

RATES OF PHOTOBROMINATION OF FLUORENE  
AND 2-METHYLNAPHTHALENE

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The enhanced effect of iodine as carrier in the dark-room bromination of fluorene (1) raises the question of its influence on the photobromination of this molecule (2). In the first part of the present paper it is shown that the presence of iodine reduces the formation of 9-bromofluorene in the photobromination. By the passage of light from a six-inch mercury arc through iodine filters, effects have been secured which range from no production of 9-bromofluorene to where all the bromination takes place in the 9-position.

A Coleman Universal Spectrophotometer, Model 14, has been used to extend the photochemical study. The effect of different wave lengths of monochromatic light on the bromination of fluorene and 2-methylnaphthalene in both carbon tetrachloride and carbon disulfide has been examined. 2-Methylnaphthalene was selected because of the strong tendency of the bromine to enter the favored 1-position of this molecule, rather than the side-chain.

## EXPERIMENTAL

## EFFECT OF IODINE ON THE PHOTOBROMINATION OF FLUORENE

In Table I the samples of fluorene (1.66 g.), dissolved in 10.00 ml. of carbon tetrachloride and 10.00 ml. of the same solvent containing the quantity of iodine indicated, were refluxed in an Erlenmeyer flask attached to a condenser by a ground-glass joint with a 6" mercury arc placed  $\frac{3}{4}$ " from the flask; 10.00 ml. of molar bromine-carbon tetrachloride solution was added down the condenser; after 3 minutes the arc was cut off, excess sodium thiosulfate solution added to stop the bromination, and the carbon tetrachloride was separated, washed and analyzed for 9-bromofluorene by the sodium iodide method (3).

The presence of 0.2899 g. of iodine reduces markedly the formation of 9-bromofluorene even under the conditions of strong irradiation and high temperature. In order to determine if all the bromination took place in the 9-position in the presence of iodine, analyses were made on the same solutions both by the sulfite and sodium iodide methods. (Table II). Previous work (4) has shown that the former analysis gives the total bromination, while the latter gives the percent of 9-bromofluorene only. The experiments were made with one Mazda lamp (200W) at 3" for 4 minutes in a thermostat at 41°.

From Table II it is apparent that 0.0289 g. iodine reduced the formation of 9-bromofluorene to one-third of the total bromination. How much of this effect was due to the absorption of the irradiation by the iodine in the solution? As an approach to this screening effect of iodine, the light from a 200-W Mazda bulb was passed through one and one-eighth inch of an iodine solution before reaching the flask containing 1.66 g. of fluorene in 20.00 ml. of pure carbon tetrachloride; the total distance of the bulb from the reaction flask was  $3\frac{1}{8}$ "; the reaction time, 4 minutes at 41°.

Several interesting observations can be drawn from a comparison of Table II and III. The passage of light through the screen of pure carbon tetrachloride did not reduce the rate of bromination. The 0.0029 iodine filter slowed down the reaction, but strangely enough, all the bromine still entered the 9-position. On the other hand, the passage of light through the 0.0289 iodine filter reduced sharply the total bromination, and only one-

half of the bromine now entered the 9-position. When this same strength of iodine (0.0289 g.) was present in the reaction mixture, the total bromination was greater but only one-third of the bromine entered the 9-position. Finally, the 0.2899 iodine filter absorbed all the irradiation, for when several brominations were performed in a dark room at 41° for 4 minutes, the average was 12% bromination by the sulfite analysis and 0% bromination by the sodium iodide method for 9-bromofluorene.

TABLE I  
FORMATION OF 9-BROMOFLUORENE IN THE PRESENCE OF IODINE

CONC. I <sub>2</sub> (g.)	9-BR-FL. %	CONC. I <sub>2</sub> (g.)	9-BR-FL. %	CONC. I <sub>2</sub> (g.)	9-BR-FL. %
0.2899	13	0.0289	77	0.0029	90
0.2899	10	0.0289	75	0.0029	90
0.2899	12				

TABLE II  
AMOUNT OF 9-BROMOFLUORENE IN THE TOTAL BROMINATION WITH IODINE PRESENT,  
41°, 200 W MAZDA LAMP

CONC. I <sub>2</sub> (g.)	9-BR-FL. (NAI ANAL.)	TOTAL BROM. (Na <sub>2</sub> SO <sub>3</sub> ANAL.)
0.0289	12%	35%
0.0289	13%	34%
Pure CCl <sub>4</sub>	70%	72%
Pure CCl <sub>4</sub>	69%	72%

TABLE III  
ABSORPTION OF IRRADIATION BY IODINE FILTERS

SOLUTION IN FILTER (G. PER 10.00 ML.)	9-BR-FLUORENE (NAI ANAL.) %	TOTAL BROMINATION (Na <sub>2</sub> SO <sub>3</sub> ANAL.) %
0.2899	0	11
.0289	7	15
.0289	7	14
.0029	44	44
.0029	44	44
Pure CCl <sub>4</sub>	69	70
Pure CCl <sub>4</sub>	70	69

#### USE OF SPECTROPHOTOMETER

A Coleman Universal Spectrophotometer, Model 14, has been used to determine the effect of different wave lengths of monochromatic light on the bromination of fluorene and 2-methylnaphthalene, both with and without iodine present in the solvents, carbon tetrachloride and carbon disulfide. The instrument was adapted for temperature control by connecting the well in the same with a constant temperature bath. The spectrophotometer was set at a desired wave length with the galvanometer dials in full counterclockwise position. A cuvette containing 0.005 mole of purified hydrocarbon in 5.00 ml. solvent was placed in the cuvette well at 41°; 10.00 ml. *M*/2 bromine in carbon tetrachloride or carbon disulfide (0.005 mole) were added. Anhydrous conditions were maintained by having a calcium chloride tube on the outlet for the hydrogen bromide. After a given length of time

TABLE IV  
PHOTOBROMINATION OF FLUORENE AND 2-METHYLNAPHTHALENE, 0.005 MOLE, 41°

EXPER.	IRRADIATION (Å°)	EXPOSURE (MIN.)	IODINE (g.)	SOLVENT	TOTAL BROM. %	SIDE-CHAIN BROM. %
<i>Effect of change in wave length with fluorene</i>						
1-4	3750	20	—	CCl <sub>4</sub>	22.9	1.8 <sup>a</sup>
5-8	4250	20	—	CCl <sub>4</sub>	23.7	3.1 <sup>a</sup>
9	5000	20	—	CCl <sub>4</sub>	24.2	13.5
10	5000	20	—	CCl <sub>4</sub>	25.7	13.3
11-16	5250	20	—	CCl <sub>4</sub>	31.4	15.4 <sup>a</sup>
17-20	6250	20	—	CCl <sub>4</sub>	26.2	9.3 <sup>a</sup>
21-27	6750	20	—	CCl <sub>4</sub>	21.2	2.1 <sup>a</sup>
28	7500	20	—	CCl <sub>4</sub>	17.4	0.9
29	7500	20	—	CCl <sub>4</sub>	17.4	1.1
<i>Change in solvent with fluorene</i>						
30	3750	20	—	CS <sub>2</sub>	22.9	1.8
31	3750	20	—	CS <sub>2</sub>	23.8	1.8
32-35	5250	20	—	CS <sub>2</sub>	21.7	5.1 <sup>a</sup>
36-39	6750	20	—	CS <sub>2</sub>	22.0	2.6 <sup>a</sup>
<i>Iodine effect with change of solvent and time of irradiation of fluorene</i>						
40-43	5250	20	0.0015	CCl <sub>4</sub>	58.5	1.7 <sup>a</sup>
44-47	5250	20	0.0002	CCl <sub>4</sub>	29.5	9.3 <sup>a</sup>
48	5250	5	—	CCl <sub>4</sub>	20.3	6.7
49	5250	5	—	CCl <sub>4</sub>	20.5	5.5
50	5250	3	—	CCl <sub>4</sub>	19.1	3.7
51	5250	3	—	CCl <sub>4</sub>	18.6	3.5
52-55	5250	1	—	CCl <sub>4</sub>	20.5	3.2 <sup>a</sup>
56-59	5250	3	—	CS <sub>2</sub>	18.6	2.1 <sup>a</sup>
60-63	5250	3	0.0002	CCl <sub>4</sub>	24.0	2.2 <sup>a</sup>
<i>Change in wave length with 2-methylnaphthalene</i>						
64	3600	20	—	CCl <sub>4</sub>	43.3	3.3
65	3600	20	—	CCl <sub>4</sub>	43.5	3.0
66	4250	20	—	CCl <sub>4</sub>	31.5	5.2
67	4250	20	—	CCl <sub>4</sub>	31.5	4.6
68-71	5250	20	—	CCl <sub>4</sub>	34.7	6.7 <sup>a</sup>
72	6000	20	—	CCl <sub>4</sub>	41.6	4.0
73	6000	20	—	CCl <sub>4</sub>	38.4	5.1
<i>Iodine effect on 2-methylnaphthalene</i>						
74-77	5250	20	0.0015	CCl <sub>4</sub>	54.1	3.9 <sup>a</sup>

<sup>a</sup> Average of number of experiments indicated.

the reaction was stopped by pouring the contents of the cuvette into 15.00 ml. *M*/2 sodium sulfite-sodium acetate solution, and the excess was titrated with *M*/4 iodine solution to determine the percent of total bromination. A sodium iodide analysis (4) on the residue from the carbon tetrachloride layer gave the percent of active bromine (9-bromofluorene

or 2-bromomethylnaphthalene) formed during the reaction. All experiments were run for 20 minutes; in a number of experiments the reaction was exposed for the time indicated in column 3 of Table IV to the wave length given in column 2; the irradiation was always done at the beginning of the 20 minutes period.

#### DISCUSSION OF RESULTS

*Effect of change in wave length on the rates of photobromination.* Four decades ago Bruner (5) determined with the aid of filters that yellow and green light (5000–5800 Å) was more effective in side-chain bromination of toluene in carbon tetrachloride. Four years later LeBlanc and Andrich (6) reported a constant rate of photobromination of toluene between the wave lengths 3270–5790 Å when the reaction was carried out in an atmosphere of oxygen. The next year these authors (7) published a series of three articles on the photobromination of toluene: they reported that the more oxygen present, the higher the yield of benzyl bromide, and they confirmed the constant yield of benzyl bromide between 3250–5790 Å; finally, they found the reaction rate decreased rapidly below 4000 Å and that it was not light sensitive between 2000 and 3000 Å.

Our results show that the photobromination of fluorene and 2-methylnaphthalene differ from the above picture for toluene in several ways. An examination of Table IV reveals that the total bromination of fluorene was little influenced by change in wave length from 3750–7500 Å; (Exper. 1–29), but that the rate of formation of 9-bromofluorene, corresponding to side-chain bromination, increased seven-fold up to 5250 Å and then dropped off again with continued increase in wave length. And our data reveal (Exper. 64–73) that the photobromination of 2-methylnaphthalene resulted chiefly in nuclear bromination, and neither the nuclear nor the side-chain reaction was influenced markedly by change in wave length, although the latter did reach a definite peak at 5250 Å. Kozak (8) reported a maximum rate at 5160 Å.

*Effect of change in solvent.* The rate of photobromination of fluorene in carbon disulfide followed the same general pattern as that in carbon tetrachloride (Exper. 30–39), except the peak of 9-bromofluorene formation at 5250 Å was only about one-fourth that in carbon tetrachloride. The rates for total bromination and for formation of 9-bromofluorene were almost identical for the two solvents at the extremes of 3750 and 6750 Å.

*Iodine effect with change in solvent and time of irradiation.* The literature on the use of iodine in photobrominations is not extensive, although this carrier has been employed widely in non-photobrominations. In 1875 Jannasch (9) obtained only ring bromination when he used 25 g. iodine and 100 g. bromine in the bromination of toluene in sunlight. Bruner (10) added traces of iodine to destroy the "after effect" in the photobromination of toluene; he secured high yields of benzyl bromide by using high ratios of toluene to bromine (up to 200 to 1). Kharasch (11) explains these "after effects" as due to the presence of peroxides, which are removed by the addition of such reagents as iodine, hydrogen bromide and excess toluene<sup>1</sup>.

<sup>1</sup> Neither fluorene nor 2-methylnaphthalene gave a positive test for peroxides when our purified samples were tested by Nozaki's method (12).

Brewster (13) and Hopper (14) have employed a crystal of iodine in their photochemical preparations of *p*-nitrobenzyl bromide.

The presence of 0.0015 g. iodine in the bromination of fluorene in carbon tetrachloride with 20 minutes exposure to 5250 Å almost doubled the rate of total bromination, but it decreased the formation of 9-bromofluorene to one-tenth its value in pure carbon tetrachloride (Exper. 11-16, 40-43). On the other hand, 2-methylnaphthalene showed an increase of about 50% in nuclear bromination and a corresponding decrease in side-chain bromination in the presence of the same iodine concentration (Exper. 68-71, 74-77).

The photobromination of fluorene showed some "after effect" in the absence of iodine, for reducing the time of irradiation at 5250 Å to five minutes cut the rate of total bromination to two-thirds and the formation of 9-bromofluorene to about one-third the value for the 20 minute irradiation (Exper. 11-16, 48-49). With only 1 minute of irradiation, the rate of total bromination remained the same as for 5 minutes, but there was only one-fifth the amount of 9-bromofluorene formed (Exper. 48-49, 52-55).

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#### SUMMARY

1. The presence of iodine reduced the amount of 9-bromofluorene found during the photobromination. By the passage of light from a 6" mercury arc through a series of filters, effects have been produced which range from no production of 9-bromofluorene to those where all the bromination took place in the 9-position.

2. With the aid of a Coleman Universal Spectrophotometer the following facts characterized the photobromination of the two hydrocarbons under investigation in 0.005 *M* solution:

a. The total bromination of fluorene was little influenced by a change in wave length from 3750-7500 Å, but the rate of formation of 9-bromofluorene increased sevenfold to a maximum at 5250 Å.

b. The rate of formation of 9-bromofluorene and the rate of total bromination of this molecule were about the same in the two solvents, carbon tetrachloride and carbon disulfide, at the extremes of 3750 and 6750 Å. But at 5250 Å the rate of formation of 9-bromofluorene in the latter solvent was only about one-fourth of that obtained in carbon tetrachloride.

c. The photobromination of 2-methylnaphthalene resulted chiefly in nuclear bromination, but with a definite peak at 5250 Å for side-chain bromination.

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