

## Photobromination of Methyl-naphthalenes

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As part of a general study of methyl-naphthalene reactions the photobromination with bromine of 1-methyl-naphthalene, 2-methyl-naphthalene, and 2,6-dimethyl-naphthalene was found to yield, almost exclusively, the bromomethyl, dibromomethyl, and tribromomethyl derivatives. The bromination process was simulated on an analog computer with the assumption that the mechanism involved a free-radical chain reaction. By varying relative rate constants in the machine, a good match was obtained between computed and experimentally determined product compositions. The substitution of the first bromine atom into the  $\beta$ -methyl group was 47 times faster than substituting the second. The  $\alpha$ -methyl group was monobrominated 2.8 times faster than the  $\beta$ -methyl group; however, substituting a second bromine into an  $\alpha$ -bromomethyl group was only 0.49 times as fast as substituting the second bromine into a  $\beta$ -bromomethyl group. The presence of a 6-methyl, 6-bromomethyl, and 6-dibromomethyl group slowed the relative bromination rate in groups substituted in the 2-position by factors of 1.00, 0.40, and 0.35, respectively. From these relative rate constants the product compositions are predicted for the photobromination of other dimethyl-naphthalene isomers.

Included in our general study of the reactions of methyl-substituted naphthalenes was the halogenation of mono- and dimethyl-naphthalenes. Photobromination of these methyl-naphthalenes with molecular bromine under appropriate conditions yielded almost exclusively side-chain substituted products. Less than 5% of the bromine substituted on the naphthalene rings, even when preparing the di- and tribromomethyl derivatives. Since the naphthalene ring is reported to be seven times easier to brominate than the benzene ring<sup>2</sup> and is easily brominated under free-radical conditions,<sup>3</sup> we expected considerable ring substitution.

The photobromination of toluene and xylenes to yield bromomethyl and dibromomethyl derivatives is well documented.<sup>4,5</sup> On the other hand, the photobromination of methyl-naphthalene is only briefly mentioned in the literature<sup>6,7</sup> and the photobromination of polymethyl-naphthalenes using molecular bromine, as far as we know, has not been reported. The preparation of bromomethyl and dibromomethyl derivatives of naphthalene from polymethyl-naphthalenes has been accomplished with the brominating agent, N-bromosuccinimide.<sup>8-11</sup> Since recent literature suggests that bromine and N-bromosuccinimide behave similarly in free-radical substitution reactions<sup>12-14</sup> we might have predicted that photobromination would give high yields of side-chain substituted products. Our results confirm this prediction.

The bromination of 1-methyl-, 2-methyl-, and 2,6-dimethyl-naphthalene was extensively studied. A complex mixture of side-chain brominated products resulted in almost all cases and the composition of this mixture was a direct function of the number of bromine equivalents used in the reaction. From these data we were

able to determine relative rate constants for the bromination of the starting methylated naphthalene and the myriad of brominated naphthalene intermediates by simulating the reaction mechanism on an analog computer. With these determined relative rate constants we were able to predict the distribution of brominated derivatives on photobromination of other dimethyl-naphthalene isomers. In this paper we will present our data, discuss our method for obtaining relative rate constants, and predict the product composition for the photobromination of other dimethyl-naphthalene isomers.

### Photobromination Results

A conventional procedure was used for brominating these methyl-naphthalenes.<sup>5</sup> In essence, a carbon tetrachloride solution of bromine was slowly added dropwise to a stirred, refluxed, nitrogen-purged, dilute solution of the methyl-naphthalene in carbon tetrachloride. In most cases a 200-w. incandescent light catalyzed the reaction, but a free-radical catalyst, such as azobisisobutyronitrile, was found to be equally effective. In order to maximize the ratio of side-chain to nuclear bromination, the unreacted bromine was maintained at low concentrations and the hydrogen bromide formed was removed as rapidly as possible with a nitrogen purge.

The monomethyl-naphthalenes were photobrominated by adding the bromine in approximately 0.25-equiv. portions. After the addition of each portion a small sample was taken and analyzed. Tribromomethyl-naphthalene in these samples was determined by hydrolysis followed by isolation of naphthoic acid. The 2,6-dimethyl-naphthalene was brominated by adding approximately 1.0, 1.5, 2.0, 3.0, or 4.0 equiv. of bromine and then isolating the product mixture. All these product mixtures were analyzed by a combination of g.l.c. and n.m.r. procedures.

Under these bromination conditions, the amount of nuclear bromination was very small even when high cumulative amounts of bromine were used. This was confirmed by the following procedure. After adding approximately 2 equiv. of bromine to 2-methyl-naphthalene, the brominate was isolated and refluxed with alcoholic potassium hydroxide. This alcoholysis replaced all reactive bromines in the methyl groups but did not remove any ring bromines. Analysis of this

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(4) E. F. M. Stephenson, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 984.

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(11) W. Ried and H. Bodem, *Chem. Ber.*, **91**, 1981, 2479 (1958).

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alcoholysis product showed only 1.6% bromine which amounted to approximately 3% nuclear halogenation. The same alcoholysis procedures on 1-methylnaphthalene and 2,6-dimethylnaphthalene brominates at high cumulative bromine to methylnaphthalene ratios showed equally small amounts of nuclear substitution.

The results of the photobromination of 2-methylnaphthalene, 1-methylnaphthalene, and 2,6-dimethylnaphthalene as well as a mixture of 1- and 2-methylnaphthalene are summarized in Tables I through IV, respectively.<sup>15</sup> These results show that the total amount of dibromomethyl groups increases proportionately to the extent of bromination. However, the buildup of any particular intermediate depends on its relative ease for bromine substitution.

TABLE I  
PHOTOBROMINATION OF 2-METHYLNAPHTHALENES

Br equiv. reacted <sup>a</sup>	Brominate analysis, <sup>a</sup> mole %			
	[2(0)]	[2(1)]	[2(2)]	[2(3)] <sup>b</sup>
0.20	80.0	20.0	0	0
0.21	79.2	20.8	0	0
0.43	57.2	42.8	0	0
0.43	57.2	42.8	0	0
0.70	33.2	63.7	3.1	0
0.74	31.5	63.2	5.3	0
1.00	12.0	75.0	13.0	0
1.00	10.0	79.6	10.4	0
1.23	0	77.4	22.6	0
1.46	0	54.5	45.5	0
1.56	0	46.8	50.8	2.4
1.82	0	26.2	65.8	8.0
1.99	0	8.1	84.5	7.4
2.16	0	4.2	85.6	10.2

<sup>a</sup> Calculated from quantitative n.m.r. analysis of brominate product mixture. <sup>b</sup> Determined by hydrolysis of brominate and isolating 2-naphthoic acid.

TABLE II  
PHOTOBROMINATION OF 1-METHYLNAPHTHALENE

Br equiv. reacted <sup>a</sup>	Brominate analysis, <sup>b</sup> mole %		
	[1(0)]	[1(1)]	[1(2)]
0.23	76.6	23.4	0
0.48	52.1	47.9	0
0.75	25.8	73.2	1.0
0.97	5.5	91.8	2.7
1.22	0.1	77.5	22.4
1.47	0	53.2	46.8
1.67	0	32.7	67.3
1.79	9	21.1	78.9

<sup>a</sup> Determined from brominate analysis. <sup>b</sup> Analyses by g.l.c. of methoxy derivatives. No 1-tribromomethylnaphthalene was found in these brominates since on hydrolysis 1-naphthoic acid was absent.

### Discussion

Evidence exists which supports a free-radical chain mechanism for the photobromination of alkyl aromatics<sup>16</sup> as illustrated in eq. 1-3.

(15) For convenience we introduce the following notational scheme for identification of compounds: [2(2),6(2)] ≡ 2,6-bis(dibromomethyl)naphthalene. The square brackets enclose the complete compound code. An integer inside the brackets, but not in parentheses, denotes the position of a methyl group on the naphthalene ring. An integer in parentheses denotes the number of bromine atoms substituted into the methyl group identified by the associated position integer. As further example, note that [2(2),5(0)] represents 2-dibromomethyl-5-methylnaphthalene whereas [1(3)] denotes 1-tribromomethylnaphthalene.

(16) See, for instance, C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 369-373.

TABLE III  
BROMINATION OF 2,6-DIMETHYLNAPHTHALENE

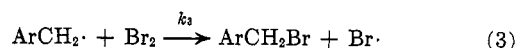
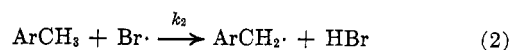
Br equiv. reacted <sup>a</sup>	Brominate composition, <sup>b</sup> mole %					
	[2(0), 6(0)]	[2(1), 6(0)]	[2(2), 6(0)]	[2(1), 6(1)]	[2(2), 6(1)]	[2(2), 6(2)]
0.92	18	65	1	16	0	0
1.10	17	63	0	20	0	0
1.07	15	64	3	18	0	0
1.63	6	40	10	32	12	0
1.32	9	55	4	27	5	0
1.80	0.5	29	7	57	6	0.5
1.30	5	57	6	25	6	1
1.68	6	36	9	39	10	0
2.05	0	16	8	48	21	7
1.97	0	24	9	44	19	4
1.96	0.5	20	8	51	19	1.5
2.00	0	14	10	54	21	1
1.93	0.5	25	9	56	8	1.5
2.93	0	0	0	28	54	18
3.90	0	0	0	3.5	22	74.5
3.85	0	0	0	1	19	80

<sup>a</sup> Total bromine determined by combustion analytical techniques. <sup>b</sup> N.m.r. and g.l.c. analysis of methoxy derivatives. Only traces of naphthalenecarboxylic acid (tribromomethyl derivatives) were detected by acidifying the aqueous phase of the methanolysis products of the last two brominates listed. None was detected in the others.

TABLE IV  
PHOTOBROMINATION OF 1- AND 2-METHYLNAPHTHALENE MIXTURE

Br equiv. reacted <sup>a</sup>	Brominate analysis, <sup>b</sup> mole %					
	[1(0)]	[2(0)]	[1(1)]	[2(1)]	[1(2)]	[2(2)]
0	54.5	45.5	0	0	0	0
0.18	39.9	42.0	14.0	4.1	0	0
0.42	24.6	33.6	30.4	11.4	0	0
0.66	9.3	24.3	44.2	22.2	0	0
0.86	1.5	12.8	52.0	33.6	0	0
1.13	0	0.4	46.8	39.3	5.6	7.9
1.31	0	0	39.8	29.3	12.2	18.7

<sup>a</sup> Determined from analyses. <sup>b</sup> All except initial compositions were determined by quantitative n.m.r.



Now,  $k_3$  is expected to be much larger than  $k_2$  and, employing the usual steady-state assumption, we find that the rate of formation of  $\text{ArCH}_2\text{Br}$  is therefore determined by eq. 4. It follows that the relative rate of

$$\frac{d}{dt}[\text{ArCH}_2\text{Br}] = k_2[\text{ArCH}_3][\text{Br}\cdot] \quad (4)$$

brominating two different alkyl aromatics (or two alkyl groups on one aromatic nucleus) depends on their relative concentration and the relative magnitude of rate constants  $k_2$  as in eq. 5.

$$\frac{d}{dt}[\text{ArCH}_2\text{Br}] = \left(\frac{k_2}{k_2'}\right) \frac{[\text{ArCH}_3]}{[\text{Ar}'\text{CH}_3]} \quad (5)$$

The determination of these relative rates and concentrations in the photobromination of a dimethylnaphthalene, such as 2,6-dimethylnaphthalene, becomes complicated by the possibility of two reaction sites in

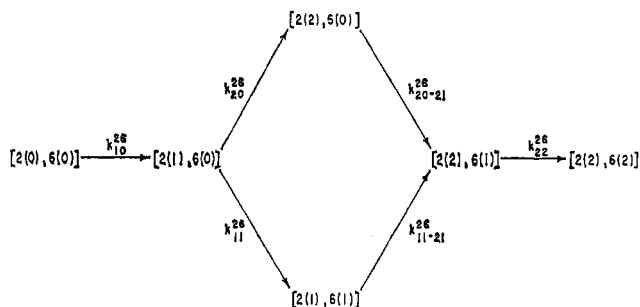


Figure 1.—Photobromination reaction sequence for 2,6-dimethylnaphthalene [2(0),6(0)].

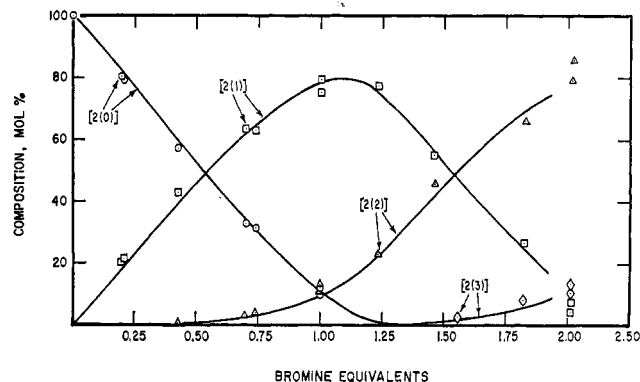


Figure 2.—Photobromination of 2-methylnaphthalene [2(0)]; points observed, curves computed.

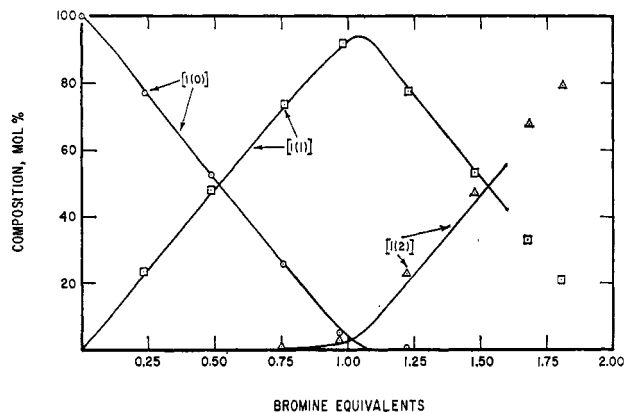


Figure 3.—Photobromination of 1-methylnaphthalene [1(0)]; points observed, curves computed.

each molecule and the fact that the instantaneous concentration of each intermediate depends on its rate of formation as well as disappearance. For instance, Figure 1 illustrates the sequence of reactions which can and do occur in the photobromination of 2,6-dimethylnaphthalene.<sup>17</sup> We shall ignore the formation of [2(3),6(2)] and [2(3),6(3)]. Their relative rates of formation are apparently insignificant as evidenced by analysis of brominates in the experimental reactions.

(17) The relative rate constants are annotated consistent with our scheme of compound identification. The superscript refers to the position of the methyl groups on the naphthalene ring. The subscript refers to the number of substituted bromines in the product compound in the methyl group corresponding to the superscript position integer. When more than one precursor is possible it is also indicated in the subscript. For example,  $k_{1,1}^{1,6}$  indicates the relative rate of formation of [1(1),5(1)] or 1,5-bis(monobromomethyl)naphthalene and  $k_{2,0}^{2,6}$  indicates the relative rate of formation of [2(3)] or 2-tribromomethylnaphthalene; however, note that  $k_{2,0-2,1}^{2,6}$  indicates the relative rate of formation of [2(2),6(1)] from [2(2),6(0)] only.

By reference to Figure 1 it can be seen that the differential equations describing the kinetics of the reaction sequence are as follows.

$$[2(0),\dot{6}(0)] = -k_{1,0}^{2,6}[2(0),6(0)][\text{Br}\cdot] \quad (6)$$

$$[2(1),\dot{6}(0)] = \{k_{1,0}^{2,6}[2(0),6(0)] - (k_{1,1}^{2,6} + k_{2,0}^{2,6})[2(1),6(0)]\}[\text{Br}\cdot] \quad (7)$$

$$[2(1),\dot{6}(1)] = \{k_{1,1}^{2,6}[2(1),6(0)] - k_{1,1-2,1}^{2,6}[2(1),6(1)]\}[\text{Br}\cdot] \quad (8)$$

$$[2(2),\dot{6}(0)] = \{k_{2,0}^{2,6}[2(1),6(0)] - k_{2,0-2,1}^{2,6}[2(2),6(0)]\}[\text{Br}\cdot] \quad (9)$$

$$[2(2),\dot{6}(1)] = \{k_{1,1-2,1}^{2,6}[2(1),6(1)] + k_{2,0-2,1}^{2,6}[2(2),6(0)] - k_{2,2}^{2,6}[2(2),6(1)]\}[\text{Br}\cdot] \quad (10)$$

$$[2(2),\dot{6}(2)] = k_{2,2}^{2,6}[2(2),6(1)][\text{Br}\cdot] \quad (11)$$

Finally

$$[\dot{\text{Br}}\cdot] = -\{k_{1,0}^{2,6}[2(0),6(0)] + (k_{1,1}^{2,6} + k_{2,0}^{2,6})[2(1),6(0)] + k_{1,1-2,1}^{2,6}[2(1),6(1)] + k_{2,0-2,1}^{2,6}[2(2),6(0)] + k_{2,2}^{2,6}[2(2),6(1)]\}[\text{Br}\cdot] \quad (12)$$

where

$$[i(j),\dot{m}(n)] \equiv \frac{d}{dt} [i(j),m(n)]$$

The set of differential equations (6–12) was programmed for numerical solution on an electronic analog computer. For the nonlinear type of program required, the error in numerical results contributed by computer components was less than 1%. Computed solutions for trial rate constant values were compared with experimentally observed reaction data until the computed compositions as a function of bromine consumed agreed with the experimental data. The set of relative rate constants thus obtained was considered to be the best possible. Variation of any of the values in this best set by as little as  $\pm 5\%$  caused the computed results to deviate significantly from the observed experimental data. Therefore, we estimate that the values for these constants are accurate within this limit of  $\pm 5\%$ .

Similar computer analyses were made on data from the bromination of 1-methylnaphthalene, 2-methylnaphthalene, and mixtures of the two. In these cases, the reaction sequences are simpler than for the dimethylnaphthalenes, as shown in eq. 13. The monomethylnaphthalene is brominated sequentially to bromomethylnaphthalene, dibromomethylnaphthalene, and, finally, tribromomethylnaphthalene.

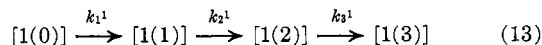


Figure 2 is a graphical representation of the data from the photobromination of 2-methylnaphthalene (Table I) and the solution curve from the analog computer which best matched this data. Similarly, Figure 3 represents the data for the bromination of 1-methylnaphthalene (Table II) and the best match from the analog computer. In both of these cases the experimental data can be matched very well and the determined relative rate constants are estimated to be well within the numerical error of  $\pm 5\%$ . The computed curves were not carried out to 100% bromine consumption because the reaction slows down exponentially with consumed bromine and integration errors in the computer become significant for extremely slow rates.

Figure 4 represents the data and the computed curves for the bromination of a mixture of 1-methylnaphthalene and 2-methylnaphthalene. The match partially deteriorates above 0.75 equiv. of bromine, probably ow-

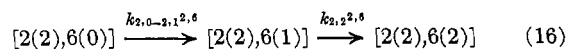
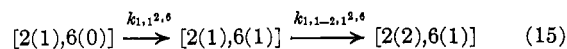
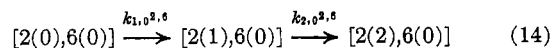
ing to errors in n.m.r. analyses. However, this experiment was designed to find the relative rates for brominating 1-methylnaphthalene and 2-methylnaphthalene and use is made only of the initial portion of the curves. The ratio,  $k_1^2/k_1^1$ , was thus determined to be 0.360 (*i.e.*, 1-methylnaphthalene brominates almost 2.8 times faster than 2-methylnaphthalene). The entire set of relative rate constants determined by computer analysis for both the 1-methylnaphthalene and 2-methylnaphthalene brominations including adjustments for the  $k_1^2/k_1^1$  ratio are presented in Table V.

TABLE V  
RELATIVE RATE CONSTANTS DETERMINED FOR  
1- AND 2-METHYLNAPHTHALENE BROMINATIONS

$k$	Found <sup>a</sup>	Corrected <sup>b</sup>	Per hydrogen <sup>c</sup>	Relative to $k_1^1$ per hydrogen
$k_1^1$	1.000	1.000	0.333	1.000
$k_2^1$	0.0141	0.0141	0.0071	0.0213
$k_3^1$	<i>d</i>	...	...	...
$k_1^2$	1.000	0.360	0.120	0.360
$k_2^2$	0.0811	0.0292	0.0146	0.0438
$k_3^2$	0.0071	0.0026	0.0026	0.0078

<sup>a</sup> Determined from computer analysis of bromination of [1(0)] and [2(0)] individually. <sup>b</sup> Correction factor of 0.360 =  $k_1^2/k_1^1$  determined from bromination of mixture applied to 2-methyl case. <sup>c</sup> Corrected for number of available hydrogen atoms at the reaction sites. <sup>d</sup> Apparently negligible since no 1-tribromomethylnaphthalene was detected by chemical analysis, even for large total bromine additions.

Figure 5 illustrates the data from the bromination of 2,6-dimethylnaphthalene (Table III), along with the best match from the analog computer. Since there are many more rate constants involved in the bromination of dimethylnaphthalenes than in the bromination of monomethylnaphthalenes, obtaining a good curve fit of the experimental data is much more difficult. However, by reference to Figure 1 and eq. 14-16, it can be



seen that there are three distinct paths wherein bromination of 2-methyl groups occurs while the rest of the molecule remains structurally constant. Assuming that the relative rates of the mono- and dibromination steps are the same along each of these paths, we assign the ratios

$$\frac{k_{1,0^2,6}}{k_{2,0^2,6}} = \frac{k_{1,1^2,6}}{k_{1,-2,1^2,6}} = \frac{k_{2,0-2,1^2,6}}{k_{2,2^2,6}} \equiv \frac{k_1^2}{k_2^2} = 8.21$$

which were determined experimentally from the bromination of 2-methylnaphthalene. The six-parameter problem is now reduced to finding the relative values of three parameters,  $k_{1,0^2,6}$ ,  $k_{1,1^2,6}$ , and  $k_{2,0-2,1^2,6}$ , while maintaining the ratio assumed above.

Re-examining Figure 5 shows that the computer is unable to match some of the data especially around the point where 2 equiv. of bromine has been substituted. Notice at this point the brominate mixture contains all possible brominated 2,6-dimethylnaphthalene intermediates. This considerably taxed our composition analysis methods and we think the deviation from the computed curves is due to the relatively large error in

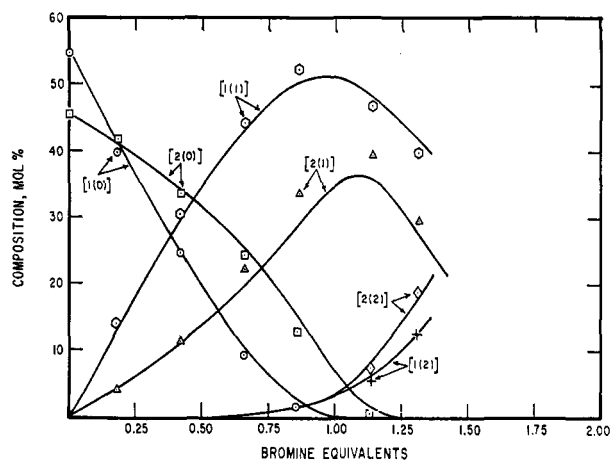


Figure 4.—Photobromination of a mixture of 1- and 2-methylnaphthalene [1(0)] and [2(0)]; points observed, curves computed.

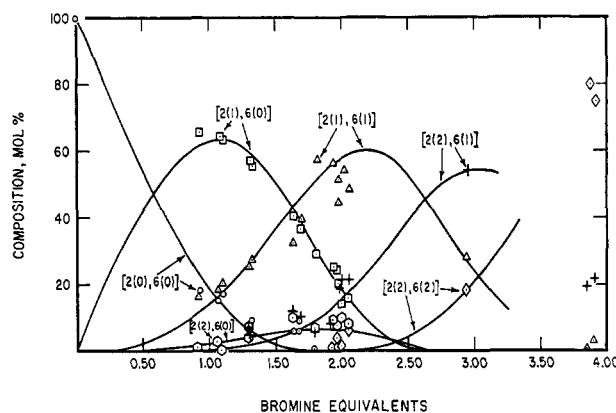


Figure 5.—Photobromination of 2,6-dimethylnaphthalene [2(0),6(0)]; points observed, curves computed.

these analyses. The experimental data at this point are probably no better than  $\pm 10\%$ . The much better match between the data and computed curves early and late in the bromination gives us confidence that our interpretations and conclusions are correct. At these points the mixtures are simpler and, thus, easier to analyze, the limit of error being  $\pm 5\%$ .

The relative rate constants for the photobromination of 2,6-dimethylnaphthalene thus determined are summarized in Table VI.

TABLE VI  
RELATIVE RATE CONSTANTS FOR  
2,6-DIMETHYLNAPHTHALENE BROMINATION

$k$	Found <sup>a</sup>	Per hydrogen	Relative to $k_{1,0^2,6}$ per hydrogen
$k_{1,0^2,6}$	1.000	0.167	1.000
$k_{1,1^2,6}$	0.200	0.0667	0.400
$k_{2,0^2,6}$	0.0406	0.0203	0.1218
$k_{1,-2,1^2,6}$	0.0324	0.0081	0.0486
$k_{2,0-2,1^2,6}$	0.175	0.0583	0.3498
$k_{2,2^2,6}$	0.0141	0.0071	0.0426

$$k_{1,0^2,6}/k_{1,1^2,6}/k_{2,0-2,1^2,6} = 1.00:0.399:0.349$$

<sup>a</sup> Actual relative values determined by computer. <sup>b</sup> Corrected for number of available hydrogens at reaction sites.

There are three major factors which affect the relative rate constants in the photobromination of dimethylnaphthalenes. For convenience we shall call

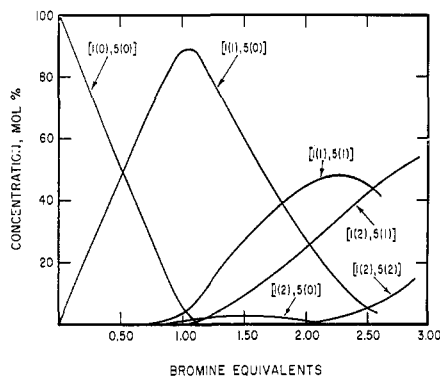


Figure 6.—Predicted photobromination of 1,5-dimethylnaphthalene [1(0),5(0)].

these the ring effect, side-chain bromine effect, and substituent effect.

The ring effect can be defined as all those steric and electronic effects on the rate of bromination caused by the naphthalene ring. Molecular orbital calculations by Hanna<sup>18</sup> have determined the relative stability of an  $\alpha$ -naphthylmethyl to be greater than that of a  $\beta$ -naphthylmethyl radical. He found the relative spin density of  $\alpha$ -C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>· to be 0.450 while that of  $\beta$ -C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>· is 0.529. Our data show  $\alpha$ -methylnaphthalene monobrominates 2.8 times faster than the  $\beta$  isomer. This validates our steady-state kinetic assumption in that the relatively high stability of the  $\alpha$  radical is indicative of a higher rate of formation. Although, according to spin density values, the  $\beta$  radical is more reactive, the step involving bromination of the free radical proceeds much faster than free-radical formation in both the  $\alpha$  and  $\beta$  case and therefore has little effect on the over-all kinetics. In the case of the dibromination (*i.e.*, the monobromination of a monobromomethylnaphthalene) we note a reversal in reaction rates, the  $\beta$  reaction being about twice as fast as the  $\alpha$  reaction. Although we would expect the relative stability of the  $\alpha$ -monobromo isomer to still be greater than the  $\beta$ , we expect that steric shielding by the *peri*-hydrogen has a pronounced influence upon the attack of a large group such as bromine.

The side-chain bromine effect will be defined as the change of rate constants caused by one or more bromines already substituted on the methyl group. As found, the substitution of one bromine on a methyl group lowers the rate constant for the substitution of the second bromine on the same group. Two bromines dramatically lower the rate constant for the substitution of a third bromine. Electronic as well as steric factors undoubtedly control this sequential reduction in reaction rate, but it is difficult to identify clearly the relative importance of each factor. The side-chain bromine effects are noticeable in the large reduction of the relative rate constants for substituting one, two, and three bromines into a particular methyl group. The  $k_1^1/k_2^1$  ratio is 47, and the  $k_1^2/k_2^2$  ratio is 8.21. The much larger ratio in the 1-methylnaphthalene case is probably due to the steric hindrance of the *peri*-hydrogen and that is why we assumed  $k_3^1$  would be much smaller than 0.0077 ( $k_3^2$ ).

(18) Private communication from Melvin Hanna, Colorado University, Boulder, Colo.

The substituent effect on relative rates refers to the nature and position of substitution on the naphthalene ring other than at the reaction site. It has been shown that substituted naphthalenes follow a Hammett  $\sigma$ - $\rho$  relationship similar to that found in substituted benzenes.<sup>19-23</sup> Deactivating groups such as methyl or dibromomethyl would, therefore, be expected to reduce the relative rate constants.

Consider the proportionality of  $k_{1,0}^{2,6}:k_{1,1}^{2,6}:k_{2,0-2,1}^{2,6}$  as found for eq. 14-16. A 6-bromomethyl group reduces the relative rate constant in the 2-position by a factor of 0.399. The 6-dibromomethyl group reduces the relative rate at position 2 by 0.349. It is interesting to note that the dibromomethyl group has just a slightly greater effect upon the rate than the bromomethyl group.

If one assumes that the reaction constant ( $\rho$ ) is the same in the naphthalene series as it is in the benzene series ( $-1.36$ )<sup>13,24</sup> and the  $\sigma$  for the methyl group is  $-0.170$ ,<sup>24</sup> then the naphthalene substituent constant ( $\sigma_n$ ) of the 6-bromomethyl group on the 2-position is calculated to be 0.13 and that of the dibromomethyl group is 0.17. This compares well with the  $\sigma$  of 0.184 found for the chloromethyl group.<sup>25</sup> Since in the naphthalene series  $\sigma$  values are found to be slightly smaller than those in the benzene series,<sup>21</sup> our data are consistent with previous literature.

### Predictions

With this information about the relative rates of photobrominating methylnaphthalenes, it should be possible to predict with reasonable accuracy the product composition on brominating other dimethylnaphthalene isomers. As long as the methyl groups are not adjacent to one another, the ring, side-chain bromine, and substituent effects should be the same as or similar to those determined for the 1-methyl-, 2-methyl-, and 2,6-dimethylnaphthalene brominations. A slight difference in the substituent effect could exist. Price has shown that the rate of base hydrolysis of ethyl nitro-2-naphthoates varies, depending on whether the nitro and the ester group are conjugated (*para*) or not conjugated (*meta*).<sup>19</sup> A 6-nitro group has a greater effect upon the saponification rate than the 7-nitro group. Fischer and co-workers<sup>21</sup> have shown that in the hydrolysis of the ethyl nitro-1-naphthoates, the nitro group exerts a slightly smaller polar effect in the naphthalene series than in the benzene series, especially when the nitro group is in the 5-, 6-, or 7-position. Data compiled by Wells and Ward<sup>23</sup> show that a chloro or bromo group in the naphthalene system exhibits a small but definite substituent effect upon the benzoylation of chloronaphthylamines in benzene at 25° and solvolysis of naphthylmethyl bromides in 90% aqueous methanol. The chlorine and bromine  $\sigma$  values are similar and range from 0.30 to 0.50, depending upon the position of attachment to the naphthalene ring. The substituent effect of the bromomethyl and dibromomethyl

(19) C. C. Price and R. H. Michel, *J. Am. Chem. Soc.*, **74**, 3652 (1952).

(20) C. C. Price, *et al.*, *ibid.*, **76**, 5131 (1954).

(21) A. Fischer, *et al.*, *J. Chem. Soc.*, 4358 (1957).

(22) A. Fischer, *et al.*, *ibid.*, 1426 (1958).

(23) P. R. Wells and E. R. Ward, *Chem. Ind. (London)*, 528 (1958).

(24) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(25) Y. Ogata and I. Sugiyama, *Kagaku (Tokyo)*, **19**, 232 (1949).

group should be and is smaller than bromine owing to the insulation of the methylene group.

From the above one would expect bromination of 1,5-dimethylnaphthalene to be entirely predictable. The ring and side-chain effects should be the same as in the 1-methylnaphthalene case. As in 2,6-dimethylnaphthalene, the methyl groups in 1,5-dimethylnaphthalene are conjugated and the substituent effects should be similar to those found in the photobromination of 2,6-dimethylnaphthalene. Assuming this, the relative rate constants were calculated for the photobromination of 1,5-dimethylnaphthalene and are tabulated in Table VII. The composition curves produced from the analog computer are illustrated in Figure 6.

TABLE VII  
RELATIVE RATE CONSTANTS CALCULATED  
FOR 1,5-DIMETHYLNAPHTHALENE

$k$	Per hydrogen <sup>a</sup>	$k \times \text{no. of hydrogens}^b$	Relative to $k_{1,0}^{1,5}$
$k_{1,0}^{1,5}$	1.000	6.000	1.000
$k_{2,0}^{1,5}$	0.0213	0.0426	0.0071
$k_{1,1}^{1,5}$	0.399	1.197	0.200
$k_{1,1-2,1}^{1,5}$	0.0085	0.0340	0.0057
$k_{2,0-2,1}^{1,5}$	0.349	1.047	0.174
$k_{2,2}^{1,5}$	0.0074	0.0148	0.0025

<sup>a</sup> Calculated from constants in Tables V and VI. <sup>b</sup> Multiplied by number of available hydrogens at reaction sites.

It is noticed that the shapes of these 1,5-dimethylnaphthalene concentration curves are much different from those of 2,6-dimethylnaphthalene. The concentration of  $[1(1),5(0)]$  builds up to almost 90% before being diminished by further bromination. By this same reasoning the bromination of 1,4-dimethylnaphthalene should show the same distribution predicted for the 1,5 isomer.

The dimethylnaphthalene isomers considered so far contained equivalent methyl groups (*i.e.*, a center of symmetry existed). This is not the case with 1,6-dimethylnaphthalene so the photobromination of 1,6-dimethylnaphthalene should produce a much more complicated mixture of brominated compounds. The monobromination of the  $\alpha$ -methyl group will give a different product from the monobromination of the  $\beta$ -methyl group (see Figure 7 for the sequence of reactions). In the 1,6 isomer the methyl groups are also not conjugated which should result in the reduction of the substituent effect. Wells and Ward<sup>23</sup> show that  $\sigma$  may be reduced by as much as 40 to 50%. On reducing the  $\sigma$  constant by 50% and recalculating the relative rates, we found an effect of only 2% on the shape and magnitude of the composition curves. This is because the ring and side-chain bromine effects are considerably larger than the substituent effects and essentially dictate the shape of the curves.

Therefore, we assumed the same substituent effect in the bromination of 1,6-dimethylnaphthalene as in the bromination of 2,6-dimethylnaphthalene. The calculated relative rate constants are summarized in Table VIII and the projected composition of brominated products is shown in Figure 8. The shape and magnitude of the curves turned out quite differently from those of either 2,6-dimethylnaphthalene or 1,5-dimethyl-

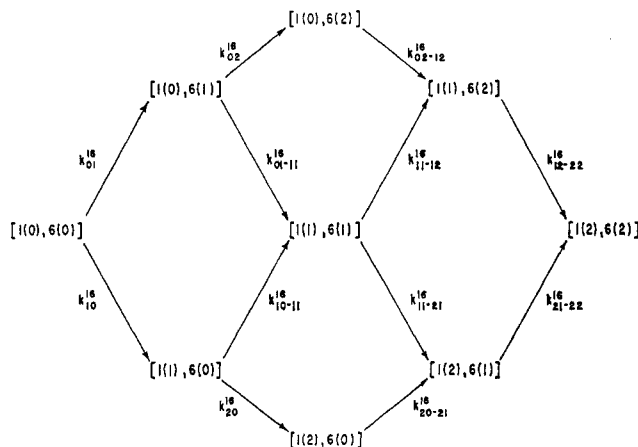


Figure 7.—Photobromination reaction sequence for 1,6-dimethylnaphthalene  $[1(0),6(0)]$ .

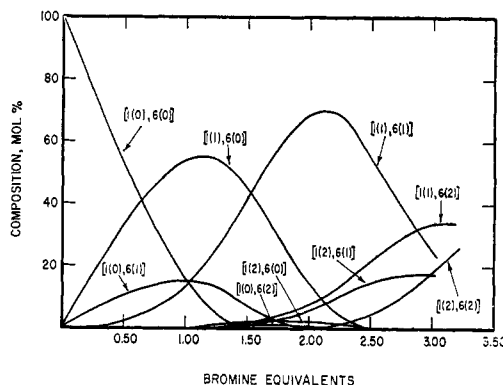


Figure 8.—Predicted photobromination of 1,6-dimethylnaphthalene  $[1(0),6(0)]$ .

naphthalene. This is due to the asymmetry of the methyl groups and the different relative rates for brominating  $\alpha$ - and  $\beta$ -methyl groups.

TABLE VIII  
RELATIVE RATE CONSTANTS CALCULATED FOR  
1,6-DIMETHYLNAPHTHALENE

$k$	Per hydrogen <sup>a</sup>	$k \times \text{no. of hydrogens}^b$	Relative to $k_{1,0}^{1,6}$
$k_{1,0}^{1,6}$	1.000	3.000	1.000
$k_{2,0}^{1,6}$	0.0213	0.0426	0.0142
$k_{0,1-1,1}^{1,6}$	0.399	1.197	0.399
$k_{1,1-2,1}^{1,6}$	0.0085	0.0170	0.0057
$k_{0,2-1,2}^{1,6}$	0.349	1.047	0.349
$k_{1,2-2,2}^{1,6}$	0.0074	0.0148	0.0049
$k_{0,1}^{1,6}$	0.360	1.080	0.360
$k_{0,2}^{1,6}$	0.0439	0.0878	0.0293
$k_{1,0-1,1}^{1,6}$	0.144	0.432	0.144
$k_{1,1-1,2}^{1,6}$	0.0175	0.0350	0.0117
$k_{2,0-2,1}^{1,6}$	0.125	0.375	0.125
$k_{2,1-2,2}^{1,6}$	0.0153	0.0306	0.0102

<sup>a</sup> Calculated from constants in Tables V and VI. <sup>b</sup> Multiplied by the number of available hydrogens at reaction site.

By the same procedure it is possible to predict the compositions for the photobromination of 2,7-dimethylnaphthalene and 1,7-dimethylnaphthalene. The composition curves would resemble closely those of 2,6-dimethylnaphthalene and 1,6-dimethylnaphthalene, respectively.

We have no way of knowing what effect *ortho*-substituted methyl groups would have on each other and,

therefore, cannot predict the composition of products from the bromination of 1,2-, 2,3-, and 1,8-dimethylnaphthalene. We would expect the substituent and side-chain bromine effects to change and yield an entirely different set of composition curves. We will study these cases in the future.

### Experimental

**Photobrominations.**—1-Methylnaphthalene, 2-methylnaphthalene, and 2,6-dimethylnaphthalene were each photobrominated by similar procedures, the molar ratio of bromine to aromatic being varied for different product compositions. The following are examples of these procedures.

**Bromination of 2,6-Dimethylnaphthalene.**—To a 500-ml., three-neck flask, equipped with a stirrer, dropping funnel, reflux condenser, nitrogen inlet tube, and heating mantle was added 10 g. (0.064 mole) of 2,6-dimethylnaphthalene (Aldrich Chemical Co.) in 200 ml. of carbon tetrachloride. Bromine (10.2 g., 0.064 mole) was dissolved in 100 ml. of carbon tetrachloride and placed in the dropping funnel. The molar ratio of bromine to 2,6-dimethylnaphthalene in this case was 1.0. With stirring and a nitrogen purge, the 2,6-dimethylnaphthalene solution was brought to reflux, and a 200-w. incandescent light was placed such that it illuminated the reaction mixture. The bromine in carbon tetrachloride was added dropwise to this stirred solution over a period of 2 hr., hydrogen bromide being continually evolved and removed by the nitrogen purge. Care was taken to maintain the drop rate slow enough to prevent any sizable buildup of molecular bromine. After complete addition, the mixture was stirred, purged, and refluxed for an additional 0.5 hr. and then cooled with stirring. The brominated 2,6-dimethylnaphthalene mixture was recovered by complete evaporation of the solvent and was analyzed by the g.l.c. techniques described below.

**Bromination of 1-Methylnaphthalene (2-Methylnaphthalene).**—In a similarly equipped 2-l. reaction flask was placed 1-methylnaphthalene (50 g., 0.352 mole) and 1 l. of carbon tetrachloride. With a 200-w. incandescent light as the catalyst it was photobrominated as above with 14.0 g. (0.087 mole), or approximately 0.25 equiv., of bromine. At this point a 5-ml. sample of the reaction mixture was taken for analysis and the reaction mixture was again photobrominated with 14.0 g. of bromine. This stepwise bromination was continued until 2 equiv. of bromine was added. Each intermediate sample and final brominate was analyzed by the g.l.c. or n.m.r. techniques described below.

**Analytical Procedure.**—In most cases the photobromination of methylnaphthalenes produced a complex mixture of bromomethyl and dibromomethyl derivatives. These brominates were labile and high boiling and could not be analyzed directly by gas chromatography. A gas chromatography analysis procedure was possible, however, by first forming the more stable methyl ether derivatives of the brominate mixture. The bromomethyl and dibromomethyl groups were converted to the methoxymethyl and methyl acetal groups, respectively. Any tribromomethyl groups present were transformed into sodium carboxylate groups and isolated as such from the reaction mixture.

Approximately 1 g. of the brominate mixture was refluxed with 1–2 g. of sodium methoxide in 200 ml. of absolute methanol for

at least 6 hr. The methanolysis product could be isolated by adding 3 vol. of water and extracting into ether; however, the reaction mixture could be analyzed directly by g.l.c.

The g.l.c. analyses for 2,6-dimethylnaphthalene derivatives were performed on a 2-m. 20% gum rubber column programmed from 100 to 350° at 10°/min. The 1-methylnaphthalene methyl ether derivatives were analyzed on the same column at 170°. Pure methoxymethyl derivatives were isolated from some of the reaction mixture and purified in order to make up standard mixtures. These standard mixtures were used to determine the relative retention time and molar response factors are given in Table IX. Some of the compounds in Table IX were not available or isolable from the reaction mixtures. Their molar response factors were considered equal to the available methoxy derivative nearest in molecular weight and retention time. Since our g.l.c. analyses were only repeatable within  $\pm 5\%$  and these unavailable compounds were generally in low concentration, this estimate did not greatly affect the analysis accuracy.

TABLE IX  
RELATIVE RETENTION TIME AND MOLAR RESPONSE OF  
METHANOLYSIS PRODUCTS FROM 2,6-DIMETHYLNAPHTHALENE  
AND 1-METHYLNAPHTHALENE BROMINATES

Derivative	Relative retention time <sup>a</sup>	Molar response factor <sup>b</sup>
2,6-Dimethylnaphthalene	1.00	1.00
2-Methoxymethyl-6-methylnaphthalene	1.31	0.87
2,6-Bis(methoxymethyl)naphthalene	1.58	0.82
2-Dimethoxymethyl-6-methylnaphthalene	1.46	0.82 <sup>c</sup>
2-Dimethoxymethyl-6-methoxymethylnaphthalene	1.71	0.82 <sup>c</sup>
2,6-Bis(dimethoxymethyl)naphthalene	1.84–1.97	0.82 <sup>c</sup>
1-Methylnaphthalene	1.00	1.00
1-Methoxymethylnaphthalene	2.05	0.835
1-Dimethoxymethylnaphthalene	4.17	0.835 <sup>c</sup>

<sup>a</sup> Relative retention times are based on the parent aromatic, 2,6-dimethylnaphthalene or 1-methylnaphthalene. <sup>b</sup> The molar response factor was used to correct area per cent into mole per cent. <sup>c</sup> The molar response factor of these compounds could not be determined directly. They were assumed to be approximately equal to the value for 2,6-bis(methoxymethyl)naphthalene.

The 2-methylnaphthalene brominate mixtures were analyzed directly by quantitative n.m.r. spectroscopy. The  $\beta$ -methyl group protons adsorption band appeared at 2.41 p.p.m., the  $\beta$ -bromomethyl protons at 4.50 p.p.m., and the  $\beta$ -dibromomethyl protons at 6.70 p.p.m. The aromatic protons appeared further downfield and did not interfere.

**Acknowledgment.**—The authors wish to acknowledge the valuable help of Dr. A. L. Schlage of the Marathon Oil Company who did the n.m.r. analytical work for us and to Professors C. H. DePuy and M. W. Hanna of the University of Colorado for the benefit of many enlightening discussions regarding our work.