on carbon, fractional distillation of these two esters was undertaken in an attempt to obtain samples of analytical purity. Ethyl β-ethyl-α-bromoacrylate (170 g.) which had been obtained from several runs was distilled through a 30-cm. column packed with 3-mm. glass helices and provided with a heating jacket. Eleven fractions (15–20 g. each) were collected with refractive indices (25°) ranging from 1.4760 to 1.4745; b.p. 80–92° (13 mm.).

In a similar fashion, 130 g. of ethyl α-bromocrotonate was fractionally distilled, n^{25}_D 1.4772–1.4778 with the exception of the first fraction where the value was 1.4764; b.p. 79–89 (20 mm.). The analytical results are included in Table I.

α-Bromocrotonic Acid.—Ethyl α-bromocrotonate (9.6 g., 0.05 mole) and 100 ml. of 20% potassium hydroxide were heated at 50–55° for 40 minutes. The mixture was cooled and acidified with 45 ml. of 6 *N* hydrochloric acid, the temperature of the mixture being carefully maintained at 10–15°. The mixture was extracted with three 75-ml. portions of ether and the combined extracts dried over anhydrous sodium sulfate. The ether was removed leaving a yellow, crystalline residue; yield 6.1 g. (74%); m.p. 91–98°. One recrystallization from water gave white crystals, m.p. 104–108°.[9] A sample was recrystallized several times for a neutral equivalent determination, m.p. 107.5–108.5°.

Calcd. for $C_4H_5BrO_2$: neut. equiv., 165.0. Found: neut. equiv., 164.4.

***p*-Bromophenacyl α-Bromocrotonate.**—A *p*-bromophenacyl ester could readily be prepared,[10] m.p. 94–97°. A sample for analysis was obtained by two recrystallizations from ethanol, m.p. 96.5–97.5°.

Anal. Calcd. for $C_{12}H_{10}Br_2O_3$: C, 39.81; H, 2.78. Found: C, 39.79; H, 2.71.

***p*-Bromoanilide of α-Bromocrotonic Acid.**—α-Bromocrotonyl chloride was prepared[11] by heating 2.4 g. of α-bromocrotonic acid and 2.9 g. of thionyl chloride under reflux for two hours. The 1.8 g. of the acid chloride obtained by distillation was added to 3.5 g. of *p*-bromoaniline dissolved in cold, dry benzene. The mixture was allowed to stand for one hour and the amine hydrochloride was removed by filtration. The benzene was removed *in vacuo* and the residue extracted with anhydrous ether. The ether was removed leaving a white, crystalline residue, yield, 3.8 g.; m.p. 92–93°. The material was twice recrystallized from 70% ethanol to give white needles, m.p. 93.5–94.5°.

Anal. Calcd. for $C_{10}H_9Br_2NO$: C, 37.65; H, 2.84. Found: C, 37.81; H, 2.80.

Acknowledgment.—This investigation was supported in part by a Frederick Gardner Cottrell grant from the Research Corporation.

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[9] α-Bromocrotonic acid melts at 106.5°, and the geometric isomer, α-bromoisocrotonic acid, melts at 92°, A. Michael and L. M. Norton, *Am. Chem. J.*, **2**, 15 (1880).

[10] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 157.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER CO.]

The Bromination of Naphthalene[1]

BY FRANK R. MAYO[2a] AND WILLIAM B. HARDY[2b]

The bromination of naphthalene was investigated in several solvents at 20–25°. In carbon tetrachloride in the dark, about 15% addition to the nucleus normally accompanies substitution. Although both reactions are accelerated by ascaridole and retarded by air and isoamyl nitrite, the addition reaction is more susceptible to acceleration and inhibition. Under illumination, more than 80% of the bromine may react by addition. Substitution is accelerated by solvents of higher dielectric constant. Addition is less affected. In benzene and toluene solutions in the absence of light and catalysts, both addition and substitution in naphthalene occur without significant attack on the solvent. In toluene, in the presence of light or ascaridole, side-chain substitution in toluene becomes the predominant reaction, and addition to naphthalene is also accelerated, both at the expense of nuclear substitution in naphthalene. The ratio of side-chain substitution in toluene to addition to naphthalene increases as the bromine concentration decreases. It is concluded that, as in the benzene series, substitution in naphthalene occurs by a polar or molecular mechanism while addition takes place by a free radical mechanism. However, in contrast to benzene derivatives, there is a also a radical mechanism for substitution and a non-radical mechanism for addition, but these have not been fully identified and resolved. Some reactions of 1,2,3,4-tetrabromo-1,2,3,4-tetrahydronaphthalene are described.

The object of this research was to distinguish between addition and substitution reactions in the bromination of naphthalene in terms of polar and free radical mechanisms. Substitutions of chlorine and bromine in benzene are recognized as polar reactions,[3] while the photochemical or peroxide-catalyzed[4] additions to the nucleus proceed through a free radical-chain mechanism. Bromination and chlorination of toluene result in nuclear substitution under conditions favoring a polar mechanism, in side-chain substitution[5] or in both side-chain substitution and nuclear addition[4] by a free radical mechanism. Addition to toluene is favored over side-chain substitution by higher chlorine concentrations,[4] suggesting that the addition reaction is of higher order in chlorine, and the vapor phase photo-addition of chlorine to benzene is considered to involve both a chlorine atom and a chlorine molecule in the rate-determining step.[6] In all these instances, the distinction between the polar mechanism and the free radical mechanism is clear-cut, and the reaction may be directed to give nearly 100% of either type of product. Addition and substitution in the bromination of phenanthrene are similarly distinguished, although a polar mechanism for the addition has also been found.[3,7]

The halogenation of naphthalene has not been studied from the standpoint of competing substitution and addition reactions or of polar and radical

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[1] The work in carbon tetrachloride and "other solvents" is condensed from the Ph.D. Dissertation of William B. Hardy, University of Chicago, December, 1940. The remainder is the work of the senior author as Contribution No. 104 from the General Laboratories of the U. S. Rubber Co. Presented at the XII International Congress of Pure and Applied Chemistry, New York, September, 1951.

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[3] C. C. Price, *Chem. Revs.*, **29**, 37 (1941).

[4] M. S. Kharasch and M. G. Berkman, *J. Org. Chem.*, **6**, 810 (1941).

[5] M. S. Kharasch, P. C. White and F. R. Mayo, *ibid.*, **3**, 33 (1938).

[6] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., p. 294, 308.

[7] C. C. Price, THIS JOURNAL, **58**, 1834, 2101 (1936); M. S. Kharasch, P. C. White and F. R. Mayo, *J. Org. Chem.*, **2**, 574 (1938).

mechanisms. Chlorination in the cold and in the dark is said to give first the 1,4-addition product, which dehydrohalogenates to α-chloronaphthalene.[8,9] Similarly, bromination is reported to give some reactive bromide,[10] suggesting addition. The best yields of α- or monohalides have been obtained in polar solvents,[11,12] or in the presence of a carrier, while chlorination in carbon tetrachloride without carrier yields polychlorides directly, suggesting substitution *via* addition. Chlorination[9] and bromination[10] in the light yield the tetrahalide addition products. On heating, the tetrabromide decomposes to give bromine, hydrogen bromide, and polybrominated naphthalenes.[13] The over-all bromination of naphthalene is faster in acetic acid than in hexane[14] and is retarded by the hydrogen bromide formed. In dilute solution in acetic acid, the over-all reaction is stated[15] to be a composite of three reactions, first order in naphthalene and first, second and third order in bromine. In the presence of iodine, naphthalene is reported to brominate faster than toluene,[16] but toluene is said to protect naphthalene from chlorination in the absence of iodine,[11] the product being benzyl chloride. Wibaut and co-workers[17] have recently studied the relations between α-, β- and polybromides in the bromination at higher temperatures.

Although this paper reports a large number of experiments on the bromination of naphthalene, it does more to point out the complexities in the bromination of naphthalene than to settle them. However, since the present authors are now unable to continue this work, its publication may stimulate further work to settle the problems raised. The bromination was studied first in a relatively inert, non-polar solvent, carbon tetrachloride, using a sealed tube technique and was then extended to a few other solvents. The results in toluene solution suggested that this solvent be studied in more detail. These last experiments were carried out by regulated addition of bromine solution to the reaction mixture under nitrogen.

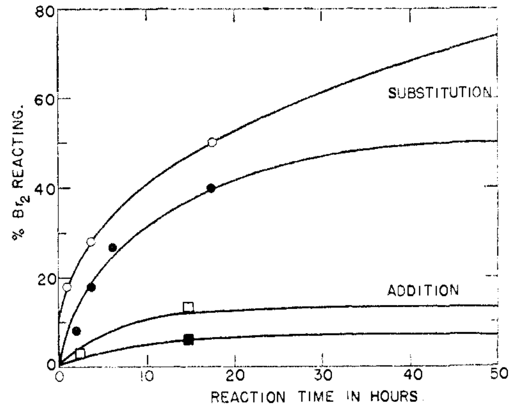

Fig. 1.—Reaction of 0.21 *M* bromine with 1.07 *M* naphthalene in carbon tetrachloride at 25°: ○, □, air absent; ●, ■, air present.

The Bromination of Naphthalene in Carbon Tetrachloride—In the experiments in this section, five moles of naphthalene were present per mole of bromine and the quantities of catalysts and inhibitors are referred to the initial quantity of bromine used. Reactions were carried out at room temperature (22–25°), blank experiments being used for comparisons of rates. Results are expressed as percentages of the initial bromine reacting by addition and substitution, the total reaction being measured by disappearance of bromine, substitution by formation of hydrogen bromide, and addition by difference.

The reaction of 0.212 molar bromine with 1.07 molar naphthalene in carbon tetrachloride solution and in the absence of light and air will be used as a basis of reference. One to two per cent. of the bromine seemed to react instantaneously in a reaction which has not been accounted for (see Experimental part). Figure 1 shows that 30–35% reaction takes place in the first four hours, reaction thereafter becoming slower, and reaching 85–90% in 50 hours. About six times as much bromine eventually reacts by substitution as by addition, but relatively more addition occurs in the early stages. The slow rate in the later stages is due to the hydrogen bromide formed, which, according to Lauer and Oda,[14] complexes with the unreacted bromine. Air retards both substitution and addition by 25–40%.

The blank experiments in Table I show that relatively more addition occurs at lower reagent concentrations. The effects of isoamyl nitrite, which stops aliphatic brominations,[18] and of ascaridole (menthene peroxide), an accelerator of free radical chain reactions, suggest (1) that bromination is predominantly non-radical at higher concentrations, because it is more subject to acceleration than inhibition by free radical reagents, (2)

TABLE I

THE EFFECTS OF ISOAMYL NITRITE AND ASCARIDOLE ON THE BROMINATION OF NAPHTHALENE[a]

Time		Blank	*i*-AmONO	Ascaridole
$[Br_2]_0 = 0.21\ M$; $[C_{10}H_8]_0 = 1.07\ M$; [added reagent] = 0.015 *M*				
3 hours	% addition	9	5	45
	% substitution	13	3	19
$[Br_2]_0 = 0.041\ M$; $[C_{10}H_8]_0 = 0.21\ M$; [added reagent] = 0.0015 *M*				
3 hours	% addition	12	0.5	12
	% substitution	6	3	5

[a] Each value is average for three runs. These experiments were carried out in brown bottles where more instantaneous reaction was found.[23]

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(8) A. Laurent. *Ann. chim.*, [2] **52**, 275 (1833).

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(10) J. R. Sampey, J. M. Cox and A. B. King, *ibid.*, **71**, 3697 (1949).

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(15) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 100 (1948).

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(17) J. F. Suyver and J. P. Wibaut, *Rec. trav. chim.*, **64**, 65 (1945); J. P. Wibaut, F. L. J. Sixma, J. F. Suyver and L. M. Nijland, *Proc. Koninkl. Nederland. Akad. Wetenschap.*, **51**, 776 (1948); J. P. Wibaut, F. L. J. Sixma and J. F. Suyver, *Rec. trav. chim.*, **68**, 525 (1949); F. L. J. Sixma and J. P. Wibaut, *ibid.*, **69**, 577 (1950).

(18) M. S. Kharasch, W. Hered and F. R. Mayo, *J. Org. Chem.*, **6**, 818 (1941).

that the predominating addition at lower concentrations is largely a free radical reaction, because it can be stopped by isoamyl nitrite but not further accelerated, and (3) that both reagents affect addition more than substitution.

Light is a powerful accelerator for the addition reaction. A run with the concentrations of the reference experiment proceeded nearly to completion in three hours under an incandescent lamp. Sunlight was much more effective; within 15 minutes, 83% of the bromine reacted by addition, 11% by substitution. Two hours in sunlight followed by 15 hours in the dark give 81% addition and 16% substitution, indicating that little reaction occurred after the first few minutes except for possible loss of hydrogen bromide by the addition product. Only about one-fourth of the added bromine was found as the crystalline tetrabromide, and the remainder must appear as unknown dibromides and isomeric tetrabromides. Experiments on the thermal decomposition and chemical dehalogenation of the known tetrabromide are summarized in the Experimental part.

Packing a reaction tube with broken Pyrex increased the rates of both substitution and addition by 20–200% but the results were not reproducible.

The experiments on the thermal bromination of naphthalene in carbon tetrachloride show that both substitution and addition occur spontaneously in the dark. Both are affected by accelerators and retarders of free radical reactions, but the addition reaction becomes the predominating reaction in the presence of ascaridole or light.

The Bromination of Naphthalene in Other Solvents —In the experiments in this section, the solvent was 75% by volume of the one indicated, 25% by volume of carbon tetrachloride. The reaction of naphthalene in benzene or toluene in the dark was about as fast as in carbon tetrachloride and gave the same ratio of substitution to addition products. Careful search for bromobenzene showed that less than 2% (if any) of the reacting bromine attacked the benzene in spite of a mole ratio of benzene:naphthalene of 10:1.

The rates of bromination of naphthalene in carbon tetrachloride, acetic acid and nitrobenzene in the dark are compared in Fig. 2. Tests showed no reaction of these solvents with bromine in the absence of naphthalene. Since addition and substitution were not resolved in acetic acid and since addition accounted for only 10–15% of the total reaction in the other solvents, the fraction of bromine reacting is plotted against time. Figure 2 shows that the rates of reaction of bromine increase with the dielectric constants of the solvents. The acceleration is due mostly to an increase in the rate of substitution, 84% in one hour against 10% in carbon tetrachloride, but there is also an increase in the rate of addition, 7% in one hour in nitrobenzene, 4% in carbon tetrachloride. These effects of solvents on rates are characteristic of polar or ionic, not of free radical, mechanisms. Thus we have evidence of polar as well as free radical mechanisms of both substitution and addition.

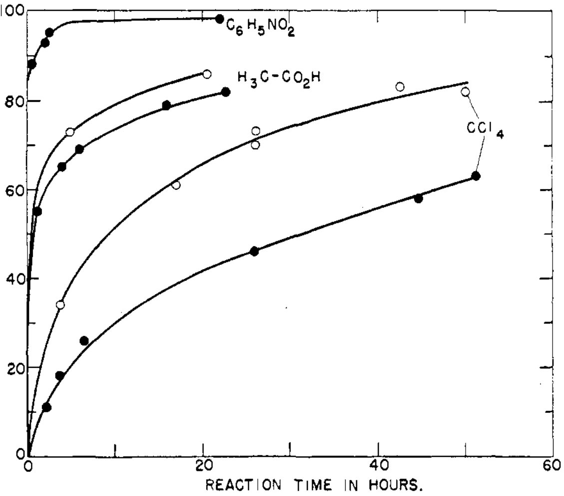


Fig. 2.—Reaction of 0.21 *M* bromine with 0.105 *M* naphthalene at 25° in solvents: ○, air absent; ●, air present.

Experiments in toluene solution in Table II show a clear distinction between the radical and polar mechanisms of addition. In the absence of light and peroxides, both addition and substitution in naphthalene occur without attack on the toluene. However, in the presence of ascaridole or light, which promote addition to naphthalene, side-chain substitution in toluene exceeds both addition and substitution in naphthalene, although naphthalene addition now predominates over naphthalene substitution. Thus the spontaneous addition to naphthalene, presumably polar in the presence of air, occurs without affecting toluene, but the accelerated addition to naphthalene, presumably radical, is outrun by substitution in the toluene side-chain, by a free radical mechanism.

TABLE II

THE BROMINATION OF NAPHTHALENE IN TOLUENE SOLUTION

Conditions	Time, hr.	% initial bromine reacting by Nuclear substn.	Side-chain substn.	Addition
Dark, air present	4.8	22	0	4
	23	38	3	5
	25	39	0.5	8
	45	45	0	5
Dark, air present 3 mole % ascaridole	17	7	83	8
Hg arc, air present	0.08	10	77	13
Hg arc, air absent	.08	11	75	14
	.12	13	73	14

Bromination of Naphthalene–Toluene Mixtures in the Light —The above experiments suggested that both the accelerated addition to naphthalene and the side-chain substitution in toluene might involve bromine atoms and hydrocarbon in the rate-determining steps and that the relative reactivities of the two hydrocarbons toward bromine atoms might be measured in competitive reactions. The experiments show, however, that the relative reactivities depend on the bromine concentration and therefore that the two brominations have different rate-determining steps.

The results obtained are summarized in Table III. The indicated quantities of hydrocarbons in 110 ml. of carbon tetrachloride were treated with 20 ml. of 1 *M* bromine in carbon tetrachloride at

TABLE III

PHOTOCHEMICAL BROMINATION OF TOLUENE AND NAPHTHALENE IN CARBON TETRACHLORIDE AT 20°

Expt. no.	Millimoles		Reaction time,[a] min.	Br_2 found,[b] %	Total substn.,[c] %	% Br reacting by			$\frac{k_{substn.}}{k_{addn.}}$[g]
	$C_6H_5CH_3$	$C_{10}H_8$				Substn. $C_6H_5CH_3$[f]	Substn. $C_{10}H_8$[e]	Addn. $C_{10}H_8$[d]	
9	200	...	20	102.5	97.0	100			
10	200	...	12	97.3	95.8–101.2				
16	200	...	13	101.0	98.1				
11	...	200	123 + 75	98.4	9.7–12.9		10	90	
15	...	200	106 + 14	99.3	8.6–10.6				
12	100	100	50	99.0	94.1–96.1	94	1	5	19
17	100	100	43	101.3	84.3	82	2	16	5
23	100.3	100	1 + 2	98.3	69.8–73.2	69	3	28	2.5
18	40	160	170 + 2	97.0	84.9–90.9	89	1	10	36
20	40	160	230 + 2	97.2	84.9–90.5				
19	40.5	160	5 + 2	99.7	63.2–63.8	59	4	37	6
21	40	160	5 + 2	95.5	60.2–68.3	63	4	33	8
24	250	250	70 + 1	97.7	91.1–95.7	93	1	6	15

[a] The first period is the one during which bromine solution was added; the second is the additional period of illumination (if any was required) during which the solution became colorless (except expts. 11 and 15). [b] Fraction of original bromine accounted for as hydrogen bromide and organic halogen. [c] The first value is the yield of hydrogen bromide found; the other is an upper limit calculated on the assumption that all the missing halogen is hydrogen bromide. This limit is too low if carbon tetrachloride fragments appear in the reaction product. [d,e,f] Probable values calculated on basis that [d] all bromine not reacting by substitution reacts by addition to naphthalene, [e] that substitution in naphthalene is one-ninth as extensive as addition, and [f] that all remaining substitution is in the side-chain in toluene. [g] Rate of side-chain substitution in toluene divided by rate of addition to naphthalene, after correcting for relative concentrations of hydrocarbons.

20° during the indicated periods, as described in more detail in the Experimental part. The bromine reacted completely except in experiments containing no toluene. Because of experimental difficulties, the principal error is probably due to loss of hydrogen bromide and the fraction of bromine reacting by substitution is estimated accordingly (*cf.* footnote *c*, Table III).

The first group of experiments shows that toluene reacts exclusively by substitution in the side chain. This reaction occurred rapidly in the light and the bromine solution could be added in 10–15 minutes without imparting any more than local color to the stirred reaction mixture. Two out of the three runs listed showed that an excess of halogen is accounted for, suggesting that some carbon tetrachloride residues may have been incorporated in the bromination products.

In the second group of experiments, with naphthalene alone, the photochemical bromination of naphthalene is found to be slow and incomplete: in expts. 11 and 15, 0.40% and 1.77% of the initial bromine was recovered. Since the stronger bromine colors would lighten rapidly, the observations point to a higher order reaction with respect to bromine. After removal of bromine by distillation, solutions of the residues in toluene retained a light red-brown color, but since treatments with aqueous potassium iodide and sodium thiosulfate failed to affect the color, the evidence points to a colored reaction product rather than to an equilibrium involving free bromine. In the photobromination of naphthalene, about 90% of bromine reacted by addition, 10% by substitution. This proportion of substitution to addition in naphthalene was assumed to hold in competitive experiments and is not large enough to affect the toluene substitution–naphthalene addition ratios. Further, determinations of reactive halogen on products from competitive experiments are almost always larger than the calculated, so that more than the estimated substitution in naphthalene is very improbable. All solutions absorbed bromine less readily as reaction progressed, presumably because of accumulation of hydrogen bromide.

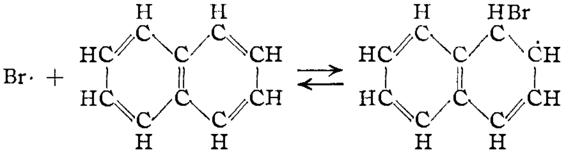
In expts. 12 and 17, containing an equimolecular mixture of hydrocarbons, bromine could be passed into the reaction mixture only about one-fourth as fast as with toluene alone if permanent color was to be avoided, although the toluene concentration had been reduced by only one-half and although less than 20% of the bromine reacted with naphthalene. Experiment 23 indicates that lack of agreement in these experiments may be partly due to variations in local bromine concentrations: when the bromine was added very rapidly, yielding a deeply colored solution, more reaction with naphthalene occurred. Both the rate and concentration effects are confirmed by the next four experiments where a higher ratio of naphthalene to toluene in the feed was employed and where satisfactory checks were obtained. The failure of the higher proportion of naphthalene to increase the proportion of the bromine reacting with naphthalene in slow additions of bromine indicates that bromine concentration is more important than toluene–naphthalene ratio.

The last experiment, using the highest practical concentrations of hydrocarbons (a small portion of the naphthalene would not dissolve until some reaction had occurred) showed a distinctly slower reaction than in the equimolecular mixture with lower concentrations, but no significant difference in the relative rates of the toluene substitution–naphthalene addition reactions.

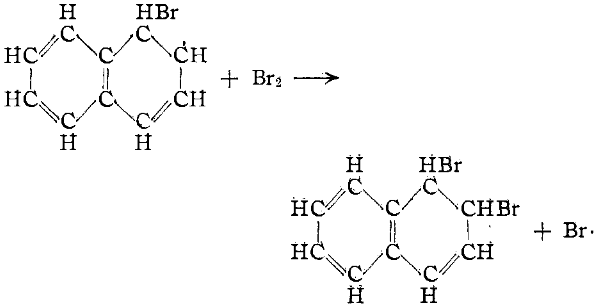
The dependence of the relative rates of the two reactions on the concentration (rate of addition) of bromine shows that the rate-determining step in the addition of bromine to naphthalene requires more bromine than the side-chain substitution in toluene. If the latter reaction involves

$$Br\cdot + C_6H_5{-}CH_3 \longrightarrow HBr + C_6H_5{-}CH_2\cdot$$

then a reasonable formulation for addition to naphthalene is addition of a bromine atom to naphthalene (in the α-position if the same first step is to result in both 1,2- and 1,4-dibromides),



followed by a rate-determining reaction of the resulting radical with bromine in the 2- or 4-position



A second molecule of bromine may then add to the remaining double bond. This formulation shows how naphthalene can retard the side-chain bromination of toluene without reacting extensively itself, by picking up bromine atoms in a reversible reaction, and increasing the chance that a bimolecular reaction with some other radical will occur before the next propagation step occurs.[19] Similar relations have been found in the addition of chlorine to benzene[6] and in addition and side-chain substitution in toluene.[4]

Summary and Conclusions

From this and previous work on the halogenation of naphthalene, we conclude that there are at least three primary reactions of bromine with naphthalene, at least two mechanisms of substitution, and at least two mechanisms of addition. It is clear also that further work is needed. The three primary reactions are: (1) a direct substitution to give α-bromonaphthalene, favored by polar solvents and high bromine concentrations, like the polar or "ionic" substitution reactions of benzene derivatives, (2) a spontaneous addition of bromine to naphthalene, and (3) an accelerated addition. Because the latter addition is initiated by light or ascaridole and retarded by oxygen or isoamyl nitrite, it must proceed by a free radical-chain mechanism. The distinction between the spontaneous and accelerated additions is established by the behavior of the solvent, toluene, which participates in the presence of the accelerated addition but not in the spontaneous reaction. Although the competition between the accelerated addition to naphthalene and side-chain substitution in toluene is dependent on the bromine concentration, Table II establishes the difference between the spontaneous and accelerated additions in the absence of concentration effects. Acceleration of the spontaneous addition by polar solvents indicates that it occurs by a polar or ionic mechanism.

One substitution and two addition mechanisms are accounted for above. The effects of free radical catalysts and retarders on substitution require at least one more mechanism of substitution involving free radicals, either in a direct substitution in naphthalene or in elimination of hydrogen bromide from an addition product, and there is reason to expect both. The postulated unstable $C_{10}H_8Br\cdot$ radical, which reacts with bromine to give an addition product, should also be able to react with bromine to give a substitution product and hydrogen bromide, thus accounting for the 10% substitution accompanying addition in the light. The present and earlier work on dichloride,[8] tetrachloride[9] and tetrabromide[13] addition products shows that these lose hydrogen halide, at least on warming, to give substitution products.[20] Such a substitution path accounts for the high proportions of polyhalide substitution products formed from naphthalene in non-polar solvents,[11,12] for the relatively higher proportion of addition as compared with substitution in the early stages of the uncatalyzed reaction, and for the higher proportion of substitution at higher temperatures.

The present work has not established the kinetics of any mechanism for the reaction of bromine with naphthalene, which may be closely analogous to the bromination of phenanthrene.[3,7] The high proportions of bromine reacting by addition in the light and the low yields of crystalline tetrabromide isolated point to the formation of dibromides or other tetrabromides, as do also the colors in the residues from naphthalene reactions, and different yields of silver bromide formed by the action of alcoholic silver nitrate (71% on two hours refluxing with the known tetrabromide, 52% on standing at room temperature with the unknown mixture of addition products). Several isomers of both dibromide and tetrabromide addition products are possible and their properties are unknown. No information is available on the effect of bromine concentration on the competition between naphthalene addition and either toluene substitution at high bromine concentrations or napthalene substitution at any bromine concentration. The slight instantaneous reaction on mixing reagents is unaccounted for and the possible incorporation of carbon tetrachloride fragments in the reaction products should be noted. The recently reported formation of a complex from naphthalene and bromine suggests still other complications.[21]

Experimental

Reagents.—For the sealed tube experiments, carbon tetrachloride was refluxed with aqueous potassium permanganate, dried with calcium chloride and fractionally distilled. Benzene and toluene were washed with cold concentrated sulfuric acid and then with water, dried with calcium chloride and fractionally distilled. Reagent bromine was dried with calcium bromide and distilled. For the competitive rate

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[19] Formulation of the rate-determining step as $C_{10}H_8 + Br_3\cdot \rightarrow C_{10}H_8Br_2 + Br\cdot$ accounts for the concentration effect, but not the retarding effect of naphthalene.

[20] A preliminary experiment with naphthalene at 70°, otherwise like expts. 11 and 15 in Table III, indicated 38% substitution as compared with 10% at 20°.

[21] N. W. Blake, H. Winston and J. A. Patterson, THIS JOURNAL, 73, 4437 (1951).

experiments, reagent grade carbon tetrachloride, toluene and bromine were employed without further purification. Naphthalene and other solvents were fractionally distilled, the former at reduced pressure.

Procedure in Sealed Tube Experiments.—Runs in the presence of air were usually carried out in sealed Pyrex tubes using 3 ml. of a 1.3 molar solution of naphthalene in the principal solvent employed and 1 ml. of a standard solution of bromine in carbon tetrachloride. Light was excluded by keeping the tubes in a can from which only the necks of the tubes protruded during sealing. The reaction mixtures were degassed and the tubes evacuated for runs in the absence of air.

Analyses in Sealed Tube Experiments.—After the desired reaction time, the reaction tubes were emptied into excess aqueous potassium iodide, and unreacted bromine and hydrogen bromide formed were determined by titration with sodium thiosulfate and potassium iodate.[22] This method indicated an instantaneous reaction of 1–2%[23] of the bromine with naphthalene, confirmed by another method: a solution to be titrated was added to excess sodium sulfite, and after acidification, the bromide ion was titrated by the Volhard method. Titration immediately after mixing the reagents showed 1.3% reaction by the sodium sulfite method, while the sum of unreacted bromine and hydrogen bromide as determined by the potassium iodide–sodium iodate method, showed that 1.6% reaction had occurred. The reliability of the usual method was confirmed by a bromine balance on a larger run, analyzing the organic reaction product for bromine. α-Bromonaphthalene and naphthalene tetrabromide were found in this product.

In reactions carried out in toluene solution, after titration of bromine and unreacted hydrogen bromide, the organic layer was separated and the aqueous layer extracted three or four times with ether. The ether extracts were combined, and washed with water until free of halide. The ether was evaporated at reduced pressure; excess alcoholic silver nitrate was added to the residue, and the mixture was refluxed for two hours. The silver bromide was washed well with water and ether, dried, and weighed. Blanks on naphthalene tetrabromide alone showed that 71% of the bromine was removed under these conditions; in toluene–naphthalene runs, the amount of benzyl bromide was determined by correcting the amount of silver bromide formed for that coming from the addition product known to be present, assuming that all the addition product is the known isomer of naphthalene tetrabromide. Although results below cast doubt on this assumption, the general conclusions reached are not affected.

Procedure in Competitive Rate Experiments.—Brominations were carried out in a 300-ml. 3-necked Pyrex flask, fitted with a thermometer, a motor-driven stirrer, and a bromine inlet of capillary tubing connected to a 50-ml. buret, all extending to the bottom of the flask, and gas inlet and exit tubes at the top of the flask. Ground joints were used for connections and the tight ground glass stirrer bearing was kept lubricated and gas-tight with carbon tetrachloride. The gas exit tube was connected successively to traps kept in solid carbon dioxide and liquid nitrogen baths. The reaction flask was kept in a water-bath of heavy Pyrex glass and illuminated from below by a 75-watt clear-glass incandescent lamp in a 4″-diameter reflector, nearly in contact with the bath. The temperature was usually maintained at 19–21° by regulation of water flow through the bath.

The hydrocarbons were weighed out to 0.01 g. and made up to 100 ml. with carbon tetrachloride. This solution was added to the reaction flask, previously flushed with commercially purified nitrogen, and the volumetric flask was rinsed with 10 ml. more of carbon tetrachloride. The gas exit tube was connected; a slow stream of nitrogen was passed through the system, and after temperature equilibrium was attained, addition of bromine was begun. About 20 millimoles of bromine solution in 20 ml. of carbon tetrachloride was used in each experiment, the strength of this solution being checked regularly. In general, an attempt was made to add bromine rapidly without imparting a persistent color to the reaction mixture, but this object was not always attained in mixtures containing a high proportion of naphthalene and was unattainable in the absence of toluene, where some unreacted bromine was always recovered, even after considerable standing.

Analyses in Competitive Rate Experiments.—Subsequent manipulations were designed to prevent loss of hydrogen bromide gas, to collect it in the liquid nitrogen trap, and to replace all the carbon tetrachloride with toluene so that halogen analyses could be made on the reaction products. After completion of the reaction, the flow of nitrogen was increased for a few minutes to sweep out most of the hydrogen bromide. Subsequent procedures were varied but the following were found most effective. The nitrogen stream was shut off and the traps were connected to vacuum with very gentle suction. The gas exit tube of the reaction flask was stoppered and the gas inlet tube was connected to the traps so that air was sucked in through the bromine inlet. The stirrer was then cautiously removed and rinsed with toluene (carbon tetrachloride when free bromine remained) and the flask was connected to a fractionating column packed with 15 cm. of glass helices. Gentle suction was then applied to the column, through the traps, and the gas inlet tube was replaced with a glass stopper. The thermometer and closed gas exit tube were left on the flask. Except when free bromine remained, about 25 ml. of toluene was added and most of the carbon tetrachloride was removed at 200 mm. pressure, with final reduction of pressure to about 150 mm. and heating of the liquid residue to a temperature of 55°. At this point, the traps were emptied and their contents were titrated. Only in naphthalene runs containing no toluene was any bromine recovered, and then almost entirely in the solid-carbon dioxide trap. In mixtures containing both bromine and hydrogen bromide, the bromine was determined iodometrically with potassium iodide and sodium thiosulfate. Addition of potassium iodate then liberated an additional equivalent of iodine for each equivalent of acid present. In the absence of bromine, hydrogen bromide was determined by titration with 0.5 *N* sodium hydroxide. The most effective way of transferring hydrogen bromide quantitatively from the liquid nitrogen trap was to connect the trap to a gentle stream of nitrogen and to a sintered glass filter stick dipping into water. Slow warming of the trap then gave a satisfactory evolution of hydrogen bromide.

To the residue in the distilling column was added 25 ml. of toluene and distillation was continued slowly at 50 mm. pressure until the liquid temperature again reached 55°. More toluene was then added and removed in the same way to remove as much carbon tetrachloride as possible from the high-boiling bromination products. All distillates and trap contents were titrated for additional hydrogen bromide. The residue from the distillation was then transferred to a volumetric flask and the flask and column were rinsed by short refluxing with more toluene. The solutions were then made up to 100 ml. with toluene. A test of the distillation procedure for removal of 100 ml. of carbon tetrachloride from 0.1 mole of naphthalene and 0.3 mole toluene showed that only 0.045 *milli*equivalent of halogen remained.

The reaction products were analyzed for total halogen (as bromine) and also for reactive halogen (benzyl bromide plus part of the added bromine),[24] but since these analyses serve mostly to give a bromine balance (in Table III) or to confirm (usually within 5%) the total bromine in benzyl bromide and addition products, no details will be given.

Naphthalene Tetrabromide.—1,2,3,4-Tetrabromo-1,2,3,-4-tetrahydronaphthalene was prepared by gradual addition, over a period of 4–6 hours, of 20 g. of bromine in 50 ml. of carbon tetrachloride to 16 g. of naphthalene and 3 mole % of ascaridole in 100 ml. of carbon tetrachloride, under stirring and illumination with a 500-watt incandescent lamp. When the addition of the bromine solution was complete, the solution was immediately evaporated under reduced pressure and the remaining solid was collected on a filter (wt. 9 g.). Three recrystallizations from chloroform gave 6.7 g. (12% yield based on the added bromine), which melted with decomposition at 111–112°.[12] Melting points were taken by placing the melting point tube in a bath at about 108° and allowing the temperature to rise at the rate of about 1° per minute. They were uniformly reproducible. The tetrabromide was analyzed for halogen by the Parr bomb method.

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[22] H. P. A. Groll, G. Hearne, F. F. Rust and W. E. Vaughan, *Ind. Eng. Chem.*, **31**, 1239 (1939).

[23] 5% in some early experiments in brown glass-stoppered bottles.

[24] The products of three naphthalene runs released 49.7 ± 0.2% of their total bromine, 52.4 ± 0.3% of their added bromine, on treatment with alcoholic silver nitrate for 8 hours at room temperature. Note that the known tetrabromide released more bromine under reflux.

Anal. Calcd. for $C_{10}H_8Br_4$: Br, 71.4. Found: Br, 71.8.

As deposited from chloroform solution, the crystals were transparent; they become opaque on standing, although no other evidence of decomposition was noted over a period of two months.

When 3.9 g. of tetrabromide was heated at 140° for three hours, bromine and hydrogen bromide were evolved. Fractional sublimation of the 2.5 g. of residue at 18 mm. pressure yielded 0.41 g. of α-bromonaphthalene and 1.8 g. of a solid analyzing for 52.8% bromine (corresponding to 82 mole % of dibromonaphthalenes and 18 mole % of monobromonaphthalenes). On this basis, 8.7 millimoles of naphthalene tetrabromide gave 3.2 millimoles of monobromonaphthalenes and 5.4 millimoles of dibromonaphthalenes.

Behavior of the addition compound toward several reagents is summarized in Table V, the reactions being carried out by refluxing 0.2 g. of tetrabromide in 10 ml. of solution. The extent of reaction was determined by titration of the bromide ion in experiments 1–4, by titration of iodine[25] in experiments 5–6.

TABLE IV

DEHALOGENATION OF NAPHTHALENE TETRABROMIDE

Expt.	Solvent	Reagent	Br removed, %	Time, hr.
1	60% EtOH	H_2O	39	2.5
2	75% EtOH	4% NaOH	63	2.3
3	75% EtOH	4% NaOH	62	5.0
4	75% EtOH	$AgNO_3$	71	2.5
5	99% MeOH	Excess KI	94	1.5
6	99% MeOH	Excess KI	96	2.0

Since not more than 50% of the halogen could be removed by simple elimination of hydrogen bromide (to give dibromonaphthalenes), it appears that the action of alkali must cause some hydrolysis or effective elimination of bromine as well. Since no acid is formed in the reaction of potassium iodide with the addition compound, the reaction of potassium iodide with the tetrabromide is represented by the equation

$$C_{10}H_8Br_4 + 4I^- \longrightarrow C_{10}H_8 + 2I_2 + 4Br^-$$

SCHENECTADY, N. Y.

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[25] R. T. Dillon, W. G. Young and H. J. Lucas, THIS JOURNAL, **52**, 1953 (1930).

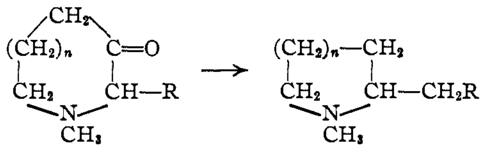
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Rearrangement of α-Thiaketones During Clemmensen Reduction[1,2]

BY NELSON J. LEONARD AND JOHN FIGUERAS, JR.

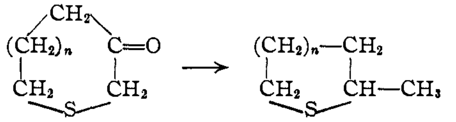
It has been shown that monocyclic six- and seven-membered ring α-thiaketones undergo rearrangement during Clemmensen reduction. Specifically, 3-ketothiacyclohexane is converted to 2-methylthiacyclopentane and 3-ketothiacycloheptane is converted to 2-methylthiacyclohexane upon reduction with zinc amalgam and hydrochloric acid.

Reports from this Laboratory[3] have indicated that monocyclic α-aminoketones of the type I undergo reduction–rearrangement to II when subjected to treatment with zinc amalgam and hydrochloric acid. It was reasonable to expect that analogous monocyclic α-thiaketones would undergo similar ring contraction during Clemmensen reduction. This prediction has been confirmed by the observation that 3-ketothiacyclohexane (IIIa) and 3-ketothiacycloheptane (IIIb) are converted to 2-methylthiacyclopentane (IVa) and 2-methylthiacyclohexane (IVb), respectively, under Clemmensen reduction conditions.



I II

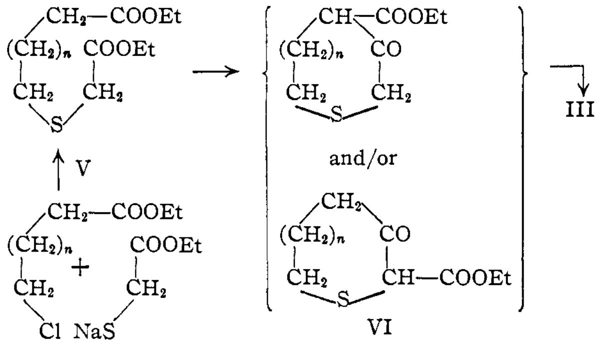
(R = alkyl or H, n = 1 or 2)



III IV

(a, n = 1; b, n = 2)

3-Ketothiacyclohexane (IIIa) was obtained by hydrolysis and subsequent decarboxylation of the β-ketoester (VIa) resulting from the Dieckmann ring closure of carbethoxymethyl γ-carbethoxypropyl sulfide (Va). The diester sulfide (Va) was available through the condensation of ethyl γ-chlorobutyrate with the sodio derivative of ethyl thioglycolate. While the position of the carbethoxyl group in the β-keto ester (VIa) is regarded as equivocal, either of the possible structures would produce 3-ketothiacyclohexane (IIIa). The structure of the α-thiaketone IIIa was confirmed by analysis, infrared absorption spectrum, and the formation of ketone derivatives. The seven-membered ring α-thiaketone IIIb was synthesized by the same route (Vb → VIb → IIIb), starting with ethyl δ-chlorovalerate.



(a, n = 1; b, n = 2)

The identity of the cyclic sulfides resulting from the Clemmensen reductions of IIIa and IIIb was established by comparison of their infrared spectra with those of authentic samples of 2-methylthiacyclopentane (IVa) and 2-methylthiacyclohexane

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[1] Reported at the Twelfth National Organic Symposium of the American Chemical Society, Denver, Colorado, June 14, 1951.

[2] This work was supported in part by a grant from E. I. du Pont de Nemours and Company, Inc.

[3] N. J. Leonard and W. V. Ruyle, THIS JOURNAL, **71**, 3094 (1949); N. J. Leonard and E. Barthel, Jr., *ibid.*, **71**, 3098 (1949); N. J. Leonard and E. Barthel, Jr., *ibid.*, **72**, 3632 (1950).