Electrophilic Substitution in Acenaphthene and Related Compounds. II.[1] Bromination and Chlorination of Bromo- and Chloroacenaphthenes

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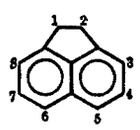
3-Bromo-, 3-chloro-, 5-bromo-, and 5-chloroacenaphthene have been brominated and chlorinated and the products identified. The 3-halo compounds undergo further substitution almost completely in the 6 position. 5-Bromo- and 5-chloroacenaphthenes react with sulfuryl chloride to give, mainly, 5,6-dihalo compounds. Side-chain bromination of 5-bromoacenaphthene is found under a variety of conditions. However, reaction with bromine vapor gives small amounts of 3,5- and 3,6-dibromoacenaphthenes while bromination with hypobromous acid gives 5,6-dibromoacenaphthene as the major product.

Little is known about the orientation of the substituent groups on dihalogenation of acenaphthene (**1**). A significant proportion of the starting material remained unaccounted for in all reported preparations of dihaloacenaphthenes, and no comprehensive study has been published. This paper reports a detailed study of further bromination and chlorination of 3-bromo-, 3-chloro-, 5-bromo-, and 5-chloroacenaphthenes.



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Goto and Ngai[2,3] carried out extensive studies on the chlorination of 5-chloroacenaphthene and obtained the 5,6-dichloro compound in yields ranging from 52.6 (using molecular chlorine with zinc powder as catalyst[2]) to 58% (using sulfuryl chloride with iodine as catalyst[3]). Dashevskii and Petrenko[4] increased the yield to 75–78% by using aluminium chloride as the catalyst with sulfuryl chloride, though later workers[5] obtained only 40% by this method. Sulfuryl chloride, in the presence of Lewis acids, has been shown to be a good aromatic nuclear chlorinating agent.[6]

Only one dibromoacenaphthene is known and this (reported in 10–40% yields[5,7]) was originally assigned the 5,6 structure. It was shown[8] by X-ray crystallography in 1962 that this compound was in fact 3,5-dibromoacenaphthene. Dibromination is not unique with regard to this orientation as Nightingale and Brooker reported[9] the same behavior for acylation and nitration of 5-chloro- and 5-bromoacenaphthenes.

Only one of the possible bromochloroacenaphthenes has been reported. Karishin[10] prepared 5-bromo-6-chloroacenaphthene in 67% yield by allowing 5-bromoacenaphthene to react with sulfuryl chloride at room temperature in the presence of anhydrous ferric chloride.

A quantitative study of monobromination and chlorination has been made. Denisova, *et al.*,[11] showed that, in both cases, 5- and 3-haloacenaphthenes were formed in ratios varying from 2.24 (chlorine in 90% acetic acid–water) to 48.2 (bromine in 90% acetic acid–water). In a previous paper[1] it was shown that the proportion of 3-bromo compound depends markedly on the conditions, varying from 3.4 (bromine in acetic acid) to 32.4% (hypobromous acid in 75% dioxane–water).

A kinetic study[12] of the bromination of acenaphthene showed that the positions *para* to the bridge are extremely activated to electrophilic attack. In further substitution of the 3 isomer therefore, on electronic grounds the expected major product would be the 3,6 derivative, with minor quantities of 3,5- and 3,8-dihaloacenaphthenes being possible. With the 5 isomer, electronic considerations alone place the expected products in the order 5,6- (main), 3,6-, and 3,5-dihaloacenaphthenes. However, steric effects, especially in dibromination, would act against formation of the 5,6 product.

Results and Discussion

Bromination and Chlorination of 3-Bromo- and 3-Chloroacenaphthenes.—In each case, only one ring dihalo compound (at least 90% of the total products) was produced and this was shown to be the 3,6 isomer. The infrared (ir) spectrum of each of these four previously unreported compounds contained two strong peaks of approximately equal intensity in the 800–830 cm^{-1} range (two adjacent hydrogens) and no significant peak in the 750–790 cm^{-1} region (three adjacent hydrogens).

This substitution pattern gives rise to two AB systems in the nmr spectrum and, except with 3,6-dibromoacenaphthene, the eight lines were readily distinguishable. In each spectrum the 8 proton[13] occurred as half an AB system at higher field than the other lines. These peaks were broadened by coupling with the protons on C-1 and were easily recognized. The

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other half of this AB overlapped with the other AB pattern. For 3,6-dibromoacenaphthene, the H-4,5 AB collapsed to virtually a single line. All four compounds had $J_{7,8} \sim 7.8$ Hz, $J_{4,5} \sim 9.0$ Hz.

This substitution is in accord with the result expected from electronic considerations, though the complete absence of any 3,8 substitution from chlorination was surprising.

Chlorination of 5-Chloroacenaphthene.—Under the chlorinating conditions used, the only compounds formed were 3,6- and 5,6-dichloroacenaphthenes (90% yield) in the ratio 1:5. The 5-chloroacenaphthene used contained some 3-chloro isomer (see Experimental Section) and the product ratio was not significantly different from the ratio of 3-/5-chloroacenaphthenes in the starting material. Assuming that the 3-chloroacenaphthene reacted completely to give the 3,6-dichloro compound, this result indicates that only a very minor amount of the 5-chloroacenaphthene substituted further in the 8 position.

It is evident that the steric hindrance of a chlorine atom in the 5 position toward attack by the chlorinating reagent at the electronically active 6 position is negligible.

Chlorination of 5-Bromoacenaphthene.—Gas chromatography of the reaction mixture showed three products. Two of these were 5-bromo-6-chloroacenaphthene (60% of the total product) and 5-chloroacenaphthene (10%). The third peak (20%) was resolved into three components on a polyphenyl ether column, the major one being identified as 5,6-dichloroacenaphthene. The second was 3-chloro-6-bromoacenaphthene and the third component was not identified. The 5-chloroacenaphthene presumably arose from halogen exchange in the presence of the ferric chloride catalyst employed and some underwent further chlorination to give the 5,6-dichloro compound. Though bromine has a larger effective size than does chlorine, it appears that the steric hindrance in 5-bromoacenaphthene to attack by sulfuryl chloride in the adjacent 6 position is not significantly greater than that in 5-chloroacenaphthene, at least in the presence of ferric chloride. It is also apparent from these two results that chlorination of a 5-haloacenaphthene leads to formation of a smaller proportion of product containing chlorine in a position adjacent to the bridge than does chlorination of acenaphthene itself.

Bromination of 5-Bromoacenaphthene.—This compound was most reluctant to undergo further ring bromination. With liquid bromine under various conditions, including those unfavorable to free-radical formation (*e.g.*, bromine in aqueous acetic acid in the presence of iodine), extensive and predominent side-chain bromination occurred. The products obtained, which have all been reported[14,15] previously, depended on the conditions and the amount of bromine used. Further investigation of the reactivity of the bridge is being carried out.

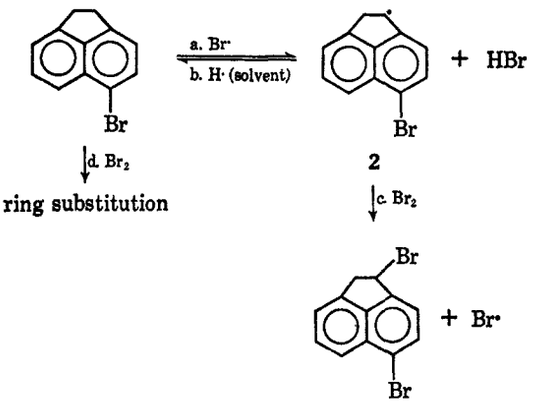
Ring substitution was observed when bromine vapor was employed. These were the conditions previously reported[5] to give 3,5-dibromoacenaphthene. This experiment of Letsinger, *et al.*, on acenaphthene was repeated. Glpc analysis showed the product mixture to contain *ca.* 80% 5-bromoacenaphthene and 10% material subsequently isolated by liquid chromatography and identified by ir analysis as a mixture of 3,5- and 3,6-dibromoacenaphthenes (glpc gave poor separation of these isomers). Recrystallization of this material gave the pure 3,5 isomer. Thus, the unaccounted for product in Letsinger's experiment was almost completely monobromination product.

These experimental conditions were then repeated on 5-bromoacenaphthene. With 4 mol of bromine, glpc of the product mixture indicated *ca.* 10% ring dibromo products, the remainder being unreacted starting material. Infrared analysis showed the dibromoacenaphthene fraction to contain approximately equal amounts of the 3,5- and 3,6-dibromo compounds. With 5 mol of bromine, the amount of ring dibromo product was increased slightly but higher molecular weight halogenated products (probably side chain) were also formed.

Under these experimental conditions, the 3-bromoacenaphthene impurity in the starting material was still present in the product mixture and the 3,6- and 3,5-dibromoacenaphthenes were therefore formed from the 5-bromo isomer.

The difference in conditions between the bromine vapor and liquid experiments seems to be solely in the concentration of bromine present at any time. The virtual exclusion of side-chain products in the vapor experiments can possibly be interpreted on this basis, as depicted in Scheme I.

SCHEME I



It is assumed that the initial side-chain product arises through the normal free-radical chain process. Under conditions of low bromine concentration, the radical (**2**) is more likely to abstract a hydrogen atom from the solvent (b) than to react with another bromine molecule (c). Thus the slower, but irreversible ring substitution (d) alone leads to significant reaction.

The best condition for ring bromination was found when hypobromous acid was used in dioxane solvent. No side-chain bromination was observed. The products (75% yield), apart from unchanged 5-bromoacenaphthene, were a mixture of the 3,5- and 3,6-dibromo derivatives and another compound subsequently identified as the hitherto unknown 5,6-dibromoacenaphthene. This latter was the major product (73% by

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glpc) while the mixture (27%) of 3,5 and 3,6 isomers consisted (ir) of approximately equal amounts of each. The structure of the 5,6-dibromoacenaphthene was assigned from spectral data. The ir spectrum was very similar to that of 5-bromo-6-chloroacenaphthene while the nmr spectrum consisted of one AB system (J = 7.5 Hz) with the 3(8)-proton lines at higher field and broadened by long range coupling with the bridge protons. With the use of a bulky substituting entity such as molecular bromine, the steric effect of the 5-bromo group apparently precludes further attack in the 6 position and the bromine is forced to substitute in positions adjacent to the bridge. However, when a "positive bromine" species from hypobromous acid is employed, the electronically activated 6 position is accessible and the major product is the 5,6-dibromo compound.

A priori, the formation of comparable amounts of 3,5- and 3,6-dibromoacenaphthenes was unexpected since this result indicates that the 5-bromo substituent has a similar electronic effect on the transition states for bromination in the 3 and 8 position. While transition state data are not available, ground-state measurements from pK determinations[16] do support this observation. Thus, 4-bromo-2-naphthoic acid is only slightly stronger than 5-bromo-2-naphthoic acid (ΔpK = 0.11).

Such an explanation might seem to require that 3-bromoacenaphthene would undergo further substitution at a similar rate in the 5 and 6 positions, contrary to the experimental results. By reference to another naphthalene analogy it can be seen that this is not necessarily so. 3-Bromo-1-naphthoic acid is rather stronger than 5-bromo-1-naphthoic acid[16] (ΔpK = 0.24). These results indicate that an α-bromine atom conjugates better with a naphthalene ring than does a bromine in a β position. Thus, the difference in behavior of 3- and 5-bromoacenaphthenes in further bromination is not inconsistent.

Further work is in progress on electrophilic substitution reactions of various monosubstituted acenaphthenes.

Experimental Section

Except where stated otherwise, glpc analyses were carried out on a GE-SE30 silicone rubber column at 200–220°. Infrared spectra were run as Nujol mulls and CCl_4 was employed as the solvent for nmr measurements, with tetramethylsilane (TMS) as internal standard. Microanalyses were carried out by the Australian Microanalytical Service.

Materials. 3-Bromo- and 3-Chloroacenaphthene.—3-Nitroacenaphthene was reduced in high yield with hydrazine and palladium–charcoal in boiling ethanol. Diazotization of the resulting 3-amino compound[17] gave 3-bromoacenaphthene, mp 63–64° (lit.[11] 64.5–65.5°), and 3-chloroacenaphthene, mp 74–75° (lit.[11] 76–77°).

5-Chloroacenaphthene.—This was obtained, mp 69–70° (lit.[11] 68.5–69°), by treating acenaphthene with sulfuryl chloride in chloroform solvent. The product contained 15% 3-chloro isomer (glpc).

5-Bromoacenaphthene.—Bromination of acenaphthene under standard conditions gave this product, mp 50–52° (lit.[11] 53–54°), containing 3% 3-bromo isomer.

Purification from the 3 isomer was not achieved in either case as recrystallization and liquid chromatography did not alter the isomer proportions significantly. The 5-haloacenaphthenes were not prepared in the same way as the 3 isomers because of the reported[18] difficulty found in obtaining pure 5-nitroacenaphthene.

"Standard" Reaction Conditions. A. Chlorination.—The compound (1 mol) was dissolved in ice-cold chloroform, sulfuryl chloride (1.4–1.5 mol) and anhydrous ferric chloride (0.1 mol) were added, and the mixture was allowed to stand at room temperature in the dark for 1–2 days.

B. Bromination.—Bromine (3 mol) was added to the compound (1 mol) in 75% ethanol–water and the mixture was refluxed in the dark for 1 hr.

In both reactions, the product mixture was analyzed by glpc. Where the trace showed only one product, the solvent was removed and the residue was recrystallized from ethanol. When a number of products were formed, identification was achieved from samples isolated by glpc and further purified by sublimation, or by comparison of retention times with those of authentic samples.

The following compounds were prepared in these ways. 3,6-Dibromoacenaphthene (from 3-bromoacenaphthene) had mp 71–73°; ir 1110 (s), 1090 (m), 1063 (s), 860 (m), 845 (m), 830 (s), 800 (s) cm^{-1}. *Anal.* Calcd for $C_{12}H_8Br_2$: C, 46.15; H, 2.6; Br, 51.25. Found: C, 46.45; H, 2.4; Br, 51.5. 3-Bromo-6-chloroacenaphthene (from 3-bromoacenaphthene) had mp 69.5–71°; ir 1110 (s), 1080 (s), 871 (m), 850 (m), 830 (s), 800 (s) cm^{-1}. *Anal.* Calcd for $C_{12}H_8BrCl$: C, 53.9; H, 3.0; Cl, 13.3. Found: C, 54.2; H, 2.85; Cl, 13.5. 3,6-Dichloroacenaphthene (from 3-chloroacenaphthene) had mp 94–96°; ir 1130 (s), 1110 (s), 1082 (s), 890 (m), 855 (m), 830 (s), 804 (s) cm^{-1}. *Anal.* Calcd for $C_{12}H_8Cl_2$: C, 64.5; H, 3.6. Found: C, 64.2; H, 3.75. 6-Bromo-3-chloroacenaphthene (from 3-chloroacenaphthene) had mp 74–75°; ir 1130 (s), 1110 (s), 1068 (s), 885 (m), 848 (m), 830 (s), 802 (s) cm^{-1}. *Anal.* Calcd for $C_{12}H_8BrCl$: C, 53.9; H, 3.0. Found: C, 54.2; H, 3.0. 5,6-Dichloroacenaphthene had mp 158–160° (lit.[2] mp 160°). 5-Bromo-6-chloroacenaphthene (from 5-bromoacenaphthene) had mp 152–155° (lit.[10] mp 153–155°); ir 1115 (s), 1025 (s), 865 (m), 838 (s), 815 (s), 742 (w), 720 (m) cm^{-1}.

Vapor Bromination of 5-Bromoacenaphthene.—This was carried out in 95% ethanol and the 3,5-dibromoacenaphthene, mp 138–139° (lit.[5] mp 138–140°), was isolated according to the method previously reported:[5] ir 1095 (s), 1020 (w), 865 (s), 832 (m), 825 (m), 775 (s), 742 (m) cm^{-1}.

5,6-Dibromoacenaphthene.—5-Bromoacenaphthene (2.0 g) was dissolved in dioxane (60 ml). Perchloric acid (12 ml, 72% solution) and silver sulfate (6 g) were added. To the stirred solution, at room temperature in the dark, was added a solution of bromine (1.2 g) in dioxane (10 ml) and the mixture was left overnight. Extraction with ether gave the crude product. This was recrystallized once from chloroform and once from acetic acid and chromatographed on silica gel (petroleum ether eluent). The product was recrystallized from aqueous acetic acid to give pale yellow needles, mp 165–168° after shrinking: ir, 1105 (s), 1022 (s), 1010 (w), 835 (s), 810 (s), 740 (w), 706 (w) cm^{-1}. *Anal.* Calcd for $C_{12}H_8Br_2$: C, 46.15; H, 2.6. Found: C, 45.8; H, 2.6.

Registry No.—**1**, 83-32-9; 3-bromoacenaphthene, 5209-31-4; 3-chloroacenaphthene, 5573-31-9; 5-bromoacenaphthene, 2051-98-1; 5-chloroacenaphthene, 5209-33-6; 3,6-dibromoacenaphthene, 19202-58-5; 3-bromo-6-chloroacenaphthene, 19190-89-7; 3,6-dichloroacenaphthene, 19202-59-6; 6-bromo-3-chloroacenaphthene, 19190-90-0; 5,6-dibromoacenaphthene, 19190-91-1.

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