the addition of I₂ to the reaction system and the removal of the formed I₂ by Na₂S₂O₃ brought about no effect on the orientation. These results along with the effect of solvents and no influence of oxygen as a radical scavenger suggest a mechanism via a complex between methyl iodide and the aromatics which is different from a direct radical attack.

Methyl iodide, which has a UV absorption [λ_{\max} 257 nm (ϵ 380)], decomposes on UV irradiation to give methyl radical and atomic iodine.² It is expected that methyl radical reacts with aromatics to produce methylated aromatics and that atomic iodine leads to molecular iodine by coupling or to hydrogen iodide by H atom abstraction. Furthermore, there is a possibility of the participation of molecular iodine in the reaction of methyl iodide with aromatics, since I₂ can form a σ complex with the benzene ring.³

In the title reaction, we obtained results different from those expected from the normal radical reaction; thus we report here the photochemical behavior of methyl iodide dissolved in aromatic compounds.

Results and Discussion

Photolyses of methyl iodide in aromatic compounds were carried out at -60 to +70 °C. In order to examine the effect of light wavelength on the product distribution, 254 or >290-nm light was used. The 254-nm light is absorbed by both methyl iodide and aromatics, while >290-nm light is absorbed only by methyl iodide.

Products and Isomer Distribution. Product yields and isomer distributions are summarized in Table I. About 30% methyl iodide was decomposed after 20 h of irradiation. The yields of ring-methylated products were fairly high compared with those reported for thermal reactions of methyl radical (e.g., 8% for the decomposition of acetyl peroxide).⁴ The products produced from H atom abstraction from the side chain by a radical, e.g., ethylbenzene and bibenzyl from toluene, were not observed, and also, virtually none of the other byproducts expected from toluene were detected. The yield of methane, formed by H atom abstraction with methyl radical, was below 10% in both photolyses. The iodine component of methyl iodide was converted into molecular iodine, hydrogen iodide, and/or iodo aromatics, their yields depending on the wavelength. That is, I₂ was formed almost quantitatively at 254 nm, while I₂ was formed in only 20% yield together with HI and iodo aromatics for >290-nm irradiation.

The orientation of the aromatic methylation is appreciably different from that ($o/2 > p > m/2$) for ordinary radical substitution by methyl radical in the dark;⁴ i.e., the

Table I. Products Yields and Isomer Distributions of Methylated Aromatics in the Photochemical Reaction of MeI with Aromatic Solvents (C₆H₅R)^a

R	λ , nm	% MeI dec	yield, ^b %	
			MeC ₆ H ₄ R (ortho/meta/para ratio)	I ₂
Me	254	25–34	50–70 (39:40:21)	~100
Me	>290	18–27	~50 (42:36:22)	20–30
Me ^c			8 (56:27:17)	
OMe	254	<i>d</i>	<i>e</i> (57:24:19)	<i>e</i>
OMe	>290	<i>d</i>	<i>e</i> (56:22:22)	<i>e</i>
Et	254	28	<i>e</i> (39:42:19)	96
H	254	37	79 ^f	95

^a Irradiation at 27 °C for 20 h except for the reaction with toluene which was irradiated at -60 to +70 °C. Initial concentration of MeI, [MeI]₀ = 0.1 M. ^b Based on decomposed MeI. ^c Thermolysis (70 °C) of acetyl peroxide in toluene for 10 h. ^d The concentration of MeI by iodometry could not be measured due to the interference of anisole. ^e Not determined. ^f Product is toluene.

Table II. Photochemical Reaction of Toluene with MeI in Various Solvents^a

solvent	λ , nm	% MeI dec	yield, ^b %	
			xylenes (ortho/meta/para ratio)	I ₂
toluene	254	29.3	69 (41:38:21)	98
<i>n</i> -hexane	254	18.9	12 (35:40:25)	78
EtOH	254	19.9	17 (38:41:21)	84
EtOH-H ₂ O ^c	254	20.5	30 (43:36:21)	25
CCl ₄	254	24.2	2 (42:36:22)	95
toluene	>290	27.2	38 (46:31:23)	20
<i>n</i> -hexane	>290	18.1	6 (43:33:24)	70
EtOH	>290	10.7	4 (45:34:21)	61
MeOH	>290	13.1	5 (49:29:22)	76

^a Irradiation at 27 °C for 20 h; [MeI]₀ = 0.1 M and [PhMe]₀ = 0.4 M. ^b Based on decomposed MeI. ^c Ratio of 60:40 (v/v %).

statistical ratio of orientation ($o/2 \approx m/2 \approx p$) was observed for this MeI reaction in toluene and ethylbenzene. No effect of the temperature on the orientation was observed at -60 to +70 °C in toluene, where no thermolysis of methyl iodide occurred. Furthermore, the orientation was influenced neither by the reaction time nor the concentration of methyl iodide.

Photoreaction in Solvent. The reaction of toluene with methyl iodide was carried out in a number of solvents, the results being shown in Table II.

A few byproducts derived from solvents were detected, e.g., heptane and hexyl iodide in the case of *n*-hexane as a solvent. The yields of xylenes at 254 nm increase with

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(3) Andrews, L. *J. Chem. Ber.* 1954, 54, 713.

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Table III. Effect of Toluene Concentration on the Orientation of the Photochemical Reaction of MeI with Toluene in *n*-Hexane^a

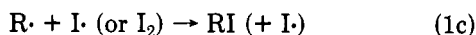
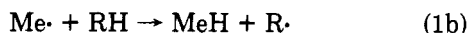
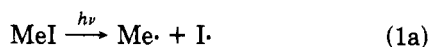
[PhMe] ₀ , M	% MeI dec	yield, ^b %	
		xylenes (ortho/ meta/para ratio)	I ₂
0	18.8	<i>c</i>	80.2
0.10	17.7	5.4 (35:38:27)	79.5
0.50	16.8	16.4 (36:41:23)	78.8
1.00	19.0	22.7 (37:41:22)	80.4
9.5 ^d	28.0	75.2 (40:39:21)	97.9

^a Irradiation with 254-nm light at 26 °C for 20 h; [MeI]₀ = 0.1 M. ^b Based on decomposed MeI. ^c Two products (heptane and hexyl iodide) were detected by GC/MS. ^d Toluene was used as a solvent.

increasing polarity of solvents; especially, the yields in EtOH-H₂O attained to over 30%, while the yields in CCl₄ were very low. This low yield may be due to the consumption of methyl iodide by a solvent radical, probably via a chain mechanism.⁵ Molecular iodine was also produced in high yield in nonhydroxylic solvents, while the photolysis in EtOH-H₂O gave a low yield of I₂ and an appreciable amount of HI. This fact shows that HI is photolyzed easily in nonhydroxylic solvents to give I₂ by a radical mechanism,⁶ but HI is rather stable in hydroxylic solvents due to its ionic dissociation.

In contrast, the reaction at >290 nm in solvents gave lower yields of xylenes and higher yields of I₂ than those in neat toluene. The low yields of xylenes may be due to the same reason as that at 254 nm. The higher yield of I₂ compared with that in neat toluene at >290 nm may be ascribed to less consumption of I₂ by photoreaction of a toluene-I₂ complex, which increases with increasing concentration of toluene (see below). But the orientation was unchanged irrespective of the solvent.

The effect of toluene concentration on the yields of xylenes and I₂ was also examined in *n*-hexane as a solvent, and the results are summarized in Table III. The yields of xylenes increase with increasing concentration of toluene. Heptane and hexyl iodide were detected as products other than xylenes by GLC and GC/MS. This fact suggests that methyl iodide in *n*-hexane containing a low concentration of toluene was directly photolyzed to give methyl radical and atomic iodine, which react with solvent (*n*-hexane, RH in eq 1a-d).⁷ Therefore, the decrease of the yields of xylenes in *n*-hexane may be due to an increase of these side reactions.



RH = solvent

Effect of Molecular Iodine. In order to examine the effect of molecular iodine formed during the photolysis of methyl iodide, I₂ was added initially to the reaction system on one hand, while I₂ was removed by aqueous Na₂S₂O₃ solution on the other. The results are listed in Table IV. Apparently, no change of the orientation of isomeric

Table IV. Effect of Iodine Concentration on the Orientation of Photochemical Reaction of MeI with Toluene^a

λ, nm	[I ₂] ₀ , M	% MeI dec	yield, ^b %	
			xylenes (ortho/ meta/para ratio)	I ₂
254	0	33.3	50.6 (40:39:21)	98.5
254	0.02	27.6	68.5 (42:39:19)	93.6
254	0 ^c	48.5	33.8 (39:41:20)	
254	0 ^d	42.7	37.2 (41:38:21)	<i>e</i>
254 ^f	0.50	<i>e</i>	<i>e</i> (41:39:20)	<i>e</i>
>290	0	27.2	54.3 (44:35:21)	13.1
>290	0.20	26.3	27.1 (47:30:23)	<i>f</i>
>290	0 ^c	37.1	45.7 (41:39:20)	

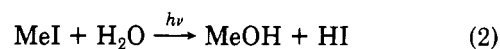
^a Irradiation at 27 °C for 20 h; [MeI]₀ = 0.1 M. ^b Based on decomposed MeI. ^c Molecular iodine was trapped by 5% aqueous Na₂S₂O₃ during the reaction. ^d Water alone was added as a controlled run for the trapping of I₂ by 5% aqueous Na₂S₂O₃. ^e Not determined. ^f [MeI]₀ = 0.05 M.

Table V. Effect of Oxygen on the Photochemical Reaction of MeI with Toluene^a

λ, nm	condi- tion	% MeI dec	yield, ^b %	
			xylenes (ortho/ meta/para ratio)	I ₂
254	air	33.3	50.6 (40:39:21)	98.5
254	O ₂	34.5	46.8 (40:40:20)	99.7
254	N ₂	32.5	47.3 (42:39:19)	95.3
>290	air	26.2	38.4 (44:35:21)	20.3
>290	O ₂	22.7	39.1 (44:34:22)	19.0
>290	N ₂	27.3	41.7 (45:33:22)	24.6

^a Irradiation at 27 °C for 20 h; [MeI]₀ = 0.1 M. ^b Based on decomposed MeI.

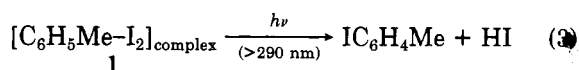
xylenes was observed under both conditions. A decrease of the yields of xylenes and a high conversion of methyl iodide were observed by addition of aqueous Na₂S₂O₃ at both 254 and >290 nm. This may be due to the consumption of methyl iodide by the preliminary hydrolysis of methyl iodide with water present in the trapping system (eq 2).⁸ In fact, methanol was detected by GLC and GC/MS in the trapping system.



The smaller effects at >290 nm than those at 254 nm are attributable to the smaller extinction coefficient of methyl iodide at >290 nm (e.g., ε_{300nm} 6) than that at 254 nm (ε_{254nm} 380).

In spite of an increase of xylene yield on addition of I₂ at 254 nm, the yields of xylenes decreased remarkably at >290 nm on addition of I₂, while iodotoluenes were formed in appreciate yields, suggesting the secondary reaction of iodine with toluene at >290 nm.

It is well-known that iodine forms a complex with aromatics,³ e.g., toluene-iodine complex 1 (λ_{max} 306 nm, ε 8400).⁹ Complex 1 (eq 3) was found to decompose on >290-nm irradiation to give iodotoluenes in high yields.¹⁰



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(7) (a) Benson, S. W.; O'Neal, H. E. *J. Chem. Phys.* 1961, 34, 514. (b) Sullivan, J. H. *J. Phys. Chem.* 1961, 65, 722.

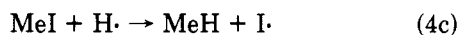
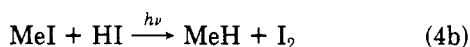
Table VI. Effect of Molecular Iodine on Decomposition of Acetyl Peroxide (APO) in Toluene

10[APO] ₀ , M	10[I ₂] ₀ , M	% APO dec	10[I ₂], M	yield, ^a %	
				xylenes (ortho/meta/ para ratio)	PhEt
1.89 ^b	0	69	0	8.3 (57:27:16)	4.7
1.89 ^b	0.20 ^c	74	0	6.2 (56:28:16)	4.2
1.89 ^b	2.01	72	0.71 ^d	trace	trace
1.96 ^e	0	59	0	2.8 (51:35:14)	14.1
1.96 ^e	0.20	53	0.06	17.6 (39:38:23)	5.9
1.96 ^e	2.01	62	0.87	28.2 (40:38:22)	trace

^a Based on decomposed APO. ^b Thermolysis at 70 °C for 10 h. ^c The color of I₂ was disappeared after 30 min. ^d I₂ was consumed (65%), and methyl iodide was obtained as a main product. ^e Irradiation with 254-nm light at 27 °C for 20 h.

On the other hand, the observed high yield of iodine in the >290-nm photolysis of PhMe–MeI in diluted solution may be ascribed to low concentration of the toluene–iodine complex (1).

Hydrogen iodide, which is another product, should be formed in a high yield in the system with added molecular iodine. Hence, the yields of xylenes at >290 nm may be lowered by the reaction of methyl iodide with hydrogen iodide⁶ (eq 4).



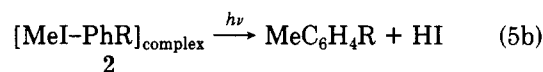
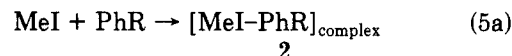
In contrast, irradiation with 254-nm light showed little consumption of iodine even in the system added with I₂, which may be due to the weak absorbance of the complex 1 at 254 nm.^{3,9}

Mechanism. The formation of methyl radicals in the photolysis of methyl iodide has been confirmed by ESR and other techniques.¹¹ But our results are inconsistent with a direct attack of free radical. In fact, the introduction of oxygen into the reaction system¹² showed no effect, i.e., negative evidence for trapping radicals (Table V). Moreover, the results of the thermolysis of acetyl peroxide in toluene in the presence of I₂ are quite different from those of the photolysis (Table VI); i.e., the addition of I₂ in the thermolysis decreased the yields of xylenes and ethylbenzene, which are the ordinary products of toluene–methyl radical reaction, while the addition increased the yield of methyl iodide. On the other hand, the photolysis of acetyl peroxide in toluene in the presence of I₂ gave a similar distribution of products as that in the photolysis of methyl iodide in toluene. Therefore, methyl radical generated by the thermolysis or photolysis of acetyl peroxide is trapped by I₂ to give methyl iodide.

Furthermore, as mentioned above, the yield of methane in the photolysis of methyl iodide in toluene is much lower than that in the thermolysis of acetyl peroxide (ca. 70%).¹³ These facts suggest that free methyl radical reaction is unimportant in the photolysis of PhMe–MeI.

This photolysis may proceed via a complex 2 between methyl iodide and alkylbenzene (PhR) which may be formed in the ground state^{3,14} or via photoinduced electron

transfer from the aromatic to methyl iodide, leading to the observed products under irradiation (eq 5a,b), where hy-



drogen iodide is easily photolyzed to give iodine. Iodine thus generated also forms complex I₂–PhR (1), which is then photolyzed at >290 nm to give iodo aromatics.

In the reaction in some solvents (Table II), the yields of xylenes decrease probably due to a decrease of the concentration of the MeI–PhMe complex (2) and to the side reaction of radicals with the solvents (eq 1). The side reactions may be more significant at >290 than at 254 nm, since the absorbance of the complex 2 leading to xylenes is much weaker at >290 nm.¹⁵ The increase of the yields of xylenes with increasing content of hydroxylic solvents may be ascribed to an increase of the stability of the complex 2 in view of its polarized nature.

The methylation of aromatic compounds via complex 2 may proceed by a short-lived and highly active Me radical in a solvent cage, since there is no evidence for a free-radical reaction out of the cage, and the hot radical would give the statistical orientation as observed. Formation of hot radicals in photolysis of methyl iodide by absorption of light energy in excess of the C–I bond energy has been reported by several workers.¹⁶

Experimental Section

Materials. Toluene, anisole, ethylbenzene, and benzene were of guaranteed grade and purified by fractionation before use. Methyl iodide was of guaranteed grade. No impurities were detected by GLC analysis of these materials. Authentic samples of *o*-, *m*-, and *p*-methylanisoles were prepared by the methylation of the corresponding cresols with dimethyl sulfate.¹⁷ Xylenes were of first grade. All these materials were identified by IR and NMR spectroscopies and they had single GLC peaks.

Analysis. The concentration of methyl iodide was determined iodometrically according to the following procedure. The sample solution was washed by aqueous 5% Na₂S₂O₃ until the disappearance of the brown color. One milliliter of the solution was added to a mixture of 10% AcONa–AcOH (10 mL) containing bromine, and then aqueous 10% AcONa (10 mL) was added. The excess bromine was removed by adding aqueous formic acid. A mixture of saturated KI (2 mL) and 4 N H₂SO₄ (5 mL) was added,

(15) The absorption spectrum of methyl iodide–toluene complex may be close to the overlap of the components.

(16) (a) Riley, S. J.; Wilson, K. R. *Faraday Discuss. Chem. Soc.* 1972, 132. (b) Palmer, R. E.; Padrick, T. D. *J. Chem. Phys.* 1976, 64, 2051. (c) Donohue, T.; Wiesenfeld, J. R. *J. Phys. Chem.* 1976, 80, 437. (d) Rice, J. K.; Truby, F. K. *Int. J. Chem. Kinet.* 1977, 9, 693; *Chem. Abstr.* 1977, 87, 52461.

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and after being allowed to stand for 5 min, the mixture was titrated with 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$.

The iodine was determined by titration with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ after addition of the sample solution (2 mL) to 4 N H_2SO_4 (30 mL)-saturated KI (1 mL).

The reaction products were analyzed with a Yanagimoto G 180 gas chromatograph using Bentone 34-DIDP (5 + 5%), PEG 20M, and Porapak QS columns. The identification of products was done by comparison of GLC peaks with those of the authentic samples and by GC/MS (JEOL JMS-D300 mass spectrometer). The yields were estimated by GLC with mesitylene as an internal standard.

Photolysis. The solution of methyl iodide (0.1–0.2 M) in aromatic solvents were irradiated by a Halos 30- or 60-W low-pressure Hg lamp in a cylindrical 10 × 200 mm quartz cell or a Halos 1-kW or 300-W high-pressure Hg lamp in a Pyrex cell. Low-temperature experiments at -70 to -20 °C were conducted

by cooling a reaction cell with a Yamato Neocool DIP Model BD-21 cooling apparatus.

Analyses of Gaseous Products. The gaseous products evolved by photolysis were collected in a gas buret (50-mL volume) connected with a capillary tube to the photolysis vessel and were replaced with He. The gas collected was analyzed by GC/MS and GLC with two sorts of columns packed with Porapak Type T and Porapak Type QS, and analyses of mass peaks were carried out by comparison with standard samples.¹⁸ Ethane was not detected in the gas in both the 254- and >290-nm irradiations.

Registry No. Toluene, 108-88-3; anisole, 100-66-3; ethylbenzene, 100-41-4; benzene, 71-43-2; MeI, 74-88-4.

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Trisannulated Benzenes. Preparation, Properties, and Photoelectron Spectra

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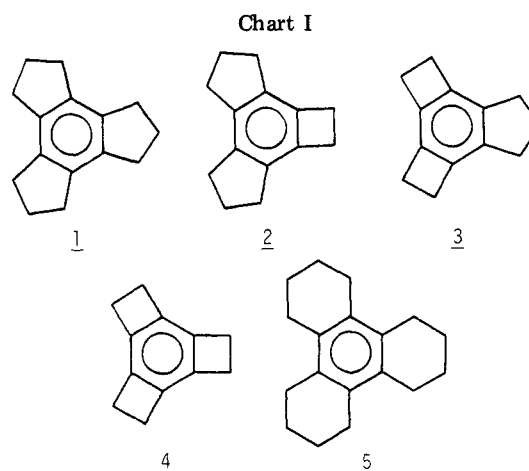
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The preparation of tricyclobutabenzene and its next two higher homologues is described. The synthetic approach involves the [4 + 2] cycloaddition of dimethyl 1,2-cyclobutenedicarboxylate to an appropriate diene followed by hydrolysis of the ester functions, bisdecarboxylation, and aromatization. The NMR, ultraviolet, and photoelectron spectra of these small-ring trisannulated benzenes are presented. The properties of all three molecules are reasonably consistent, and no evidence is shown for any serious perturbation of aromaticity.

Until recently, the smallest known trisannulated benzene system was trindan (tricyclopentabenzene, 1). Our preparation of a series of bisannulated benzenes¹ and study of their properties² has consequently led us to consider the lower homologues of trindan, 2–4 (Chart I). Beyond the synthetic challenge involved, we were also interested in the interaction of reactive, strained ring systems with resonance-stabilized aromatic nuclei.³ This paper describes the general synthetic approach to trisannulated benzenes and some of the more salient physical properties of these systems.

Synthesis

Trindan (1) was first reported in 1897 as a minor product of the action of HCl on cyclopentanone.⁴ Although this condensation approach has been used in the preparation of several trisannulated benzenes, it is unsatisfactory for the preparation of 4 as well as unsymmetrical analogues. A second approach to symmetrical trisannulated benzenes is the cyclotrimerization of a cycloalkyne. Molecules such as trinorbornabenzene⁵ and tribullvalenobenzene⁶ have been prepared in this manner. The unlikelihood of generating cyclobutene makes this route unsatisfactory for the synthesis of 4. A notable exception, however, is the copper-bronze-promoted cyclization of 1,2-diiodoperfluorocyclobutene which provides the perfluoro analogue of 4 in reasonably good yield.⁷



There have been several recent reports of pyrolytic reactions which might have led to the formation of tricyclo-

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