catalysts.[8,9] At 420–470°, however, these values tend to converge for catalysts A and C. A marked increase in the catalytic activity of alumina for hydrocarbon reactions has been observed to occur above 400° and has been ascribed to the conversion of passive acidic sites into active ones.[10] In the present case the production of active sites for the methylation process may be especially large on catalyst C for temperatures above 400°. However, it should be noted that A, B, and C do not show equivalent catalytic properties even in this temperature range, since differences in the distribution of methylated naphthalenes and in isomeric compositions still persist.[6] This may be due to nonequivalence in the nature and geometric arrangements of active sites on A and C, with attendant differences in orienting influences on the adsorbed substrates.

The formation of several minor product components, *viz.* naphthalene (XI), 1-methylnaphthalene (XII), 2-methylnaphthalene (XIII), 2,7-dimethylnaphthalene (XV), and 1,2,3-trimethylnaphthalene (XVI), cannot be accounted for by the proposed general mechanism. Direct reduction of the naphtholic group in I, VI, and V would, however, lead to XI, XII, and XIII, respectively. In fact XII (free from XIII) was found as a minor product from VI (Table I, footnote *g*). The small yield of 1,3-dimethylnaphthalene from 2,4-dimethyl-1-naphthol (expt 7 and 8) indicates that the same type of reaction occurs. Analogously XV could be derived from an intermediate 2,7-dimethyl-1-naphthol (not experimentally detected). The low yields of XI–XIII and XV from reactions of I[2] up to 550° imply that sequential methylation steps proceed in preference to direct reduction of the naphtholic group. A different pathway is likely for the formation of XVI, which is the main by-product in the reaction of methanol with 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene (IX).[3] As noted previously IX may be methylated at C-3 before reduction–rearrangement occurs.[3]

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(9) J. B. Peri, *J. Phys. Chem.*, **69**, 231 (1965).
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Experimental Section

Apparatus, Materials, and Procedure.—The apparatus and experimental procedure were essentially the same as described previously.[2,3] For each run 35 g of fresh alumina catalyst (A, from aluminum isopropoxide; or C Houdry hard alumina)[2] was employed and the methanol–naphthol molar ratio was 50:1 (methanol, 0.63 mol; naphthol, 0.0125 mol). The methylnaphthols V, VI, and VIIa (about 99% pure, as based on chromatographic analysis) were synthesized by the methods given previously.[2] Product components (Table I) were isolated by gas chromatography and were identified by comparison of their pmr and infrared spectra, as well as their relative chromatographic retention volumes, with those of pure reference samples.[2] Gas chromatographic analysis of methylnaphthalene products was effected by means of a modified Bentone-34 column; and that of acidic (naphtholic) fractions, by means of Bentone-34 and Carbowax 20M columns.

Registry No.—Methanol, 67-56-1; I, 90-15-3; V, 7469-77-4; VI, 10240-08-1; VII, 4709-20-0.

Electrophilic Substitution in Acenaphthene and Related Compounds. I. Monobromination

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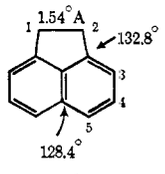
Isomer distribution in the bromination of acenaphthene has been determined for a variety of conditions and reagents. A wide variation was found in the per cent of *ortho* product. Isomer distributions for 1,8-dimethylnaphthalene, perinaphthane, and pleiadane were similar to those for acenaphthene using similar procedures.

There has been considerable recent interest[2-6] in the reactions of acenaphthene (1) and the related 1,8-dimethylnaphthalene (2). Electronic considerations suggest electrophilic attack would lead to a mixture of 3- and 5-substituted acenaphthenes or the corresponding 2- and 4-substituted 1,8-dimethylnaphthalenes.



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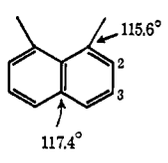

2

Molecular dimensions[7,8] suggest that substitution *ortho* to the ethylene bridge in acenaphthene might not be as sterically hindered as 2-substitution in 1,8-dimethylnaphthalene.

Whereas it has been known[9] that reasonable (approximately 20%) yields of 3-nitroacenaphthene can be separated from 5-nitroacenaphthene after the treatment of acenaphthene with nitric acid in acetic anhydride, until recently no investigation had been made into isomer proportions in monosubstitution reactions of acenaphthene. Electrophilic substitution in 1,8-dimethylnaphthalene has been assumed to enter the 4

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(2) E. Berliner, D. M. Falcione, and J. L. Riemenschneider, *J. Org. Chem.*, **30**, 1812 (1965).
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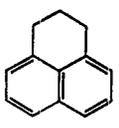
position.[2,10,11] An infrared investigation[6] has recently been made of the reaction products in the halogenation of acenaphthene in methanol and in 90% acetic acid, but some polyhaloacenaphthenes may also have been present.

Accurate information on isomer proportions in monosubstitution reactions of **1** and **2** is needed since the products reported to be isolated on disubstitution (either by further reaction on the hydrocarbon or by subsequent reaction with an already isolated monosubstituted compound) are sometimes unexpected on electronic and steric considerations. For example, such considerations would suggest that a 5-haloacenaphthene would undergo further electrophilic substitution at the 8 position. However, 5-chloroacenaphthene is reported[9] to yield considerable amounts of the 3-nitro compound on treatment with nitric acid in acetic anhydride, to chlorinate[12] in the 6 position, and to acylate[13] in the 3 and 8 positions. 5-Bromoacenaphthene is reported[9,13] to give a 28% yield of the 3-nitro derivative when treated with nitric acid in acetic anhydride but to afford[3] the 6-nitro derivative when nitrated in acetic acid, to brominate[14] in the 3 position, and acylate[13] in the 3 and 8 positions. 5-Iodoacenaphthene is reported[15] to iodonate further in the 3 position. All these results are based on product isolation and the intermediate 5-haloacenaphthene was not always isolated in the dihalogenation reactions. No results appear to be available for further substitution in 3-haloacenaphthenes. The bromination[16] of 4-bromo-1,8-dimethylnaphthalene apparently gives only 2,4-dibromo-1,8-dimethylnaphthalene.

We are at present undertaking a detailed investigation into this situation and the recent report[6] of a few results on the halogenation of acenaphthene prompts us to report our own rather more detailed study on the bromination of acenaphthene, 1,8-dimethylnaphthalene, perinaphthane[17] (**3**) and pleiadane[18] (**4**). Further investigations are in progress on disubstitution reactions and on the π electron distribution in acenaphthene.



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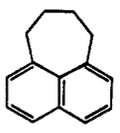

4

Results and Discussion

We chose to investigate bromination because the reagents and conditions are relatively easy to standardize and the products can be analyzed by vapor phase chromatography. Since a considerable number of entities have been used as brominating reagents and solvents employed, we investigated a range of such procedures using acenaphthene. We kept the initial concentrations of acenaphthene and brominating species approximately constant throughout to aid comparison. Conditions were such that only part of the acenaphthene was brominated and disubstitution was detected in only one case. Results are shown in Table I in which the *ortho* product (3-bromoacenaphthene) is shown as a percentage of the total monosubstituted material. We found no evidence for 4 substitution, in agreement with previous workers,[6] but tests with authentic 4-bromoacenaphthene indicated it had a similar retention time to the 5-bromo isomer and trace amounts would thus not be detected by our procedure. However, any such small amounts would hardly affect our results.

TABLE I

BROMINATION OF ACENAPHTHENE[a] AT 20°

Condition	Brominating agent	Solvent	% *ortho* product in monobromination
1	Br_2	HOAc	3.4[b]
2	$BrPy_2OAc$	HOAc–Py	3.6
3	Br_2	Py	4.9
4	NBS	DMF	5.0
5	$BrPy_2NO_2$	Py	5.9
6	Br_2	CH_3NO_2	5.9[c]
7	Br_2	DMF	6.3
8	Br_2	CCl_4	8.1[d]
9	BrOAc	CCl_4	9.5
10	IBr	CCl_4	10.6
11	HOBr	25% aqueous HOAc	24.0[e]
12	HOBr	25% aqueous dioxane	32.4

[a] Acenaphthene, 0.005 mol; brominating species, 0.0025 mol. [b] Not significantly changed by trace amounts of added iodine or water. [c] Contained a trace amount of iodine. [d] Not significantly changed by a trace amount of added iodine. [e] Some disubstitution detected. Run contained either 0.23 mol of perchloric acid or 0.02 mol of sodium acetate and gave comparable results.

The results show a variation in per cent of *ortho* product from 3.4% with bromine in acetic acid to 32.4% with hypobromous acid in aqueous dioxane. This marked dependence of product composition on reagents and solvents used may be useful to help choose the best conditions for avoiding or aiding *ortho* attack in related compounds (but see below).

Our results from bromination of acenaphthene with hypobromous acid in acetic acid are somewhat less meaningful than the others in Table I since not all the acenaphthene immediately dissolved and some dibromination resulted. Similar results obtained in an acetate buffer or in the presence of perchloric acid are interesting, nevertheless, since the percentage of *para* bromination in diphenyl has been reported[19] to change from 46% (0.2 *M* perchloric acid) to 79% (0.02 *M* sodium acetate) under these conditions.

Further comments on some of the brominations are pertinent. Nitromethane was chosen since the chlorination of toluene in this solvent is reported[20] to give the lowest percentage (34%) of *ortho* chlorotoluene in a series of reactions with molecular chlorine in various media. In acetic acid a considerably larger (60%) yield of the *ortho* isomer was obtained. Our figures show the opposite order. N-Bromosuccinimide, which is more usually employed for the side chain bromination

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(16) G. J. Hutchinson and R. D. Topsom, unpublished results.
(17) 2,3-Dihydrophenalene.
(18) 7,8,9,10-Tetrahydrocyclohepta[*d,e*]naphthalene.
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of alkyl aromatics in the presence of a radical initiator such as benzoyl peroxide, can also be used[21] for nuclear bromination in polar solvents. It has been suggested[22] to be a source of bromonium ions when used in dimethylformamide. However, our results suggest that the brominating agent is likely to be molecular bromine rather than a positive species.

We selected conditions 1, 4, 8, and 12 (Table I) as being representative and used these for similar product ratio studies on 1,8-dimethylnaphthalene (**2**), perinaphthane (**3**), and pleiadane (**4**). The results are summarized in Table II.

TABLE II

COMPARISON OF THE PERCENTAGE *ortho* BROMINATION UNDER VARIOUS CONDITIONS AT 20°

Conditions (Table I)	Compd 1	2	3	4
1	3.4	4.4	4.0	5.3
4	5.0	6.3	3.6	5.5
8	8.1	4.6	6.4	5.3
12	32.4	29.8	38.8	38.4

Surprisingly, compounds **2**, **3**, and **4** show little variation in percentage *ortho* bromination under the first three conditions. The amount of the *ortho* isomers obtained with hydrobromous acid in aqueous dioxane (condition 12) is remarkably high in relation to the expected increase in steric hindrance to such substitution. Some increase in strain in the transition state for *para* substitution would be expected in **2**, **3**, and **4** compared to acenaphthene (**1**) because of interaction with the *peri* hydrogen and this may partly offset the effect at the *ortho* position.

We also ran competitive experiments with pairs of compounds to compare rates of bromination. The percentage of isomeric products was not significantly altered for any one compound in the presence of another. Considering the total amount of monobromination and arbitrarily assigning a rate of unity to perinaphthane we found that the rates of bromination in acetic acid (condition 1) were acenaphthene > perinaphthane > pleiadane > 1,8-dimethylnaphthalene in the ratio 9.74 > 1.00 > 0.56 > 0.24. A similar order was obtained for condition 12 in the ratio 3.18 > 1 > 0.66 > 0.46. The more selective brominating conditions gave a greater spread as expected.

Experimental Section

Reagents.—Acenaphthene (mp 96°), 1,8-dimethylacenaphthene (mp 61–62°), perinaphthane[23] (mp 64.5°), and pleiadane[24] (mp 57–58°) were recrystallized samples tested for purity by vpc.

The hydrocarbon (0.04 mol) in acetic acid (200 ml) was allowed to react with bromine (0.04 mol) in acetic acid (50 ml) over 6 hr with stirring at room temperature in the absence of light. The mixture was poured into water (500 ml) and the mixture then extracted with three 25-ml portions of benzene. The benzene layer was washed with water and dried over anhydrous sodium carbonate. Distillation under reduced pressure followed by recrystallization from pentane–ethanol gave 5-bromoacenaphthene,[25] mp 53–53.5° (*Anal.*[26] Calcd for $C_{12}H_9Br$: Br, 34.33. Found: Br, 34.52); 4-bromo-1,8-dimethylnaphthalene,[10] mp 31–31.5° (*Anal.* Calcd for $C_{12}H_{11}Br$: Br, 34.04. Found: Br, 33.76); 6-bromoperinaphthane, mp 24–25° (*Anal.* Calcd for $C_{13}H_{11}Br$: Br, 32.40. Found: Br, 32.62); 7-bromopleiadane, mp 26.5–27°) (*Anal.* Calcd for $C_{14}H_{13}Br$: Br, 30.66. Found: Br, 30.65).

Authentic samples of 3- and 4-bromoacenaphthenes and 3-bromo-1,8-dimethylnaphthalene were available from other work.[10,25]

Bromine, acetic acid, carbon tetrachloride, dimethylformamide, dioxane, pyridine, and nitromethane were purified by standard methods and fractionated before use. Iodine monobromide was a commercial sample titrated against sodium thiosulphate. Bromine dipyridine nitrate[27] had mp 76–77°. Bromine dipyridine acetate was prepared[28] in solution before use.

Bromination.—The general procedure (conditions 1–8, 10) was to place the hydrocarbon (0.005 mol) in 10 ml of the chosen solvent in a reaction vessel containing the brominating entity (0.0025 mol in 5 ml of solvent) in a second chamber. The vessel was immersed in a thermostated bath at 20° for 20 min and the brominating solution then added to the stirred hydrocarbon solution over 30 min. Reaction was continued for a further 30 min. The contents of the reaction vessel were then shaken with benzene (20 ml) and sodium sulfite solution (10 ml, 10%). The benzene layer was washed with water and dried over anhydrous sodium carbonate, and the solvent was evaporated. The residue was analyzed by vpc. Three experiments were conducted for each set of conditions and three vpc analyses made on each product. The results shown in Table I represent the average values of the nine determinations for each, but significant variation was not found in individual analyses. Bromine acetate (condition 9) was prepared[29] by adding bromine (1 ml) in carbon tetrachloride (20 ml) over 30 min to a suspension of silver acetate (4 g) in the same solvent (160 ml). The mixture was then shaken for 90 min and the precipitated silver bromide removed. The solution was titrated against sodium thiosulfate. The bromine acetate solution (0.0025 mol, 25 ml) was added to acenaphthene (0.005 mol) in carbon tetrachloride (25 ml) and the reaction otherwise was carried out as above.

The hypobromous acid solution for runs 11 and 12 was prepared from bromine, water, and silver sulfate and distilled under reduced pressure. It was standardized against sodium thiosulfate. The acenaphthene (0.005 mol) was dissolved in 75 ml of the chosen solvent and the hypobromous acid (0.0025 mol) made up to 100 ml. The acenaphthene was not completely dissolved initially when acetic acid was used and the reaction mixture was therefore allowed to stand overnight before the products were isolated. Some dibromination was detected (vpc). The acenaphthene was completely dissolved when dioxane was used as a solvent and no dibromination occurred.

Gas Chromatography.—A Pye "Argon" gas chromatograph with an Sr-90 ionization detector was used for the analyses. The columns were packed with 10% poly(ethylene glycol) adipate or 7.5% polyethylene adipate–2.5% Apiezon L (for bromo-1,8-dimethylnaphthalenes) and used at a temperature of 175°. The products from the bromination of each hydrocarbon gave three peaks. The first peak was readily identified as unchanged hydrocarbon. The compound corresponding to the third and major peak was isolated and shown to be a monobromo hydrocarbon in each case, and further identified with the known 5-bromoacenaphthene and 4-bromo-1,8-dimethylnaphthalene in these instances. The generally small intermediate peak obtained in the bromination of acenaphthene was identified with an authentic sample of 3-bromoacenaphthene and the other intermediate peaks assumed to be the corresponding *ortho* isomers by analogy and by noting their marked increase in each case when hypobromous acid was used as a brominating agent. Authentic samples of 4-bromoacenaphthene and 3-bromo-1,8-dimethylnaphthalene had longer retention times than the minor peaks obtained in the

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(26) Analyses by the Microanalytical Laboratory (Dr. A. D. Campbell) of the University of Otago.
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bromination of the corresponding hydrocarbons. It was also shown that side chain brominated products produced by use of N-bromosuccinimide in carbon tetrachloride in the presence of benzoyl peroxide, gave peaks with different retention times. (1-Bromoacenaphthene decomposed on the column to give acenaphthylene.)

The chromatograph was calibrated directly with mixtures of the hydrocarbons and their *para* bromo derivatives and with 3-bromoacenaphthene. It was shown that 3- and 5-bromoacenaphthenes gave equal responses and equivalent result for the other pairs of bromo isomers was shown by checking the results with a gas chromatograph with a gas density balance as a detector.

Registry No.—**1**, 83-32-9; **2**, 569-41-5; **3**, 479-58-3; **4**, 14622-16-3; 6-bromoperinaphthane, 15733-72-9; 7-bromopleiadane, 15733-73-0.

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The Kinetic Isotope Effect in the Formation of Anthraquinone[1,2]

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The rate of formation of anthraquinone from 2-(2′-deuteriobenzoyl)benzoic acid is less than the rate for the protium analog, k_H/k_D varying from 1.28 in 97% sulfuric acid to 1.20 in 104% sulfuric acid. The product anthraquinone retains from 56 to 62% of one deuterium. The mechanistic implications of these results are discussed.

Isotope effects in aromatic substitution processes have been examined for many reactions by two different approaches. On the one hand there are direct comparisons of the rate of reaction of a protium compound and of its deuterium analog. Many examples typically show little or no isotope effect.[4] For example, in the nitration of nitrobenzene-d_5[5] k_H/k_D is 1.0 to within about 5%; similar results have been reported by De la Mare, Dunn, and Harvey[6] for the bromination of benzene and benzene-d_6. In other situations, however, there is observed a substantial deuterium isotope effect ($k_H/k_D \gg 1$). These situations have been characterized as ones in which the removal of the aromatic hydrogen is achieved by a general base in the rate-limiting step.[7,8] In still other cases intermediate values for k_H/k_D have been obtained. These results have been interpreted as indicating that the rate of proton loss from the Wheland intermediate is of about the same magnitude as the reversal of the attack of the substituting species upon the aromatic compound.[9]

The secondary isotope effects which accompany the formation of the Wheland intermediate are generally small. Berliner and Schueller[10] have concluded that in the bromination of biphenyl the formation of the Wheland intermediates is rate limiting with a secondary effect of $k_H/k_D = 1.15$. More recently Helgstrand and Lamm[11] have observed that the secondary isotope effect in the azo coupling reaction of *p*-chlorobenzenediazonium ion with trimethoxybenzene is inverse, $k_T/k_H = 1.13$. Very recently Kresge and Chiang[12] also reported an inverse secondary isotope effect in the aromatic hydrogen exchange of trimethoxybenzene, $k_H/k_D = 0.90$. Streitwieser[13] has pointed out that only modest secondary effects are to be expected in the formation of the Wheland intermediate as a result of the counterbalancing influences of the change in hybridization and of hyperconjugation. The results of Kresge and Chiang[12] and of Helgstrand and Lamm[11] suggest that the resultant of these influences will generally be a very small inverse effect. This is consistent with the results of Batts and Gold.[14]

Particularly pertinent to the present discussion are the results of Schubert and his students on the mechanism of the decarbonylation of aromatic aldehydes[15] which showed that proton attack on the aromatic ring of mesitaldehyde or of 2,4,6-triisopropylbenzaldehyde was not solely the rate-limiting step, but that the decomposition of the Wheland intermediate was partly rate limiting. Evidence for this was adduced from the observed isotope effect with mesitaldehyde-α-d and the solvent isotope effect.

There are studies of deuterium isotope effects in aromatic acylation reactions of the Friedel–Crafts type, which have been of the second-type, competitive experiments. Denney and Klemchuk[16] have reported that the cyclization of 2-(2′-deuteriophenyl)benzoic acid to fluorenone under a variety of conditions shows an isotope effect as measured by the deuterium content of the product. Jensen has reported[17] that benzene-d_6 is benzoylated 1.6 times more slowly than benzene; that toluene-4-d_1 shows k_H/k_D of 2.4 on benzoylation in

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(2) Supported in part by Grants G-13125 and GP-1572 from the National Science Foundation.

(3) National Science Foundation Cooperative Graduate Fellow, 1961–1962; National Institutes of Health Predoctoral Fellow, 1962–1963.

(4) It is not the purpose of this discussion to attempt to present a comprehensive review. For leading references and an excellent discussion the reader is referred to the reviews by Melander ("Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960), by Zollinger ("Advances in Physical Organic Chemistry," Vol. II, V. Gold, Ed., Academic Press Inc., New York, N. Y., 1964, pp 163–200), and by Halevi ("Progress in Physical Organic Chemistry," Vol. I, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, Inc., New York, N. Y., pp 109–221).

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